Bragg and magnetic diffuse scattering in MnO

Intensity distribution in the (hhl) plane of MnO in the paramagnetic phase at 200 K measured with the Flat-cone diffractometer E2. Giant red trees of Bragg reflections and smooth mountains of magnetic diffuse scattering are visualized. Magnetic interaction energies could be determined for the first time directly from the diffuse scattering distribution using a mean field theory with a Onsager correction term.

(For further details see p. 22: D. Hohlwein, Magnetic interactions in MnO from paramagnetic diffuse scattering)

The cover was designed by screenworks, Kreuzbergstrasse 7, D-10965 Berlin, www.screenworks.de

Editorial:

The Berlin Neutron Scattering Center (BENSC) is a department of the Hahn-Meitner-Institut Berlin GmbH. BENSC develops and runs the Neutron Scattering Instruments at the Berlin Research Reactor BER II and is responsible for the service to external users. The Hahn-Meitner-Institute (HMI) is a national research institution financed by the Federal Republic of Germany and the City State of Berlin.

Address:

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Fax: +49 - 30 - 8062 2523
Email: bensc@hmi.de
Net: http://www.hmi.de/bensc
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The BENSC Experimental Reports are intended as interim summaries. In view of the short time available between the termination of certain experiments and the deadline for this report, the results presented here have to be considered as very preliminary. The inclusion of reports in this volume does not constitute a publication in the usual sense. Final results will be submitted for publication in regular scientific journals.

Notice:
The quality of figures in CD and electronic version - especially in colour presentation – is remarkably higher than in print version
Introduction

The present volume contains 250 BENSC Experimental Reports and gives an overview on the experimental work carried out on BENSC during the year 2002.

BENSC User Service

BENSC is open to both, the national and the international user community, whereby about 70 percent of the beam time is available to external users; 20% for long term collaborating groups from German universities and other research institutions and 50 % for peer reviewed short term projects.

Detailed descriptions of all essential BENSC neutron scattering instruments are available - and updated - on the BENSC Webpage.

http://www.hmi.de/bensc/instrumentation

A colour printed version (brochure HMI-B 577) is on the market since March 2001 and available on request.

BENSC puts special emphasis on sample environment under extreme conditions: high fields, high pressure, high, low and ultra low temperatures. The sample environment group has published a detailed technical handbook on BENSC sample environment. The handbook is updated continuously and available in the INTERNET under

http://www.hmi.de/bensc/sample-env/home.html

Scientific Selection Panel

The short term project beam time allocations for the scheduled instruments are established on a semi-annual basis in collaboration with a scientific selection panel, the "user committee". The 2002 beam time quota for the short term projects of the external user groups were allocated at two user committee sessions in November 2001 and May 2002. Ten external and two in-house committee members have been involved:

External members:
- Prof. Dr. P. Baglioni, 
  Univ. Firenze, Italy
- Prof. Dr. G. Decher, 
  Univ. Strasbourg, France
- Prof. Dr. M. Lerch, 
  Techn. Univ. Berlin, Germany
- Prof. Dr. P. Fratzl, 
  Univ. Leoben, Austria
- Prof. Dr. M. Jansen, 
  MPI-FK, Stuttgart, Germany
- Prof. Dr. M. Loewenhaupt, 
  Techn. Univ. Dresden, Germany
- Prof. Dr. D. Kaczorowski, 
  Polish Acad. of Sciences, Wroclaw, Poland
- Dr. L. Pintschovius, 
  FZ Karlsruhe, Germany / LLB Saclay, France
- Prof. Dr. V. Sechovsky, 
  Charles Univ. Prague, Czech Republic
- Prof. Dr. B. Toudic, 
  Univ. Rennes I, France

Internal members:
- Prof. Dr. F. Mezei, 
  HMI-Berlin
- Dr. H.A. Graf 
  HMI-Berlin

Support for European Access to BENSC from the European Commission

The access of European research groups to BENSC is generously supported by the European Community under the Access to Research Infrastructures action of the Improving Human Potential Programme (IHP). The EU support under IHP is available for groups from European Member States as well as for groups from the Associated States; for groups from Switzerland slightly modified rules apply. As listed on page IX, an important proportion of the contributions in this volume report on EU supported experiments.

The "European Access to BENSC" action turned out to be very successful and the share of these BENSC users in the number of BENSC publications in high-ranking journals is super-proportionally high.

Rainer Michaelsen
List of BENS Instruments

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April 2003

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How to Apply for BENS C Beam Time

BENS C is open to both the national and the international user community with up to 70% of the beam time available to external users. The main portion of this beam time is foreseen for short term research proposals. Applications for short term beam time will be examined by a scientific selection committee twice each year,

deadlines for submission of proposals are 15 March and 15 September.

Requests for urgent experiments (Directors's discretionary time) and for industrial use may be submitted at any time.

Applications for BENS C beam time should be made electronically. The BENS C ONLINE PROPOSAL SUBMISSION (OPS) system is available in the internet via

http://www.hmi.de/bensc/user-info/user-info_en.html

Further information on BENS C instrumentation can be obtained from the internet via

http://www.hmi.de/bensc/instrumentation/instrumentation_en.html

The latest four-colour printed version of the instrumentation brochure (HMI-B 577) is on the market since March 2001 and available on request:

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Germany
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Fax: +49 - 30 - 8062 2523
Email: bensc@hmi.de
Acknowledgement for Support by the European Commission

**FP5, IHP, Access to Research Infrastructures**

For most of the groups from European Community Member States and Associated States, the access to BENSC has been supported by the European Community under the Access to Research Infrastructure Action of the Improving Human Potential Programme (IHP)

Results of IHP supported groups are contained in 62 reports of this volume.


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EXPERIMENTAL REPORT

Effect of magnetic field on magnetic and charge ordering in LaSr$_2$Mn$_2$O$_7$

Principal Proposer: T.G. Perring, ISIS Facility, RAL, UK
Experimental Team: T.G. Perring, D.T. Adroja, (ISIS Facility)
J. Klenke, S. Danilkin (BENSC)

Date of Experiment: May 2002
Date of Report: Jan. 2003

The colossal magnetoresistance (CMR) effect found in cubic perovskite manganites, RE$_{1-x}$A$_x$MnO$_3$, at hole doping x~0.2-0.4 has attracted great attention in the field of condensed matter physics. More recently, pronounced CMR has been observed in the two dimensional analogues, bilayer, La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ (x=0.3-0.4), albeit with reduced $T_C$ ~120K. The bilayer manganite with x=0.5, just like the cubic systems, exhibits a semi-conductor type resistivity behaviour at all temperatures, but with an anomalous maximum in the resistivity at ~170K. Below 180K Mn moments show A-type antiferromagnetic ordering (AFM). X-ray and neutron diffraction studies show the presence of super-lattice peaks at (-1/4, 1/4, 0) between 210K and 100K due to charge and orbital ordering.

The aims of the present experiment were twofold: (I) to determine if a magnetic field applied to the low temperature A-type AFM phase ($T<<100K$) results in an FM component to the ordering, thereby offering an explanation for the magnetoresistance within the framework of the double exchange model and, (II) to test the hypothesis that the application of a magnetic field melts the charge and orbitally ordered structure that exists between ~100K and ~200K. Unfortunately, due to many problems with the positioning of the analyser table and sample rotation stick, only part (I) of the proposal was completed. (It should be noted also that the baffles on the sample stick were discovered to be magnetic, which resulted in the sample stick being pulled down into the cryomagnet when high fields were applied). The main results obtained from the present experiment are summarised in Figs 1 and 2. It has been observed that the intensity of the FM component, visible at the (004) and (110) positions, increases gradually with an applied field between 5K and 230K, while that of the AFM component, seen at (003) below 100K, decreases gradually with the field. Surprisingly, the intensity of (111) peak changes dramatically at very low field (below 0.5T). We did not observe any sign of hysteresis in the FM and AFM peaks with field cycling. However, the (111) peak shows a weak hysteresis below 0.5T.

![Fig.1 Field dependence intensity of the AFM and FM peaks](image1)

![Fig.2 Temperature dependence intensity of the FM and AFM peaks at 0T and 12T](image2)
Magnetic structure and soft modes in non-stoichiometric Ni2MnGa alloys

Present investigation is focused on in-situ neutron diffraction study of magnetic structure of the magnetic shape memory Ni$_{1.99}$Mn$_{1.14}$Ga$_{0.87}$ single crystal, possessing more than 5% magnetic field induced strain at room temperature. The Curie and phase transformation temperatures of this alloy are: $T_C = 374$K, $A_s = 310$K, $A_f = 310$K, $M_s = 303$K, $M_f = 302$K. The unit cell of martensite in the studied single crystal was determined earlier as modulated orthorhombic with $\alpha' = 0.421$ nm, $b = 0.562$ nm, $c' = 2.105$ nm at 296K. In present work we index the tetragonal martensite lattice with $c = 0.562$ nm and $b = a = \sqrt{2a'^2}$, as cubic (L2$_1$) structure corresponding to the parent austenitic unit cell.

**Experiment:** Measurements were performed with E1 spectrometer (\(\lambda = 0.1218\) nm). The single crystalline sample was aligned to have (100) plane coinciding with the scattering plane. Before experiments the specimen was magnetised along the [001] direction. Magnetic field of 0 to 2.5 T was applied using horizontal cryomagnet HM2.

**Results:** (1) Studied alloy is ferromagnetic with single magnetic sublattice, coinciding with crystalline structure. Figures (1-2) show changes in the magnetic diffraction pattern vs. temperature and applied magnetic field. At T=200 K, the applied magnetic field of 0.4T-2.5T causes (200) martensite peak broadening, while at T=4 K magnetic field (up to 2.5T) does not affect the diffraction pattern. Contribution of the inelastic scattering in the region of the superstructure peak from 5-layered modulation (1.04\(I_{\text{elastic}}\) at T=200K and 1.24\(I_{\text{elastic}}\) at T=4K) is much higher than in the main martensite peak (0.6\(I_{\text{elastic}}\) at T=200K and 0.7\(I_{\text{elastic}}\) at T=4K).

(2) Contribution of the inelastic scattering to intensity of the superstructure peak changes with temperature stronger than for the main (200) martensite peak.

**References:** N. Glavatska et al. BENSC experimental reports, 2001, p. 186.
Magnetic ordering and superconductivity are in general considered as mutual exclusive, but the rare-earth nickel borocarbides belong to a small group of materials where these two phenomena coexist. The coexistence offers a unique possibility to study the interplay between superconductivity and magnetism. This work concerns the rare-earth nickel borocarbide ErNi$_2$B$_2$C, a material that is superconducting at temperatures below $T_c=11$ K in zero applied field. If the material is further cooled below the Néel temperature $T_N=6$ K, the magnetic moments of the Er$^{3+}$ ions form a transversely polarized spin-density wave with the moments parallel to the [010] direction and a modulation wave vector $\mathbf{Q}=(Q_x, Q_y, 0)$ with $Q_x \approx 0.55$ rlu and $Q_y \approx 0$ rlu.

The results of the experiments are summarized in a phase diagram of ErNi$_2$B$_2$C for a field applied in the [110] direction, shown in figures A and B. We have observed three magnetic phases characterized by different spin density modulation wave vectors. The diagram A shows the variation of the $x$ component of the modulation wave vector, and the diagram B shows the variation of the $y$ component. The different magnetic phases are separated by intermediate phases.

The general behaviour of the magnetic structures as function of field and temperature as well as the bulk magnetisation properties are well described by a mean field model proposed by J. Jensen [1]. However, the model fails to explain the finite $Q_y$ component of the modulation wave vector. Further experiments with field applied in the $ab$ plane are required in order to clarify whether this feature is unique for a field applied along [110], or if it is present independent of field direction. If the latter is the case, it is interesting to study if the appearance of a finite $Q_y$ component is correlated with the upper critical field for superconductivity $H_{c2}$, as fig. B may suggest, and not just a result of the interaction between the applied field and the magnetic structure.

FIGURE A, B: magnetic phase diagram of ErNi$_2$B$_2$C for an applied field along the [110] direction. Fig. A describes the variation of the $Q_x$ component of the modulation vector $\mathbf{Q}=(Q_x, Q_y, 0)$. We have observed three different magnetic phases separated by intermediate phases. Fig. B describes the $Q_y$ component $-0.005$ rlu $< Q_y < 0$. $H_{c2}$ is the upper critical field for superconductivity determined by Bud'ko et al.[2]. Notice the proximity of $H_{c2}$ to the phase line separating regions with $Q_y=0$ and $Q_y<0$.

**Introduction** \( \text{Cs}_2\text{CuBr}_4 \) has the orthorhombic crystal structure with the space group \( Pnma \) and magnetic \( \text{Cu}^{2+} \)-ions make a distorted triangular lattice within the \( bc \)-plane, as shown in Fig. 1. For the isostructural \( \text{Cs}_2\text{CuCl}_4 \), the magnetic properties are well investigated by the elastic and inelastic neutron scattering technique [1, 2].

\( \text{Cs}_2\text{CuBr}_4 \) undergoes magnetic phase transition at Néel temperature \( T_N = 1.4 \text{ K} \). Below \( T_N \), the magnetization plateau was observed at approximately one third of the saturation magnetization for the field direction \( H || b \)- and \( c \)-axis which are in the triangular lattice plane [3]. Since the magnetization plateau is observed irrespective of the field direction within the \( bc \)-plane, the origin of the plateau is attributed to quantum effect. It is expected that the collinear up-up-down spin structure is realized at the plateau.

In the present measurement, we have performed elastic neutron scattering experiments, in order to determine its magnetic structure in the magnetic field applied parallel to the \( c \)-axis up to plateau region.

**Experiments** Measurements were performed at E1 triple axis spectrometer installed at experimental hall. A single crystal with \( 1 \text{ cm}^3 \) in volume was mounted on the sample stage of the dilution stick DS-X. Dilution stick was loaded into VM-1 14.5 T vertical superconducting magnet. Measurements were performed for the \( (a, b) \) and the \( (b, c) \) horizontal scattering planes. Incident neutron energy was fixed at \( E_i = 14.04 \text{ meV} \left( k_i = 2.603 \text{ Å}^{-1} \right) \). The horizontal collimation sequence was chosen as 40’ – monochromator – 40’ – sample – 40’ – analyzer – open – detector.

**Result** Figure 2 shows the typical profile scanned along the \( b^* \)-direction around at \( T = 60 \text{ mK} \). Magnetic Bragg reflection appears at \( Q = (0, 0.575, 0) \). This fact indicates the magnetic structure is incommensurate with the lattice along the \( b \)-axis. The origin of this incommensuration is the frustration between \( J_1 \) and \( J_2 \).

Figure 3 shows the field dependence of the ordering vector \( Q = (0, q, 0) \) at \( T = 60 \text{ mK} \). With increasing field, \( q \) increases continuously, and is locked at \( q = 0.662 \) above the critical field \( H_{c1} = 13.15 \text{ T} \) indicated by the arrow. This result shows the excellent agreement with the critical field \( H_{c1} \) at the beginning of the magnetization plateau [3]. This fact implies obviously that the up-up-down spin structure parallel to the magnetic field direction is realized at the plateau. To the best of our knowledge that the present result is the first experimental example of the one-third plateau stabilized by quantum fluctuation in triangular antiferromagnet.

Anomalies in the field dependent magnetization of CsCuCl₃ at low temperatures have stimulated many experimental and theoretical studies during the last decade [1-4]. It is now basically understood that these anomalies are a consequence of the influence of quantum fluctuations at low and thermal fluctuations at higher temperatures.

CsCuCl₃ is a hexagonal perovskite which undergoes a structural phase transition at 423 K due to the cooperative Jahn-Teller effect from the Cu²⁺ ion. The lattice symmetry changes from $P6_3/mmc$ to $P6_22$ in the low temperature phase. The lattice consists of chains of face sharing distorted Cl₆-octahedra centered by the Cu²⁺ ions along the $c$ axis. These chains are arranged on a triangular lattice in the $ab$ plane.

Long-range magnetic order of the Cu²⁺ moments occurs below 10.65 K. A triangular spin arrangement of the 120°-type structure is formed in the $ab$ plane and an incommensurate spiral along the $c$ axis with a repetition length of about 71 layers. The 120° structure results from the antiferromagnetic coupling on the triangular lattice. CsCuCl₃ belongs to the family of frustrated magnetic systems. The reduction of the ordered moment to 0.58 $\mu_B$ for the moment of the $S=1/2$ spin of the Cu²⁺ ion is not uncommon in frustrated triangular-lattice antiferromagnetic (TLA) systems. The magnetic interaction along the $c$ axis is predominantly ferromagnetic. An additional Dzyaloshinskii-Moriya interaction - possible by the low symmetry in the local structure due to the Jahn-Teller distortion - accounts for the observed incommensurate magnetic helix along the $c$ axis.

After having established the magnetic phase diagram recently [5] we have now focussed to determine the magnetic structure in an in plane field in more detail. Our measurements were extended in $q$-range to look for higher harmonics of the type $(1/3 1/3 + nq)$. Beside reflections with $n=1$ and 2 already seen in our former experiments we could for the first time observe reflections with $n=4$ at field strengths above 9 Tesla. No clear indication for magnetic Bragg intensity was observed at $n=3, 5-9$. A Fourier analysis is underway to get a more specific knowledge about the magnetic spiral distorted by the applied field. The observed 4.th harmonics is important to test for the different proposed magnetic spin arrangements.

Transition metal oxides with the perovskite structure \(\text{ABO}_3\) (\(A=\) rare earth, alkali-earth metal and \(B=\) transition metal) have been the subject of intense research activity due to their unusual electrical and magnetic properties. A very interesting system that has mainly been studied for the chemically induced metal-to-insulator transition is the perovskite solid solution \(\text{LaNi}_{x}\text{Co}_{1-x}\text{O}_3\). The above system exhibits metal-to-insulator transition around a critical concentration \(x_c = 0.35\) and giant negative magnetoresistance (GMR) for \(x < x_c\). Recently, detailed dc and ac magnetic susceptibility studies have revealed that the system exhibits remarkably complex magnetic behaviour, which has not been fully explored and/or related to the magnetoresistance effect [1]. On the basis of the above, the purpose of this experiment was to collect neutron diffraction patterns for both \(x = 0.5\) and \(0.2\), i.e. above and below the critical concentration \(x_c\), at low and high temperatures both in zero and in a non-zero magnetic field in order to determine the magnetic structure of the solution. The application of high magnetic fields is necessary to examine the extent to which magnetic interactions are related to the observed magnetoresistance effect (e.g. magnetic cluster growth) as well as to the metal-to-insulator transition. Phase purity of both samples was checked by X-ray powder diffraction. All neutron diffraction experiments were performed in the E2 flat-cone diffractometer of the reactor BER II in Berlin. A neutron wavelength of \(\lambda = 1.21\) Å was chosen by a Ge crystal monochromator with a collimation of 30°. 5 gr of powdered sample were placed in a vanadium can of 5mm diameter in He atmosphere and immersed in a cryostat. The magnetic field was applied, always normal to the scattering vector and only during the heating procedure.

Measurements for the \(x = 0.5\) compound were performed at 2 K, 120 K and 300 K in zero magnetic field and at 300 K and 2 K in a magnetic field of 6.5 T (Fig. 2). The difference diffractograms in temperature and in field didn’t show any residual intensity despite the long counting time. We conclude that either the ordered magnetic moment is very weak, at the border sensitivity of the diffractometer (~ 0.3 \(\mu_B\)), or that the compound does not exhibit a true magnetically long ranged order. All spectra were analysed with the Rietveld method in the \(R\bar{3}c\) space group. Diffraction spectra for the \(x = 0.2\) compound were obtained at 300 K in H= 0 T then at H= 6.5 T and back at H= 0 T. We didn’t observe any transition in the sensitivity limit of the diffractometer, however, the obtained diffractograms could not be analysed in the same crystallographic space group as for \(x = 0.5\). The latter is warrant of further investigations.
EXPERIMENTAL REPORT

Crystallographic and magnetic structure of Tb$_2$PdSi$_3$

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Date of Experiment: 18.02.02 – 26.02.02
Date of Report: 14.03.02

We performed a neutron diffraction experiment using a Tb$_2$PdSi$_3$ single crystal of excellent quality. The series R$_2$PdSi$_3$ (R = rare earth metal), crystallizing in an AlB$_2$ derived hexagonal structure, have been found to exhibit strong anisotropic magnetic properties and a giant magneto-resistance behavior [1]. The atomic positions are given according to space group P 6/mmm. The magnetic rare earth ions occupy the Al positions of the AlB$_2$ structure while the non-magnetic Pd and Si atoms are supposed to be statistically distributed on the B positions [2].

The neutron diffraction experiment was performed within a temperature range from 1.5 K to 300 K using both the germanium (\(\gamma=1.21\) Å) and the PG monochromator (\(\gamma=2.39\) Å; additional \(\gamma/2\)-, \(\gamma/3\)-filters). The single crystal was oriented in such a way that the scattering planes were \((H, 0, L)\), \((H, L, H)\) and \((H, K, 0)\).

The main results of our experiment are shown in Fig. 1. We found a crystallographic superstructure yielding satellite reflections at \((1/2, 1/2, L)\) at room temperature as marked in Fig. 1a. Within the resolution of our neutron diffraction experiment we determined the values of \(L\) to be \(L = n/8\) where \(n\) is an integer.

While using the flat-cone method of E2 we verified these values with the observation of corresponding reflections in \((h, k, 2/8)\)- and in \((h, k, 3/8)\)-planes. The existence of a crystallographic superstructure in ternary intermetallic 2-1-3-compounds was often quoted but never definitely verified [3].

Below the antiferromagnetic ordering temperature of \(T_N = 24\) K we found magnetic satellites at \((i/2, j/2, L')\) where \(i, j\) are integers (Fig. 1b). In this case the \(L'\) values seem to be \(L' = n/16\) where \(n\) is again an integer. As one can see in Fig. 1b a clear separation of the magnetic satellites is in some cases hardly feasible, especially close to the nuclear reflections.

Fig. 1: Neutron diffraction pattern (contour plot) of our high quality Tb$_2$PdSi$_3$ single crystal. Reflections result from the crystallographic superstructure (a) and from the antiferromagnetic structure (b) marked by arrows.

Critical magnetic behaviour of a cubic antiferromagnet with an integer spin: NiO

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In numerous investigations of transition metal compounds with a quenched orbital moment and a well defined spin quantum number it was observed that the temperature dependence of the (normalized) magnetic order parameter, $m_s(T)$, can be described in the whole range $0<T<T_c$ by only two temperature power functions with an analytical change (crossover) at the intersection of these functions [1]. The power function for $T\to0$ with exponent $\varepsilon$ is $m_s(T)=1-c^* T^\varepsilon$. For $T \to T_c$ the well known critical power law $m_s(T) \sim (T_c-T)^\beta$ holds. Normally, the crossover between the two functions is at about $0.85^* T_c$.

For the empirical exponent $\varepsilon$ six universality classes are now firmly established [2]. It can be assumed that the conjugated exponents $\beta$ of the $T\to T_c$ power law are like the exponents $\varepsilon$ also rational numbers. In isotropic (cubic) materials with a half-integer spin ($\varepsilon=2$) the mean field value $\beta=1/2$ was frequently confirmed [3]. For integer spins ($\varepsilon=9/2$) $\beta=4/11$ was proposed which is in close agreement with the well known Heisenberg value. Unfortunately, we know of no cubic ferromagnet with an integer spin.

The cubic antiferromagnet NiO with $S=1$ due to the Ni$^{2+}$ ion is a promising candidate to test $\beta=4/11$. For this material it was reported that the Néel transition is second order and that $\beta=0.38$ [4].

Fig.1 shows our results for the antiferromagnetic order parameter, i.e. the square root of the 1/2,1/2,1/2 scattering intensity vs. $(T_N-T)^{9/2}$. The Néel temperature was evaluated by the maximum of the critical diffuse scattering. A sharp crossover from the critical power law to the $T^{9/2}$ power law can be noticed. This event clearly indicates the limit of the critical range.

A precise verification of $\beta=4/11$ was not possible with our NiO single crystal because of rather large diffuse scattering intensities and difficulties in their correct subtraction. However, restricting to the choice between $\beta=1/2$ and $\beta=4/11$ a clear decision in favour of 4/11 can be made. We therefore consider the empirical rule as further confirmed that in isotropic (cubic) magnets with an integer spin the conjugated (critical) exponents are $\varepsilon=9/2$ and $\beta=4/11$ but for half-integer spin they are $\varepsilon=2$ and $\beta=0.5$.

Na$_2$MnF$_5$ belongs to the class of quasi one-dimensional magnetic chain compounds. Due to a small but finite inter-chain exchange the compound exhibits long-range antiferromagnetic order at low temperatures. The magnetic structure was first investigated by powder neutron diffraction [1]. A purely antiferromagnetic spin arrangement characterized by a propagation vector of $k=(0, \frac{1}{2}, 0)$ with ordered magnetic moments of $\mu_{\text{ord}}=3.3 \ \mu_B$ being aligned along the crystallographic $c$-axis has been proposed [1]. However, susceptibility measurements on single crystalline samples indicated an additional canting of the spins by approximately $5^\circ$ away from the chain direction, in agreement with preliminary single crystal neutron diffraction experiments. A complex $B$-$T$ phase diagram has been established by field dependent magnetic measurements. Within the 3D antiferromagnetically ordered state of Na$_2$MnF$_5$ at low temperatures, a spin flop transition is induced by an external magnetic field of approx. 3 T resulting in a weak ferromagnetic high-field phase.

We have started to investigate the magnetic ordering process and the $B$-$T$ phase diagram of Na$_2$MnF$_5$ by single crystal neutron diffraction experiments on the flat-cone diffractometer E2 at the HMI, Berlin (compare with experimental reports PHY-01-1011 and PHY-01-1012 published in the BENSC EXPERIMENTAL REPORTS 2001). In the present experiment, we completed this study by establishing in detail the field dependence of the magnetic structure of Na$_2$MnF$_5$ at various temperatures which remained previously unexplored. Exemplarily, we show the $(h, k, 0)$ reciprocal lattice plane of Na$_2$MnF$_5$ at $T=25$ K and $T=1.6$ K. At $T=25$ K, within the quasi 1D state of Na$_2$MnF$_5$, vertical lines of strong diffuse scattering reflect magnetic fluctuations along the chains. At $T=1.6$ K, within the magnetically ordered state, these lines of diffuse scattering become bent due to magnetic excitations with a well defined dispersion relation [2]. A significant spin canting away from the chain direction could be confirmed. This additional magnetic component becomes reversed upon the application of an external magnetic field and therefore is at the origin of the field induced spin flop transition. The results are currently being published.

![Fig. 1 Reciprocal (h, k, 0) plane of Na$_2$MnF$_5$ at T=25 K (upper panel) and T=1.6 K(lower panel).](image)

The hexagonal Tb$_2$PdSi$_3$ compound show complex magnetic behavior [1]. In order to investigate the microscopic properties of the different magnetic phases we performed a neutron diffraction experiment on E2 using a Tb$_2$PdSi$_3$ single crystal of excellent quality. We utilised the dilution stick DS2 for temperatures down to 50 mK and the vertical magnet VM2 for applying magnetic fields up to 6.5 T. All data was obtained using the PG monochromator (\(\lambda = 2.39\) Å; additional PG filters).

The single crystal was oriented within the scattering plane \((H, H, L)\). The magnetic field was applied in the ab-basal plane in direction perpendicular to a axis which represent the magnetic hard direction in the basal plane.

From a previous experiment on the same crystal we determined the propagation vector \((1/2, 1/2, 1/16)\) for the zero field magnetic structure at \(T = 2\) K [2]. Additionally, diffuse magnetic scattering at positions beside the antiferromagnetic satellites occurs.

In the first part of the here reported neutron scattering experiment we found no phase transition between 50 mK and 2 K. The diffuse magnetic scattering shows also no qualitative changes. Applying a magnetic field we observed modifications of the antiferromagnetic satellites as well as strong changes in the diffuse magnetic scattering. Both phenomena could be measured simultaneously due to the excellent signal-background ratio and good resolution of the instrument E2.

At \(T = 2\) K and increasing magnetic field, reflections at \((1/2, 1/2, n/16)\) \((n = \text{odd integer})\) could be observed up to 3.0 T. Additional antiferromagnetic satellites at \((1/2, 1/2, m/4)\) \((m = \text{integer})\) occur from 0.1 T up to the maximum applied field of 6.5 T (marked by arrows in Fig. 1b). The intensity at positions of nuclear reflections increases from \(\mu_0H = 0.1\) T continuously corresponding to ferromagnetic ordering. However, the intensity of all reflections decreases slightly due to a misalignment forced by magnetic fields above 5 T.

At the positions of the diffuse scattered intensity a transition from short to long-range magnetic order was observed for magnetic fields \(\mu_0H = 1.5 \ldots 2.5\) T (see arrows in Fig. 1a). The correlation length is anisotropic with values of about 500 Å in the \(a\) direction and about 100 Å in \(c\) direction, respectively. The new antiferromagnetic satellites change their positions at \(\mu_0H = 2.5\) T. Above 5 T their intensity decreases and is below the detection limit at 6.5 T.

Surprisingly, after decreasing the field from 6.5 T to zero we still observed remaining ferromagnetic components and new antiferromagnetic satellites whose positions did not match exactly the positions of the previously described antiferromagnetic satellites. After applying a magnetic field of 0.5 T the diffraction pattern is the same as starting from the virgin state in zero field.

Fig. 1: Neutron diffraction pattern (contour plot) of Tb$_2$PdSi$_3$ single crystal for two characteristic magnetic fields at a temperature \(T = 2\) K.

Nd_{1-x}Pb_xMnO_3 belongs to the perovskitic mixed-valent manganites of type R_{1-x}A_xMnO_3 (R is La or a rare earth and A a divalent ion) displaying metallic ferromagnetism and colossal magnetoresistance (CMR) in the doping-range 0.2 < x = 0.5. In such manganite systems, the magnetic moments of R-ions may act as probe for the magnetism of the Mn-O-subsystem, or they may undergo an ordering transition at lower temperature. As shown in Fig. 1 the particular system Nd_{0.7}Pb_{0.3}MnO_3, which orders ferromagnetically at T_c = 150 K, displays below 50 K an anomaly which may indicate the onset of Nd-ordering with ferrimagnetic component or a spin-canting. Specific heat data reveal a low-temperature anomaly, similar to a Schottky anomaly, which may be due to single Nd-ions or signals a further magnetic transition.

To investigate the magnetic structure, neutron diffraction for a Nd_{0.7}Pb_{0.3}MnO_3 single crystal grown at IISc Bangalore [1] was performed on the E2-flat-cone instrument using neutron-wavelength ?=2.39 Å. Based on powder data for Nd_{0.7}Pb_{0.3}MnO_3-material and room-temperature x-ray Laue-diffraction of the crystal itself, it had been indexed in space-group Pbnm with (a=5.47, b=5.47 and c=7.75 Å) and pre-oriented for mapping the (hk0)-reciprocal plane. Superlattice Bragg-peaks in a square pattern (Fig. 2) and missing Bragg-peaks in the (hk1)-plane, expected for Pbmn-symmetry, indicate another modification of the ideal perovskite structure in this crystal (space group P4/mmm) with a=b=7.78, c=3.48 Å and a=ß=?=90°, i.e. a structure with low distortions away from ideal cubic structure but with a cell-doubling as already observed for Nd_{1-x}Pb_xMnO_3 crystals of compositions x=0.2 and 0.5 [1,2].

Fig. 1: Nd_{0.7}Pb_{0.3}MnO_3: (left) magnetization M vs. T after field-cooling (FC) and zero-field-cooling (ZFC) in 100 Oe; (right) specific-heat C vs. T of Nd_{0.7}Pb_{0.3}MnO_3. Inset shows Schottky-like low-temperature anomaly in C/T vs T.

For a choice of (hk0)-Bragg-peaks the temperature evolution was measured (example in Fig. 3), which demonstrates a change of the ordered spin-structure taking place at low temperature T = 20 K. The analysis of these data will require at least some auxiliary data from ongoing powder diffraction experiments.

Fig. 2: (hk0) plane of Nd_{0.7}Pb_{0.3}MnO_3 single crystal measured with E2 instrument at T=1.5 K (indexed according to space-group P4/mmm a=b=7.78 Å).

Fig. 3: Integral intensity of (020) Bragg-peak vs. temperature

EXPERIMENTAL REPORT

Hyperfine induced nuclear polarization in Nd

Proposal N° PHY-01-1179
Instrument E2
Local Contact Dietmer Hohlwein

Date(s) of Experiment
9-15 September, 2002

Principal Proposer: Tapan Chatterji, ILL, Grenoble
Experimental Team: Dietmer Hohlwein, BENSC
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Among the light rare earth elements the magnetic structure of Nd has been intensely investigated for several decades [1]. However the observed neutron diffraction pattern of Nd at different temperatures are so complex that a complete understanding of the magnetic structure of Nd has not yet been achieved. Nd has a double hexagonal closed packed (dhcp) crystal structure with the stacking ABAC. In the dhcp crystal structure atoms on the A-layer have neighbour distribution typical of the cubic structure whereas those on B and C-layers have hexagonal nearest neighbour environments. The existence of two kinds of sites (cubic and hexagonal) with different local symmetry is a further complication. Nd orders at $T_N = 19.9\text{ K}$ with a longitudinal sine-wave amplitude-modulated phase on the hexagonal site. The modulation vector lies in the basal plane in the b direction and is incommensurate with the crystal structure. The magnetic moments also lie in the basal plane. The moments on the neighbouring hexagonal sites are ordered antiferromagnetically. Simultaneously a c-axis moment (plus a small component in the basal plane) with the same wave vector is induced on the cubic sites by the anisotropic two-ion coupling. As the temperature is lowered further a first-order transition to a double-$k$ structure takes place. At $T = 8.2\text{ K}$ the planar components of the moments on the cubic sites begin to order. Several phase transitions occur in Nd as the temperature is lowered further and finally at the lowest temperature a complex quadruple-$k$ structure is realized.

Our inelastic neutron scattering investigation [2] on the back scattering neutron spectrometer IN16 of the Institute Laue-Langevin suggested the possibility of observing hyperfine induced nuclear polarisation in Nd at millikelvin temperature. The scattering process from nuclear magnetic moments is basically different from the dipolar scattering from electronic moments. So we expect appearance of extra reflections in Nd at millikelvin temperature. From the strong nuclear polarisation peak observed in Nd$_2$CuO$_4$ [3] we know that $b^+ - b$ for $^{143}$Nd and $^{145}$Nd, which have natural abundances of only 12.18 and 8.29% respectively, must be very favourable. We have measured the intensities in the hk0 reciprocal layer of Nd on the flat-cone diffractometer E2 of the Berlin Neutron Scattering Center (BENSC) at millikelvin temperatures. We have not detected any new reflection corresponding to nuclear polarisation effect. However, the intensities of the magnetis satellite reflections which become saturated at $T = 1.5\text{ K}$ starts increasing again at about $T = 200\text{ mK}$. This increase in intensity follows approximately the square of the Brillouin function corresponding to the Nd nuclear spin $I = 7/2$ of the $^{143}$Nd and $^{145}$Nd isotopes. The results are very similar to that observed by us previously in Nd$_2$CuO$_4$ [3]. We interpret this increase in intensity of the satellite reflection to be due to the hyperfine induced nuclear polarisation of the Nd nuclear moment $I = 7/2$.

![Graph](image)

Fig. 1 – Temperature variation of the intensity of the satellite reflection corresponding to one of the propagation vectors of the quadruple-$k$ structure of Nd at millikelvin temperatures. The continuous curve is just a guide to the eye.

References:
The alkali-dysprosium double tungstates belong to the class of magneto-elastics with interrelation between magnetic and elastic ordering. The compounds with formula ADy(WO4)2 (ADyW), where A is alkali ion, are characterised by low-symmetry and by low-dimensionality. Scientific interest is mainly connected with structural phase transition (SPT) of the cooperative Jahn-Teller effect (CJTE) type which occurs in them at several kelvins region and with the magnetic ordering at subkelvins region.

The SPT of the CJTE type from paraelastic to antiferroelastic state were observed at 6.38K, 4.9K and 9.5K, ~29K for KDyW, RbDyW and CsDyW, respectively, in thermodynamical, magnetic and spectroscopic experiments and lately also in neutron scaterring experiment (PHY-01-899 for KDyW). The magnetic phase transitions take place at 0.60K, 0.82K and 1.33K (K-, Rb-, CsDyW, respectively). The neutron diffraction studies are expected to give information on the crystalline and magnetic structure.

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The neutron scattering experiment, in the frame of the project PHY-01-1180 was directed to determine the structure of the magnetic state of the KDy(WO4)2. The neutron scattering measurements were made on powdered sample in the CD3OD (deuterized methanol) because of the problem with temperature stabilizing and sorptive properties of the powder of the “pure” potassium dysprosium double tungstate.

The set of nominally selected temperatures was following: 35, 200, 400, 500, 550, 600, 700 and 1630 mK. The neutron scattering spectra in paramagnetic state (1.63K) are composed from several lines with the first, most intensive reflex at about 22.6 degrees (for wavelength 2.396A; mono.: graphit). Background of the spectra is enough high. It is due to the high neutron absorption of dysprosium ions in the sample. It is a main reason of not small experimental errors.

The new Bragg reflexes were found in subkelvin temperature region. The low angle reflexes are at about 17.2, 20.2, 21.6, 24.5, 26.2, 27.8, 29.5o for example – see Figure 1. The intensity of reflexes is nearly constant below 500mK, decreases with further temperature increase and diminishes for 700mK – Figure 2. This temperature dependence clearly indicates 609±30mK as temperature of the magnetic phase transition what was confirmed in specific heat [1] and magnetic susceptibility experiments made earlier [2]. We expect to solve the magnetic structure of (probably) antiferromagnetic or more complex state after the full analysis of the experimental data.


This work was partially support by Polish State Committee on Science (KBN) - project No.2P03B14118.
In recent years many publications have been focused on investigations of Heusler-type Ni$_2$MnGa ferromagnetic alloys. In these materials an enormous strain can be induced by a magnetic field, which makes them very attractive for applications as mechanical actuators. The reversible magnetic field induced strain is denoted as magnetic shape memory effect (MSME). It is caused by the preferential growth of martensitic twin variants favorably oriented in relation to the applied magnetic field.

Intensity distributions in the martensitic phase of a Ni$_2$MnGa alloy were measured below phase transformation temperature which is close to room temperature. In cooperation with N. Glavatska from Institute for Metal Physics, Kiev, we shared a single crystal for our investigations on the Flat-Cone Diffractometer E2 using a wavelength of 2.39 Å. Magnetic field was applied in the direction of easy magnetisation.

Fig. 1: Intensity distribution within reciprocal space (hk0) at T = 244 K and H = 0

The magnetic field was changed in several steps. First from 0 - 1.1 Tesla and then back to zero Tesla. In the following measurement the external magnetic field was increased from 1.3 up to 3.0 Tesla and afterwards decreased to 0 Tesla.

Fig. 2: Variation of reflex intensity in the martensite phase with magnetic field

The results show that a magnetic field applied in the direction of easy magnetisation induces crystallographic texture that is stable in zero field. The strain caused by the applied magnetic field increases continuously while applying magnetic field in correlation with the change of the crystallographic structure.

References:

The paramagnetic rare earth metal holmium reveals a complex magnetic structure behaviour below its Néel temperature of $T_N \approx 133$ K. Below this magnetic ordering temperature the structure is reported as a basal plane spiral in which the magnetic moments are confined to the ferromagnetic planes. But from plane to plane the orientation of the magnetic moments is slightly rotated, producing an incommensurate propagation vector and turns satellite reflections along the reciprocal $c^*$-axis around the nuclear bragg peaks. (Fig. 1, Fig. 2).

We investigated a holmium single crystal in a temperature range from 1,6 to 154 K. The experiment was carried out at the flat-cone diffractometer E2 using the pyrolytic graphite monochromator with wavelength $\lambda = 2,369$ Å.

References:


Fig. 1: Satellite reflections along the reciprocal $c^*$-axis below $T_N$ at $T = 1,6$ K around $O_{\text{Sample}}=115,425$

Fig. 2: Diffuse scattering at $T = 133,1$ K $> T_N$ within the paramagnetic regime
We investigated the lattice and magnetic properties of the La$_{1-x}$Sr$_x$MnO$_3$ perovskites using the flat-cone diffractometer E2. In the compound LaMnO$_3$ ($x=0$) we found six even distributed twin domains of the orthorhombic structure (Pbmn $a=5.56$ Å, $b=5.53$ Å, $c=7.68$ Å). The antiferromagnetic phase transition temperature to the paramagnetic phase was determined as $T_N=139.5$ K. The intensity of the antiferromagnetic peak was fitted by the phenomenological formula $I(T) = C (1 - (T/T_N)^d)^e \sim M^2$ [1] with $d = 2.1$ and $e = 0.46 = 2\beta$ (fig. 1).

As continuation of the measurements of complete reciprocal layers [2] for analysing the magnetic diffuse neutron distributions over a large temperature range was supplemented by restricted area measurement near the phase transition (fig. 2). The diffuse scattering was fitted with the software TVtueb (R. Schneider and J.-U. Hoffmann) by an extended mean field theory. We determined the exchange parameter along the c-axis $J_c = -4.31$ K. The exchange parameter $J_{ab}$ varied with temperature without renormalization from $J_{ab}(150K) = 6.9$ K to $J_{ab}(200K) = 9.2$ K. The resultant microscopic inverse susceptibility at the antiferromagnetic peak position (001) is plotted in figure 3.

Hexagonal manganites REMnO$_3$, space group $P6_3cm$, consist of layers of 2D connected distorted MnO$_5$ bipyramids, separated by distorted layers of RE, leading to frustrated Mn$^{3+}$-O$^-$-Mn$^{3+}$ in plane (superexchange) and frustrated Mn$^{3+}$-O$^-$-O$^-$-Mn$^{3+}$ inter plane exchange paths (super-superexchange). Below $T_N$ this leads to the typical 120° in plane spin arrangement of a XY-antiferromagnet, the inter plane interaction is described by a 6$_3$' axis, but can be changed by rare earth ordering to a 6 axis [1,2]. Below $T_N$ the reciprocal susceptibility gained by SQUID magnetization data of YMnO$_3$ showed an unusual strong deviation from Curie Weiss law up to room temperature (not shown here), indicating magnetic correlations far above $T_N$.

As the Mermin-Wagner theorem forbids 2D long range order [3] and superexchange is usually far stronger than super-superexchange, 2D magnetic short range order within the $ab$-plane had to be expected in hexagonal manganites and was confirmed for RE=Ho,Y recently [4,5].

Indeed, single crystal diffraction data of the $h0l$-plane at $T=78$ K of ErMnO$_3$, Fig.1, reveal streaks comparable to Weissenberg images of REMnO$_3$, RE=Ho,Y, see also [6].

EXPERIMENTAL REPORT
Spin canting in hexagonal manganites due to rare earth ordering

Proposal No. EF
Instrument E2
Local Contact D. Hohlwein

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Due to the position of Mn near (1/3,0,0) a magnetic structure determination in the structure class of hexagonal manganites REMnO$_3$ is problematic: two different magnetic structures, e.g. $P6_3cm$ and $P6_3'cm'$ are nearly homometric [1]. For HoMnO$_3$ we were able to solve this problem by a development of a new statistical qualifier and we detected a rare earth induced low temperature phase transition between precisely the nearly homometric magnetic space groups $P6_3cm$ and $P6_3'cm'$ by neutron powder diffraction recently [2]. Furthermore neutron single crystal diffraction revealed hints of a small distortion of the magnetic Mn lattice due to a re-ordering of the Ho(2a) position at lower temperatures [3], thus we proposed a symmetry reduction, as a canting of the Mn lattice and ordering in Ho(2a) is forbidden in $P6_3cm$.

New low temperature neutron powder diffraction data of HoMnO$_3$ (50mK<T<800mK) confirmed the results of the single crystal data: a small but significant distortion of the magnetic spacegroup $P6_3cm$ to $P3$, due to a canting of the Mn lattice of about 4°, accompanied by a reordering of the magnetic Ho(2a) positions was detected, Fig. 1.

Attempts to induce the spin canting of the Mn lattice at higher temperatures via a dilution of the superexchange dominated Mn lattice by double exchange in $Y_{1-x}Ca_xMnO_3$, $x = 0.01, 0.02, 0.04, 0.08$, remained unsuccessful, a second nuclear phase had to be refined, while there were no significant changes of the magnetic symmetry detectable compared to YMnO$_3$ (not shown here).


Fig. 1. Low temperature data of HoMnO$_3$ reveals a canting of the Mn lattice and a small but significant magnetic moment of Ho(2a).
The influence of the rare earth ordering process on the magnetic Mn lattice in hexagonal manganites REMnO₃ provides a good possibility for the analysis of the competition of magnetic exchange interactions. E.g. for RE=Ho ($\mu=10.6 \, \mu_B$), a precursor ordering accompanies a magnetic phase transition of $P6_3/c'm$ to $P6_3/c'm'$ [1], while Ho ordering leads to a first order phase transition and reduces the symmetry further to $P3$ [2,3]. Thus a similar behaviour can be assumed for RE=Er ($\mu=9.58 \, \mu_B$) at lower temperatures. Indeed the integrated intensity of single crystal diffraction data, (100), Fig.1, shows a precursor ordering of Er for 70K>T>10K, while contrary to RE=Ho, this does not lead to a change of magnetic symmetry as can be seen in the regular gradient of (101), cf [4]. Comparable to RE=Ho, Er ordering leads to a first order phase transition (100), Fig.1, distorting the Mn lattice (001), Fig.2, accompanied by a jump of intensity of (301), Fig.2. Tentatively we propose a canting of the Mn lattice for the full temperature range $T<T_N$ (001) due to RE precursor ordering and a low temperature phase transition at 1.8K (301) due to RE ordering in ErMnO₃.

[2] Th. Lonkai et al., BENSC Experimental reports 2001, PHY-01-0068_1
EXPERIMENTAL REPORT
Changes in the Magnetic Structure of $Y_{0.1}Ca_{0.9}MnO_3$ by Gallium Doping

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In previous measurements [1,2] we studied the influence of iron doping on the magnetic structure of $Y_{0.1}Ca_{0.9}Fe_xMn_{1-x}O_3$. In this measurement we studied for comparison the effect of Gallium doping on the magnetic structure.

The magnetic structure of the Mn/Ga-sub-lattice of $Y_{0.1}Ca_{0.9}Ga_xMn_{1-x}O_3$ is for $x=0$ that of a canted antiferromagnet, which consist of three components $A_z$, $C_x$, and $F_y$. Gallium doping affects like iron all of these components.

Data were collected at the E2 instrument with wavelengths 1.21 and 2.39 Å as a function of temperature for the compounds $Y_{0.1}Ca_{0.9}Ga_xMn_{1-x}O_3$ with $x = 0.04$ and 0.08.

The temperature dependence of the components of the magnetic moment is shown in Figs. 1,2,3 by plotting the intensities of specific reflections.

Unlike the iron doped sample there is a clear shift in the phase transition temperature for almost all components. Only for the $F_y$ component and for high concentrations of Gallium (8 percent) for the $C_x$ component is the intensity significantly reduced.

The magnetic moments determined by simultaneous Rietveld refinement of neutron and x-ray data will be compared with the electrical conductivity of the samples.

Magnetic Structures in iron doped $Y_{0.1}Ca_{0.9}MnO_3$

Changes of the magnetic structure in $Y_{0.1}Ca_{0.9}MnO_3$ by iron doping.

Fig.1: Intensity change connected with the $C_x$ component

Fig.2: Intensity change connected with the $A_z$ component

Fig.3: Intensity change connected with the $F_y$ component
In previous measurements [1] we studied the influence of iron doping on the magnetic structure of \( \text{Y}_{0.1}\text{Ca}_{0.9}\text{Fe}_{x}\text{Mn}_{1-x}\text{O}_3 \). In this measurement we studied additional concentrations of iron. The magnetic structure of the Mn/Ga-sublattice of \( \text{Y}_{0.1}\text{Ca}_{0.9}\text{Fe}_{x}\text{Mn}_{1-x}\text{O}_3 \) is for \( x=0 \) that of a canted antiferromagnet, which consist of three components \( A_z \), \( C_x \) and \( F_y \). Iron doping has an effect on all of these components.

Data were collected at the E2 instrument with wavelengths 1.21 and 2.39 Å as a function of temperature for the compounds \( \text{Y}_{0.1}\text{Ca}_{0.9}\text{Fe}_{x}\text{Mn}_{1-x}\text{O}_3 \) for \( x = 0, 0.005, 0.01, 0.04 \) and 0.08.

The temperature dependence of the components of the magnetic moment is shown in Figs. 1, 2, 3 by plotting the intensities of specific reflections. The 0.08 concentration is only included in the plot of the \( A_z \) component, because the reflections corresponding to \( C_x \) and \( F_y \) were lost in the background intensity.

[1] BENSC Experimental Report 2001, EF/E2 Magnetic Structures in iron doped \( \text{Y}_{0.1}\text{Ca}_{0.9}\text{MnO}_3 \)
Magnetic interaction parameters in crystals can be deduced from magnon dispersion curves determined by neutron inelastic scattering. But this can be done only in the long-ranged ordered phase at lower temperature. At higher temperature, above the magnetic phase transition, the interaction parameters can considerably vary due to structural change or phase transition. But also in the case of very small structural changes, it is important to know the size of magnetic fluctuations or short-range order to characterize the paramagnetic phase as a function of temperature. In the past, we have shown for the model system MnF$_2$, that the mean-field or RPA (random phase approximation) theory has to be extended by an Onsager parameter [1].

MnO is a frustrated cubic (fcc) antiferromagnet with a first order magnetic phase transition at $T_N = 118$ K. At the same temperature starts a cubic-to-rhombohedral lattice distortion. The magnetic structure is of type 2 and consists of ferromagnetic sheets parallel to the (111) plane with the moment directions within the plane and directions antiparallel in adjacent sheets.

A single crystal of about $0.5$ cm$^3$ has been mounted with a <110> axis vertical at the E2 instrument. The diffuse scattering has been recorded in complete (hhl) layers with wavelength of 1.21 Å ($E_0 = 56$ meV). A picture of the diffuse scattering distribution can be seen on the cover page of the BENSC Reports 2002.

To apply a generalized mean-field theory, we have to check that the quasi-static approximation ($E_0 >> ?E$) is fulfilled. For this purpose we have measured the energy width of the diffuse scattering at several points of the Brillouin zone. This has been done with constant-Q scans in the inelastic mode of E2 [2]. Some energy widths (fwhm of Lorentzians) are shown in Fig. 1. At higher temperature the energy transfer $?E$ goes up to $\pm 4.5$ meV. This value is still small compared to the incoming energy of $E_0 = 56$ meV.

The diffuse integral scattering was first fitted with fixed $J_1 = -4.8$ K and $J_2 = -4.2$ K values ( from magnon measurements [3]) and a parameter $?T$ for the Onsager field. The Onsager parameter can also be calculated by a Fourier sum of the diffuse scattering in a Brillouin zone. The good agreement between $?T$ determined in two ways is shown in Fig. 2. This result demonstrates that the mean-field theory extended by an Onsager term describes well the paramagnetic phase. Finally we have fitted $J_1$ and $J_2$ directly to the data, calculating the Onsager term for each refinement step. The result for 140 K was $J_1 = -4.70$ K and $J_2 = -3.60$ K, not very different to the values from magnon measurements (given above) determined at 4 K.

Fig. 1 and 2:

Over the years remained the details of the magnetic behavior of UCuGe an unresolved task. Some of the studies (see [1]) claimed that antiferromagnetic ordering exist below 58 K, some of them reporten spin glass reentrant behavior. Recently, even the correctness of the crystal structure has been brought in question. For the presented study we have used a large good quality single crystal grown by a Czochralski method.

We have collected using the E4 diffractometer in zero field two sets of reflections, at 70 K and at 2 K (for each of two basic crystal orientations) and followed intensity of few reflections as a function of temperature. In addition we scanned the l=0 and l= 1/2 reciprocal planes at temperatures well above and below the magnetic phase transition using the E2 diffractometer.

Analysis of the 70 K unique data set, shows that all the reflection can be indexed using the hexagonal symmetry with lattice parameters a = 418.4 pm and c = 379.5 pm. These values are in good agreement with literature [1]. However, by analysis of the integrated intensities we came to conclusion that the crystal structure of the CeCd$_2$ type ($P\overline{3}m1$ space group) reported in the literature is questionable. Equivalently good agreements were obtained for few other crystal structures that include the SrPtSb type structure with the $P\bar{6}m2$ space group. The two structures differ in the number of symmetry operations depending whether there is (or not) a preferential occupation of Cu and Ge atoms. We presume that the SrPtSb type structure is correct. In this type U atoms occupy the (1a), Cu atoms the (1d) and Ge atoms the (1f) site.

As the temperature goes below the magnetic phase transition of about 50 K, new intensity due to magnetic order occur. All new reflections can be indexed using two propagation vectors: $q_1 = (1/2, 0, 0)$, and $q_2 = (1/2, 0, 1/2)$ together with hexagonal equivalents. On top of it, intensity could be discerned on top of few nuclear reflections.

**Fig. 1:** Temperature dependence of one magnetic and one nuclear reflection of UCuGe suggesting non-collinear arrangement of U moments.

Analysis of the magnetic structure turned out to be rather difficult. At the moment the most probable structure consists from ferromagnetic chains of moments oriented along the a axis and coupled within the hexagonal plane antiferronagnetically to the neighbouring chain. The next layer along the c axis consists from moments that are turned by 90 degrees with respect to the original one. The magnitude of U moments is critically depends on the number of symmetry operations of the crystal structure. For the SrPtSb type of structure it amounts to 1.4 $\mu_B$.

**Reference**

Most of the uranium silicides UT$_2$Si$_2$ ($T$ transition metal) crystallize in the tetragonal structure (ThCr$_2$Si$_2$-type) with the space group $I4/mmm$, among them UNi$_2$Si$_2$ and UPd$_2$Si$_2$, as well as the pseudoternary U(Ni$_{1-x}$Pd$_x$)$_2$Si$_2$ system ($0 \leq x \leq 1$). Owing to similarity of lattice parameters the Ni – Pd substitution is possible in the whole concentration range. Both border compounds order antiferromagnetically (AF) below the Néel temperatures $T_N = 125$ K and 133 K, respectively [1]. All their magnetic structures are formed by ferromagnetic basal planes with $U$ magnetic moments $\mu_U \approx 2.2 \mu_B$ parallel to the c-axis [1,2,3,4]. The individual magnetic phases depend on various stacking or modulation of these planes along the c-axis, described by various propagation vectors expressed generally as $q = (0, 0, q_z)$.

In UNi$_2$Si$_2$ the ground-state phase AF3 is an uncompensated antiferromagnet (UAF) with the $++--$ stacking of the basal planes ($q_z = 2/3$). In UPd$_2$Si$_2$ the ground-state phase is just the AF2 structure with $+-+-$ stacking.

In UNi$_2$Si$_2$ was found that the formation of the UAF phase is promoted in high magnetic fields parallel to the c-axis [4] or in elevated pressures [5]. This caused natural question about the concentration stability of the UAF phase in U(Ni$_{1-x}$Pd$_x$)$_2$Si$_2$ system. We tried to find the critical concentration of Pd, where the UAF ground state converts into the AF2. The pilot powder neutron diffraction study had shown that this concentration should be lower than $x = 0.25$ [6].

To solve that we have grown a series of single crystals with different Pd concentration. From the bulk measurements results we selected 2 crystals with $x = 0.09$ an 0.135 for a detailed neutron diffraction study on E4 in 6T horizontal cryomagnet.

In the $x = 0.135$ crystal the ground state is the AF2-phase as in pure UPd$_2$Si$_2$ and the magnetic field of at least 0.25 T is necessary to produce the UAF structure. On the other hand, the co-existence of AF2 and UAF phases was found as a ground state of the $x = 0.09$ crystal. Here, with the increasing magnetic field the intensity of the AF2 reflections irreversibly drops down revealing the rapid diminishing of the AF2 volume fraction.

All the available data enabled us to construct magnetic phase diagrams for both samples (see Fig. 1) which at temperatures above ~ 60 K strongly resemble that of pure UNi$_2$Si$_2$ [1,4].

References:

**Fig. 1:** Magnetic phase diagrams of U(Ni$_{1-x}$Pd$_x$)$_2$Si$_2$ for $x = 0.09$ and 0.135, respectively, in moderate magnetic fields parallel to the c-axis.
Introduction

CePtSn crystallizes in the orthorhombic TiNiSi-type structure with the space group $Pnma$. It is characterized as metallic Kondo compound and it orders antiferromagnetically (AF) at $T_N = 7.5$ K. In the ordered region CePtSn exhibits another order-to-order magnetic phase transition at $T_{M=5}$ K in zero magnetic field. Magnetic properties of CePtSn are highly anisotropic. In the previous neutron diffraction experiments two magnetic propagation vectors were found at 2 K: $\vec{q}_1 = (0, 0.470, 0)$ and $\vec{q}_2 = (0, 0.428, 0)$.

The b-axis magnetoresistance at around 2 K shows a sharp drop (by more than 30%) at $B \sim 3$ T which appears to be irreversible upon field removal [1] (see solid line in Fig. 1). Just a tiny step in the magnetization was observed at the same field, but both experiments show the same behaviour - the transition is absent when sweeping the field back to zero, indicating that the "field-induced" phase persists to 0 T.

Experiment and Results

In order to investigate microscopically the GMR effect observed at 2 K we performed a neutron diffraction experiment on a single crystal of CePtSn. Since the magnetic propagation vector is parallel to the field direction for observation of GMR a horizontal magnetic field must have been used. Fig. 1 shows the field dependence of the integrated intensity of the two magnetic propagation vectors. Previously observed negative GMR is clearly connected with the $\vec{q}_2$-related magnetic reflection which disappears also at about 3 T. Since E4 together with HM1 cryomagnet gives access to a very limited $\vec{q}$-space we could study only the magnetic reflections originating from the primary beam. Recent study of other magnetic peaks shows that the loss of intensity is not connected with spin reorientation but most likely with redistribution of magnetic domains with different $\vec{q}$. We conclude that there are two types of AF domains in the sample that have very similar magnetic properties but very different resistivity. Application of magnetic field favors the $\vec{q}_1$-related domains. Such a process is irreversible upon field removal and the sample can come back to its initial state only after being heated up above 3 K.

Detailed k-scan of the $(0, -q_1, 0)$ magnetic reflection with 20’ collimator reveals splitting of the reflection. Comparison with similar k-scan over the nuclear reflection and field dependence of the magnetic reflection profile suggest that the splitting is neither an instrumental artifact nor due to crystal imperfections. It can be caused by faults in the spin-slip structure. Random occurrence of such faults in the magnetic structure could explain observed discrepancies in the results of several previous neutron diffraction experiments.

Figure 1: Field dependence of the integral intensity of the two magnetic propagation vectors as scaled to fit the magnetoresistivity data.

The recently discovered family of heavy fermion (HF) compounds: CeMIn₅ (M=Rh,Ir,Co) has been found to have a variety of ground states where superconductivity (SC) and static magnetic order can coexist. The most striking properties of this series of compounds are the high values of Tₐ (0.3K< Tₐ <2.2K) and the robustness of the SC ground state upon doping, or pressure. In those systems magnetism and SC are closely related and there is increasing experimental and theoretical evidence that AFM spin fluctuations mediate Cooper pairing and that anisotropic SC appears in the vicinity of a quantum-critical point.

CeRhIn₅ is an AFM heavy fermion (Tₐ=3.8 K) which becomes SC upon pressure (Pₐ=16-17kbar). Its magnetic structure is AFM helical structure characterised by k=(0.5,0.5,0.297). Substitution of Rh by Ir tunes the ground state to SC and for extended values of Ir doping it has been observed coexistence of AFM and SC.

The aim of this experiment was to determine if the AFM order (Tₐ=3.2K) disappears or persist when the CeRh₀.₆₅Ir₀.₃₅In₅ compound becomes SC (Tₐ=0.6K) as well as to study the evolution of the magnetic structure at the SC transition and the effect of a magnetic field on the magnetic structure. We performed a single crystal diffraction experiment at E4 using the 14.5T cryomagnet. A single crystal of CeRh₀.₆₅Ir₀.₃₅In₅ was oriented so its (hhl) was in the scattering plane.

The results of our experiment revealed that the magnetic structure of CeRh₀.₆₅Ir₀.₃₅In₅ is different from the parent compound. At 50mK we found a magnetic structure characterised by two magnetic propagation vectors: k₁=(0.5,0.5,0.29), k₂=(0.5,0.5,0.5). The temperature scan performed through Tₐ and Tₐ=0.6K (Fig.1) shows that within the error bars, the magnetic structure of this compound is not modified at Tₐ. This result is quite unexpected since Ce has only one 4f electron that contributes to the long-range magnetic order and is supposed also to be responsible for SC. In addition, the onset of the commensurate and incommensurate components appears to be at different temperatures.

The magnetic field applied in the [110] direction revealed the existence two magnetic field transitions at 0.5T and 1T (Fig.2). The effect of the magnetic field on the magnetic structure is to transform the magnetic structure to a commensurate AFM (Kc₁=(0.5,0.5,0.25)) k₂=(0.5,0.5,0.5)). The magnetic field induced transitions do not happen at the critical fields for the suppression of SC (Hc₂=2.5T). These results seem to indicate that in these compounds the static magnetic order and the SC are two independent processes.

**Fig. 1** Magnetic field dependence of the magnetic Bragg peaks in CeRh₀.₆₅Ir₀.₃₅In₅

**Fig. 2** Temperature dependence of the magnetic Bragg peaks in CeRh₀.₆₅Ir₀.₃₅In₅
Ferroelectromagnetic compounds of the composition \(REMnO_3\), with \(RE = \text{Lu, Y, Ho, Er, Tm, Yb or Sc}\) crystallize in a hexagonal structure, space group \(P6_3cm\). The compounds exhibit a ferroelectric ordering at high temperatures (above 500 K) and an antiferromagnetic ordering below about 80 K. Both transitions have been the subject of our former studies at HMI.

The rare-earth ions occupy the 2a and 4b sites; consequently any ordered magnetic moment of these ions is restricted to be parallel to the c-axis for symmetry reasons valid for \(P6_3cm\).

During our investigations of the magnetic diffraction as function of temperature, we have found that the \(RE\)-magnetic moments are aligned due to the ordering of the Mn ions at 80 K, an alignment that gradually increases upon cooling, as if the moments align due to an external magnetic field. Finally, at the lowest temperature (about 5 K) the \(RE\) moments exhibit an ordering transition as evident from e.g. our specific heat measurements. This ordering is very sensitive for external magnetic fields. In fig. 1 we show the magnetization of YbMnO\(_3\) as function of field.

A similar result was obtained for ErMnO\(_3\), where the major step is at 9000 Oe. No steps are found in TmMnO\(_3\) up to 70000 Oe.

In the present experiment on single crystals we have measured the field dependence of the (100), (103) and (104) lines (B//c-axis). The first line represents the \(RE\) alignment/ordering, while the others are mainly governed by the Mn ordering. Other diffraction lines could not be seen due to the geometry of the HMI magnet. Figure 2 and 3 show the results for Yb- and ErMnO\(_3\).

Clearly, the steps in the bulk magnetization are reproduced in the diffraction intensities. A complete disappearance of a magnetic diffraction line within an external magnetic field certifies an increase of magnetic symmetry of the \(RE\) moments. A small field dependence of the (103) and (104) lines, which leads us to believe that the Mn orientation is influenced via the \(RE\) reorientation.

The temperature dependence of the Mn ordering revealed a critical exponent for the magnetization of about 0.2 for our single crystals of Tm-, Er- and YbMnO\(_3\).
The single crystal with nominal composition Lu$_2$Fe$_{18}$ was selected for the diffraction studies with sample arrangement - b-axis $\parallel$ H (in VM2) $\parallel$ axis of rotation of diffractometer E4 $\parallel$ axis of CuBe pressure cell and c-axis $\parallel$ beam. As was expected, an incommensurate helical magnetic structure with Fe moments in the basal plane has been detected below the Néel temperature $T_N = 274$ K where the magnetic satellites with propagation vector $(0;0;\tau_z)$ have been observed down to temperature 130 K. At ambient pressure, the $\tau_z$ decreases rapidly down to zero with decreasing temperature (see Fig.1) and a length of the helix increases to infinity at a transition into ferromagnetic phase below 130 K. Application of pressure expands the range of stability of the helical phase down to the lowest temperatures. A pressure induced increase of the propagation vector indicates an increase of the negative interlayer magnetic interactions with decreasing Fe-Fe distances. These interactions are only slightly affected by temperature under pressure.

Starting from the ambient pressure measurements, we collected a set of nuclear and magnetic reflections at different external fields. An application of a critical magnetic field $H_C$ induces a transition from helical into forced ferromagnetic structure. Two interesting features of this transition were discovered. Firstly, the field above $H_C = 0.3$ T is enough to change the structure. Secondly, a disappearance of the satellites with practically unchanged value of the $\tau_z$ indicates that the transition does not proceed by the rotation of the moments in the planes. However, no evidence of a presence of a magnetic fan structure in the Lu$_2$Fe$_{17}$ has been obtained and no second order satellites were detected.

At high pressures above 0.5 GPa, the forced ferromagnetic phase is induced by magnetic field above $H_C \approx 1$ T, however, traces of the satellites exist up to 3 T (see Fig.2). This is compatible with results of pressure measurements of magnetization of the Lu$_2$Fe$_{17}$ single crystal in EMD where magnetization didn’t reach the saturation value even at external fields up to 5 T - after the transition at $H_C$. Again, the satellites disappeared at field without any change of their position (see Fig.2), i.e. with practically unchanged value of the $\tau_z$. Moreover, an intensity of the nuclear $(002)$ reflection is almost unaffected by the field at temperature 5 K in contrast to a behavior of the $(101)$ reflection which reflects the transition into forced ferromagnetic phase by a significant increase of its intensity, see below.

These phenomena and the temperature dependence of $\tau_z$ under pressure below 0.5 GPa urgently need more detailed investigations in the near future.
The interaction of magnetism and superconductivity (SC) is a significant and long-standing problem in condensed matter physics. In many strongly correlated electron systems the magnetism and SC are closely related and there is increasing experimental and theoretical evidence that antiferromagnetic (AFM) spin fluctuations mediate Cooper pairing and that anisotropic SC appears in the vicinity of a quantum-critical point. In the heavy fermion superconductors (HFS), SC and magnetism can coexist. These systems provide an opportunity to explore the interaction of magnetic and SC order parameters as a function of control parameter (pressure, magnetic field, chemical substitution).

CeCoIn₅ is a HFS (Tc=2.2K) and the substitution of Co by Rh gives rise to the development of AFM and SC ground state. In this experiment we focussed in the CeCo₀.₅Rh₀.₅In₅ compound.

The aim of this experiment was to determine the magnetic structure of the compound CeCo₀.₅Rh₀.₅In₅, to study the evolution of the magnetic structure at the SC transition and the effect of a magnetic field in order to be able to find any links that could exist between the long range magnetic order and the superconductivity.

We performed a single crystal diffraction experiment at E4 using the 14.5T cryomagnet. The CeRhIn₅ AFM parent compound has been found to have a helical magnetic structure with propagation vector (0.5,0.5,0.297), and for that reason we choose the (hhl) in the CeRh₀.₅Co₀.₅In₅ single crystal used in this experiment to be in the scattering plane.

The results of our experiment revealed that the magnetic structure of CeCo₀.₅Rh₀.₅In₅ is different from the magnetic structure of the parent compound. At 50mK we found a magnetic structure characterised by three magnetic propagation vectors $k_1=(0.5,0.5,0.303)$, $k_2=(0.5,0.5,0.402)$ and $k_3=(0.5,0.5,0.5)$. Fig.1 shows the temperature dependence of 3 magnetic Bragg peaks. The intensity of those peaks is not apparently modified at $T_C$. This result is quite unexpected since Ce has only one 4f electron that contributes to the long-range magnetic order and is supposed also to be contributing to SC.

The magnetic field applied in the [110] direction revealed the existence two magnetic field transitions at 1T and 3T (Fig.2). The effect of the magnetic field on the magnetic structure is to transform the magnetic structure to a commensurate 3D AFM with a propagation vector (0.5,0.5,0.5). Further experiments will be required to perform the full refinement of the magnetic structure.
UNiGa forms in the hexagonal ZrNiAl type of structure and orders antiferromagnetically below 40 K. There are 6 magnetic phases in UNiGa at low temperatures and in fields up to 1 T applied along the c axis. Long time ago the complete magnetic phase diagram has been determined. However, recently prepared second crystal revealed somewhat modified magnetic phase transition temperatures. Also, some doubts about the correctness of the magnetic structure with the propagation vector \( q = (0, 0, 1/3) \) have emerged. The aim of the present experiment was to determined unambiguously this magnetic structure.

Crystal has been prepared by a modified Czochralski method and heat-treated for a week at 700 K in vacuum. Neutron diffraction was performed at E4 with the wavelength of 2.44 Å. Magnetic field produced by the horizontal HM2 magnet was applied along the hexagonal c axis.

In Fig. 1 we show temperature development of reciprocal scans between 30 and 40 K in which four magnetic transitions appear. With respect to the previous crystal, the temperature region which is described by \((0 \ 0 \ 1/3)\) propagation vector is larger. On the contrary, the "1/8" phase with \( q=(0 \ 0 \ 1/8) \) and \( (0 \ 0 \ 3/8) \) is reduced. Incommensurate and the ground state AF structures are also indicated. All phases consist from ferromagnetic planes coupled in a different way along the c axis.

Macroscopic measurements show that the magnetization of the 1/3 phase is zero. This implies that three possibilities exist: a, + 0 - sequence, b, + - - sequence with two different moments (- has a half value of +) and c, sequence + - - with equal + and - , however, with AF domains that compensate for the total moment.

We can exclude possibility c, because it leads to non-zero intensity on some of the nuclear reflections. Possibilities a, and b, are hard to distinguish because the only difference is the scaling factor for all the magnetic reflections. However, it is reasonable to suppose that the moment magnitude varies with temperature smoothly. Then, its magnitude should be only slightly smaller than in the "1/8" phase. From this point of view is the a, possibility slightly preferred.

![UNiGa (h=1, k=0)](image)

Fig. 1: Temperature development of q scans measured on UNiGa single crystal.

Field dependence of several nuclear and magnetic reflections revealed in addition the existence of a strong magnetoelastic coupling which alternates the extinction. This manifests itself in existence of magnetic reflections of the \((0 \ 0 \ 1/3)\) type which should be with moments along the c axis extinct.

Reference
URhSi is reported to exhibit a ferromagnetic (F) order [1] with nearly the same Curie temperature (9.5 K) as the isostructural ferromagnetic superconductor URhGe. Application of magnetic field has been found to have profound effects in these compounds: e.g. the electrical resistivity is reduced by 40% near $T_C$.

Single crystal of URhSi has been for the first time prepared by a modified Czochralski method. The magnetization (Fig. 1) and the magnetic susceptibility $\chi(T)$ were measured by means of a SQUID magnetometer between 1.7 and 300 K in fields up to 5.5 T along the principal axes. Neutron diffraction was performed at E4 with the wavelength of 2.44 Å.

Crystal structure determination have been performed from the 15K data set which confirmed that URhSi forms in the orthorhombic TiNiSi-type of structure (space group Pnma) [1]. All the atoms occupy the 4(c) crystallographic site but with distinct position parameters. The quality of the fit was significantly improved when the occupation numbers were set as free parameters. Deficiency of Si of the order of 4-5% was detected. This is in good agreement with EPMA analysis.

Our low-temperature experimental data point to ferromagnetic order in URhSi below 10.5 K (Fig. 2). The discrepancy with respect to literature value of 9.5 K is tentatively attributed to the Si deficiency. Similar to previous powder neutron-diffraction experiments, our neutron single-crystal data are consistent with a collinear ferromagnetic ordering of U moments of 0.58 $\pm$ 0.09 $\mu_B$/U oriented along the $c$-axis.

Such a collinear structure is a little bit surprising in view of magnetization data which suggest non-zero a and b axes components (Fig. 1), however, this can be explained by a strong polarization of the conduction electrons.

No superconductivity has been detected at temperatures down to 50 mK produced by dilution refrigerator.

Reference
U$_2$Pd$_2$In crystallizes in the tetragonal structure (space group P4/mmb, \(Z=2\)) that is built of two basal plane layers alternating along the c axis. One is formed by uranium atoms only which occupy 4(h) positions and the other contains Pd atoms in 4(g) positions and In in 2(a) positions.

Bulk measurements showed antiferromagnetic ordering below 37 K in this system. At higher temperatures stronger magnetic response is found perpendicular to the c axis. At low temperatures, however, higher magnetic signal found along the c axis. Previous powder and single crystal neutron diffraction studies revealed that U magnetic moments of about 1.6 \(\mu_B\) form a non-collinear magnetic structure (Fig. 1a). U$_2$Pd$_2$In exhibits, no metamagnetic transition (MT) up to 57 T for fields applied along the c axis. For the a axis the MT is observed with increasing field at about 29 T. For the [110], the MT occurs at about 26 T. It has been proposed that these observations can be explained by modifications of the magnetic structures as shown in Fig. 1. It should be noted that this picture assumes that the U moments are confined to [110] type planes suggested by ab initio calculations.

Crystal of U$_2$Pd$_2$In has been prepared by a mineralization method and the neutron diffraction was performed at E4 with the wavelength of 2.44 Å. Magnetic field has been produced by the 14.5 T cryomagnet and field enhanced up to 17 T by the Dy pole tips. 17 T is, however, by no means sufficient to change magnetic state of U$_2$Pd$_2$In at low temperatures. However, at 33 K we have been able to produce field induced transitions with field along [110] and [100].

Our neutron studies confirm the ground state magnetic structure of U$_2$Pd$_2$In as determined from previous studies. Experiments in magnetic fields led to structures that are in agreement with theoretical predictions (albeit for low temperatures). Upon application of a magnetic field within the tetragonal basal plane, we find that U moments like to stay in the [110] type mirror planes. At 33 K, and magnetic field of 17 T applied perpendicular to the c axis merely reverses the direction of some of the moments within those mirror planes (depending on the in-plane field direction – see Fig. 1). It seems that U magnetic moments can exist only in these mirror planes. The monotonic changes of integrated intensities with field suggest that this reversal is not of a spin-flip type, but that the moments that are oriented antiparallel to the applied field are initially suppressed with field and then grow again in the opposite direction, still being in mirror planes.

**Reference**

Nd$_{2-x}$Ce$_x$CuO$_4$ (NCCO) is a high-temperature superconductor ($T_{c, \text{max}} \sim 25$K), which unlike the more widely studied compounds La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) and YBa$_2$Cu$_3$O$_y$ (YBCO), is electron instead of hole-doped. Like all the cuprate superconductors, magnetic and superconducting phases are closely related in NCCO. It exhibits an antiferromagnetic phase that is stable with respect to charge-carrier doping over a very wide range. Superconducting samples exhibit remnant static magnetism and inelastic commensurate magnetic fluctuations.

We used the two-axis fixed-energy diffractometer E4 and the 14.5 Tesla high-field magnet to examine the magnetic field dependency of the scattering at the antiferromagnetic wave-vector (1/2 1/2 0) in a single-crystal sample of Nd$_{1.82}$Ce$_{0.18}$CuO$_4$ ($T_c=20$K). The sample was mounted such that the magnetic field was perpendicular to the copper-oxygen planes. Scattering was restricted to the (H K 0) zone.

As shown in the figure, we observe a field-induced enhancement of the scattering intensity at (0.5 0.5 0) at low temperature. Although the effect is greatly reduced at higher temperatures, higher statistics data indicate that the effect is not strictly correlated with the superconducting transition temperature.

The low-temperature magnetic field dependence of the scattering at (0.5 0.5 0) (shown below) indicates that the enhancement onsets at low fields. Loss of intensity at higher fields indicates a possible two-component nature to the scattering. This would be consistent with the zero-field magnetic structure of NCCO. Antiferromagnetic ordering of the copper atoms is known to induce a neodymium magnetic moment for temperatures below $\sim 30$ K. Field-dependence of the scattering at the $(1 1 0)$ structural reflection shows a $\sim H^2$ increase in intensity resulting from the increasing ferromagnetic polarization of the neodymium moments along the field direction.

The complex interplay between the copper and neodymium magnetic sublattices makes interpretation of possible competing effects difficult. A clear field-induced enhancement of scattering at the antiferromagnetic wave-vector has been observed, but the origin of the effect remains unclear. The high-field capabilities of BENSC are needed in order to access the complete evolution of the magnetic structure. However, this places constrictions on the sample size that require long counting times. Further experiments to more fully investigate the phenomenon as a function of field, temperature and doping are required.
It is well known that the sensitivity to magnetic signal can be greatly improved using neutron beam that is polarized. However, on the other hand, this technique is by far more delicate, in particular, guiding field that keeps the polarization of neutrons should be provided.

The aim of this experiment was three-fold: 1, to check whether the implementation of the new shielding box at E4 did not hampered the polarization option at E4, 2, to check whether it is possible to use the symmetric-field cryomagnet VM1 for polarization experiments and 3, to observe a diamagnetic signal from Bi single crystal.

The first question can be answered as follows: if the polarizing bender is placed after the shielding block and guiding field are provided the whole path from the bender to the analyzing bender, the polarization degree reaches 94 %, a value that is rather good. However, when the bender is placed inside the neutron channel, i.e. before the shielding box that does not contain any guiding magnetic field, the polarization degree drops to about 70 %. From this follows that guiding field has to be implemented to this box.

To answer the second question we made a series of experiments with different position of the flipper with respect to permanent magnets generating guiding fields, shielding box and the VM1 cryomagnet with various magnetic fields. The results can be summarized as follows: With no magnetic field in VM1 (with only remanent field present) and in configuration similar to that one in the first part (bender inside the channel), the polarization drops further to 32%. However, with non-zero field that generates stray field outside the cryomagnet of the same direction as is present in the polarizing benders (i.e. acting as the guiding field), the polarization degree can be increased up to 50 %. Disadvantage is that at each field one has to use different current through the compensating coil.

A better solution is to place flipper inside the soft iron joke that shields the flipper from the stray field and put it inside the shielding box. In such a way, polarization degree of 74% can be achieved at 14.5 T (Fig. 1 shows the scans through the one of the Bragg reflections of the Heusler crystal with no analyzer). However, in this case only part of the beam comparing the zero-field experiment has been used (above the midpoint of the split-pair coil). From this follows that polarization experiments using symmetric VM1 cryomagnet are certainly possible.

In the observation of a diamagnetic signal of Bi we were also successful. The flipping ratio of the (003) reflection measured for 2 hours at 14.5 T amounts to 1.014 ± 0.003 and has the same sign as in the case of the Heusler crystal (the interaction in the Heusler crystal is negative and has therefore the same sign as in the case of a diamagnetic material as Bi). At 1 T it is reduced to 1.008 ± 0.003 and having correct sign. Obviously, although new field of research is open by a such observation, a lot more work is needed to exclude all possible influences that lower the sensitivity of the presented experiment.
2-amino-5-chloropyridinium (5CAP) copper (II) chloride (CAPCC) is one of a family of S=½ square antiferromagnets of general formula A₂CuX₄ (where A is related to 5CAP through substitution of other groups such as methyl for chlorine, and X = Cl, Br) 1-4. These materials are of interest in relation to the magnetic behaviour of high-T_c superconducting materials based on layered cuprates, and related low-dimensional, low-moment antiferromagnets5. In particular, CAPCC has a relatively low value of in-plane magnetic exchange J (0.57 K) which means that the magnetic properties may be tuned significantly through the application of experimentally accessible applied magnetic fields6.

The structure and basic magnetic character of CAPCC have been determined for the protonated material, revealing T_N = 0.75 K. We prepared crystals of a perdeuterated sample of the material7 to perform neutron diffraction studies of static magnetic correlations on E4 at BENSCE. Single crystal of CAPCC of volume ≅ 20 mm³ was mounted with a* and c* in the horizontal scattering plane, and a survey made of likely magnetic reflections at 30 mK. Of the reflections that were accessible to our measurements, additional scattering was found at (101), (10-1), (301), (30-1) in comparison with the scattering at 1 K. This is compatible with a simple 2-sublattice collinear array of moments in the magnetic (ab) planes, with an antiferromagnetic arrangement between such planes, as would be anticipated for a magnet with this exchange geometry.

The intensity, I_{101}, of the strongest magnetic reflection, (1 0 1), was studied as a function of T and H, where H was applied perpendicular to the scattering plane. I_{101} was least-squares fitted to the standard expression for the critical exponent β for sublattice magnetisation: I_{101} = A.exp(-ε²β), (where ε = (T_N−T)/T_N) with optimised values T_N = 751(1) mK and β = 0.32(1) for temperatures above 630 mK (Figure 1). T_N was observed to drop as H was increased, and an approximate phase diagram for the transition from the collinear phase to the phase with saturated magnetisation (Figure 2).

This work confirms the prevailing belief that the static spin structure of this class of magnet is conventional, and will form the basis for further work to explore non-classical behaviour in applied magnetic fields where H/J is large6.

References


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Magnetic field effect on static magnetic order in Nd$_{1.85}$Ce$_{0.15}$CuO$_4$

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Understanding of the interplay between antiferromagnetism and superconductivity (SC) is one of the most important unresolved issues in the physics of high-transition temperature (high-$T_c$) superconductivity. The electron doped Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ (NCCO) is interesting because of its achievable upper critical field in neutron experiments. Recently, we have discovered that on application of a few Tesla field, the elastic intensity at $(\pi,\pi)$, that is $(1/2,1/2,0)$, increases dramatically. However, it is not clear whether the field-induced effect is two-dimensional or three-dimensional in reciprocal space. To address this issue, we orient the crystal in the [H,H,L] zone and applied the horizontal magnetic field along the c-axis direction.

The neutron scattering experiments were performed on the two-axis spectrometer E4. The horizontal collimation was 40'-Sample-40' in sequence from reactor to analyzer with fixed incident neutron energy $E_i=13.6$meV. Two pyrolytic graphite filters were placed in front of the sample to eliminate higher-order contamination. The superconducting CuO$_2$ planes were aligned perpendicular to the horizontal plane and in the [H, H, L] zone. Indices in this paper are represented in the chemical unit cell of tetragonal symmetry of NCCO (space group I4/mmm). We used a split-coil superconducting magnet HM2, and the magnetic field $B$ was applied up to 4T perpendicular to the CuO$_2$ planes and along the c-axis.

Figure 1 shows the effect of a $B//c$-axis field on the scattering at (a) $(1/2,1/2,2)$ and (b) $(3/2,3/2,2)$. We observed enhancement of the peak at AF Bragg reflection $(1/2,1/2,3)$. The peak width almost equals to resolution width and is the same for both field on and field off. This result suggests that the three dimensional (3-D) correlations are not affected by the field. However, we found quite different field dependence for $(3/2,3/2,2)$, as shown in Fig. 1(b). When the magnetic field is applied, the background intensity decreases, and the peak at $(3/2,3/2,0)$ is slightly enhanced. Clearly, more careful measurements are necessary to sort out the differences between these two reflections.

Nevertheless, observed field effects at $(1/2,1/2,3)$ and $(3/2,3/2,0)$ strongly indicate the induced antiferromagnetic order is 3-D in nature.
Crystallographic and Magnetic structure of YTiO$_3$

The interplay between spin and orbital degrees of freedom in transition metal oxides has been studied extensively in the past decades. Recently, also dynamic effects in the spin and orbital sector have become interesting. It has been demonstrated that the antiferromagnetic Mott insulator LaTiO$_3$ possesses a novel state where orbital fluctuations dominate [1]. In this experiment we have determined the magnetic structure of YTiO$_3$ [2], the ferromagnetic sister compound of LaTiO$_3$.

The YTiO$_3$ sample was an untwined single crystal of volume 0.4 cm$^3$ grown by the floating zone technique. Elastic neutron scattering experiments were performed at the four-circle diffractometer E5 at the HMI. For the measurements neutron wavelengths of 2.36 Å or 0.902 Å were selected by a PG or a Cu monochromator, respectively, and the data were collected with a 2D position sensitive $^{3}$He-detector. A set of 1359 structural Bragg reflections could be refined with the orthorhombic space group $Pbnm$ ($a = 5.3584(9)$ Å, $b = 5.6956(8)$ Å, $c = 7.6371(11)$ Å) in agreement with previous reports [3]. Our data provide no indication of a structural phase transition down to 10 K.

The presence of magnetic intensity could be established from the temperature dependence of primitive Bragg reflections, some of which show a spontaneous increase in intensity below $T_C = 27$ K (Fig. 1.a). The reflections (2,0,0), (0,2,0), (1,1,0) and (1,1,2) show the strongest magnetic intensities, indicating a predominantly ferromagnetic coupling of the Ti-moments as previously reported [3]. In addition, weak magnetic Bragg reflections were also observed at (0,1,1), (1,0,1), (0,0,1), and (0,0,3), (Fig. 1.b). This indicates the presence of hitherto unobserved staggered components of the ordered moment. A full analysis of the magnetic diffraction pattern at $T = 10$ K gives a basically ferromagnetic structure, i.e., $F_z$ ($0.554(11)$ $\mu_B$), with weak additional antiferromagnetic components, i.e. $G_x$ ($0.082(12)$ $\mu_B$) and $A_y$ ($0.047(13)$ $\mu_B$). The total magnetic moment at 10 K is 0.553(11) $\mu_B$/Ti$^{3+}$-ion. Since the magnetic Bragg peak intensity is not saturated at 10 K, this extrapolates to 0.71 $\mu_B$ at 0 K, somewhat lower than the saturated moment of 0.84 $\mu_B$, reported for samples with proportionally higher $T_C$ [4].

Fig. 1. (a) Ferromagnetic and (b) $G$-type antiferromagnetic components of the magnetic moment in YTiO$_3$. The inset gives a pictorial representation of the experimentally determined crystallographic and magnetic structure.

Molecular magnets, *i.e.*, magnetic units assembled in a supermolecular aggregate consisting of organic components, are soft materials. Therefore, they are sensitive to the application of external pressure. In consequence, applying pressure to a molecular magnet affects its properties by variation of the distance between the magnetic ions and the geometry of the exchange path. To understand the interplay of structural and magnetic properties in molecular magnets both the pressure dependence of structural and magnetic parameters need to be determined.

In this context we present a study of the structural parameters of a molecular magnet, FePM\(_2\)Cl\(_2\) (PM = pyrimidine = C\(_2\)N\(_2\)H\(_2\)), as function of pressure. The material crystallizes in a tetragonal \(I\overline{4}22\) lattice \((a = 7.4292\AA, c = 20.364\AA)\), with the Fe ions connected via PM-rings and forming a three-dimensional network of Fe-PM complexes. A PM ring mediated superexchange yields magnetic coupling between Fe, causing a transition into an antiferromagnetic state at \(T_N=6.1\)K \([1]\). The magnetically ordered state has directly been observed by powder neutron diffraction of non-deuterated samples, yielding an ordered moment \(\mu_{\text{ord}}=3.8\mu_B\) \([2]\).

We have performed neutron powder diffraction under applied hydrostatic pressure. The experiments have been carried out on non-deuterated material at the BENSC, utilizing the Focusing diffractometer E6 with a neutron wavelength \(\lambda=2.448\AA\) at temperatures ranging from 1.5K to room temperature. The pressure has been generated in a clamped pressure cell. The applied pressure has been determined from the lattice parameter of NaCl, of which a piece was included in the sample space. In Fig. [1] we plot the neutron diffraction spectra of FePM\(_2\)Cl\(_2\) taken at 10K at ambient pressure and 2.2kbar, respectively. In the plot, in addition to the Bragg peaks from FePM\(_2\)Cl\(_2\), those from the pressure standard NaCl can be observed as indicated. From our data we find no indication for a change of the crystallographic symmetry of the overall lattice or of sub-units of the lattice. The Bragg peak positions shift with pressure, from which we obtain a lattice parameters reduction along \(a\) by 0.56(10)% and \(c\) by 0.35(10)%. We derive the bulk modulus \(B=V(\Delta p/\Delta V)\), which we evaluate to 15GPa. This is a very small value, reflecting the softness of this material. Typical intermetallic compounds, for instance, generally have bulk moduli of the order of 100GPa \([3,4]\).

Interestingly, the anisotropy of the compression is strongly temperature dependent. An analogous scattering experiment carried out at room temperature yields a reduction of the lattice parameters \(a\) by 0.9(1)% and \(c\) by 0.0(1)% under an externally applied pressure of 3kbar. Then, the bulk modulus is evaluated to 17GPa, closely resembling the low temperature value. However, at this temperature the compression is highly uniaxial, in contrast to the fairly isotropic compression at low temperatures. These observations highlight the relevance of a detailed structural analysis as function of temperature for the interpretation of pressure experiments.

[R. Feyerherm, BENSC Experimental Reports (1999) 104.]


The compound PbNi$_2$V$_2$O$_8$ is a classic example of an S=1 quasi-one dimensional antiferromagnet that exhibits a non-magnetic singlet ground state and a gap in its excitation spectrum. The interest in the compound as a model Haldene-gap system is heightened because it exhibits considerable inter-chain interactions and is therefore very close to the phase boundary of a long-range magnetically ordered ground state [1]. The criticality of the compound has been investigated structurally with the introduction of non-magnetic [2] and magnetic dopants [3] (BENS Proposal: PHY-01-948) along the Ni (S=1) chains. The present experiment further aimed to probe the criticality of PbNi$_2$V$_2$O$_8$ via an investigation of the magnetic phase diagram with respect to hydrostatic pressure. The experiment was in fact a repeat of PHY-01-1050, which was unsuccessful in applying significant pressure to the powder samples. During the allocated, compensating, time of 6 days on E6 (σ= 2.448 Å), and despite various ‘difficulties’ in using the supplied pressure cells, we were able to apply pressures, sustained at low temperature, of P= 2 kbar and P= 7 kbar. The corresponding diffraction patterns are plotted in Figures 1 and 2.

Figure 1 shows the diffraction patterns obtained for PbNi$_2$V$_2$O$_8$ both with and without pressure in the ILL CuBe clamped pressure cell with a long counting time (24 hrs each). The pressure within the cell at 1.5 K was estimated from the NaCl (111) reflection positions as 2 kbar [it was corresponding to 5.5 kbar at room temperature (RT)]. The pressure retained within this cell was found to only weakly transmit from the pressure (load) applied ‘outside’ the cell at RT.

Further experimentation was performed using the Bridgman pressure cell (supplied by BENS via Prague, with the help of visiting researcher K. Prokes). With this cell, a maximum pressure of 7 kbar was retained at 1.5 K (see Figure 2). At this pressure the PbNi$_2$V$_2$O$_8$ $I4_1/cd$ lattice was significantly compressed. Namely, at P= 1 bar: a= 12.233(2) Å, c= 8.345(3) Å and at P= 7 kbar: a= 12.181(2) Å, c= 8.3341(3) Å, both measured at 1.5 K.

Till today, the parent compound shows no evidence for magnetic Bragg scattering at any of the measured pressures at low temperatures. However, and clearly from the data, statistics are too low in order to successfully observe magnetic scattering of the intensity [staggered moment of ~0.9(1) μB] seen in doped (with Mg, S= 0 or Co, S= 3/2) samples. A considerable drop in statistics and overall data quality was notable due to the pressure cell and the “Flutec” liquid pressure medium.

**References:**

It has been observed that low doping with Cr on Mn site in charge ordered (CO) and orbital ordered (OO) manganites with the CE (charge exchange) structure, which are known to be antiferromagnets and insulators (AF-I) induces a transition to ferromagnetic and metallic (FM-M) states [1-5]. The appearance of FM is attributed to phase separation [6]: FM clusters are formed within the AF matrix which grow at the expense of the AF structure: as the doping of Cr increases the FM clusters are spread into layers. The transition from an AF-I state to FM-M one is very interesting because of their electric properties. In our project we investigate if on rich doping of the Mn-sublattice by Cr we get the same transitions.

Powder diffraction experiments were carried out on the manganite Nd$_{0.6}$Ca$_{0.4}$Mn$_{0.5}$Cr$_{0.5}$O$_3$. The parent compound Nd$_{0.6}$Ca$_{0.4}$MnO$_3$ is known to be AF and has CO-OO CE type structure. The experiments were performed on the E6 diffractometer using a wavelength 2.4422Å from a pyrolytic graphite monochromator. The data were recorded over an angular range 10-95$^\circ$ after it was observed that no reflections were present below 10$^\circ$ at any temperature in the range 1.8-300K. At 1.8K patterns were also recorded with applied magnetic field up to 5T in intervals of 1T using the vertical cryomagnet VM3.

The compound has been found to belong to the orthorhombic Pnma structure at all temperatures. Mn and Cr shared the same site. No additional reflections were observed or any splitting in any of the reflection indicating CO-OO state.

In Fig. 1 the development of the intensity of the reflections below the transition temperature is shown. Below 160K the intensity of certain reflection increase consistent with the development of a magnetic unit cell which entails a quadrupling of the original orthorhombic unit cell volume, 2axbx2c and can be indexed using the two propagation vectors $k_1=[\frac{1}{2},0,0]$ and $k_2=[\frac{1}{2},0,\frac{1}{2}]$. The Cr and Mn ions are distributed in the sixteen sites derived from the $b$ site of the Pnma space group. The moments are directed along a axis in a FM way forming zigzag AF chains on the basal plane, $z=0$. These chains are alternatively AF coupled with the chains on the plane $z=1/2$. The applied field up to 5T did not affect the spectra drastically, but small changes in the intensity of some reflections is observed. Probably it would require much larger field in order to change the state of the material. Down to the lowest temperature the Nd sublattice did not show long range magnetic ordering.

**References.**
**Experimental Report**

**Neutron-powder diffraction study of Nd$_{0.92}$Ca$_{0.08}$MnO$_3$.**

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**Date of Report:** 8/01/03

**Introduction.**
This paper is a part of a work devoted to establish the magnetic phase diagram of the mixed valence manganite Nd$_{1-x}$Ca$_x$MnO$_3$ for small values of $x$ for which very little is known. In the present work we have established the magnetic structure for $x=0.08$.

**Experimental.**
A sample in powder form with the nominal composition Nd$_{0.92}$Ca$_{0.08}$MnO$_3$ was prepared by the usual ceramic method. The purity of the sample was tested by X-rays. Neutron diffraction experiments were carried out at E6 diffractometer, BENSC, Berlin, using a pyrolytic graphite monochromator and wavelength 2.4422Å. Patterns were collected at temperatures between 200 and 1.8K.

**Results.**
In fig. 1 the neutron diffractograms at selected temperatures are shown. The refinement of the data led to the orthorhombic $Pnma$ type structure in agreement with X-rays. The occupancy of the elements was as in the nominal composition. The relation of the lattice parameters were found to be $c<a<b\sqrt{2}$ at all temperatures.

Data analysis showed that the MnO$_6$ octahedron is distorted. One of the equatorial Mn-O bond lengths gets shorter while the other and the apical bond length elongate with decreasing temperature, and rotates around the b axis, the angle of rotation being close to 160 degrees.

**Magnetic Structure**
The intensity of certain Bragg reflections increase even at 195K, showing more clearly in the range of the lowest angles, indicating the presence of a ferromagnetic (FM) long range interaction. The best fit was obtained with the Mn magnetic moment of $2 \mu_b$ directed along the a-axis. From 150K the forbidden (100) and (001) reflections appear, Fig.1, increasing with decreasing temperature indicating the presence of long range (AF) order. The simultaneous decrease of the FM reflections and the increase of the AF reflections with temperature is evidence of the rotation of the Mn moment and not of the presence of two phases as it has been assumed for $x=0.1$[1]. The moments below 130K are lying on the (110) plane and they are AF coupled along the c axis. Along the a axis the $\mu_a$ and $\mu_b$ are coupled ferromagnetically while along the c axis are antiferromagnetically coupled. At the lowest temperature measured, i.e. 1.8K, the rotation is completed and the Mn moment is directed along the b axis forming AF coupled planes perpendicular to the c axis. At the low temperature region the Nd moment orders FM along the c axis with a magnetic moment closed to $1\mu_B$/ion.

**Fig. 1.-** Selected neutron diffraction patterns.

**References**
The stoichiometric ternary rare earth compound YbRh$_2$Si$_2$ crystallizes in the tetragonal ThCr$_2$Si$_2$-type structure and is the first Yb-based compound exhibiting pronounced non-Fermi-liquid behavior above a low-lying antiferromagnetic transition at $T_N \approx 65$ mK. The antiferromagnetic order is evidenced by sharp maxima in the specific heat, the dc-magnetization in small magnetic fields and by an anomaly in the electrical resistivity [1, 2]. An ordered moment of below 0.1 $\mu_B$/Ce was estimated from an analysis of the dc-magnetization [2] and confirmed by recent $\mu$SR measurements [3]. However, the commensurate antiferromagnetic order of the isostructural CePd$_2$Si$_2$ with ferromagnetic planes stacked antiferromagnetically along [110] suggests a similar ordering in YbRh$_2$Si$_2$. To shed light on the origin of the non-Fermi-liquid behavior in YbRh$_2$Si$_2$ it is essential to have knowledge about the magnetic order.

The aim of the experiment on the diffractometer E6 was to search for antiferromagnetic ordering in YbRh$_2$Si$_2$. Therefore we used 6g of powder mounted in the horizontal 4 T magnetic using a $^3$He-$^4$He dilution stick. By cooling down the sample in a horizontal magnetic field (in the scattering plane) we aligned the powder, since the susceptibility in the basal plane is larger than along the tetragonal c-axis by roughly an order of magnitude. At lowest temperature ($T \approx 40$ mK) the field was switched off and the measurement was performed in zero field because the critical field of the AF state is a few ten mT. Diffraction pattern at lowest temperatures $T< T_N$ as an indication of antiferromagnetic order.

![Figure 1: Powder diffraction pattern of YbRh$_2$Si$_2$ taken at low temperatures ($T < 1$ K) before (uniformly distributed powder) and after applying a horizontal field of $B = 4$ T in the scattering plane (field-aligned powder).](image)

References

[3] K. Ishida et al., cond-mat/0207464; D. E. MacLaughlin et al., cond-mat/0207461.
Recently a new series of magnetic 221 intermetallic plumbides was discovered. Here rare earth elements (R) from Gd to Lu and Y can be combined with Ni and Pb. The crystal structure has orthorhombic symmetry of the Mn₂AlB₂ type (space group Cnmm) and it can be described as a naturally occurring multilayer structure consisting of stacked a-c planes of various kinds. Planes consisting only from R are intercalated between planes of only Pb atom on one side and Ni atoms on the other. As one moves along the b axis, the sequence reads: Pb-R-Ni-R-Pb-R-Ni-R-Pb. All the R atoms occupy the same crystallographic position.

Bulk measurements suggest various different magnetic phases to appear at low temperatures. These phases are very sensitive in an anisotropic way to applied magnetic fields. Sharp metamagnetic transitions and a giant magnetoresistance accompanying these transitions were observed [1]. In order to connect macroscopic an microscopic information we have performed powder diffraction experiment on three compounds with R = Dy, Ho, Er.

Samples were prepared by arc melting of appropriate amount of pure elements under vacuum and checked for the stoichiometry and homogeneity using electron probe micro-analysis. Neutron-diffraction patterns were collected at appropriate temperatures at the multicounter diffractometer E6 with the incident-neutron wave length of 2.44 Å.

In all samples we have detected presence of different propagation vectors that coexist and develop with temperature. For instance, in the case of Dy₂Ni₂Pb, the bulk measurements suggest two distinct magnetic phase transitions: one antiferromagnetic at $T_N = 14.5$ K and the other at $T_m = 3.5$ K below which a ferrimagnetic or canted ferromagnetic structure was anticipated. On the contrary neutron measurements, which were made in the range 1.5 - 20 K, showed that Dy₂Ni₂Pb has a complicated noncollinear antiferromagnetic spin structure of the same type in the whole temperature range studied. The magnetic structure is described by two commensurate propagation vectors $q_1 = (0, 0, 0)$ (collinear) and $q_2 = (1/3, 0, 0)$ (cycloidal component). As a result, Dy moments remained confined to the a-c plane (see Fig. 1). A smooth development of the two magnetic moment components at low temperatures indicates that the magnetic structure remains antiferromagnetic. Because of stability reasons another order-order magnetic phase transition at lower temperature can be expected.

Reference
Neutron diffraction measurements were carried on a powder sample of NdMn$_{1.55}$Fe$_{0.45}$Ge$_2$ in the function of the temperature (1.5 – 290 K) and pressure at ambient and 5 and 10 kbar. An analysis of the nuclear intensities in the neutron diffraction patterns indicates that the Nd atoms occupy the 2(a) site, the Mn and Fe atoms occupy randomly the 4(d) site and the Ge atoms are in the 4(e) site.

An analysis of the magnetic contributions to the peak intensity on the neutron diffraction patterns obtained in the ambient pressure gives the following model for the magnetic structures:

- At 1.5 K the Nd moments equal to 3.16(12) $\mu_B$ form a collinear structure with the moment direction parallel to the $c$-axis, while the Mn moments equal to 2.70(18) $\mu_B$ form a noncollinear Fmc- type of structure [1]. This type of magnetic structure is observed at 40 K;
- In the temperature range 100 - 210 K the Mn moments form a noncollinear antiferromagnetic AFmc - type of structure, while at 260 K the moments form a collinear antiferromagnetic AFl structure.

In the two canted structures, Fmc and AFmc, the components of the Mn magnetic moments in the (001) plane form the antiferromagnetic structure of the AFI-type while the components perpendicular to this plane form ferromagnetic (for Fmc) or an antiferromagnetic (for AFmc) structures.

The results of the neutron diffraction measurement under a pressure of 5 kbar and 10 kbar give similar peaks as under atmospheric pressure. The analysis of the peak intensities of the neutron diffraction pattern measured at different temperatures reveals a magnetic order similar to those observed under atmospheric pressure. Only a decrease of the Nd and Mn magnetic moments with increasing pressure was detected. The decrease of the Nd moment is near 9 % for p=5 kbar and it does not change under further increase of pressure up to 10 kbar, while the Mn moment linearly increases with increase of the pressure $\frac{d\mu}{dp} = 5 \cdot 10^{-2} \frac{\mu_B}{kbar}$ at low temperature.

Fig. 1 shows the thermal variation of the lattice constants a and c. In the temperature dependence of the a parameter is clearly visible the contraction of this value between the ferromagnetic and antiferromagnetic phases, equal to 2.4 % at ambient pressure, 1.5 % at 5 kbar and 1.0 % at 10 kbar. The c - constant changes slightly with the temperature and pressure. Fig. 2 shows the thermal dependence of the linear compressibility $k_a=a^{-1}\frac{da}{dp}$ along the a-axis determined from the measurements at 5 and 10 kbar. The values of $k_a$ are higher for the ferromagnetic than for the antiferromagnetic phase. A similar effect was observed in SmMn$_2$Ge$_2$ [2]. The values obtained for $k_a$ are slightly smaller than those observed in the isostructural RMn$_2$Ge$_2$

![Fig. 1](image1.png)  ![Fig. 2](image2.png)

Fig. 1

Fig. 2

compounds which at room temperature (RT) are equal to 36 $10^{-3}$ kbar$^{-1}$ for R=La and 45 $10^{-3}$ kbar$^{-1}$ for R=Nd. Both above compounds are ferromagnets at RT [3]. The above results confirm that the compressibility in the ferromagnetic phase higher that in the antiferromagnetic.

Experimental Analysis of the neutron diffraction patterns revealed several significant features that could be discerned from initial analysis of the neutron diffraction patterns. First, the lattice parameters of La$_{1-x}$Y$_x$Mn$_2$Si$_2$ were reduced by ~0.5 GPa as expected. The a-lattice and c-lattice parameters decreased ~0.20% and ~0.14% respectively over the temperature range 2-300 K. Second, at ambient pressure the presence of a 2-phase region is revealed by a pronounced dip in the intensity of the antiferromagnetic (111) peak over the temperature range ~150–280 K (the (110) peak provides a sensitive indication of antiferromagnetic ordering within the (001) planes [2]). By comparison at ~0.5 GPa, this region can barely be discerned, demonstrating that the extent of the 2-phase region is decreased significantly in the pressurised state. Also significant is the point that while the broadening observed in the (110) peak at ambient pressure [1] was found to persist in the applied pressure runs (indicating the co-existence of ferromagnetic and antiferromagnetic phases), the maximum in this (110) peak broadening shifted from ~200 K to ~250 K. Combined with the intensity variation of the (111) reflection (Figure 1), these findings demonstrate a weakening in the ferromagnetic-like component to this 2-phase region in favour of persisting antiferromagnetic interactions. This is shown clearly by Figure 1 – at ambient pressure the intensity of the antiferromagnetic (111) peak starts to decrease at ~140 K whereas at high pressure the intensity of the (111) peak is almost constant up to 200 K, indicating stronger antiferromagnetic exchange over this region. These features are in good agreement with our predictions based on the magnetic phase diagram [1].

Figure 1. The variation of the intensity of the (111) peak of La$_{0.8}$Y$_{0.2}$Mn$_2$Si$_2$ with temperature at ambient pressure (open circles) and at ~ 0.5 GPa (closed squares). The arrows indicate the temperatures at which the intensity of the antiferromagnetic (111) peak starts to decrease.

The present results demonstrate the central finding that the ferromagnetic region in La$_{0.8}$Y$_{0.2}$Mn$_2$Si$_2$ at ambient pressure is suppressed at a pressure of ~0.5 GPa and that the influence of antiferromagnetic exchange is extended to a higher temperature region. Analysis of the neutron diffraction patterns is continuing.

References

Introduction: The experiments were carried out on the E6 diffractometer at BENS. The investigations require the challenging combination of low temperatures ~2-300 K and applied pressures ~0-0.5 GPa. There were two factors that partly hindered the progress of our experiments. First, the initial ‘orange’ cryostat provided had a vacuum leak and second the pressure cell was found to be restricted in its pressure range compared with the expected specified performance. Additional neutron beam-time was made available to us to compensate the loss due to failure of the cryostat.
**EXPERIMENTAL REPORT**

**Test of a correlated behaviour of the magnetic order parameter for T\(\rightarrow\)0 and T\(\rightarrow\)\(T_c\)**

Principal Proposer: U. Köbler, IFF, FZ-Jülich
Experimental Team: U. Köbler, IFF, FZ-Jülich
A.Hoser, Inst. f. Kristallographie RWTH Aachen

Proposal N° PHY-01-1145
Instrument E6
Local Contact N. Stüßer

Date(s) of Experiment
21.01. - 25. 01 2002

Date of Report: 08.01.2003

From the experimentally well established fact [1] that the deviations of the (normalized) magnetic order parameter from saturation at absolute zero follow a simple power law according to \(1- \frac{\nu(T)}{\nu(T_c)} = cT^\beta\) it can be concluded that \(T=0\) is a singular point similar as the critical temperature \(T_c\). In the vicinity of those points simple power functions hold. On the other hand, the well known critical power law describes the deviations from \(T_c\) according to \(T_c-\frac{\nu(T)}{\nu(T_c)} = m T^{1/\beta}\).

As we have shown recently [2], the standard behaviour of \(\nu(T)\) consists in a direct crossover from the \(T\rightarrow0\) to the \(T\rightarrowT_c\) power function at the intersection of the two functions. Normally, this crossover is at about 0.85\(T_c\).

For the empirical exponents \(\epsilon\) the six fold universality scheme of Table I is now firmly established [1].

<table>
<thead>
<tr>
<th>Integer Spin</th>
<th>Half-Integer Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\epsilon = \frac{9}{2})</td>
<td>(\epsilon = 2)</td>
</tr>
<tr>
<td>(\epsilon = 2)</td>
<td>(\epsilon = \frac{3}{2})</td>
</tr>
<tr>
<td>(\epsilon = 3)</td>
<td>(\epsilon = \frac{5}{2})</td>
</tr>
</tbody>
</table>

It can be assumed that a similar universality scheme holds also for the conjugated exponents \(\beta\). In other words, the \(T\rightarrow0\) and the \(T\rightarrowT_c\) behaviour can be expected to be correlated. In Table II we show the proposed critical exponents \(\beta\) which are assumed to be like the exponents \(\epsilon\) rational numbers.

<table>
<thead>
<tr>
<th>Integer Spin</th>
<th>Half-Integer Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\beta = \frac{4}{11})</td>
<td>(\beta = \frac{1}{2})</td>
</tr>
<tr>
<td>(\beta = \frac{1}{2})</td>
<td>(\beta = \frac{1}{8})</td>
</tr>
<tr>
<td>(\beta = \frac{1}{3})</td>
<td>(\beta = \frac{1}{3})</td>
</tr>
</tbody>
</table>

In order to further confirm the correlations between the exponents of Table I and of Table II we have performed neutron diffraction measurements on FeF\(_2\) \((S=2)\), MnF\(_2\) \((S=\frac{5}{2})\) and FeCl\(_2\) \((S=2)\) powder samples. The two fluoride compounds with the rutile structure are known to be typical 1D systems [3]. This can be understood by assuming that the interactions in the a-b plane are below the threshold value to be thermodynamically relevant. As a consequence, the thermodynamics is exclusively due to the dominating interactions along the fourfold symmetry axis.

Fig.1 shows the square root of the (100) scattering intensities (order parameter) of FeF\(_2\) on a \(T^3\) scale. The exponent \(\epsilon=3\) is typical for a 1D system with an integer spin. Crossover to the (not well resolved) critical power law with \(\beta=1/3\) is clearly visible.

Fig.2 shows similar experimental data for MnF\(_2\) but on a \(T^2\) scale. For this 1D material with \(S=\frac{5}{2}\) the \(T\rightarrow0\) exponent is \(\epsilon=5/2\). The data in the critical range are consistent with \(\beta=0.33\). This value was obtained with a high precision in ref.4.

As a result, the presented experiments on FeF\(_2\) and MnF\(_2\) confirm \(\beta=1/3\) for 1D systems with integer as well as half-integer spin quantum number.

For most of the RCo$_3$ compounds, a transition from a weak ferromagnetic state into a strong ferromagnetic state (SFM) is observed. In ErCo$_3$, this transition occurs at about 100 K, where the molecular field exceeds the critical field for this transition (82 T) [1,2]. In Er$_{0.7}$Y$_{0.3}$Co$_3$ (where Er is substituted by Y), the compound shows in addition to the SFM transition (at about 35 K), a spin reorientation at about the same temperature. The substitution of the magnetic Er atoms by the nonmagnetic Y atoms weakens the molecular field.

It was the goal of this experiment (PHY-01-1210/E6) to study the influence of a magnetic field on both, the SFM transition as well as the spin reorientation in the Er$_{0.7}$Y$_{0.3}$Co$_3$ compound.

The E6 neutron experiment revealed, that the spin reorientation is strongly effected by a magnetic field, in contrast to the SFM-transition, where nearly no field dependence was found (reflected in the intensity of the (1,0,1) peak - see Fig. 1). This is obviously due to the fact, that for the SFM transition a molecular field of about 82 T is needed. The highest field available in this experiment was 5 T, which hardly influences the SFM transition.

The spin reorientation can be understood as a rotation of some of the Er moments out of the c-direction when the Er is partly substituted by Y. Applying a magnetic field, this non-collinear spin arrangement is stabilized up to higher temperatures. Fig. 2 shows the temperature variation of the (0,0,3) reflection, which has a finite intensity only in the case when some of the Er moments are aligned out of the crystallographic c-direction. The transition broadens considerably for higher magnetic fields (see Fig. 2). One of the problems comes from the fact, that both transitions (SFM and spin reorientation) occur nearly at the same temperature, which causes difficulties (at least up to now) in the data analysis. Another problem is the fixing of the powdered sample in the sample holder when applying a magnetic field. The used CD$_3$OD-C$_2$D$_5$OD mixture caused additional lines in the spectra.

We observed, that even the remanent field of the superconducting magnet caused a preferred orientation of the sample during cooling down below the melting point of the used CD$_3$OD-C$_2$D$_5$OD mixture. This preferred orientation causes further difficulties in the data analysis.

References:
Neutron diffraction studies of polycrystalline $R_3Cu_4X_4$ (R=Tb, Dy, Ho, Er; X=Ge, Sn) intermetallic compounds with the orthorhombic $Gd_3Cu_4Ge_4$-type crystal structure (space group $Immm$, no. 71) indicate the existence of different magnetic structures. Rare earth atoms occupy two nonequivalent 2d and 4e sublattices. The rare earth magnetic moments order at low temperatures in all these compounds.

For R=Tb, Er and X=Ge with the decrease of temperature first the 2d sublattice magnetic moments order; the 4e sublattice magnetic moments order at lower temperatures. For R=Dy, Ho; X=Ge both sublattices order simultaneously although the moment values are different for each of them. In the compounds with R=Tb, Er and X=Ge near the Néel temperature a change of the magnetic structure, connected with the 2d sublattice, is observed. This is a transition from the commensurate structure, described by the $k=(0,\frac{1}{2},0)$ propagation vector at low temperatures to the incommensurate one with $k=(0,\frac{1}{2}+d,0)$ at higher temperatures (however still below the Néel temperature).

For R=Tb, Dy; X=Sn the magnetic structures below the Néel temperature are described by the $k=(0,0,\frac{1}{2}+d)$ propagation vectors. In these compounds both rare earth sublattices order. For R=Ho; X=Sn the magnetic structure is more complicated. There are two vectors; one of them is $k=(0,\frac{1}{2},0)$ whereas the second one changes with temperature. For the Er/Sn-compound there is the $k=(0,\frac{1}{2},\frac{1}{2})$ propagation vector, which describes the magnetic ordering in the 2d sublattice. At low temperatures it is accompanied with the other $k=(0,0,d)$ vector describing the ordering in the 4e sublattice.

In the case of Tb$_3$Cu$_4$Ge$_4$ the neutron diffraction patterns at different temperatures between 1.5 and 28 K were measured. They are shown in Figs. 1 and 2a.

![Fig 1. Neutron diffraction patterns of Tb$_3$Cu$_4$Ge$_4$ measured at 1.5, 12, 19 and 28 K. The indexes 1 and 2 by the hkl-s indicate two different propagation vectors describing the magnetic ordering in the two rare earth sublattices.](image1)

![Fig 2. Parts of the neutron diffraction patterns of Tb$_3$Cu$_4$Ge$_4$ measured as function of temperature (a) and the temperature dependence of the magnetic peak intensities. The meaning of the indexes 1 and 2 - as it was previously.](image2)
EXPERIMENTAL REPORT
Neutron diffraction studies of the hexagonal RTIn compounds.

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Experimental Team: S. Baran, Institute of Physics, Jagiellonian University, Krakow, Poland
J. Hernandez-Velasco, BENSC

Date(s) of Experiment: 12.11.2002-18.11.2002
Date of Report: 10.01.2003

The neutron powder magnetic scattering data were collected for the following compounds: NdNiIn, TbNiIn, HoNiIn, PrNiIn, DyNiIn and CeAuIn. Analyses of the nuclear peaks confirmed, that all the compounds have the hexagonal ZrNiAl-type structure (Space group 189). Lattice constants at 1.5 K for investigated compounds are presented in table below.

<table>
<thead>
<tr>
<th>Compound:</th>
<th>$a$ [Å]</th>
<th>$c$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrNiIn</td>
<td>7.505</td>
<td>3.907</td>
</tr>
<tr>
<td>NdNiIn</td>
<td>7.508</td>
<td>3.889</td>
</tr>
<tr>
<td>TbNiIn</td>
<td>7.429</td>
<td>3.741</td>
</tr>
<tr>
<td>HoNiIn</td>
<td>7.386</td>
<td>3.706</td>
</tr>
<tr>
<td>DyNiIn</td>
<td>7.373</td>
<td>3.753</td>
</tr>
<tr>
<td>ErNiIn</td>
<td>7.494</td>
<td>3.752</td>
</tr>
<tr>
<td>CeAuIn</td>
<td>7.625</td>
<td>4.233</td>
</tr>
</tbody>
</table>

Collected data let us to determine magnetic structures in that family:
- PrNiIn – long-range magnetic order was not observed.
- NdNiIn – was found to be a ferromagnet. At 1.5 K magnetic moments of about 2.5 $\mu_B$ lie along the $b$ axis of crystal unit cell.
- TbNiIn – additional magnetic peaks were observed. Magnetic neutron diffraction pattern at 40 K can be indexed with magnetic cell, where all Tb magnetic moments of 3.8 $\mu_B$ build a non-collinear structure in the $ab$-plane. At 1.5 K additional magnetic peaks are visible, that peaks can be described with propagation vector $k = (0.5; 0; 0.5)$. Tb magnetic moments are equal to 7.8 $\mu_B$.
- HoNiIn – magnetic structure can be described by simple ferromagnetic structure with magnetic moments parallel to the $c$-axis of the crystal unit cell. Ho magnetic moments are equal to 6.2 $\mu_B$ at 1.5 K. See Fig. 1.
- DyNiIn – magnetic structure is similar to that observed for TbNiIn at 1.5 K. Dy magnetic moments of 5.1 $\mu_B$ lie in the $ab$-plane. Magnetic unit cell is doubled along the $a$ direction.
- ErNiIn – was found to be a ferromagnet with magnetic moments of 5.2 $\mu_B$ (at 1.5 K) parallel to the $c$-axis [1].
- CeAuIn – At 1.5 K Ce magnetic moments of 1.2 $\mu_B$ form a non-collinear structure in the $ab$-plane. Magnetic cell is doubled along the $c$ direction – propagation vector $k = (0; 0; 0.5)$ [1].

Following conclusions can be made:
- Compounds of RNiIn type can be ferromagnets distinct from RAuIn family. That can be connected with quite different $c$ lattice parameter for that compounds. Moreover density of states DOS at fermi level is much higher for RNiIn compounds due to Ni 3d states [2].
- Crystal field (CEF) influence was observed resulting with decreasing of rare earth magnetic moments values and their different orientation – parallel or perpendicular to the distinguished $c$-axis.

Fig.1 Neutron diffraction pattern for HoNiIn.

REFERENCES:
EXPERIMENTAL REPORT
The Study of Crystal Structure and Magnetic Ordering in Rare-Earth Ferricyanides

Project N°: PHY-01-1216
Intrument E6
Local Contact N. Stüßer

Date(s) of Experiment 18.-20.12.2002
Date of Report: 15/01/2003

Introduction

Rare-earth ferricyanides RE[Fe(CN)$_6$]$_n$H$_2$O, belonging to the group of molecule-based magnets, have been studied intensively in the last 30 years. While La-compound adopts hexagonal crystal structure, compounds where RE = Sm, Eu, Gd, … Lu, Y are orthorhombic and compounds with RE = Ce, Pr, Nd could be obtained in two modifications – hexagonal and/or orthorhombic. The crystal structure and magnetic properties of compounds are dependent on the number of water molecules in the unit cell. Removal of 1H$_2$O per formula unit reduces the hexagonal symmetry to orthogonal [1].

Experimental and Results

The powdered samples of composition Dy[Fe(CN)$_6$]$_n$D$_2$O and Pr[Fe(CN)$_6$]$_n$D$_2$O have been investigated at wavelength $\lambda$ = 2.45 Å covering a range from 6 to 85 degrees. In procedure of sample preparation deuterium atoms were directly implemented into our compounds instead of hydrogen. All samples were characterized in terms of X-ray diffraction [2]. Because of large absorption of Dy[Fe(CN)$_6$]$_n$D$_2$O we used an aluminium double wall container. An absorption correction has to be applied in order to take into account a special shape of the sample holder [3]. The Pr[Fe(CN)$_6$]$_n$.nD$_2$O samples were stored in a standard vanadium container. The diffraction patterns were taken in the temperature range 1.6 - 40 K. The sample with composition Pr[Fe(CN)$_6$]$_n$.nD$_2$O do not order magnetically down to lowest temperature (1.6 K) e.g. no significant difference between low and high temperature pattern has been found. Dy[Fe(CN)$_6$]$_n$D$_2$O sample orders magnetically bellow 2.8 K. Analysis of magnetic contributions to the pattern, displayed in fig. 1, leads to ferrimagnetic ordering as it is expected in [1]. The diffraction patterns taken at temperatures 1.76 K, 2.12 K, 2.45 K, 2.76 K, 3.06 K, 3.37 K and 9.63 K show gradual development of magnetic moment as temperature decreases (fig.2). The magnetic structure is currently having been refined.

V. K and M. L. acknowledge a support of EU and BENSCH-HMI Berlin.

References


Fig. 1 (a) Diffraction pattern of Dy[Fe(CN)$_6$]$_n$D$_2$O at 1.6 K and 30 K, (b) a magnetic contribution $I_{1.6K}$-$I_{30K}$.

Fig. 2. Dy[Fe(CN)$_6$]$_n$D$_2$O at different temperatures. The data are shifted for clarity.
The compound \((\text{Ce}_3\text{N})\text{In}\) crystallises in the anti-perovskite type structure \([1]\). From X-ray and neutron powder diffraction at ambient temperature \((a = 504.72(1) \text{ pm, } \text{Pm3m})\) \([2]\) and from chemical analyses the composition \((\text{Ce}_3\text{N}_{0.9})\text{In}\) was deduced for a microcrystalline sample prepared from \(\text{Ce}_2\text{In}\) and \(\text{CeN}\) in several heating cycles. In measurements of the magnetic susceptibility, magnetic transitions between 6 K and 10 K were observed.

A neutron diffraction experiment carried out on \((\text{Ce}_3\text{N}_{0.9})\text{In}\) at 1.5 K (fig. 1) showed that additional strong reflections do exist, which can be explained by a spin structure with an antiferromagnetic ordering \(\vec{k}_{\text{mag}} = \frac{1}{2} \frac{1}{2} \frac{1}{2}, I\text{-centred unit cell: } a = 1007.58(7) \text{ pm}\).

Fig. 1: Neutron diffraction patterns of \((\text{Ce}_3\text{N}_{0.9})\text{In}\) at various temperatures (\(\lambda = 245.22 \text{ pm}\)) from bottom to top: 9.7 K, 8.0 K, 6.2 K, 4.5 K, 3.0 K, and 1.5 K.

No indication for an additional magnetic ordered phase between 6 K and 10 K as suggested by the magnetic susceptibility measurements was visible from neutron diffraction experiments in this temperature region, but unusual slow ordering response of the magnetic structure on the temperature change was observed (6 h). Thus, we studied the kinetics of the magnetic transition in the range of \(30^\circ \leq \theta \leq 50^\circ\) at the temperatures of 1.5 K, 3 K, 4.5 K, 6.2 K, 8 K, 9.7 K, and 11.2 K. Fig. 2 shows the development of the magnetic reflections (211) at \(\theta = 34.8^\circ\) and (310) at \(\theta = 45.3^\circ\) compared to the nuclear structure reflection (110) at \(\theta = 40.4^\circ\) at 1.5 K. The analysis of these data is still in progress.

Fig. 2: Neutron diffraction patterns of \((\text{Ce}_3\text{N}_{0.9})\text{In}\) after different waiting times at 1.5 K (\(\lambda = 245.22 \text{ pm}\)) from bottom to top in steps of 0.5 h. The sample was held at 1.5 K for nearly 12 h, heated to 30 K to destroy the magnetic ordering (0.25 h) and then again cooled down to 1.5 K (0.1 h), before the 12 runs (6 h) were started.

References


**Experimental Report**

Coexistence of ferromagnetism and antiferromagnetism in YIG and NiCo$_3$

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**Principal Proposer:** U. Köbler, IFF, FZ-Jülich  
**Experimental Team:** U. Köbler, IFF, FZ-Jülich  
A.Hoser, FZ Jülich + RWTH Aachen

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Yttrium Iron Garnet (YIG = Y$_3$Fe$_5$O$_{12}$) is a well known ferrimagnet. In a ferrimagnet an ordered antiferromagnetic component and an ordered ferromagnetic component coexist. The same applies for the weak ferromagnet NiCo$_3$. While the phenomenon of weak ferromagnetism has been explained by a canting of the two spins in the unit cell of NiCo$_3$ due to antisymmetric exchange interactions according to Dzialoshinski [1] a collinear spin structure is assumed for YIG.

The two different spin structure models for YIG and NiCo$_3$ are not consistent with each other in view of the perfect magnetic isotropy of the two materials. We have therefore compared the normalized temperature dependence of the antiferromagnetic component (using neutron scattering) with the macroscopic spontaneous magnetization.

Fig. 1 shows on a $T^2$ scale the spontaneous magnetization of YIG from ref.2 together with the square root of two neutron scattering intensities obtained on instrument E6. Additionally, normalized NMR frequencies are displayed [3].

The observed $T^2$ dependence and the mean field exponent of $\beta=0.5$ conform to the fact that YIG has a half-integer spin of $S=5/2$ and a magnetic isotropic cubic lattice [3]. Antiferromagnetic and ferromagnetic component are not proportional mainly because the first is discontinuous but the second is continuous at $T_c$. Moreover, an amplitude crossover between two $T^2$ functions occurs in the ferromagnetic component but not in the antiferromagnetic component.

In contrast to YIG the two magnetic components of NiCo$_3$ are perfectly proportional to each other (Fig.2). The crossover from the $T^{w/2}$ power law to the critical power law with $\beta=4/11$ (~Heisenberg value) is typical for an isotropic system with an integer spin. Only at low temperatures the exchange anisotropy becomes relevant and induces an exponent crossover from $\epsilon=9/2$ to $\epsilon=2$.

The qualitatively different behaviour of ferromagnetic and antiferromagnetic component in YIG qualifies the two components as two different order parameters. These can be assumed to be orthogonal in a mathematical and in a geometrical sense. In NiCo$_3$ the two magnetic components belong to the same order parameter.

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The \textit{Immm}-R$_2$BaCoO$_5$ oxides (R=Rare Earth) present quite interesting magnetic behaviour: one-dimensional (1D) correlations of antiferromagnetic (AF) character within (CoO$_6$)$_n$ chains have been shown around RT [1], as it is inferred from the lack of the Co$^{2+}$ magnetic moment contribution to the susceptibility. At lower temperatures, 3D-AF ordering takes place. The 1D-AF correlations are observed in the M$^{2+}$ sublattices from above RT to T$_N$, at this critical temperature both the R$^{3+}$ and M$^{2+}$ sublattices become magnetically ordered, $k=[\frac{1}{2},0,\frac{1}{2}]$ being the propagation vector. However depending on the R$^{3+}$ and M$^{2+}$ cations, different spin arrangements are adopted, the orientation of the magnetic moments will depend on the distinct anisotropy and exchange forces that take place in the system. In this sense, the intrachain M-M coupling being the strongest one, the intersite R-M interaction must be dominant over intrasite R-R and interchain M-M, as it is inferred from the fact that both R$^+$ and M$^+$ sublattices order at the same temperature T$_N$. In the case of Ho$_2$BaCoO$_5$ oxide it is about 79 K. When saturation is reached (see Table below), the observed $m_{\text{Ho}} = 9.4(2) \mu_B$ value is close to $gJ=10\mu_B$, while the $m_{\text{Co}}=2.4(2)\mu_B$ experimental value at 6.1 K is near $2S=3\mu_B$ but somewhat lower. This shows the strong covalency and low dimensional effects in the Co$^{2+}$ subsystem (quantum spin fluctuations) which tend to decrease the magnetic moment value from the expected one.

<table>
<thead>
<tr>
<th></th>
<th>Ho</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_X$ ($\mu_B$)</td>
<td>0</td>
<td>-2.25(15)</td>
</tr>
<tr>
<td>$m_Y$ ($\mu_B$)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$m_Z$ ($\mu_B$)</td>
<td>-9.39(19)</td>
<td>0.83(4)</td>
</tr>
<tr>
<td>$</td>
<td>m</td>
<td>$ ($\mu_B$)</td>
</tr>
<tr>
<td>$\theta$ (°)</td>
<td>180</td>
<td>-70°(1)</td>
</tr>
</tbody>
</table>

The fit of the experimental data, Fig.1, agrees with a $B_g (F,F_z)$ symmetry representation, which means that the Co and Ho magnetic moments are restricted to the ac plane. The Ho magnetic moments $m_{\text{Ho}}$ are parallel to the c-axis, as shown in Fig. 2, while $m_{\text{Co}}$ are oriented antiferromagnetically along the a-axis with a small canting in the z direction. The order is ferromagnetic in the b direction (sublattice magnetization are canceled due to the translational symmetry of the AF lattice). Metamagnetic like transitions induced by the field are also observed, the data analysis of diffraction patterns obtained at $H \leq 5$ T is undertaken.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Neutron diffraction pattern collected at $H = 0$ T on E6 and refined using the Rietveld method. Sample weight < 0.5 g.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Representation of the Ho$_2$BaCoO$_5$ magnetic structure on one nuclear unit cell excluding the non magnetic atoms.}
\end{figure}

Neutron diffraction measurements on \textit{Pnma-}\textsubscript{Er\textsubscript{2}BaCoO\textsubscript{5}} show a strong diffuse scattering developing below 8 K that condenses in high intensity incommensurate (I) magnetic reflections around $T_N = 3.2$ K. The former is due to a short range magnetic order coming from the establishment of low dimensional spin correlations in the magnetic sublattices. In the case of the isostructural R\textsubscript{2}BaCoO\textsubscript{5} compounds where R= Tm, Lu and Y, complex magnetic phase transitions have been observed, following the scheme summarized below:

\begin{itemize}
  \item \textit{Paramagnetic State} (No long-range order)
  \item $\downarrow T_1$
  \item \textit{AF Incommensurate Structure} $k = \pm [0, k_y, 0]$
  \item $\downarrow T_2$
  \item \textit{AF Commensurate Structure}
  \item $k = [0, \frac{1}{2}, 0]$ (Tm), $k = [0, \frac{1}{2}, \frac{1}{2}]$ (Lu, Y)
\end{itemize}

By contrast with the isomorphous compounds mentioned above, the wave vector for the \textit{Er\textsubscript{2}BaCoO\textsubscript{5}} $I$-magnetic structure is $k=\pm[0,0,k_z]$, with $k_z = 0.4371(1)$, and remains constant in the whole temperature range of the measurement, \textit{i.e.} $1.4 \leq T \leq 3.2$ K (See Fig.1.a). The decreasing of the temperature below $T_N$ only shows the growing intensity of the magnetic reflections coming from a higher degree of ordered magnetic moments trying to reach saturation of sublattice magnetization, which takes place around $T \leq 2.1$ K. At 1.4 K, the integrated intensity corresponding to magnetic scattering is near to 63\% of the whole pattern. Experiments performed at lower temperatures, ranging from 0.04 K to 1 K, with a special sample environment (Dilution $^3$He/$^4$He cryostat) seem to indicate that this $I$ magnetic structure does not collapse to a $C$ one and remains surprisingly as the ground state until the lowest accessible temperature of the experiment, \textit{i.e.} 40 mK, see Fig. 1b. This striking result permits us to discard a possible amplitude modulated sinusoidal structure, which can not be stable down to 0K due to thermodynamic considerations, except in the case of a non-magnetic CEF singlet ground state, not in a Kramers ion like Er\textsuperscript{3+}($^4$I\textsubscript{15/2}).

Figure 1: 3D evolution of \textit{Er\textsubscript{2}BaCoO\textsubscript{5}} neutron diffraction patterns at low temperature: \textit{a}) showing the onset of strong magnetic reflections; \textit{b}) at temperatures below 1K; \textit{c}) at 1.7 K under applied magnetic field ($0 \leq H \leq 4.5$ T) using the vertical cryomagnet VM2.
By contrast, for the case of $R_2\text{BaCoO}_3$ with $R=\text{Lu}$ and $\text{Y}$, the $\text{Co}^{2+}$ magnetic moments change in magnitude and orientation while approaching the $C$ phase. Also in $\text{Tm}_2\text{BaCoO}_3$, variation of the pitch angle of the helimagnetic sublattices is observed in the framework of a devil’s staircase behaviour. While magnetic periodicity remains unchanged in $\text{Er}_2\text{BaCoO}_3$ ($k$ constant) which could be associated to a progressive squaring-up of the structure, which allows both an equal magnetic moments order and to reach the maximum value of sublattice magnetization. The former could explain the optical spectra that we measure elsewhere and the latter the thermodynamic stability of the I-phase in the low temperature region.

Nevertheless, on the basis of the $k$ vector proposed for $\text{Er}_2\text{BaCoO}_3$ it is possible to index all the Bragg reflections with magnetic origin. The powder pattern matching shown in Fig. 2 fits even the weaker peaks, without invoking to the presence of higher order harmonics $(2n+1)k$, as expected in square-wave modulations to account for the corresponding overtones of fundamental satellites.

FIGURE 2. Fitting of the neutron diffraction patterns below and above (inset) the Néel temperature. Refinement was done using the Rietveld method for the nuclear cell and a profile matching mode without structural model for the magnetic part of $\text{Er}_2\text{BaCoO}_3$. Open circles are the experimental data; continuous lines are the calculated profiles; differences between them are shown at the bottom of each pattern; last rows of vertical marks indicate the allowed Bragg reflections for each phase. Lattice parameters at $8.0$ K: $a = 12.244(1)$ Å, $b = 5.6928(7)$ Å, $c = 7.037$ (1) Å. Agreement factors: $\chi^2 = 10.5$, $R_a = 4.5\%$, $R_{wp} = 12.5\%$. Content of impurity phase $\text{Er}_2\text{O}_3$ (Cubic $I\bar{a}3$) < 2% weight. For the magnetic phase of $\text{Er}_2\text{O}_3$, $k=0$.

In this sense, it is worth mentioning again that sinusoildally modulated structures can not remain as pure sine-waves when the temperature is decreased, since at low temperature higher order terms in the free energy induce either a transition to a $C$ phase or a squaring of the modulation. Cases of $I$ structures in which entropic contributions are not so important include helimagnetic ordering, conical envelopes, complex spirals and square modulated structures. They could be stable down to 0K, since all magnetic moments can reach their saturation value. However, excluding the simple helix and the static spin waves, there must be a $C$ propagation vector together with the two $I$ arms of the wave vector $\pm k$ to account for the full set of magnetic reflections.

To fully characterize the complex magnetic structure of $\text{Er}_2\text{BaCoO}_3$, neutron diffraction measurements were scheduled under applied magnetic field. In this way, we expected to observe changes in the magnetic structure or a transition to a $C$ phase which could explain the upturn observed in the low temperature magnetization curves, and so to complete the phase diagram for the unusual and fascinating magnetic behaviour of $\text{Pnma-Er}_2\text{BaCoO}_3$.

To summarize, the main observed points are the low critical field which is necessary to start the development of magnetic intensity on the nuclear positions ($H < 0.4$ T) in comparison with the isostructural compounds that we have studied too, which is accompanied by a fast decrease of the intensities of the $I$ magnetic peaks (See Fig. 1c). Notice the evolution of the lowest angle strongest magnetic reflection observed in the diffraction pattern at $2\theta \approx 8.6^\circ$, which has been indexed as $(0,0,0)\pm k_z$. Its intensity should show the contribution of the magnetic structure factor from ordered Fourier components of magnetic moments held in a perpendicular direction to the scattering vector.

We mention that basis functions with $x$ and $y$ components belong to different $IR$ of $G_K$. However, the $I$ character does not completely vanish up to the highest field ($6.5$T) and $zK_i$ is needed in addition to $k=0$ in order to fit the experimental pattern. It could be seen in Fig. 3 at $H=4.5$T, above this field the stray field of the magnet VM2 allows only qualitative analysis due to the malfunction of the radial collimator in front of the detector.

FIGURE 3. $\text{Er}_2\text{BaCoO}_3$ T=1.8K H=4.5T k=(000)+hz

Intensity (a.u.)

2θ (degrees)

32000
24000
20000
16000
12000
8000
4000
-4000
-8000
-12000
-14000
-16000
10 20 30 40 50 60 70 80 90

Intensity (a.u.)

5300
4500
3700
2900
1200
500
6 18 22 26 30 34 38 42 46 50 54 58 62 66 70 74 78 82 86

FIGURE 3. $\text{Er}_2\text{BaCoO}_3$ T=1.8K H=4.5T k=(000)+hz

Intensity (a.u.)

5300
4500
3700
2900
1200
500
6 18 22 26 30 34 38 42 46 50 54 58 62 66 70 74 78 82 86

Intensity (a.u.)

5300
4500
3700
2900
1200
500
6 18 22 26 30 34 38 42 46 50 54 58 62 66 70 74 78 82 86

Intensity (a.u.)

5300
4500
3700
2900
1200
500
6 18 22 26 30 34 38 42 46 50 54 58 62 66 70 74 78 82 86

Intensity (a.u.)

5300
4500
3700
2900
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6 18 22 26 30 34 38 42 46 50 54 58 62 66 70 74 78 82 86
In the Lu₂BaCoO₅ compound, where Co²⁺ is the only magnetic atom, incommensurate (I) magnetic reflections appear in the neutron diffraction pattern at T₁ ≤ 3.8 K, which can be indexed with a wave vector k=± [0, kₓ, 0]. The magnetic order can be described as a sine-wave modulated structure. The coupling between the Fourier components mₓ of μ follows a representation with A₁C₂ modes, which means that the magnetization density is perpendicular to the propagation vector. The maximum total amplitude per each magnetic sublattice is near 4μₜ₀, but it is reached in different crystal cells. As an example, Figures 1, 2 and 3 show the modulation of some mₓ components.

However, at T₂≤2.8K, there is a locking up of the magnetic reflections that become commensurate (C) with the underlying nuclear lattice. This new set of magnetic peaks corresponds to the propagation vector k=[0, ½, ½], see Fig. 4. Nevertheless, the spin coupling remains within A₁C₂ symmetry mode. The obtained magnetic moments at 1.5 K amount to: μₓ=3.23(5)μₜ₀ ; μₓ=2.24(4)μₜ₀. The total μₓ=3.93(6)μₜ₀ > 2S accounts for a marked orbital contribution L to the magnetic moment.

In Figure 5 the neutron diffraction patterns obtained at 3.0 and 1.5 K are shown. They have been fitted using the Rietveld method for both
the nuclear and magnetic contributions to the intensity. At T=3.0 K the magnetic structure corresponds to the IC one, while at T=1.5 K the order is C and the periodicity of the magnetic cell is $a \times 2b \times 2c$. See Fig. 6.

Bulk magnetic measurements, which are shown in Fig. 7, indicate complex behaviour in the magnetization dependence on the applied field. At T=1.9K (C regime) there are two metamagnetic like steps, while the low field upturn in the magnetization curves is lost at temperatures close to $T_N$.

These transitions are confirmed by the diffraction data collected at fields between 0 and 5T, see Fig. 8. Different paths are shown depending on whether approaching from the C or IC phase to the state with induced ferromagnetic components. Both magnetic intensity on nuclear positions and new reflections appear on the patterns. Objections to the quantitative analysis due to the powder average are present taking into account the different field direction acting on each microcrystal but preferred orientations of the powder are absent. In such a way, a complete phase diagram of the system is under construction. The symmetry breaking and periodicity changes are well evidenced.
The Tm$_2$BaCoO$_5$ magnetic behaviour is quite complex due to the presence of 12 magnetic sublattices per chemical unit cell. Contrary to the whole R$_2$BaCoO$_5$ family, where R$^{3+}$ and Co$^{2+}$ sublattices order at the same critical temperature, Pnma-Tm$_2$BaCoO$_5$ shows slightly higher $T_N$ for the Co$^{2+}$ subsystem than for the Tm$^{3+}$ sublattices ($\Delta T_N < 0.4$ K). Firstly at $T=2.5$ K the IC magnetic order is similar to that described for R$_2$BaCoO$_5$ (R = Lu or Y) [1], with just the long range order of $\mu_{Co}$, but magnetic correlations of low dimensional nature are evidenced in the diffuse scattering superimposed on the background of the diffraction patterns, it should involve the rare earths magnetic interactions. Figure 1 shows the most intensive magnetic reflections at low angles collected between 3.0 and 1.4 K at H=0.

There are phase transitions and magnetic symmetry changes when Tm$^{3+}$ sublattices become magnetically ordered and the resultant IC structures can be explained as an amplitude modulation of the magnetic moments or either in the framework of 12 interpenetrating helimagnetic sublattices whose pitch angles change with temperature (Fig.2). They collapse to a new C structure through a bidimensional irreducible representation, the 3 components indicate that the transition could be first order.

The propagation vector is $k_2 = [0, \frac{1}{2}, 0]$ and the basis functions are $C_xC_yC_z$. The obtained magnetic moment for Tm $\sim 2\mu_B$ is too low compared with $gJ$, and to be explained on the basis of the crystal field splitting of the Tm$^{3+}$ ($^3H_6$) ground state. Actually it points that $\mu_{Tm}$ are induced moments not completely ordered, with origin in the polarization by the exchange field on the Co sites. In Figure 3 some of the refined neutron diffraction patterns are shown.
has been shown that in fact the transition from... expenses of flux intensity on sample position.

In this way diffraction lines are solved and it was used a non standard setting of the monochromator so reducing the spread at the expenses of flux intensity on sample position.

Y compounds (see corresponding experimental report) evidences the different anisotropy of the system, also shown in the quite distinct critical field for the metamagnetic-like transition.

To get more insight, we performed neutron diffraction measurements under magnetic field.

It is worth noting that the vector \( k_i \) shifts towards the \( C \) value while temperature decreases, it moves through a symmetry line inside the first Brillouin zone to a high symmetry point on its surface. It is seen in Fig.4. A devil’s staircase behaviour could be invoked. On the other hand, bulk magnetization measurements indicate additional magnetic phase transitions induced by the field, see Fig.5. The different shape in the isotherms compared with that on the isosctructural Lu and Y compounds (see corresponding experimental report) evidences the different anisotropy of the system, also shown in the quite distinct critical field for the metamagnetic-like transition.

To get more insight, we performed neutron diffraction measurements under magnetic field. To gain resolution at low diffraction angle it was used a non standard setting of the instrument by removing the in-pile collimation and closing the diaphragm acting on the monochromator so reducing the spread at the expenses of flux intensity on sample position. In this way diffraction lines are solved and it has been shown that in fact the transition from the AF-C ground state to induced Ferro-C goes through IC phases of different periodicity which vanish on increasing the field. See Fig.6.

**Figure 4**: Thermal evolution of the propagation vector in \( \text{Tm}_5\text{BaCoO}_5 \) (bottom) and contents of both the IC and C phases based on the percentage of integrated intensity with magnetic field. The derivatives are shown on E6 using the vertical cryomagnet VM2.

**Figure 5**: Magnetization isotherms at the indicated temperatures versus applied magnetic field. The derivatives are shown in the bottom inset on the right-hand side, while \( M \) vs \( H \) at low field is shown on the top inset. Lines are eye guides.

**Figure 6**: Neutron diffraction profiles at 1.6 K under applied magnetic field (0 ≤ \( H \) ≤ 6.5 T) for \( \text{Tm}_5\text{BaCoO}_5 \). Data collected on E6 using the vertical cryomagnet VM2.

The design of coordination polymers containing organic ligands is well suited to develop the understanding of the relationship between structure and physical properties. In this sense, molecule-based magnets has attracted great current interest. In this framework, we have carried out neutron powder diffraction measurements on some novel coordination compounds with Mn$^{2+}$ or Fe$^{2+}$ and different net topologies. The “crystal engineering” is performed through the substitution of both terminal and bridging coligands, within the former kind thiocyanate (NCS$^-$) anions have been extensively used, in the latter set we have dealt with bridging pyridyl-donor ligands like pyrazine (pyz or 1,4-diazin C$_4$N$_2$H$_4$); also pyrimidine (pym or 1,3-diazin C$_4$N$_2$H$_4$) and dicyanamide (dca or N(CN)$_2^-$). Also an interesting purely inorganic based compound was studied, namely the quasi-molecular magnet Fe(ReO$_4$)$_2$, where isolated layers of ReO$_4^-$ anions bridge the metallic centers.

Following is a brief summary of preliminary results obtained in the fully deuterated samples:

- **Mn(NCS)$_2$(pyz)$_2$**: In this compound a phase transition from the paramagnetic state to a 3D-AF order takes place at $T_N \approx 2.7$ K. Figure 1 shows the experimental neutron diffraction patterns at 4.9 and 1.5 K together with the difference curve that corresponds to the pure magnetic scattering.

![Figure 1](image1.png)

**Figure 1.** NPD data shifted on Intensity scale (E6, $\lambda$=2.449Å).

- **Mn(NCS)$_2$(pyz)$_2$**: The measurements in this case do not show the existence of diffraction with magnetic origin down to 1.8 K. Experiments at dilution temperatures will be scheduled.

- **Fe(NCS)$_2$(pyz)$_2$**: An incommensurate (I) magnetic structure with propagation vector $k=\pm[1,0,\frac{1}{4}+\xi]$ has been found to appear below $T_N \approx 6.6$ K. However diffuse scattering above $T_N$ is observed around the positions defined by the modulus of the AF-wave vector. The ground state of this system is 3D-I-AF, while its critical behaviour seems to be that of a 2D (S=1/2) Ising one. See the corresponding experimental report.

- **Fe(dca)$_2$pyz**: Both new superstructure peaks and magnetic intensity on some nuclear positions develop below $T_N \approx 3.5$ K.

- **Fe(ReO$_4$)$_2$**: This compound shows an AF structure ($T_N \approx 8.5$ K) with identical cell than the chemical one ($k = 0$). However, measurements under applied magnetic field demonstrate that there is a transition to a Ferromagnetic state even at very low field, *i.e.* $H = 350$ Oe. The reflections due to the AF spins arrangement vanish on increasing fields and subsequent magnetic intensity appears superimposed on nuclear diffraction lines. It is a genuine metamagnetic transition with low critical field. Another point that is worth mentioning is the observed concomitant magnetostriction effect, which could indicate the coupling of order parameters of lattice distortions and magnetic nature, and so the anisotropic terms in the spin Hamiltonian are rather important. See Figure 2.

![Figure 2](image2.png)

**Figure 2.** Evolution of some magnetic reflections in Fe(ReO$_4$)$_2$ under applied magnetic field (0 ≤ H ≤ 3.0 T) using the vertical cryomagnet VM3. Inset: Notice the shift to higher 2θ diffraction angle (lattice contraction) of the most intensive nuclear reflection at 2θ \^ 37°. T = 1.5 K.
EXPERIMENTAL REPORT

Zero-field magnetic structure of the 2D antiferromagnet Fe(NCS)₂(pyrazine)₂

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The use of molecular building blocks in the design and fabrication of magnetic solids is of great current interest, as mild synthetic procedures can be used to produce a vast array of compounds that exhibit a variety of crystal structures and magnetic phenomena. Generally, low-dimensional organic bridging ligands such as CN⁻, N₃⁻ and C₄O₄²⁻ (or pyz) have been utilized to structurally organize metal ions into specific architectures [1]. Beside, these diamagnetic ligands also serve as superexchange mediators between those ions and magnetic ordering ranging from few K up to 62 has been reported [2].

Of the coordination polymers that contain pyz, most of them possess low-dimensional structures, i.e. 1D chains or 2D sheets. With this in mind, and in an attempt to form asymmetric lattices that may exhibit unusual magnetic properties, an interesting alternative consists to utilize mixed-ligand systems, i.e. pyz in combination with other moities such as thiocyanate (NCS⁻) anions. In this work we have focused on Fe(NCS)₂(pyz)₂ that has been characterized as a 2D sheetlike polymer by Real et al.[3], where the thermal variation of its magnetic susceptibility (broad maximum around 9K) suggests an antiferromagnetic (AFM) ground state at low temperature.

These findings suggested that in addition to the strong AFM coupling provided by the pyz within the Fe – pyz- Fe sheets, the NCS⁻ anion that bound the Fe ion and stand above and below the Fe – pyz- Fe sheets (in an almost perpendicular fashion), must provide a weak interlayer exchange pathway. Indeed the highly polarizable sulfur atom may interact with the delocalized π-cloud of the nearly vertically-oriented pyz ligands of neighboring squares.

From this experiment we could conclude that while this system is a 3D AFM below 6.6K, its critical behavior is essentially 2D in nature. These findings allowed us to conclude that in addition to the strong AFM coupling provided by the pyz within the Fe – pyz- Fe sheets, the NCS⁻ anion that bound the Fe ion and stand above and below the Fe – pyz- Fe sheets (in an almost perpendicular fashion), must provide a weak interlayer exchange pathway. Indeed the highly polarizable sulfur atom may interact with the delocalized π-cloud of the nearly vertically-oriented pyz ligands of neighboring squares.

Recently, we have reported that a mixed crystal of composition Mn$_{0.88}$Fe$_{0.12}$WO$_4$ shows simultaneously different types of long range magnetic order [1]. The observed spin arrangements are related to the magnetic structures of the pure compounds MnWO$_4$ (AF1, AF2, AF3) and FeWO$_4$ (AF4). A coexistence of two phases in different volume elements could be ruled out and we found strong evidence that the two different structures are formed on the same lattice: one structure is embedded as a cluster within the second structure. This unusual behaviour of two interpenetrating magnetic structures becomes possible by the various superexchange couplings between adjacent Mn--Mn, Fe--Fe, and Mn--Fe-ions via one or two intervening oxygen ions. For the Mn$_{0.88}$Fe$_{0.12}$WO$_4$ compound the MnWO$_4$-type magnetic structures were found to be the dominating ones and FeWO$_4$-type spin ordering in structure AF4 is realized on a randomly diluted lattice only.

In 2002 we have continued neutron powder diffraction studies already started in 2001 in order to extend the investigations of this complex magnetic behaviour to specimens mainly with higher concentrations in Fe. Main purpose was to establish the $(x, T)$-magnetic phase diagram for Mn$_{1-x}$Fe$_x$WO$_4$ in the interesting region of coexisting magnetic phases. Results of all our measurements are summarized in the figure.

Mixed crystals Mn$_{1-x}$Fe$_x$WO$_4$ in the concentration range $0 = x = 0.29$ show a very complex and rich magnetic $(x, T)$ phase diagram. Despite the lack of a detailed knowledge of the individual exchange paths between the magnetic transition metals a qualitative understanding of the dominating phases seems to be intuitive considering the magnetic phases of the pure end members MnWO$_4$ and FeWO$_4$. The presence of random exchange can then account for some main features of the phase diagram. MnWO$_4$ type structures are only observed up to Fe concentrations of $x = 0.29$. The FeWO$_4$-type structure AF4 already forms as a high temperature phase for $x = 0.12$ due to the stronger exchange of the Fe-ions?. Mn-ions are incorporated to overcome the percolation threshold of about $x = 0.25$. At lower temperatures MnWO$_4$-type structures are still observed for $x < 0.225$. Now temperature is low enough so that an ordering becomes possible caused by the weaker exchange of the Mn-ions?. More Mn/Fe ions are ordered compared to the FeWO$_4$-type structure at higher temperature. Phase transitions are then governed by the detailed balance between energy and entropy. Regions of mixed phases occur for $0.12 = x = 0.29$.

Fig. Magnetic $(x, T)$ phase diagram of Mn$_{1-x}$Fe$_x$WO$_4$. Phases are labelled as AF1, AF2, AF3, and AF4. Phase boundaries are denoted by I, II, III and IV. Lines are guide for the eyes.

We have studied the magnetic ordering of the molecular compounds manganese tricyano-methanide, Mn[C(CN)$_3$]$_2$, and cobalt hydroxide terephthalate, Co$_2$(OD)$_2$(tp-d4), in zero and under applied magnetic field.

The magnetic interactions between the Mn$^{2+}$ ions ($S = 5/2$) in Mn[C(CN)$_3$]$_2$ through the tridentate C(CN)$_3^-$ anion can be mapped onto the “row model” for partially frustrated triangular magnets. The compound orders at $T_N = 1.18$ K.

The zero-field magnetically ordered structure (Figure 1) was solved from powder neutron diffraction data taken between 0.04 and 1.2 K. It consists of an incommensurate spiral with a temperature independent propagation vector $Q = [2Q 0 0] = [0.622 0 0]$. The ordered moment $\mu = 3.3 \mu_B$ is about 2/3 of the full Mn$^{2+}$ moment.

The magnetic-field dependence of the intensity of the $(2Q 0 0)$ Bragg reflection, measured for external fields $H \parallel Q$ (using the magnet HM-1), indicates the presence of three different magnetic phases, namely the incommensurate spiral ($H < 13.5$ kOe), an intermediate “up-up-down” phase ($13.5$ kOe $< H < 16$ kOe), and an “2-1” spin-flop like magnetic structure ($H > 16$ kOe). The saturation field is $H_{sat} = 42$ kOe. The propagation vector shows an unusual field-dependence, $Q$ varies continuously with increasing field, approaching the value 1/3, corresponding to the commensurate magnetic structure of the fully frustrated triangular lattice at $H^* = 19$ kOe. At this point, the field-dependence reverses. Except for $H^*$, the magnetic ordering is incommensurate in all three field dependent magnetic phases of Mn[C(CN)$_3$]$_2$. These results have been published in [1].

The ordered magnetic structure of fully deuterated Co$_2$(OD)$_2$(tp-d4) (tp-d4 = C$_8$D$_4$O$_4$) has been determined at various temperatures by powder neutron diffraction. Below the ordering temperature, $T_C = 48$ K, the magnetic diffraction patterns reveal the existence of different magnetic moments on two non-equivalent Co(II) ions forming ferrimagnetic layers. Zero-field cooled experiments show that the long range magnetic order is basically antiferromagnetic along the stacking axis, with possible weak canting.

After field-cooling (using the magnet VM-3), strongly canted antiferromagnetism is observed in zero field with a resulting ferromagnetic component of 1.8 $\mu_B$ along the $b$ axis on one of the Co sites. This phase is metastable, the weakly canted phase being the ground state. These results have been published in [2].

References
In the orthorhombic aluminides $LnFe_2Al_{10}$ ($Ln$ = Tb, Dy, Ho, Er) only the rare-earth ions carry a magnetic moment [1]. In a previous paper we presented the magnetic structures of TbFe$_2$Al$_{10}$ and DyFe$_2$Al$_{10}$ [2]. Below the Néel temperatures $T_N = 16.5(5)$ K and $T_N = 7.5(5)$ K the Tb and Dy moments are ordered antiferromagnetically. TbFe$_2$Al$_{10}$ shows a square wave modulated magnetic ordering of the Tb sublattice, while the Dy moments form a helical magnetic structure. Only recently an incommensurate magnetic structure of the Er sublattice in ErFe$_2$Al$_{10}$ could be observed from neutron diffraction at 100 mK [3,4]. The magnetic order of the erbium moments could be confirmed by specific heat measurements. The Néel temperature found here is $T_N = 1.77(7)$ K.

In order to investigate the magnetic order of HoFe$_2$Al$_{10}$ a neutron powder experiment has been carried out on the diffractometer E6. Powder patterns were collected at 100 mK and 2000 mK using a dilution refrigerator. The used neutron wavelength was $\lambda = 2.45$ Å. In the difference pattern no magnetic peaks could be observed. This is in agreement with our specific heat data, which do not provide any evidence for a magnetic phase transition down to 250 mK.

The Néel temperatures show a strong decrease from the Tb to the Er compound. No agreement can be found, when the values are compared to the de Gennes function $T_N \propto (g - 1)^2 J(J + 1)$ [5] where $g$ is the Landé factor and $J$ the total angular momentum of the $Ln^{3+}$ Hund’s rule ground state. For DyFe$_2$Al$_{10}$ a Néel temperature of 11.1 K is expected instead of $T_N = 7.5$ K (Fig. 1). For HoFe$_2$Al$_{10}$, the de Gennes ordering temperature is calculated to be 7.1 K, but no magnetic order could be found down to 100 mK. It is further interesting to see that ErFe$_2$Al$_{10}$ shows again an antiferromagnetic order below $T_N = 1.77$ K, compared to the expected transition temperature according the de Gennes scaling of 4.0 K. It seems obvious that the de Gennes function cannot be used for intermetallic compounds with very low lanthanide content.

In the presently investigated aluminides the magnetic order seems to be mainly influenced by the single-ion anisotropy, which is usually very strong in terbium compounds.

![Fig. 1: Experimental magnetic transition temperatures $T_N$ (solid triangles) of rare-earth ions $Ln^{3+}$ in $LnFe_2Al_{10}$ and their relation to the de Gennes function (solid circles).](image-url)

References

The magnetic structure of ZnV$_2$O$_4$ has been investigated by neutron powder diffraction on the instrument E6, using the neutron wavelength $\lambda = 2.45$ Å. ZnV$_2$O$_4$ shows a paramagnetic to antiferromagnetic transition at 40 K [1]. Below 50 K this compound crystallizes in the tetragonal spinel-type structure with the space group $I4_1/amd$ [2].

Two data sets of the antiferro- and paramagnetic phases have been collected at 1.8 K and 70 K, respectively, both between $2\theta$ values of 5 and 85°. The neutron powder pattern collected at 1.8 K showed additional relatively weak peaks at the $2\theta$ values 17.4° and 27.7°. These peaks can be ascribed to the magnetic order of the vanadium sublattice and they could be indexed as $(1, 0, 0)_M$ and $(1, 1, 1)_M$. Thus, the magnetic structure violates the $I$-centering and the reflections can be generated by the rule $(hkI)_M = (hkI)_N \pm k$, where the propagation vector is $k = (0, 0, 1)$. Due to the absence of the reflection $(0, 0, 1)_M$ the magnetic moments of the vanadium atoms are aligned parallel to the tetragonal c-axis. From our Rietveld refinements finally we obtained the magnetic moment per vanadium atom $\mu_{\text{exp}} = 0.61(5) \mu_B$ with a residual $R_M = 0.085$ ($R_M = \Sigma |I_o| - |I_c|/\Sigma |I_o|$). The observed and calculated magnetic intensities are given in Table 1.

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<th>$h$ $k$ $l$</th>
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In Fig. 1 it can be seen that one V$^{3+}$-ion has six next-nearest neighbours of oxygen atoms forming an octahedral environment. Along the a- and b-axes one finds chains of edge-sharing octahedra. Here is an direct overlap of the $d_{xy}$ (or $d_{xz}$ or $d_{yz}$) orbitals of the two V$^{3+}$-cations resulting in an anti-ferromagnetic coupling. In this case the O$^{2-}$-anions play a less obvious role in the delocalization-superexchange process (90° cation-anion-cation interaction). Fig. 1 shows that the vanadium moments form spin sequences $+-+-+-+-...$ along the x- and y-directions (chains of edge-sharing octahedra).

![Fig. 1. Magnetic structure of ZnV$_2$O$_4$.](image)

References

Zeolites are aluminosilicate crystals with pores of molecular size (called cages or channels), and so have been paid much attention as containers of atom clusters. Zeolite A and X have framework structures including micropores of about 1 nm in diameter. The Na ions located inside the micropores to keep the charge balance can be exchanged with other metal ions using the ion-exchange technique. A SQUID study [1] done on zeolite A and Y with Ni ions exchanged into the cages has shown the presence of magnetic interaction and indicated spin-glass behaviour at low temperatures. The experiment presented here was undertaken to study a possible magnetic ordering of the Ni ions at low temperature.

Samples of zeolite A and X crystals were prepared using the Gel method following [2]. The resulting crystal powder has been washed with distilled water and afterwards placed in a high-concentrated aequous solution of NiNO$_3$ in order to exchange the Na ions; the solution was replaced three times, the final product washed again and dried at 110°C in a vacuum. A part of the samples has been measured in dry state, another was saturated with D$_2$O. Analysis with RFA gave an exchange ratio of Ni/Na=2.3/1 for zeolite A and of 2.5/1 for zeolite X. These exchange ratios are slightly higher then those reported in [1].

Low temperature SQUID measurements of the samples gave no indication of magnetic susceptibility for Ni exchanged zeolite X in contrast to the literature [1]. For zeolite A the behaviour found in the literature could be confirmed (figure).

Neutron measurements have been undertaken to test the existence of a magnetic structure in these zeolites. However, no indication of changes in the diffraction patterns could be observed between 1.6 K and 40 K. No ordering of the magnetic moments seems to occur.

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Physical properties $R_2Ni_2Pb$ (R stands for Gd to Lu and Y) rare earth intermetallic plumbides were found to be very sensitive to external magnetic field [1]. For instance, already field of 1 T applied along the c axis in $R=Ho$ case reduces the electrical resistivity by more than 20 %. The crystal structure of these compounds has orthorhombic symmetry of the $Mn_2AlB_2$ type (space group Cmmm) and it can be described as a naturally occurring multilayer structure consisting of stacked a-c planes of various kinds. Planes consisting only from R are intercalated between planes of only Pb atom on one side and Ni atoms on the other. All the R atoms occupy the same crystallographic position.

In order to study field induced phases suggested by bulk measurements we have performed powder diffraction experiment on three compounds with $R = Dy, Ho, Er$. Samples were prepared by arc melting and neutron-diffraction patterns were collected at the multicounter diffractometers E6/E9 with the incident-neutron wave length of 2.44/1.79 Å in magnetic fields up to 4.5 T.

In zero field, we have detected in all samples presence of different propagation vectors that coexist and develop with temperature (see report of proposal PHY-01-1138). In the case of $Er_2Ni_2Pb$ we have found four transitions in zero field (see Fig. 1) while bulk measurements indicated three of them.

In Fig. 2 we show contour scan of a selected portion of diffraction pattern of $Er_2Ni_2Pb$ as a function of field. As can be seen, two field induced transitions exist in agreement with magnetization and magnetoresistance measurements [1]. At 4.5 T were Er moments found to be oriented in the plane perpendicular to the c axis, close to the a axis. In Dy and Ho samples were moments residing on rare earth atoms found in 4.5 T perpendicular to the b axis. Detailed analysis is under way.

**Reference**

Introduction

After the neutron diffraction experiments with antiferromagnet MnO embedded in a porous glass with the mean pore diameter 7 nm (I. Golosovsky et. al., PRL., 86, 5783, 2001.) we performed the experiments with CoO. In contrast with MnO the magnetic structure in CoO has another number of components of the order parameter. These oxides differs by electronic structures, types of crystal structure distortions and types of magnetic transition. Our objective was to compare the behavior of these oxides in the conditions of "restricted geometry".

Results

1. From the powder diffraction we found that CoO forms nanoparticles (fractal agglomerates) with averaged diameter of 100(3) Å.

2. In figure 1 the temperature dependence of magnetic moments for the bulk (triangles) and for the confinement (solid circles) are shown. Similar MnO, the averaged magnetic moment of CoO in confinement was found strongly reduced because of magnetic disordering at the surface of nanoparticle. In contrast with MnO the magnetic transition was found to be a second order and $T_N = 282(1)$ below $T_N$ of 290 K for the bulk. The critical exponent 0.34(4) corresponds to calculated one for 3D-Heisenberg model.

3. In the embedded MnO we had discovered that the structure distortion is proportional to the magnetic moment, while in the bulk this parameter is proportional to the square of the magnetic moment. It means that a molecular field approximation does not work in the confinement. The similar phenomenon was observed in CoO, however with the smaller statistical accuracy. This interesting question is still open and call for further investigations.

4. In experiments with embedded CoO we confirmed the strong increasing of the Debye-Waller factor in confinement already detected in embedded MnO. In figure 2 the Debye-Waller factors in confinement (circles) and in the bulk (triangles) are shown. We have no explanation of this phenomenon.

One of us (IVG) acknowledges the financial support of the BENS.
**Introduction**

This report presents the first experimental results with antiferromagnetic MnO embedded in the novel mesoporous matrixes, known as MCM-41 (SBA-15) with a network of the long parallel channels forming the regular hexagonal lattice. We worked with the channel diameters: 18, 32, 60 Å; wall thickness $\sim 10$ Å. Matrixes have been prepared in the Laboratoire de Chimie Physique, (Dr. C. Alba-Simionesco,) Universite Paris-Sud, Orsay and have been filled by MnO from the solution, in Ioffe Physico-Technical Institute, St.-Petersburg, Russia.

**Results**

1. Line-shape. In contrast with MnO embedded in a porous glass the line-shape of nuclear reflections has a specific profile known as "saw-tooth" profile, indicative of a 2-dimensional behavior. In figure 1 the typical profile of the MnO embedded into the channels of MCM matrix measured at low temperature is shown. Note, that the magnetic reflection of $\frac{111}{2}$, appeared below $T_N$ of 120 K, has another, Lorentzian form. In the insert of the figure the computer simulation of the diffraction profile for the particular case of two-dimensional layer is shown. Our preliminary calculations show that the layer should be very thin, about 1-2 unit-cell and its form goes from the "saw-tooth" to the Lorentzian form at the reduction of its square (i.e. the longitudinal dimensions of the layer).

It means that embedded oxide crystallized from the solution into the narrow channels can be partially in the form of the thin adsorbed film at the pore wall. The Lorentzian form for magnetic reflection can be easily explained by the magnetic domain breakdown.

2. The magnetic order appears by the second order transition similar observed in MnO embedded in a porous glass. Below the transition the trigonal (rhombic) structural distortions, driven by the magnetic order, appear in MnO. However, in contrast with the bulk and the MnO embedded in a porous glass [1] the best fitting of profile requires the additional tetragonal distortions, never observed in the bulk MnO, but known for the bulk CoO. It is known that the maximum of diffraction line from the two-dimensional layer diffraction does not coincide with the node in the reciprocal space. Nevertheless, taking in to consideration this effect calculation shows that the small tetragonal distortions still remain. Obviously, from the neutron diffraction experiments we cannot make a definite conclusion. The answer for this intriguing question can give only Synchrotron X-ray diffraction.

One of us (IVG) acknowledges the financial support of the BENS C.

**References**

EXPERIMENTAL REPORT
Neutron Response of Selected Rare-Earth Ferricyanides

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Experimental Team: M. Lukáčová, IEP SAS Košice S. Mataš, HMI Berlin

Date(s) of Experiment: 16. -17.12.2002

Introduction

The rare-earth ferricyanides $L_x[Fe(CN)_6] \cdot nH_2O$ (Lx – rare-earth, La n = 4, 5) belong to Prussian blue family of molecule-based magnets. The crystal structure and magnetic properties of compounds are dependent on the number of water molecules in the unit cell. Removal of 1$H_2O$ per formula unit reduces the hexagonal symmetry to orthogonal [1]. To our knowledge, the positions of hydrogen atoms for this type of structure have not been reported yet.

Experimental and Results

Neutron diffraction experiments were carried out at the BER II reactor. The powdered samples of composition Pr[Fe(CN)$_6$].nD$_2$O (No.1 & No.2) and Dy[Fe(CN)$_6$].nD$_2$O have been investigated at E9 instrument at a wavelength $\lambda = 1.7971$ Å covering an angular range from 6 to 156 degree. In procedure of sample preparation the hydrogen atoms were substituted by deuterium. All samples were characterized in terms of X-ray diffraction. The Rietveld refinement was performed using FULLPROF and GSAS program [3-4]. The results from x-ray confirmed that the first Pr-sample adopt hexagonal and second one an orthorhombic type of structure. Both Pr[Fe(CN)$_6$] nD$_2$O samples were stored in a standard vanadium container, however, because of large absorption of Dy[Fe(CN)$_6$].nD$_2$O sample an aluminium double wall container was used instead. The diffraction patterns with counting statistic of 12 hours / for each pattern were taken at room temperature. In addition one low temperature pattern $T=40$ K for Pr-sample (No.1) has been taken. The later neutron diffraction data however, shows the orthorhombic type of structure for both Pr-samples only (Figure 1.). The refined lattice parameters are $a= 7.492(1)$ Å, $b= 12.9526(3)$ Å, $c= 13.8205(1)$ Å. Between x-ray and neutron measurements all samples were held in the vapors of D$_2$O. It did not prevent the structural transition from hexagonal to orthogonal structure. The Dy[Fe(CN)$_6$].nD$_2$O sample adopts the orthorhombic structure Cmcm space group, with lattice parameters at room temperature $a= 7.3601(1)$ Å, $b= 12.8027(9)$ Å, $c= 13.6109(1)$ Å (Figure.2). The data were corrected for an absorption [5]. We hope that the experiment would help in localization of deuterium atoms. V. K and M. L. acknowledge a support of EU and BENSC-HMI Berlin.

References

In the literature, the magnetic properties of molecular magnetic materials are quite frequently discussed in relation to the crystal structure of these compounds determined at ambient temperature. We believe, however, that for a consistent analysis of the low-temperature magnetic properties, it is important to accurately determine the low-temperature crystal structures as well. For example, in a previous work, we have discovered a crystallographic phase transition at 290 K in Co(ox)(bpy-d8), where ox = C₂O₄²⁻ and bpy-d8 = 4,4’-bipyridine-d8 [1].

Complementing our E6 studies of the magnetic ordering of Co₂(OD)₂(tp-d4), where tp = terephthalate, and Mn[C(CN)₃]₂ (see corresponding experimental report), we have determined the low-temperature structures of these compounds. For Co₂(OD)₂(tp-d4), the structure determination could be significantly improved [2] as compared to a previous report from X-ray powder diffraction [3]. For Mn[C(CN)₃]₂ we confirmed the previously published crystal structure [4].

Moreover, on two other compounds that were synthesised in our labs at HMI, we were able to determine the previously unknown crystal structures ab initio from E9 powder neutron diffraction data, namely Fe(pyrimidine)Cl₂ and Cu(pyrimidine)(NO₃)₂ [5] (pyrimidine = C₄H₄N₂).

Hereby, we used TREOR90 for indexing the powder data, followed by building “good guess” starting structures using sterical considerations. In both cases, the final crystal structure models, shown in Figures 1 and 2, resulted directly from the Rietveld refinement of the E9 data.

Cu(pyrimidine)(NO₃)₂ has a 1D structure, resulting in S = ½ antiferromagnetic Heisenberg chain behavior [5].

Figure 1: Crystal structure of Fe(pyrimidine)Cl₂ determined ab initio from E9 powder neutron powder diffraction data.

Figure 2: Crystal structure of Cu(pyrimidine)(NO₃)₂ determined ab initio from E9 powder neutron powder diffraction data [5].

References

There is strong evidence that magnetic interactions play a crucial role in the mechanism driving high-temperature superconductivity in cuprate superconductors. Recently several experiments [1,2] and theories [3,4] have shown that a magnetic field applied in the superconducting state of underdoped La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) induces antiferromagnetic order. The field-induced antiferromagnetism has a significant ordered moment (0.23µB/Cu$^{2+}$, H=14.5T, T=2K) and is long-range (>400Å) [1]. So far all the neutron scattering experiments have been performed with the superconducting copper oxide planes of LSCO lying in the scattering plane of the spectrometer and the dependence of the field-induced antiferromagnetism with wavevector perpendicular to the superconducting plane has not been explored.

In general the magnetism in LSCO has is found to be two-dimensional where the exchange interactions acting within the superconducting plane are much stronger than those perpendicular to the superconducting plane. For inelastic measurements this is observed as constant scattering in the out-of-plane direction. Our aim in this experiment was to find out whether or not this is also the case for the elastic field-induced magnetism in underdoped LSCO.

The horizontal magnet HM1 was used for this experiment. And measurements took place around the magnetic peak [1.12,0.12, l] where the out-of-plane wavevector $l$ was varied. The figure gives the antiferromagnetic signal as a function of wavevector $h$ and $l$. Panel a shows the signal in the superconducting state (T=2K) in zero applied field. Although scattering is found for most values of $l$ the most striking feature is the absence of scattering at the reciprocal lattice point $l$=4. In an applied magnetic field of 6T (panel b) the signal around $l$=4 is greatly enhanced, while the enhancement elsewhere is much less with the result that the intensity along the out-of-plane direction is now fairly constant. When the crystal is heated up to T=30K(>T$_c$) (panel c) most of the scattering disappears.

The overall picture is of considerable modulations along the out-of-plane axis which change in a magnetic field. This is unexpected because it suggests that there are significant correlations between the superconducting planes. The results can be explained by a model where in zero-field defects give rise to magnetically ordered regions of limited spatial extent in the out-of-plane direction. In an applied magnetic field vorticies link and extend these region along the $l$ axis.

EXPERIMENTAL REPORT

Anisotropic Field-Effect in the high-$T_c$ Superconductor La$_{2-x}$Sr$_x$CuO$_4$ ($x=0.10$)

Principal Proposer: Bella Lake, Oxford University, UK
Experimental Team: Kim Leffmann, Risø National Lab, Denmark
Niels Christensen, Risø National Lab, Denmark
Gabriel Aeppli, University College London, UK

Recently several experiments [1,2] and theories [3] have shown that a magnetic field applied in the superconducting state of underdoped La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) induces significant long-range antiferromagnetic order. So far neutron scattering experiments have been performed with the magnetic field pointing perpendicular to the superconducting copper oxide planes of LSCO. This is because the field-effect is expected to be greatest for this field direction due to the strong anisotropy of the thermodynamic properties of layered cuprates [4]. Similar work on Yba$_2$Cu$_3$O$_{6.6}$ where a field has been found to suppress the 41meV resonance, shows that this effect is much greater when the field is perpendicular to the superconducting plane than when it points within the plane [5]. It is important to determine whether the observed field effect in LSCO is also anisotropic with respect to field direction. If this is the case it would prove that the phenomenon originates from the fundamental processes within the material and would eliminate the possibility that it has a more trivial origin e.g. due to a Zeeman splitting mechanism.

For this experiment we used the V2/FLEX neutron scattering spectrometer and the magnetic field was generated by the HM1 horizontal magnet. The sample was aligned so that the axis perpendicular to the superconducting plane ($c$ axis) and one of the axes within the superconducting plane ($a$ axis) lay in the instrumental scattering plane. This arrangement allowed us change the field direction by rotating the crystal within the magnet.

The data is given in the lower panel of the figure. The red circles show the antiferromagnetic signal observed with a field of 6T pointing along $c$. The blue circles give the signal with the field pointing 78.5 degrees from the $c$ axis giving it a component of 5.9T within the superconducting plane and 1.2T along $c$. The black points give the signal in zero field. Analysis shows that the signal induced for the red data points is 15.3 counts per minute while that for the blue data points is 5.6 counts per minute clearly demonstrating an anisotropic field effect. In fact the effect of field direction is even greater than first appears because of the field component of 1.2T along the $c$ axis in the blue data. Using the theoretical predictions of E. Demler et al [3] fitted to our result for the red data (see top panel of the figure), this component along $c$ induces 5.5 counts per minute. It therefore accounts for almost the entire field-induced scattering observed for this field direction and the signal induced by the component of field within the superconducting plane is negligible.

High-transition-temperature superconductors made by doping of La$_2$CuO$_4$ have a very rich magnetic phase diagram as a function of doping concentration and the nature of the dopants. In particular, neutron scattering experiments demonstrated static incommensurate spin-density wave (SDW) order in superconducting La$_2$CuO$_{4+y}$. These observations stimulated an active study of the nature of magnetic correlations and their interaction with superconductivity in cuprate superconductors. Magnetic field serves as a weak perturbation helping to probe this interaction. The SDW signal increases when the field is applied below superconducting $T_c$. This is because the field suppresses the superconducting order parameter and, as a result, the competing SDW order is enhanced, as predicted in recent theoretical model.\(^1\)

Although there is a good qualitative agreement between our previous experimental results\(^2\) and theory, a quantitative comparison has been difficult to make. This is primarily because the previous measurements have been limited to fields below 9 T and by the availability of samples of only one doping. Therefore, we have performed our magnetic field studies of superconducting La$_2$CuO$_{4+y}$ at HMI. We were able to apply higher magnetic field in order to check the predicted field dependence of the SDW peaks intensity. In addition, we have measured the effect of applied field on two samples, the optimally-doped ($T_c = 42$ K) and the underdoped samples ($T_c = 32$ K). We have found that the underdoped sample exhibit static SDW order identical to that of the optimally-doped sample. We have also found that predicted field dependence of the SDW Bragg peaks intensity describes well our results for both samples.

The use of the BENS$C$ facilities, especially the 14.5 T magnet, was crucial for the success of this experiment, as clear from the figure below.

This figure shows our main result: field dependence of SDW Bragg peak intensity $I(H)$, normalized to the zero-field intensity $I(0)$. (a) Optimally-doped sample. Our previous low-field measurements from 0 to 7 T (diamonds), are also included. (b) Underdoped sample. The fits are $H/(H_{c2})\ln(A^*H_{c2}/H)$ and linear (dashed line). $H_{c2}$ is the upper critical field of the superconducting La$_2$CuO$_{4+y}$.

The paper describing these results in great details is to be published in Physical Review B on February 1, 2003.

NDMAP is the first Haldane gap material where a field-induced quantum phase transition to a long-range ordered state has been observed with neutron scattering [1]. The transition is of a soft-mode type: one of the three Haldane gaps decreases with field and closes at some critical field $H_c$. A qualitatively new ground state emerges following a condensation of magnons. Previous measurements [2,3] were performed in magnetic fields applied parallel to the magnetic easy plane. It was observed [3] that the gap in the soft mode reopens at $H>H_c$ and increases linearly with field. Moreover, the spectrum was shown to consist of three long-lived magnon states with no sight of an excitation continuum.

It is expected that in magnetic fields applied perpendicular to the easy plane the behaviour is qualitatively different. The high-field phase in this case is a quantum-critical state. The spectrum at any $H>H_c$ is gapless, with no sharp single-magnon states, but instead a broad continuum of excitations [4]. The purpose of the present experiment was to observe such unique behavior in NDMAP. A horizontal field magnet was used to apply a field along the crystallographic c axis of a fully deuterated NDMAP single crystal sample (1.5 g). Measurements were carried out at $T=30$ mK and in field as high as 6 Tesla ($H_c=4$ Tesla in this geometry).

Typical background-subtracted data are shown in Fig. 1. Contrary to expectation the gap in the lower mode re-opens above $H_c$. Moreover, an analysis of several const-E scans performed paying special attention to instrument resolution effects, show no deviations from the single-mode approximation. The behaviour is, however, quite different from that seen previously with the field applied perpendicular to the c axis. As can be seen in Fig. 2, the increase of the gap above $H_c$ is sublinear, rather than linear. Until a more complete data analysis has been carried out, we will not be able to unambiguously identify the reasons for the stark deviations from theoretical predictions. Possible reasons include weak-but-relevant inter-chain interactions, in-plane anisotropy and a tilt of the local magnetic hard axis for $\text{Ni}^{2+}$ relative to the crystallographic c direction. Work at ORNL and BNL was carried out under US DOE Contracts No. DE-AC05-00OR22725 and DE-AC02-98CH10886, respectively. Work at RIKEN was supported in part by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science.

In the invar alloy Fe_{0.65}Ni_{0.35}),Mn_x a re-entrant spin glass (RSG) exists for x < 0.139 [1]. The spatial correlations of the magnetization were observed both in the FM and RSG phase by SANS [2] and by 3-dimensional neutron depolarization techniques[3-5] on different length scales. (0.15 nm – several μm). They depend in a pronounced way on the temperature and give evidence of the freezing of the spin components in the RSG glass phase and its irreversibility. Correspondingly, strong changes in the spin dynamics are expected. The observation of the intermediate scattering function by the paramagnetic NSE techniques will provide detailed information on spin dynamics during the freezing process.

We measured the intermediate scattering function $S(Q, t)$ and the structure factor $s(Q)$ for a sample with $x=0.113$ for scattering vectors $0.26 \text{ nm}^{-1} < Q < 1.44 \text{ nm}^{-1}$ and temperatures ranging from the ferromagnetic phase ($T_{\text{RSG}} = 90 \text{ K} < T < T_c = 220 \text{ K}$) to the strongly irreversible mixed RSG phase $T < T_2 = 50 \text{ K}$.

The data shown in Fig.1 clearly display a change in the time evolution of $S(Q, t)$ both with temperature and scattering vector $Q$. Fitting a stretched exponential decay

$$S(Q, t) = s(Q) s(Q) = \exp[-(\gamma t)^n]$$

(1)
to the experimental data shows two experimental findings:

- the inverse correlation time $\gamma$ decreases upon cooling down from FM to the first mixed RGS phase by an order of magnitude, and decreases further in the second mixed RSG phase.
- a qualitative change of the dynamics from almost exponential decay ($0.8 < n < 1$) in the ferromagnetic phase to a stretched exponential decay ($n = 0.4 - 0.5$) in the second, strongly irreversible RSG phase at the low temperature ($40 \text{ K}$).

The behaviour of $S(Q, t)$ of the sample differs from that of a classical spin glass [6,7] by the observed $Q$-dependence as will be expected for the FM phase. However, the $Q$-dependence shows up in the mixed RSG phase, too. It is appreciable at 80 K and still present, but smaller, below 60 K (cf. Fig.1).

![Fig 1: The normalized intermediate scattering function $S(Q_{\text{NSE}})$ of Fe_{0.65}Ni_{0.35})_{0.89}Mn_{0.11}$ depends on the scattering vector: (a) $Q = 0.46 \text{ nm}^{-1}$, (b) $Q = 0.85 \text{ nm}^{-1}$. The lines result from fitting equ.1 to the data.](image-url)
# EXPERIMENTAL REPORT

## Detailed observation of transverse spin freezing in Mn-Cu

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<td>Catherine Pappas, HMI</td>
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<td></td>
<td>Annemieke Mulders, Monash University, Australia</td>
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The magnetic diffuse scattering at the (0,0,1) position in neutron scattering in Mn0.9Cu0.1 is believed to originate from transverse fluctuations in the antiferromagnetic state whereas the Mn moment is directed along the c-axis. The detailed nature of these magnetic fluctuations remains not well understood. The scattering is thought to be due to components of the moment transverse to the antiferromagnetic direction which surround copper atoms and whose transverse nature is due to the frustration of the first neighbour antiferromagnetic interactions. Reentrant spin glass freezing in antiferromagnetic Mn-Cu is seen for all antiferromagnetic compositions and the glass temperature is a continuation of that seen in alloys more dilute in Mn.

Neutron scattering experiments performed at Saclay show two (or more) Lorentzian components in the dynamical transverse magnetic fluctuations of which the width narrows with decreasing temperature indicating some form of magnetic freezing [1]. The results indicate the fluctuations are faster than $10^{-11}$ s.

In contrast to this, spin echo data taken in 2000 at SPAN [2] on a relatively large single crystal of Mn-Cu showed a static signature of the fluctuations. It was clearly observed that $S(q,t) = 1$ over the whole temperature range between 2 and 300 K.

About half of the diffuse scattering is depolarized, i.e. we observe spin flip scattering on top of a depolarized signal. The ratio between the two parts remains constant as function of temperature.

At the moment it is unclear how half of the signal becomes depolarized. It possibly suggests the presence of a helical component. The dynamical behaviour of the diffuse scattering as seen in Saclay could be present in the depolarized part of the signal.

Further neutron experiments are prepared to observe the signature of this depolarized part of the signal.


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To resolve this discrepancy in results we repeated the spin echo experiment on exactly the same crystal that was used for the Saclay experiment. This crystal is smaller but of higher quality. It shows less mosaic spread and less impurities.

Spin echo data of the magnetic, spin flip scattering on the small single crystal confirm the static response as it was observed on the large crystal. $S(q,t) = 1$.

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Experimental Report

Longitudinal excitations in the high-field phase of CuGeO$_3$

CuGeO$_3$ is a spin-Peierls system where the coupling to optic phonons drives the Peierls dimerization. It is the first spin-Peierls material which is investigated in its incommensurate high-field phase, where incommensurate quantum fluctuations become statically ordered due to the 3D coupling to the phonon field. We continued our investigation of the excitations in the high-field phase (see earlier reports and [1-4]). In this experiment, V2 was configured with guide-60'-60'-60' collimation and flat analyser, 77K-Be-filter (before or after the sample) and $k_f=1.54\AA^{-1}$ fixed. The single crystal CuGeO$_3$ had a volume of about $4\times10^6\text{mm}^3$ and was mounted in the vertical 14.5T cryomagnet VM-1, with $(0, k, l)$ in the scattering plane. In a first step we completed the (0 1 0) dispersion of the magnetic excitations around the magnetic AF-point (0 1 1/2) at 14.5T and 1.5K. The results are shown in fig.1, combined with those of March 2001. The $\Delta_{\parallel}$ mode with the dispersion minimum at the incommensurate wave vector (0 1/2 0.515) is clearly visible. The dispersion was then tested at 12T, 12.5T, 12.6T, 12.8T, and 13T, (at intermediate fields only representative wave vectors) in order to follow the development from the dimer phase to the unusual dispersion of the high-field phase and detect a possible critical flattening of the dispersion. Figure 3 shows 12T, 12.5T, and 13T. We found no critical field region where the dispersion becomes flat, instead the incommensurate minimum of the $\Delta_{\parallel}$ dispersion seems to appear discontinuously.

In order to test the polarisation of the $\Delta_{\parallel}$ mode, scans at (0 3 0.5) and (0 3 0.515) were performed, as well as comparison scans at 12T. $\Delta_{\parallel}$ decreases far less in intensity than $\Delta_{\perp}$. (In order to reach other zones, configuration tests were performed with PG(114) before sample, $k_f=2.05\AA^{-1}$ fixed and scattering sense $+1,+1,1,1$.) The dispersion along $qk$ was investigated around (0 1 0.5) and (0 1 0.515) at 14.5T. $\Delta_{\parallel}$ seems to disperse much less than $\Delta_{\perp}$ (fig.3). A search for magnetic excitations at 14.5T in the paramagnetic phase (15K) showed enhanced scattering at low energies. Preliminary results are obtained at several wave vectors.


Figure 1: Magnetic excitations of CuGeO$_3$ around the AF point (0 1 1/2).

Figure 2: Magnetic excitations of CuGeO$_3$ around the AF point (0 1 1/2), at 12T, 12.5T, and 13T.

Figure 3: Magnetic excitations of CuGeO$_3$ around the AF point (0 1 1/2).
Quantum spin systems exhibit unique magnetic properties which bear no classical analogies. An example of particular relevance is the realization of magnetic quantum phase transitions driven by zero-point spin fluctuations. Within such a framework, new materials which are based on a crystalline network of dimers recently made Bose Einstein condensation (B.E.C.) expectations legitimate. Of interest are the compounds ACuCl$_3$ (A=K, Tl) in which the two Cu$^{2+}$ ions forming the dimer are antiferromagnetically coupled [1]. The dimer ground state is then a singlet with total spin $S=0$, separated by an energy gap from the excited triplet state with total spin $S=1$. The application of an external magnetic field splits the excited triplet into three components with $S=+1$, 0, -1. At a critical magnetic field $H_c$ the energy of the triplet $S=+1$ component intersects the ground state singlet and long-range magnetic order occurs, thus $H_c$ is a quantum critical point separating a gapped spin-liquid state ($H<H_c$) from a field-induced magnetically ordered state ($H>H_c$). The triplet components with $S=+1$ can be regarded as diluted bosons, thus B.E.C. occurs in these dimer compounds at the quantum critical point $H_c$ [2,3]. However, these considerations do not stem from a single gas cooled below the deBroglie temperature, but from dimer states split at high magnetic fields. The magnetic excitation spectrum associated with the condensate has been theoretically predicted to be a gapless Goldstone mode [4]. Here we summarize the complete experimental investigation of the spectrum in such a field-induced magnetic ordered state, which we accomplished by neutron scattering on TiCuCl$_3$ single crystals. Our results include the unambiguous verification of the predicted Goldstone mode characteristic of the B.E.C. of the triplet states.

The aim of the present study was to explore the full energy dispersion of the magnetic fluctuations modes, thus conclusively characterizing the typical time- and space-scale related to the spectrum in the field-induced ordered phase of a quantum spin liquid. The results at fixed $T=1.5K$ and $H=14T$ clearly indicated the coexistence of two higher-lying modes and a low-lying mode, see figure 1. The higher-lying modes are gapped and retain a quadratic dispersion around the Bragg point, whereas the low-lying mode is gapless and linear. Both have the periodicity established by the zero-field interactions. These experimental conclusions are in agreement with a comprehensive theoretical study of the field-induced ordered phase in TiCuCl$_3$ [4]. They not only allow the model description of the magnetic quantum phase transition realized in TiCuCl$_3$, but also provide a reference of general interest among dimer quantum spin liquids.

Figure 1. Contour plot of the magnetic inelastic neutron scattering intensity observed at $H=0T$ and $H=14T$, $T=1.5K$. The second high-lying mode at $H=14T$ is not shown because of weak signal. The data have been symmetrized around $q=0$. Further comments are provided in the text.

EXPERIMENTAL REPORT

High magnetic field spin dynamics for a hole doped S=1/2 Heisenberg antiferromagnet with a quantum disordered ground state

Proposal No:PHY-02-0358
Instrument V2
Local Contact
K.Habicht

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Date(s) of Experiment
17.10.– 27.10.2002
Date of Report: 15.01.2003

An ideal 2 dimensional Heisenberg antiferromagnet has no long-range order at finite temperature. The long-range antiferromagnetic order in laminar La$_2$CuO$_4$ is due to small interlayer magnetic coupling. This long-range order is susceptible to electric hole doping and disappears at 2-3% hole concentration. The doped La$_2$CuO$_4$ thus offers a great opportunity to study quantum spin liquid which exist at temperature between zero and $J/k_B$, where $k_B$ is the Boltzmann constant. Two type of spin liquids have been theoretically predicted as quantum critical and quantum disordered, which have been experimentally observed [1-4].

In this experiment, we investigate effect of magnetic field on the two type of quantum spin liquids in a single crystal of La$_2$ (Cu$_{0.94}$Li$_{0.06}$)O$_4$. For this sample, the crossover temperature between the quantum critical and quantum disordered spin liquids is about 50 K [4]. A maximum of 14.5 T of magnetic field was used in this cold neutron inelastic measurement of magnetic fluctuation spectrum. Sample scans are shown in the figure. More details will be published when data analysis is finished.

EXPERIMENTAL REPORT

Inelastic Neutron Scattering on three isostructural Mn$_{12}$ clusters

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Experimental Team:       G. Chaboussant, University of Bern
                          A. Sieber, University of Bern
                          R. Basler, University of Bern

Date(s) of Experiment:  14. – 23.07.2002
Date of Report:          January 2003

We investigated a series of three isostructural Mn$_{12}$ single-molecule magnet (SMM) clusters [Mn$_{12}$O$_{12}$(O$_2$CC$_6$F$_5$)$_{16}$(D$_2$O)$_4$] $^1$ (S = 10 ground state), (NMe$_4$)[Mn$_{12}$O$_{12}$(O$_2$CC$_6$F$_5$)$_{16}$(D$_2$O)$_4$] $^2$ (S = 19/2 ground state) and (NMe$_4$)$_2$[Mn$_{12}$O$_{12}$(O$_2$CC$_6$F$_5$)$_{16}$(D$_2$O)$_4$] $^3$ (S = 10 ground state)

The different oxidation states of the title compounds allowed us to study the axial ZFS parameters D and $B_4^0$, as a function of the electronic structure of the magnetic clusters.

The structure of $^1$ is shown in Figure 1. The reduction to $^2$ and $^3$ takes place on a Mn$^{3+}$ site of the neutral compound, to form valence trapped $^{Mn_4^{4+}Mn_7^{3+}Mn_1^{2+}}$ and $^{Mn_4^{4+}Mn_6^{3+}Mn_2^{2+}}$ clusters

Figure 1: Structure of $^1$. The small spheres are Mn$^{4+}$ ions and the large spheres Mn$^{3+}$ ions.

The low temperature data in Figure 2 revealed two isomers present in each sample. Together with the INS data collected at elevated temperatures and by applying the Hamiltonian

$$\hat{H} = D \left[ \hat{S}_z^2 - \frac{1}{3} S(S+1) \right] + B_4^0 \hat{O}_4^0,$$

where

$$\hat{O}_4^0 = 35\hat{S}_z^4 - 30S(S+1)\hat{S}_z^2 + 25\hat{S}_z^2 + 6S(S+1),$$

we could derive the axial ZFS parameters given in Table 1.

Thus, one can see that the negative axial ZFS parameter D is decreasing by about 25 % upon each step of reduction.

Figure 2: Neutron energy loss spectra of $^1$, $^2$ and $^3$, from top to bottom, respectively, collected at $\lambda_i = 5.9$ Å and $T = 1.8$ K. The resolution at zero-energy transfer is 70 $\mu$eV.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Isomer</th>
<th>D [cm$^{-1}$]</th>
<th>$B_4^0$ [cm$^{-1}$]</th>
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<td></td>
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<td>I</td>
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<td>---</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>-0.241</td>
<td>---</td>
</tr>
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</table>

Table 1: Determined ZFS parameters

Literature
We have recently performed detailed structural and magnetic studies on Fe(NCS)$_2$(d$_4$-pyz)$_2$, which is to our knowledge the only example of molecule-based systems that behaves as the 2D S=1/2 Ising square lattice while 3D ordering is achieved [1]. As already observed in several systems the 3D ordering that takes place below $T_N$ is the result of weak interlayer coupling [2]. However their critical behavior is determined only by the intralayer interactions. In the case of Fe(NCS)$_2$(d$_4$-pyz)$_2$ the global situation may be summarized as follows. From the NPD data, two regimes were observed. For $2 < T < 6.6$K, the magnetic scattering arises in the Bragg peaks and the super lattice peak positions are invariant indicating an unchanged propagation vector while above 7K, no coherent magnetic scattering is observed and the background increases slightly indicating that the sample is in the paramagnetic regime. In addition the order parameter follows the exact Osanger-solution [3] of a 2D S=1/2 Ising system, in agreement with the analysis of both $\chi(T)$ and $C_{m}(T)$ data.

The aim of the present investigation was to use inelastic neutron scattering, which is a unique source of information on the collective excitations of the material, in order to understand the apparent two-dimensional behavior of the magnetic ordering of Fe(NCS)$_2$(d$_4$-pyz)$_2$.

The experiments were performed on a fully deuterated powder sample using the high-resolution multi-chopper time-of-flight NEAT. Data have been collected at various temperatures, between 2 and 50 K, with incident neutron energy of 3.15 meV ($\lambda = 5.1\text{Å}$, $\Delta E=217 \text{μeV at the elastic peak position}$).

The observation of a large gap of about 1.64 meV below $T_N$ that is, as expected in an Ising system [4], dispersionless. Furthermore above $T_N$ a peak is observed at higher temperatures located at 1.04 meV, reflecting that in a local scale antiferromagnetic ordering is maintained within the chains. The results can be understood as follows. The critical scattering is essentially 2D in nature and long range magnetic ordering is ultimately achieved as a consequence of the strong intralayer interactions and thus long-range ordering with the planes.

$S(|Q|,\omega)$ vs. energy transfer $E$ (meV) for Fe(NCS)$_2$(d$_4$-pyz)$_2$ at selected temperatures.

We have investigated polycrystalline Fe films, which were grown on oxidised Si substrates previously coated with an Ag buffer layer of varying thickness. The surface roughness of the Ag buffer layers increases dramatically with thickness. Neutron reflectivity experiments were carried out at room temperature and in ambient conditions. A magnetic field parallel to the film plane could be applied using an electromagnet. We have studied both the specular and off-specular neutron reflectivity profiles and we have carried out polarization analysis of the reflected neutrons. The off-specular measurements are still being analysed. Therefore we restrict this report to the specular profiles.

Two different samples with different surface roughness have been studied. The smooth sample, a Fe(300Å)/Ag(40Å) bilayer, showed a very sharp magnetization reversal that is characteristic for domain wall motion, while the rougher sample, a Fe(300Å)/Ag(120Å) bilayer showed a more continuous magnetization reversal, characteristic for a combination of domain wall motion and coherent rotation. Magnetic field scans have been carried out and polarization analysis showed that in both films, the magnetization reversal mechanism is dominated by domain wall nucleation and motion. No spin flip scattering has been observed during the reversal process. Therefore additional θ-2θ scans at the coercive field (M =0) have been carried out for both samples (see figure 1). The important difference between the two graphs is situated around the edge of total reflection. The smoothest sample (see fig. 1(a)), shows a small dip in reflected intensity profile around q = 0.013 Å⁻¹. Parratt simulations showed that this dip could be contributed to the limited coherence length of the neutrons. When the coherence length of the neutrons is smaller than the domain size, the scattering process can be regarded as incoherent scattering from two sample parts with opposite magnetization. Hence, to reconstruct the observed θ-2θ intensity profile, the reflected intensities R⁺ and R⁻ for each part (R⁺/2 and R⁻/2, R is the reflected intensity for saturation magnetization) should just be added. The coherence length of the neutrons at q = 0.013 Å⁻¹ is calculated to be 109 micrometer. This means that the size of the magnetic domains at the coercive field for the smoothest sample is larger than 109 micrometer or in other words that the domains in the roughest film are smaller than 109 micrometer.

![Fig. 1 Polarized neutron reflectivity profiles, experimental and calculated, for (a) a Fe(300Å)/Ag(40Å) bilayer and (b) a Fe(300Å)/Ag(120Å) bilayer.](image)

We conclude that the roughness of the Fe films does not affect the reversal mechanism (i.e. domain wall motion). Only the number of nucleation sites with different nucleation fields, and consequently the size of the domains at the coercive field are strongly influenced. Tuning the coherence length of the neutrons would enable us to determine more accurate values of the typical domain size and also to study the growth of the domains when the reversal is continued.
The goal of our study was to measure the magnetization versus temperature of thin epitaxial Fe films on V(001) for 4, 4.5 and 5 atomic planes. One Curie temperature was expected for 4 and 5 atomic planes, whereas two Curie temperatures were expected on a fractional number of plane like 4.5. Typical ferromagnetic M(T) curves were expected on the 4 and 5 planes, whereas a superimposition of both curves were expected for 4.5 planes. In this former case, two abrupt decreases of the magnetization were expected at the two transition temperatures. We had already evidenced the occurrence of two Curie temperatures in the Fe/Ir system by working on superlattices. In the present study, our goal was to evidence this phenomenon on a single layer. The Fe/V system is particularly interesting for neutrons analysis since the absorption of vanadium is close to zero.

Consequently, measurements on a single layer were not possible. These project is possible only on layers just grown in UHV, and measured in UHV. For this purpose, the only way is to couple a MBE to the beamline.

To see the rate of counting, we have first worked on Fe/V superlattices (20 bilayers). We tried to measure the magnetic contribution on the diffraction peak due to the superperiod of the superlattice at low angle. The counting rate was very small so we did not manage to get something significant on these superlattices.
There are arguments that the surface forces influence the concentration of mobile components in objects of dimensions of some nanometers. The strength of the surface forces depends strongly on the distance between two interfaces. In nanostructured systems the dimensions often comes in the range below 20 nm. In that range the surface forces between the interfaces of small particles, of different phases or of thin layers become significant for the thermodynamic description of the system. If the effect of the surface forces on the partial free energy of the components present in the system is different, then the chemical potentials become functions of the dimensions. Consequently, mobile components will redistribute to establish thermodynamic equilibrium and the concentration of such a mobile component will become a function of the dimensions as well [1,2]. Therefore, it is interesting for numerous investigations of technical and biological structures of nanometer scale to learn more about the equilibrium distribution of mobile components as water, ions, small polar and apolar molecules, dissolved gas molecules etc. as a function of the dimension of the system. Spectroscopic measurements of the water content of polyelectrolyte multilayers [3] indicate a variation of the water/ion-pair ratio with the total layer thickness. Until now there is not a systematic investigation of this effect.

We investigated the absorption of D$_2$O in polyelectrolyte (PE) layers of 1:1 PSS(-)/PDADMAC(+) prepared by layer-by-layer deposition on Si substrates. We choose to use the neutron reflectivity, because the angular dependence of the reflectivity R(Q) is a function of the Scattering Length Density (SLD) profile perpendicular to the reflecting interface. Therefore, from the neutron reflectivity experiments we are able to obtain information about the amount of D$_2$O absorbed in the PE layer and its distribution across the layer.

The measurements were performed in a newly developed gas-tight chamber, which allows working at well-defined humidity and temperature. One sample consisting of a single polyelectrolyte bilayer PSS/PDADMAC was studied. The sample was prepared following the procedure described in [4]. First the reflectivity curve was measured in dry N$_2$ atmosphere. Two consecutive runs were performed in order to assure that the equilibrium dry state of the sample is reached. There was not a difference between the first and the second scan which shows that the equilibrium was reached within the first 8 hours, the time necessary for a single scan. Then the sample was exposed to saturated D$_2$O atmosphere and two reflectivity curves were collected again. The results are shown on Fig. 1.

The SLD profiles show that the amount of D$_2$O in the film exposed to saturated D$_2$O vapours is not equivalently distributed. The D$_2$O concentration near to the Si/PE film interface is higher. From the value of the SLD the amount of absorbed D$_2$O was estimated to be around 80% of the content of the film. This value is higher than the values reported already for thicker PE films of the same components [5]. This supports the theoretical predictions for dependence of the amount of the mobile component on the thickness of the system. More precise results will be obtained after repeated measurements with X-ray reflectivity at the same experimental conditions.

Spintronics is a new branch of physics concerned with the storage, the transfer and the manipulation of a binary information coded by the spin of the electron and not only by its charge. In order to handle spin-coded information, new types of materials are developed such as Diluted Magnetic Semiconductors (DMS), exhibiting 100 % spin polarisation below their Curie point combined with the Mn p-doped GaAs semiconducting properties. The ternary alloy Ga$_{1-x}$Mn$_x$As is a model system within the class of DMS III-V compounds grown by MBE at low temperature. The magnetization directions and the mechanism of the magnetization reversal of high-quality thin films of Ga$_{1-x}$Mn$_x$As were studied by Polarized Neutron Reflectivity (PNR).

PNR was used as a tool to elucidate the magnetization switching mechanism of two DMS thin films. Both films were grown at two different temperatures (respectively 270 °C and 330 °C). The measurements were performed at 10 K with the external magnetic field aligned along one of the anisotropic magnetic easy axes parallel to the [100] or to the [010] crystallographic axes.

The first sample is a Ga$_{0.907}$Mn$_{0.093}$As alloy grown at 270 °C (Tc = 28 K, Ms = 12.1 kA/m at 5 K). Analysis of the specular reflections showed no variation of the spin-flip cross-sections intensity although an inversion of the intensity of both the -- and the ++ cross-sections was observed. The coercive field was estimated at about 20 Oe (Fig. 1).

The measurement of the second sample, a Ga$_{0.912}$Mn$_{0.088}$As alloy grown at 330 °C (Tc = 71 K and Ms ~ 15-20 kA/m at 5 K), showed a similar variation of the non spin-flip cross-section intensities, with a coercive field of 20 Oe. But an additional spin-flip contribution was detected with a maximum at 20 Oe (Fig. 2).

The results clearly indicate the detection of an in-plane macroscopic component of the magnetization perpendicular to the initial magnetic easy axis during magnetization reversal in the second sample. This component of the magnetization, parallel to the second magnetic easy axis, was not detected in the first sample either because not existing or because the magnitude of its magnetization at 10 K was too low. This study shows that PNR can be a useful technique for analyzing the switching mechanism of the magnetization in Ga$_{1-x}$Mn$_x$As DMS thin films.
Off-specular neutron reflectivity from micropatterned films

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Experimental Team: H. Fritzsche (HMI)
K. Temst (KU Leuven)
M. J. Van Bael (KU Leuven)

In order to investigate the influence of the dots’ shape on the off-specular reflectivity we recorded reciprocal space maps for two different orientations of the sample: the long side parallel to the neutron beam and the short side parallel to the beam. The experimental results for the down-neutrons for the case of saturation is shown in Fig. 1. If the long side is parallel to the neutron beam only the first satellite is observable (left), whereas three satellites are observable if the sample is rotated by 90 degrees with its short axis along the beam (right).

This can be understood from classical diffraction theory because the form factor is decreasing much faster for the case of a large unit cell structure (long side of the dots parallel to the beam).

References:

Fig. 1: Reciprocal q_x-q_z maps for the case of saturation measured with down-neutrons with the long side parallel to the beam (left) and the short axis of the dots parallel to the beam (right).
It is of scientific and technological importance to be able to understand and investigate magnetization reversal processes in magnetic thin films. Exchange bias (EB) systems, i.e. ferromagnetic materials coupled to an antiferromagnet have been of special interest to many research groups since the discovery of the EB effect [1]. EB is usually characterized by a unidirectional shift of the magnetic hysteresis loop and by increasing coercivities with decreasing temperatures. In this state, excellent conditions exist to observe unique phenomena such as asymmetric reversal processes on opposite sides of the hysteresis loop or training effects [2]. The latter occur after cycling the magnetization several times. Polarized neutron reflectometry (PNR) provides a ready means to study magnetization reversal processes. Thus, previous investigations on a [Co/CoO/Au]20 multilayer have revealed the presence of asymmetric reversal mechanisms.

Studying the specular reflectivity at characteristic reversal fields has evidenced that the reversal at the decreasing field branch (field B, left figure) is dominated by domain wall motion while the reversal at the increasing field branch (field C, left figure) is characterized by rotation of the magnetization. Diffuse scattering experiments have further revealed the presence of a broad distribution of domain sizes for the reversal process at the increasing field branch. This is shown by the $\Theta_i - \Theta_f$ map in (C) of the figure on the right (with dashed lines referring to the specular reflection: $\Theta_i = \Theta_f$). The aim of the present investigation has been to study the reversal process during the 2nd cycle of the hysteresis loop. The reversal at the decreasing field branch of the 2nd cycle (field D, left figure) has been found to occur at a reduced coercive field of about -600 Oe in comparison with a field of nearly -900 Oe for the first cycle. A PNR study including diffuse scattering experiments shows that the reversal mechanism at the decreasing field branch changes to magnetization rotation (D in right figure) which appears to be accompanied by formation of domains with reduced size. This change is attributed to magnetic training after reversing the magnetization once to the saturation field opposed to the EB pinning direction (cooling field direction). It can be assumed that a fraction of the spins at the Co/CoO interface decouples due inhomogeneous switching of the magnetization in the course of the cycling. In order to obtain more detailed information a quantitative analysis has to be performed.

The experiment concerns to investigations of the crystal structure and lattice dynamics in ternary Cu-based superionic conductors (Cu$_{1-x}$Ag$_x$)$_2$Se. Below 373 – 473 K (depending on composition) this compound consists of AgCuSe and Cu$_2$Se-based solid solution with FCC structure. We studied the temperature of the superionic transition and phase transformations in polycrystalline sample Cu$_{1.75}$Ag$_{0.25}$Se using spectrometer E1 in conventional diffraction mode and with analyser crystal fixed to $\Delta E = 0$.

The polycrystalline sample of Cu$_{1.75}$Ag$_{0.25}$Se was prepared by solid-state reaction of high purity Cu and Se powders at 720 K. The sample (10mm diameter and 18 mm long) was measured at wavelength of 0.2417 nm in temperature range 300 – 500 K. The diffraction patterns taken on heating at temperatures close to phase transition are shown in Fig. 1.

![Fig. 1. Diffraction patterns of Cu$_{1.75}$Ag$_{0.25}$Se compound at different temperatures.](image)

The peaks from the low temperature phase AgCuSe at $\Theta = 64.5^\circ$ and 69$^\circ$ disappear at T=378 K. At higher T only reflection at $\Theta = 70.5^\circ$ from Cu$_{1.75}$Ag$_{0.25}$Se solid solution is seen. Note that position of this peak does not depend essentially on temperature except the narrow interval close to the phase transition.

The diffraction pattern of Cu$_{1.75}$Ag$_{0.25}$Se was also measured at 497 K (Fig. 2). As for the high temperature $\alpha$-Cu$_2$Se phase it can be indexed within the FCC cell formed by the Se ions. The peak at 59$^\circ$ could be related to modulated distribution of cation ions with doubled period along the [111] direction [2]. We observed such a structure in the intensity distribution in reciprocal space of single crystal $\alpha$-Cu$_2$Se [3].

The diffraction pattern measured in double crystal mode of E1 shows a presence of strong diffuse inelastic scattering with a maximum close to (220) reflection. The similar angular behaviour of the diffuse scattering was observed in $\alpha$-Cu$_2$Se at 200°C and was assigned to strong correlations among the thermal displacements of the ions [4]. However in contrast with Ref. 4 the diffuse component measured with analyser ($\Delta E = 0$ scan) is nearly suppressed (Fig. 2), probably due to a narrower elastic window, which cuts off the low-energy excitations.

![Fig. 2. Diffraction pattern of Cu$_{1.75}$Ag$_{0.25}$Se at 497 K. Upper curve – conventional double crystal scan. Lower curve – triple-axis $\Delta E = 0$ scan.](image)

References:
EXPERIMENTAL REPORT

HT - neutron diffraction study on the phase transitions in \( \alpha - \text{Na}_2\text{Si}_2\text{O}_5 \)

Proposal CHE-01-1013
Instrument E2
Local Contact D. Hohlwein

Date of Report: 29.01.2003

Introduction

Sodium disilicate (\( \text{Na}_2\text{Si}_2\text{O}_5 \)) shows a complex polymorphism [1]. At least eight different modifications have been reported as a function of temperature, pressure and synthesis conditions. Most of the sodium disilicates can be structurally classified as single layer silicates, with one short lattice constant of about 4.9 Å. This value corresponds to the translation period along the chain direction in \( [\text{SiO}_3]^2 \text{zweier} \) single chains within the tetrahedral layers.

The thermodynamically stable compound at room conditions is the so-called \( \alpha_{\text{III}} \) - phase. It is known that this compound shows two reversible thermal effects at about 676°C and 708°C, respectively. These effects have been attributed to structural phase transitions. Neutron diffraction experiments were performed to study the crystal structures of the two hypothetical HT-forms \( \alpha_{\text{II}} \) and \( \alpha_i \), respectively, in more detail.

Experimental details and results

The sample was prepared from crystallization of a stoichiometric glass. Powder diffraction patterns were measured at six temperatures between RT and 750°C at the E2/1 flat cone diffractometer with a wavelength of 1.219 Å in the range between 10° and 90° 2\( \theta \) (see Fig.1). The diffraction data were subsequently analyzed with the Rietveld technique.

According two prior X-ray diffraction studies [2] the orthorhombic \( \alpha_{\text{III}} \) phase should transform into a monoclinic \( \alpha_{\text{II}} \) phase, whereas the \( \alpha_i \) phase should adopt orthorhombic symmetry again. In our neutron diffraction experiments which were performed with sufficient high resolution we could not find any indication of a splitting of reflections in the stability field of the \( \alpha_{\text{II}} \) phase. The comparison between the diffraction pattern collected at room conditions and at 750°C shows, that several weak reflections have disappeared. The peaks of this HT-diffractogram could be indexed with an orthorhombic \( A \)-centered unit cell with lattice constants of about \( a = 6.527 \) Å, \( b = 15.459 \) Å, \( c = 5.001 \) Å. Primarily structural refinements of this data set collected in the stability field of the \( \alpha_{\text{II}} \) phase indicate, the crystal structure can be refined in the space group \( \text{Aba}_2 \). The main difference between the \( \alpha_{\text{III}} \) phase (space group \( \text{Pcnb} \)) and the \( \alpha_i \) form can be attributed to different rotation patterns of the tetrahedra belonging to neighboring layers about the \( b \)-axis (see Fig. 2). The structure refinements of the intermediate \( \alpha_{\text{II}} \) phase are still in progress.

Fig.1. Neutron diffraction patterns of \( \alpha - \text{Na}_2\text{Si}_2\text{O}_5 \) at (1) RT; (2) 670°C; (3) 690°C; (4) 700°C; (5) 720°C; (6) 750°C

Fig. 2. Side view of the structures (a) \( \alpha_{\text{III}} \)-phase (RT) and (b) HT-phase (750°C)


EXPERIMENTAL REPORT

Neutron diffraction study of Ni-doped sodium metaphosphate glasses

Proposal N° CHE-01-1092
Instrument E2
Local Contact Prof. D. Hohlwein

Date(s) of Experiment 25.02-03.03.2002
Date of Report: 14.01.2002

Transition metal oxides dissolve readily in phosphate glasses giving characteristic coloration which sensitively depends on the oxidation state and the coordination of the transition metal and arises in most cases from d-d electronic transitions. Since very few structural studies have been performed on transition metal-doped phosphate glasses so far we have carried out neutron diffraction radial distribution analysis of several (NiO)ₓ(NaPO₃)₁₋ₓ glasses (x = 0.0, 0.018, 0.033 and 0.074). All samples have been prepared by melt quenching between liquid-N₂-cooled metal blocks.

The diffraction experiments were performed at the E2 flat-cone diffractometer with an incident wavelength of λ=0.914 Å. The powder samples were loaded in a cylindrical vanadium (V) can with radius 0.415 cm. Diffraction patterns were taken for: (i) the glass samples; (ii) the empty V can; (iii) the instrumental background; (iv) a V rod (0.408 cm radius). All samples were measured at least 14 hours relative to the incident beam monitor from 3° to 83° and from 27° to 107° 2Θ. After corrections for the efficiency of the position-sensitive detector and background subtraction, the data of the two ranges for each sample were merged together and Fourier smoothed.

The scattering curve for each sample was then corrected for multiple scattering, absorption and placed on an absolute scale by dividing with the V rod counts (Fig. 1). The self-scattering terms, including the Placzek correction, were then subtracted. The corresponding total pair correlation functions g(r) (Fig. 2) were calculated using the inverse Monte Carlo program MCGR. The addition of NiO has a negligible effect on both the average P-O distance of about 1.5 Å and the average O-O distance of about 2.5 Å (Fig. 2), but leads to a slight decrease of the medium-range order between 3.8 and 8.0 Å.

Fig. 1. Normalised scattering curves.

Fig. 2. Total pair correlation functions.

Detailed interpretation of the results will be given elsewhere.
The orientational glass (OG) state was found at low temperature in the x-T phase diagram of the [Rb$_x$(NH$_4$)$_{1-x}$]$_2$H(SO$_4$)$_2$ mixed crystals [1]. The study of OG forming nature has been carried out for two single crystals, grown with rubidium concentrations x=0.11 (S1) and 0.20 (S2), on the E2 flat-cone diffractometer at room and low temperatures.

The diffraction patterns for S1 at 270K are identified by C2/c sp. gr. in the plane (a*c*)(Fig. 1). The appearance of forbidden C2/c sp. gr. reflections at 100K in (a*c*) plane shows that S1 has undergone a phase transition with cooling into a crystal structure with sp. gr. of lower symmetry and similar lattice parameters, for example P2/n (Fig. 2).

The diffraction patterns for S2 are obtained in the (a*c*) plane with $\theta$=1.215Å at 270 K (Fig. 3) and 5 K (Fig. 4), showing that the C2/c sp. gr. is not changed with cooling (also observed for the (b*c*) plane).

The aim of the present work was to study in-situ phase transformations, crystal structure and lattice parameters in martensite in non-stoichiometric ferromagnetic $Ni_{53,3}Mn_{19,1}Ga_{27,6}$ alloy within temperature range 500K – 4K.

**Experiment.** Measurements were performed with E2 diffractometer at $\lambda = 0.1217$ nm. The single crystal sample $Ni_{53,3}Mn_{19,1}Ga_{27,6}$ was aligned to have $\{100\}$ planes coinciding with scattering plane defined by the wave vectors of incident and scattering neutrons. The temperature behaviour of the crystal structure was studied *in-situ* using the Cryofurnace OF in the temperature range from 500K to 4K. Data analysis of datasets was carried out using TVtueb program [1].

**Results:**
1) the direct and inverse martensite phase transitions occur within the wide temperature interval 440K ~ 485K. Peaks belonging to the martensite are observed until 485K (Fig.1);
2) Martensite in studied alloy has non-modulated tetragonal lattice with the space group $I4/mmm$ and with lattice parameters $a=b=0.3817$ nm, $c=6.647$ nm and $c/a=1.717$ at 288K. This tetragonal structure exists within temperature interval from 485K down to 4K (Fig.2);
3) Martensite $a$-and $b$- lattice parameters decrease with cooling down whereas $c$- parameter increases (Fig. 2,3). A large contraction in the $a$- and $b$-axes under cooling down is accompanied by thermal expansion in the $c$-direction, which achieves +1.8% within temperature range 409K - 4,16K during cooling down. It means that studied crystal shows the strong thermal expansion anisotropy displaying the quite rare phenomenon of negative thermal expansion (Fig.3).

**References:**
Zirconia, ZrO2 doped with cations (e.g. Ca, Y) is a technologically important material, e.g. with respect to its high ionic conductivity based on oxygen vacancies. An alternative to create the vacancies is the doping with anions (e.g. nitrogen). New materials are quaternary phases, where the predoping with cations precludes or reduces the ordering effects on the anion sublattice. To understand the properties of the material it is necessary to know the defect structure, in particular the short range order originating by the vacancies. Depending on the amount and type of doping the structures of the well known ZrO$_2$ phases (Fm3m, P42/nmc and P21/c) can be prepared.

The diffuse scattering of a quaternary single crystal (Y$_{0.04}$Zr$_{0.96}$O$_{1.64}$N$_{0.223}$, cubic with tetragonal contribution, $a_{\text{ab}}=5.086$ Å) has been investigated by neutron diffraction at the instrument E2 using a wavelength of 0.91 Å at room temperature. New measurements show different layers of the [100]-zone additional to the layers of the [1-10]-zone measured before (OTH-01-735).

The sample shows strong diffuse scattering in the Bragg layers and also between these layers. The diffuse maxima are parts of global features such as diffuse bands perpendicular to $\langle111\rangle$ in the [1-10]-zone. The distance between these bands correspond to ¼ of the body diagonal of the fluorite structure.

First we create a model, called Cluster T, based on displacements of rigid Zr-O units away from the O-vacancy (0.177 Å) and of the octahedral oxygens around the vacancy towards it (0.05 Å). This modell fits rather well with the layers of the [1-10]-zone, but it could not explain the diffuse scattering observed in the [100]-zone.

This model seemed to be a good approximation, but it had to be refined. Therefore we added to the programm Tvtueb a “Structural Disorder” part. After the input of the undisordered unit cell (here the cubic ZrO$_2$ structure) and the choice of possible vacancies, the program will calculate the different shells of atoms around the vacancy and gives the radial vector towards the vacancy as recommended direction for the displacement. Atoms of one shell will be displaced in the same way if it is not change manually. It is also possible to constrain different shells with eachother (e.g. to create the rigid Zr-O unit). The possibility to correlate two vacancies has not been used in our case.

Using the measured data, then the absolute values of the displacements, a scale factor, a background factor and an isotropic Debye Waller factor have been refined. All six shells within the distance of $a_{\text{ab}}=5.086$ Å have been regarded and all atoms have moved radially towards or away from the vacancy. So the final model is very similar to Cluster T but the displacement values are different and more atoms have been displaced (table1).

![Diagram](image)

The diffuse scattering is calculated directly as Fourier transformation of the difference structure between ideal and displaced atom positions. The figure shows the measured and calculated diffuse scattering in the 0. layer of the [1-10]-zone.

<table>
<thead>
<tr>
<th>shell</th>
<th>atom</th>
<th>number</th>
<th>direction</th>
<th>value [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zr</td>
<td>4</td>
<td>[111]</td>
<td>0.183</td>
</tr>
<tr>
<td>2</td>
<td>O</td>
<td>6</td>
<td>[100]</td>
<td>-0.287</td>
</tr>
<tr>
<td>3</td>
<td>O</td>
<td>12</td>
<td>[110]</td>
<td>0.053</td>
</tr>
<tr>
<td>4</td>
<td>Zr</td>
<td>12</td>
<td>$\frac{1}{4}$ $\frac{1}{4}$ $\frac{3}{4}$</td>
<td>-0.061</td>
</tr>
<tr>
<td>5</td>
<td>O</td>
<td>4</td>
<td>[111]</td>
<td>0.183</td>
</tr>
<tr>
<td>6</td>
<td>O</td>
<td>6</td>
<td>[100]</td>
<td>-0.516</td>
</tr>
</tbody>
</table>

Table 1: Uncorrelated cluster
EXPERIMENTAL REPORT
Neutron diffraction investigation of orientational glass state in \([\text{Rb}_{1-x}(\text{NH}_4)_x\text{H(SO}_4)_2]\)

Principal Proposer: L.S. Smirnov, SSC RF ITEP, Moscow, Russia
Experimental Team: A. Loose, BENS, HMI, Berlin, Germany
D. Hohlwein, BENS, HMI, Berlin, Germany
J.-U. Hoffmann, BENS, Berlin, Germany
K. Wozniak, Warsaw University, Warsaw, Poland
P. Dominik, Warsaw University, Warsaw, Poland

Proposal No PHY-01-1152
Instrument E5
Date(s) of Experiment 3 June-23 June 2002

The result of the crystal structure study of the TRAHS with \(x=0.80\) (or \([\text{Rb}_{1-x}(\text{NH}_4)_x\text{H(SO}_4)_2]\) mixed crystal) at 9 K in orientational glass state [1] is presented. It is shown that long range order of this crystal is suit to sp.gr. C2/c in accordance with phase II and superstructure reflections are absent. Atomic positions of \(\text{SO}_4\) tetrahedrons and N(1), Rb(1), N(2) and Rb(2) for TRAHS with \(x=0.80\) are determined with the help of measured reflections and are presented in Table with atomic positions for TRAHS with \(x=0.89\) for the comparison.

Table. Atomic positions in \([\text{Rb}_{1-x}(\text{NH}_4)_x\text{H(SO}_4)_2]\) mixed crystals, s.g. C2/c, \(Z=4\).

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.1142(4)</td>
<td>0.2177(9)</td>
<td>0.4627(6)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.0145(2)</td>
<td>0.1846(8)</td>
<td>0.4424(5)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.1503(3)</td>
<td>0.2231(8)</td>
<td>0.6058(4)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.1289(3)</td>
<td>0.4328(7)</td>
<td>0.3981(5)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.1490(3)</td>
<td>0.0273(7)</td>
<td>0.3982(5)</td>
</tr>
<tr>
<td>N(1)</td>
<td>0.3012(2)</td>
<td>0.7757(4)</td>
<td>0.3471(2)</td>
</tr>
<tr>
<td>Rb(1)</td>
<td>0.3012(2)</td>
<td>0.7757(4)</td>
<td>0.3471(2)</td>
</tr>
<tr>
<td>N(2)</td>
<td>0.5000</td>
<td>0.2305(5)</td>
<td>0.2500</td>
</tr>
<tr>
<td>Rb(2)</td>
<td>0.5000</td>
<td>0.2305(5)</td>
<td>0.2500</td>
</tr>
</tbody>
</table>

The \(R_1/wR_2\) factors are 0.121/0.255.

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
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<td>0.2521(13)</td>
<td>0.4580(20)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.0189(7)</td>
<td>0.2300(20)</td>
<td>0.4270(20)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.1410(12)</td>
<td>0.2487(17)</td>
<td>0.6066(18)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.1428(5)</td>
<td>0.4634(17)</td>
<td>0.4010(9)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.1458(5)</td>
<td>0.0336(15)</td>
<td>0.3991(9)</td>
</tr>
<tr>
<td>N(1)</td>
<td>0.3015(4)</td>
<td>0.7530(6)</td>
<td>0.3550(7)</td>
</tr>
<tr>
<td>Rb(1)</td>
<td>0.3015(4)</td>
<td>0.7530(6)</td>
<td>0.3550(7)</td>
</tr>
<tr>
<td>N(2)</td>
<td>0.5000</td>
<td>0.2511(7)</td>
<td>0.2500</td>
</tr>
<tr>
<td>Rb(2)</td>
<td>0.5000</td>
<td>0.2511(7)</td>
<td>0.2500</td>
</tr>
</tbody>
</table>

The \(R_1/wR_2\) factors are 0.257/0.576.

The change of hydrogen atomic positions between positions in TRAHS with \(x=0.89\) at 300 K in phase II and with \(x=0.89\) at 9 K in orientational glass state is presented with the help of Fourier Fo-Fc differential nuclear density maps in Fig. 1(a-d) about atomic positions of N(1)/Rb(1) and N(2)/Rb(2). The comparison of these maps show the appearance of complex change in positions of ammonium ions NH4(1) and NH4(2). The determination of hydrogen positions in orientational glass state of TRAHS with \(x=0.80\) at 9 K is in progress.

Fig. 1(a-d). Fo–Fc differential nuclear density maps (contours from 0.0 every 0.5 1/Å³).

The hydrogen bonding system and magnetic phase transition in $K_4MnH_2(SO_4)_4\cdot2H_2O$

Bimetallic hydrogen sulfates and selenates are known only for a few number of examples. Recently, we prepared some new compounds of this class, namely $M^I_2M^{II}H_2(XO_4)_2\cdot2H_2O$ ($M^I = K, Cs; M^{II} = Zn, Mn, Mg, X = S, Se$) [1, 2] and $K_MnH_2(SO_4)_4\cdot2H_2O$ ($M^I = Zn, Mn$) [3]. The crystal structures of these compounds have been determined by single crystal X-ray diffraction [1-3]. Neutron diffraction study of $K_4MnH_2(SO_4)_4\cdot2H_2O$ (I) was required to localize protons more precisely and check an existence of antiferromagnetic phase transition below 10K [4, 5].

Neutron single crystal diffraction experiments were carried out at the BER II reactor. A single crystal of I with the dimensions of $7.0 \times 4.0 \times 4.0$ mm$^3$ has been investigated on the four-circle diffractometer E5 using a copper monochromator (220 Cu, $\lambda = 0.891$ Å). The data were collected at room temperature with a two-dimensional ($90 \times 90$ mm$^2$) position sensitive $^3$He-detector. From 1855 measured reflections, 1830 has been used for the refinement ($R_1 = 17.8\%$).

The crystal structure of I at 300 K is orthorhombic: space group $Pccn$, $a = 7.6858(2)$, $b = 21.298(5)$, $c = 10.885(3)$ Å, $V = 1781.8(8)$ Å$^3$. The structure corresponds well to that determined by X-ray single crystal diffraction at 180 K. The Mn atom is coordinated by two water molecules and four O atoms of HSO$_4$ or SO$_4$ groups at the Mn-O distances of 2.18-2.25 Å. Strong (O4-H1...O7 2.562(9) Å) and middle strong H-bonds (O9-H2...O2 2.782(9) and O9-H3...O8 2.748(9) Å) link the anions and water molecules to hexamers (Fig.1).

The measurements of the deuterated powder sample I on the neutron diffractometer E6 in the temperature range between 1.5 and 20K revealed the existence of a magnetic phase transition. The three dimensional AF-magnetic order sets about 4 K at $H = 0$. The magnetic reflections intensity shows also a dependency on the applied magnetic field (0-5 T). It points to H-induced phase transitions but remaining the periodicity of the ground state magnetic structure of $K_4MnD_2(SO_4)_4\cdot2D_2O$.

References
Acid sulphates are highly interesting materials for future applications for example as electrolytes in fuel cells. In contrast to other members of the family of alkali hydrogen sulphates, there is no hint for a super-protonic state in KHSO$_4$ at atmospheric pressure [1]. As there is a change of critical parameters leading to the super-protonic conductivity from K to NH$_4$ and Rb respectively [2, 3] we started to investigate these parameters from the structural point of view. The structure of KHSO$_4$ at ambient conditions was described in space group $Pbca$ [4, 5]. It consists of planes of potassium ions, HSO$_4$ – dimers, and HSO$_4$ – chains.

According to our measurements, KHSO$_4$ undergoes four structural phase transitions between room temperature and the melting point at 483 K. Two phase transitions were found by the observation of optical birefringence with temperature: One at 343 K which was not detected by DTA and another at approx. 400 K, supported through an exothermic signal in the DTA. These results were confirmed by changes of the temperature dependence of the cell-parameter parallel $[100]$ at 343 K, 378 K and 398 K.

From analysis of in house single crystal X-ray diffraction data of untreated samples a possible sequence of phase transitions is proposed for KHSO$_4$:

\[ Pbc \rightarrow P2_11 \rightarrow Pbc \rightarrow P2_12_12_1 \rightarrow \text{unknown} \]

The high temperature phase obtained above 453 K could not be indexed yet.

KHSO$_4$ was crystallised from aqueous solution and characterised by DTA, TG, optical microscopy and powder and single crystal X-ray diffraction. The degree of deuteration found by IR spectroscopy was approx. 60%.

Single crystal neutron diffraction of untreated samples was performed at 363 K and 423K at E5, BENSC, Berlin.

The dataset collected at 423 K in July was a test run for the furnace. For the low scattering ability of the substance the measuring time was too short to get a sufficient amount of reflections. Generally it was not possible to clearly confirm the space groups found with X-ray methods due to the poor peak to background ratio of weak reflections. Also the measured sector of the Ewald sphere was too small to give information of inconsistent equivalents.

For the room temperature the hydrogen positions were clearly found [6]. No matrix was found for the crystal measured at 363 K probably due to the existence of several domains. In the dataset measured at 423 K and refined in spacegroup $P2_1$, one of the hydrogen atoms in the chains was missing probably due to insufficient quality of the data. The dimers were not planar any more like at room temperature.

This research is supported by the German Science Foundation, DFG (grant Kn507/3-1).

References

EXPERIMENTAL REPORT

High Temperature Crystal Structure of
KDSO$_4$ - Test of the airflow furnace on E5

Principal Proposer: G.Y. Lentz, CAU Kiel
Experimental Team: A. Loose, HMI

Proposal Nº EF
Instrument E5
Local Contact Anja Loose

Date(s) of Experiment
01.07.-21.07.2002

Date of Report: 13.01.2003

The small self-made airflow furnace developed once by R. Melzer for E5 had been used again in November 2001 for the first time after years.

Proposal GEC-01-1041 involved the solution of the high temperature crystal structure of deuterated mercallite (KHSO$_4$). This material undergoes phase transitions to a superprotonic state in the T-region of 410 to 475 K [1], i. e. exactly in the region this oven is optimised for. The latter can be used for moderate temperatures up to about 600 K.

However, during the course of the experiment we encountered problems with frequent angular errors or shifts and high instability of the orientation matrix. It turned out that the reason for these problems lay in the mechanical properties of the oven rather than in the crystal quality. Due to this we were not able to determine the crystal structure of the high temperature phase by that time.

In the meantime the oven has been repaired in our in-house workshop. Now it fits again very well to the Euler cradle on E5, which had been exchanged some years ago, giving rise to a minor unevenness that made the oven lose steps in the phi-circle.

The air furnace has also been upgraded and equipped with additional thermocouples by the sample environment group. Therefore it is now possible to control the oven in a remote way via a standard Lake Shore device.

In order to make sure that the furnace will work during following experiments in the future, we decided to test it by a measurement of one of the crystals of deuterated KH$_2$SO$_4$ which was left from the first experiment.

This time, the oven worked perfectly stable concerning mechanical correctness as well as stability of the temperature. In order to achieve a stable temperature, some aluminium foil was put around the open end of the oven’s cylinder, which reduces a possible temperature gradient (Fig. 1). Up to the required 430 K a ramp was applied for heating in small steps (0.2 K / 10 s) to avoid an overshooting of the setpoint.

EXPERIMENTAL REPORT

Understanding the mechanism of the phase transition and the nature of the chemical disorder in SBT: a neutron diffraction study

Principal Proposer: P. Saint Grégoire, L2MP, Toulon France
Experimental Team: Y. Gagou, L2MP, Toulon France
M. A. Frémy, L2MP, Toulon France
D. Többens, HMI Germany

Date of Experiment:
E6: 11/03/02-21/03/02
E9: 21/03/02-28/03/02

Date of Report: 14/01/03

Strontium bismuth tantalate SrBi2Ta2O9 (SBT) is a member of Bi-layered perovskites and are expected to be the most promising materials in use in non-volatile ferroelectric memories due to its fatigue-free properties. SBT undergoes a ferroelectric transition at the Curie temperature Tc = 608 K with a structural change from tetragonal to orthorhombic systems (1).

We have carried out experiments on this compound SBT in order to get information on the symmetry change at the phase transition and on the mechanism of the transition.

No significant change was observed at low resolution, but with the high resolution instrument, noticeable changes as a function of temperature were observed.

We began to perform Rietveld refinements of the data, but till now they were not successful: we could not refine the structure satisfactorily since in the Fourier difference map, we observe excess of electron density in some regions, which could suggest that the admitted symmetry group of this compound is not the correct one.

At present time, attempts to refine the structure are still in progress. (Our results and conclusions are not reliable to write an article).

A PhD student will probably soon continue this work which possibly will need complementary neutron diffraction data acquisition, in particular to check the symmetry at room temperature.

References:
The quasi-2D organic superconductor $\beta''$-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ ($\beta''$-SF$_5$) is situated very close to an insulating phase which can be induced by applying hydrostatic pressure $p \geq 12$ kbar. Electrical resistivity measurements have clearly shown the insulating phase at high pressures and the hysteretic behavior of this pressure induced metal-insulator transition. Since organic metals are soft materials and can even undergo a structural phase transition at small hydrostatic pressures, the transition into the insulating phase in $\beta''$-SF$_5$ might also be attributed to changes in the crystal structure. To investigate the crystal structure under pressure we performed powder neutron diffraction on E6 using a wavelength of the neutrons $\lambda = 2.45 \text{Å}$. Diffraction pattern were taken at temperatures between $T = 1.5 \text{K}$ and $300 \text{K}$ and pressures $p = 0$ and $15 \text{kbar}$ using our CuBe high-pressure clamp cell with a PTFE capsule inside containing the sample and fluorinert as pressure medium.

Figures 1(a) and (b) show the diffraction pattern of $\beta''$-SF$_5$ including the effect of the pressure cell at zero and $15 \text{kbar}$ hydrostatic pressure. The most prominent difference in the pattern occurs in the range $2\Theta = 30 - 32^\circ$, visible also in the difference pattern [Fig. 1(b)]. This large effect can fully be attributed to a change in the crystal structure of PTFE under pressure as can be seen in Fig. 1(c), since the pressure medium fluorinert crystallizes in an amorphous structure. However, other peaks at $2\Theta \approx 8^\circ, 26^\circ, 28^\circ$, and $41^\circ$ are unambiguously originating from $\beta''$-SF$_5$. The shifts in $2\Theta$ of the $\beta''$-SF$_5$ peaks under pressure are most probable due to the decreasing lattice constants, whereas the crystal structure seems to be unchanged. This is supported by the fact that no additional peaks are observed under pressure. The different intensities of the peaks at ambient pressure and under pressure could indicate a movement of the atomic positions within the unit cell. However, successive measurements at $p = 0$ revealed that the intensity change is most likely due to texture of the powder.

![Diffraction patterns](image-url)

Figure 1: (a) Powder-diffraction pattern of $\beta''$-SF$_5$ and the pressure cell at $p = 0$ and $p = 15 \text{kbar}$ taken at $1.5 \text{K}$. (b) Difference pattern ($15 \text{kbar} - 0 \text{kbar}$) of the data shown in (a). (c) Diffraction pattern of the pressure cell without sample, but with pressure medium (fluorinert) and PTFE at $p = 0$ and $p > 10 \text{kbar}$ taken at $1.5 \text{K}$. 

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**EXPERIMENTAL REPORT**

The crystal structure at the metal-insulator transition in an organic superconductor

Principal Proposer: O. Stockert, Max-Planck-Institute CPI9 Dresden
Experimental Team: J. Hagel, Institute of Applied Physics (IAPD), TU Dresden

Date of Report: 15.1.2003

**Proposal N° PHY-01-1144**

Instrument: E6

Local Contact: N. Stüßer

Date(s) of Experiment: 18.-24.11.2002
Physical and chemical properties of materials are often controlled by substitutions and non-stoichiometries. Thus solid solution series especially including phase transitions are strongly recommended for reflecting dependencies of chemical composition, element ordering and microstructures as well as stability parameters as temperature and pressure.

We study the system Zn$_{2x}$Cu$_{(1-x)}$In$_{(1-x)}$S$_2$ (ZCIS), which was found to form a solid solution series with a solution gap for 0.11 $\leq$ x $\leq$ 0.38 (PHY-01-113). Samples with x<0.11 show tetragonal chalcopyrite type structure, samples with x>0.38 cubic sphalerite type structure. In the tetragonal phase exist besides orientation domains extending along all <100> directions, which occur in ZCIS single crystals as well as in powders, domains with CuAuI-ordering, which were in ZCIS firstly observed in thin films [1] and also found in single crystals. The aim of this experiment was to determine the distribution of cations on the two cation sites of the chalcopyrite structure and search for an evidence of the existence of CuAuI-ordering of the cations.

Samples were synthesized by solid state reaction of the elements in sealed evacuated silica tubes at T=950°C. The homogeneity of the powders was checked by X-ray diffraction and microprobe.

Neutron powder diffraction experiments were carried out for samples with 0.05 $\leq$ x $\leq$ 0.8. We used the focusing single crystal diffractometer E6 ($\lambda$=2.45Å). Data refinements were done by the FULLPROF program[2].

For samples with 0.251 $\leq$ x $\leq$ 0.68 we observed additional peaks, which are not consistent with the sphalerite nor the chalcopyrite structure. Also with the superstructures known for the ZCIX (X=S, Se, Te) systems, which are CuAuI-, Cu3Au- and CuPt-type ordering of the cations, this peaks cannot be explained and we have still no explanation. Additional we found no evidence for CuAuI-type ordering as described in literature for thin films and single crystals [1].

A linewidth analysis of peaks, which change intensity with different metal ordering, show a linewidth broadening for x>0.1. This points to a decrease of the tetragonal orientation domains, which is consistent to the 2-phase model discussed in PHY-01-113.

For samples with x>0.05 we observed an deviation from the statistic distribution of the Zn ions on the two metal sites of the chalcopyrite structure, which gives an evidence of the occurrence of Cu-In anti site occupation (see fig. 2).

Taking into account the anion displacement parameter derived from the experiment PHY-01-113 it was possible to determine the cation distribution for x=0.105: 82.3% of the Zn ions occupy the Me1 site (Cu site) and 17.7% of the Zn ions occupy the Me2 site (In site), which corresponds to 7.4% Cu-In anti site (i. e. 7.4% Cu occupy the In site).

[2] FULLPROF, Rietveld, profile matching and integrated intensities refinement of neutron and/or X-ray data, LLB
The aim of the neutron diffraction studies in (Ce_{1-y}Nd_y)_{10}S_{14+x}O_{1-x} oxy-sulphides is to determine their crystal structure and oxygen content more straightforward than it is possible with X-ray diffraction techniques. Based on the well known null dependence of the neutron coherent scattering lengths of the elements on electron density, in contrast with atomic scattering factors for X-rays.

These oxysulphides could present interesting industrial applications in the field of inorganic pigments, which are commonly based ontransition elements compounds, such as Fe, Pb, Co, Cu oxides and Au salts. The presence of heavy metals in their composition makes them quite toxic in most of the cases. Due to legislative regulations it seems necessary to develop new inorganic pigments with less toxicity that match or surpass the traditional materials properties.

The rare earth elements are good candidates to be introduced in new pigments, because of their low toxicity, relative high abundance and good colour properties. One of the most promising new “ecological pigments” is γ-Ce_2S_3, which is a red compound that can substitute the toxic Cd(S, Se).

The light rare earth sesquisulphides present three structure types: α (Gd_2S_3-type) below 1173 K, β (Pr_{10}S_{14-}O-type) between 1173 K and 1473 K and γ (Th_{12}P_{34}-type) above 1473 K. The β form structure and composition are very complex and still present some controversies [1, 2]. It is currently admitted that this phase forms a series of solid solutions R_{10}S_{14+x}O_{1-x} (0≤x≤1) [3] (R= Rare Earth), except in the case R = La, where β-La_{10}S_{15} = β-La_2S_3 exists.

Samples, described as (Ce_{1-y}Nd_y)_{10}S_{14+x}O_{1-x} (0≤y≤0.70) (0≤x≤1), were prepared in order to study their structure-microstructure and colour properties [4]. They mainly belong to the β form and their red colour changes with the Nd content. The optimum colour quality is found in the y=0.30 sample. The crystal parameters, obtained through X-ray powder diffraction, should decrease with the increasing Nd content in the solid solution, due the lanthanide contraction, i.e. Nd^{3+} is smaller than Ce^{3+}. However, the crystal parameters variation is related with the variable oxygen content in the different samples. The composition-structure of each compound are responsible of their good colour properties. Neutron elastic scattering is unrivaled against X-ray powder diffraction concerning the determination of the oxygen crystallographic position and occupation factors of the different chemical elements. As an example, the Rietveld refinement (E9) of a sample (Ce_{0.7}Nd_{0.3})_{10}S_{15-}O_{x} with x = 0.32(6) is shown below. It corresponds to the β-form (tetragonal; S.G. J41/acd) and lattice constants a = 15.3074(7)Å, and c = 20.2713(11)Å at RT.

Some indications for the influence of chromophore oxidation states distortions and structural defects of pyrochlores on the colour were given as early as the year 1965 by Weyl and Tcheichvili but the subject was never studied in more detail. A series of solid solutions $Y_2Sn_{2-x}Cr_xO_7\delta (x = 0, 0.02, 0.1, 0.2, 0.3, 0.4)$ recently proposed as ceramic pigments were synthesized by solid-state reaction. The purpose of present experiment was to draw the attention to possible relationship between the colour and structural defects.

Neutron diffraction (ND) experiments were realized on E9 diffractometer. The measurements of samples 5g in weight were carried out using neutron beam with wavelength $\lambda = 1.79686\ \text{Å}$. The scattered radiation was collected in the interval $2\theta = -2.1028 - 157.7350\ \text{º}$. The crystal structure parameters, Table 1, were refined by Rietveld analysis of neutron diffraction and XRD data using FullProf program, [J. Rodriguez-Carvajal, FullProf Version 3.5d Oct.1998, LLB (CEA-CNRS)], Fig.1. In the refinement process we adopted the model of random distribution for the substituting $Cr^{3+}$ ions in $16c$ Wyckoff positions of $Fd3m$ space group.

Results from Rietveld refinement of the structure indicate clearly a trend of increasing oxygen deficiency ($\delta = x/2$) with increasing chromium content ($x$). It was attributed to the formation of both intrinsic and extrinsic defects essentially vacancies in the $48f$ Wyckoff positions rather than in the alternative $8b$ sites available for the oxygen in $Fd3m$ space group.

References

The proposed experiment was an investigation of the compressibility behaviors of the superconducting layer intercalation compounds $\beta$-$A_{0.15}$ZrNCl {A= Li, K, $T_\mathrm{tr} = 15K$} [1]. We anticipated a change in compressibility behavior between the two compounds incorporating a small and a large alkali cation intercalant, A. We wished to complete the study to develop a phase diagram showing the stability of the superconductivity, by correlating high-pressure structural changes in the system with changes in the electronic behavior, observed by “in-house” high-pressure magnetic susceptibility instrumentation. The experiment was also seen, in part, as a continuation of our high-pressure experimentation at BENS (see PHY-01-1050). In this case we were investigating the practicality in using the high-resolution diffractometer E9 for such investigations.

In the period before the experiment it became apparent that the maximum pressure possible at low temperatures using the BENS clamp pressure-cell was rather low (~2kbar at 1.6 K) for a meaningful experiment to be completed on the proposed system. As a result an alternative experimental plan was decided upon. During the allocated beamtime we recorded, first, diffraction profiles of the new host material $\alpha$-ZrNBr at 1.6 K and 300 K. The diffraction profiles ($\lambda = 1.797 \text{ Å}$) were fitted to a structural model related to the published work on $\alpha$-HiNCl [2]. No structural phase transition was observed between 1.6-300 K, with refinements successful in $Pmmn$. (Refinement results: at 1.6 K, $a = 4.1144(1)$ Å, $b = 3.5955(2)$ Å, $c = 8.6433(3)$ Å ($\chi^2 = 5.00$); and at 300 K $a = 4.1166(2)$ Å, $b = 3.600(1)$ Å, $c = 8.6732(2)$ Å ($\chi^2 = 9.23$)).

Figure 1 shows the Rietveld refinement result of the 1.6 K profile. At 300 K the refinement was complicated by some Bragg scattering from the cell, $\gamma$= fluorinert scattering, and the marked extra reflections in (a) are from added NaCl. We observed little difference between the 1 bar and at 1 kbar pressure medium and 20% NaCl, as a pressure gauge. Diffraction measurements at 300 K revealed that the internal pressure had raised to 7 kbar compared to >10 kbar force, applied initially on the clamp cell through a hydraulic press. Upon cooling, at 1.6 K the remaining hydrostatic pressure had dropped to only ~1 kbar. We observed little difference between the 1 bar and at 1 kbar diffraction profiles at 1.6 K. Moreover, the diffraction profiles were heavily complicated (Fig. 2) by broad and intense Bragg scattering from the pressure-cell, which precluded Rietveld refinement. This effect would seem to negate the application of the clamp pressure cell on the E9 diffractometer.

In the second part of the experiment we returned to the pressure theme of our proposed investigations. However, we decided to measure the structurally simpler and air-stable La$_{1.875}$Ba$_{0.075}$Sr$_{0.05}$Cu$_{0.95}$O$_4$ compound using the BENS clamp pressure-cell. This compound is interesting electronically because it is related to La$_{1.875}$Ba$_{0.125}$Cu$_{0.95}$O$_4$ where superconductivity is suppressed through a structural transition from Low-Temperature Orthorhombic (LTO/ $Cmca$) to a Low-Temperature Tetragonal (LTT/ $P4_2/nmc$) phase, with concomitant “stripe-phase” formation [3]. With ionic substitution and increasing the Sr:Ba ratio the superconductivity is gradually recovered as the LTT phase formation is suppressed [4]. It is expected that at the Sr= 0.05 composition the application of hydrostatic pressure may complete the recovery of high-$T_c$ superconductivity.

In the experiment, the sample (m= 1.8g) was loaded in the CuBe clamp cell with fluorinert FC-70/77 (1:1 mixture), as pressure medium and 20% NaCl, as a pressure guage. Diffraction measurements at 300 K revealed that the internal pressure had raised to 7 kbar compared to >10 kbar force, applied initially on the clamp cell through a hydraulic press. Upon cooling, at 1.6 K the remaining hydrostatic pressure had dropped to only ~1 kbar. We observed little difference between the 1 bar and at 1 kbar diffraction profiles at 1.6 K. Moreover, the diffraction profiles were heavily complicated (Fig. 2) by broad and intense Bragg scattering from the pressure-cell, which precluded Rietveld refinement. This effect would seem to negate the application of the clamp pressure cell on the E9 diffractometer.

### References:


Besides nearly stoichiometric La$_{1.1}$Sr$_{0.9}$Co$_{3}$ perovskites, both GMR properties and metal-insulator transition have been recently observed in oxygen-deficient coaltobides LnBaCo$_{2}$O$_{6.8}$ [1, 2]. It was found that properties of these compounds can be effectively governed by a substitution of the cobalt ions with iron ones. In order to deeper understand the reasons of the unusual behaviour of the aforementioned compounds as well as to clear up the role of the iron ions we have undertook the complex investigations of the LnBaCo$_{2}$O$_{6.8}$ systems within a wide concentrational region. Here we present results of study of the crystal and magnetic structure of TbBaCo$_{1.1}$Fe$_{0.9}$O$_{5.8}$ composition at $T$= 2, 10, 100, 300 and 500 K using the Fine Resolution Powder Diffractometr ($\lambda$=1.796 Å). Given composition is limit of the TbBaCo$_{x}$Fe$_{2-x}$O$_{3.8}$ solid solutions with a maximal obtainable iron content at the conventional synthesis conditions in air from initial oxides and carbonates. According to the magnetic measurements the TbBaCo$_{1.1}$Fe$_{0.9}$O$_{5.8}$ perovskite does not have any spontaneous magnetisation in the temperature range 2<T<500 K. There is a small peak on the temperature dependence of the magnetic susceptibility at the $T$~415 K that may be connected with antiferromagnetic-paramagnetic phase transition. The additional reflections appearing on the neutron diffraction spectrum below this temperature are evidence in favour of this assumption. The structural analysis of the paramagnetic spectrum ($T$=500 K) indicates that the compound has an tetragonal symmetry of space group P4/mmm with $a_o=b_o=c_o$, and $c_o=2a_p$, were $a_p$ is the perovskite unit cell constant. The unit cell contains two oxygen deficient ABO$_2$-type perovskite units. The Tb and Ba ions are ordered forming Tb-and Ba-containing alternate planes along c axis coupled with predominant oxygen vacancies locating at the O(3) site in the Tb-containing plane. We have not observed any superstructure reflections associated with long-range ordering of the oxygen vacancies within the TbO(3)$_{1/2}$-plane. Figure 1 shows the observed and calculated intensities of the TbBaCo$_{1.1}$Fe$_{0.9}$O$_{5.8}$ at 2 K. The structural parameters at 2, and 500 K are listed in Table 1. The differences of the normalized intensity data at 2 and 500 K indicate that no magnetic intensity is superposed on the nuclear Bragg peaks and the magnetic ordering is antiferromagnetic along the a, b, and c directions. The magnetic peaks can be indexed with the propagation vector $\mathbf{q}=(1/2 1/2 0)$ in the $a_p$$\times$$a_p$$\times$$2a_p$ unit-cell. It is so called G-type magnetic structure. In our calculations the magnetic moments wea assumed to lie in the ab-plane. From refinement of the magnetic intensities the value of the Co$_{0.55}$Fe$_{0.45}$ magnetic moment is 4.1 $\mu_B$ at 2 K. This value corresponds to the high spine state of both Fe$^{3+}$ $t_{2g}$ $e_g$ $S=5/2$ and Co$^{3+}$$2t_{2g}$ $e_g$ $S=2/ t_{2g}$ $e_g$ $S=3/2$ ions. No evidence for long-range ordering of the Tb magnetic moments was detected at 2K.

![Fig. 1 Plot of the observed and calculated intensity profile for the TbBaCo$_{1.1}$Fe$_{0.9}$O$_{5.8}$ at 2 K.](image)

**Table 1** Structural parameters at 2, and 500 K.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Param.</th>
<th>2 K</th>
<th>500 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>B(Å$^2$)</td>
<td>1.42(7)</td>
<td></td>
</tr>
<tr>
<td>Tb</td>
<td>B(Å$^2$)</td>
<td>1.41(4)</td>
<td></td>
</tr>
<tr>
<td>Co/Fe</td>
<td>z</td>
<td>0.25361</td>
<td>0.253(68)</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>1.006(6)/0.90</td>
<td>1.172(7)/0.62</td>
</tr>
<tr>
<td></td>
<td>B(Å$^2$)</td>
<td>3.04</td>
<td>0.97(9)</td>
</tr>
<tr>
<td>O(1)</td>
<td>B(Å$^2$)</td>
<td>1.20(4)</td>
<td></td>
</tr>
<tr>
<td>O(2)</td>
<td>B(Å$^2$)</td>
<td>1.20(4)</td>
<td></td>
</tr>
<tr>
<td>O(3)</td>
<td>B(Å$^2$)</td>
<td>1.20(4)</td>
<td></td>
</tr>
</tbody>
</table>

A polycrystalline Ni-rich Ni-Ti shape memory alloy with a nominal Ni-concentration of 53at.% was prepared by arc melting in an argon atmosphere. The sample was encapsulated in a quartz tube (500mbar Ar), solution treated at T=1000°C for 1h and quenched in ice water. After this a subsequent heat treatment at T=400°C for 1h was employed to trigger the precipitation of Ni₄Ti₃.

Fig. 1 shows the DSC-measurement in the low temperature range for the aged Ni₅₃Ti₄₇ sample. During cooling a single step martensitic transition occurs. As suggested recently the single step transition may be explained by a martensitic transition from the B₂-phase to R-phase [1].

In order to determine the structural changes and volume fractions of the phases in the austenitic and martensitic state neutron diffractograms (ND) have been collected at T=160°C and T=-176°C, respectively.

The obtained neutron diffractogram (T=160°C) for the aged Ni₅₃Ti₄₇ sample taken at T=160°C is shown in Fig. 2. The ND data were analyzed using GSAS Rietveld refinement with the GSH description. The analysis was based on crystal structure data described by Tadaki et al. [2] for the Ni₄Ti₃ precipitates and Hara et al. [3] for the R-phase. For T=160°C reflections of the B₂-phase and the Ni₄Ti₃ phase are present. After cooling to T=-176°C only reflections of the R-phase and of the Ni₄Ti₃ precipitates can be found. According to this analysis, about 40% is Ni₄Ti₃. Following the lever rule and assuming a full decomposition of Ni₅₃Ti₄₇ in Ni-Ti and Ni₄Ti₃ precipitates, a volume fraction for the Ni₄Ti₃ precipitates of about 43.3% is expected. This leads to the conclusion that aging at 400°C for 10h is nearly appropriate to achieve a full decomposition. Furthermore, at T=-176°C, no traces of the martensitic B₁₉' phase can be found. Obviously the high amount of Ni₄Ti₃ precipitates suppresses the occurrence of the B₁₉'-phase because they represent obstacles to high transformation strains and in addition stress fields around coherent Ni₄Ti₃ precipitates may trigger the martensitic transition to the R-phase.

Further evaluation of the ND-data will be necessary to determine the crystal structure of the Ni₄Ti₃ precipitates and that of the R-phase.

In order to determine the structural changes and volume fractions of the phases in the austenitic and martensitic state neutron diffractograms (ND) have been collected at T=160°C and T=-176°C, respectively.

The obtained neutron diffractogram (T=160°C) for the aged Ni₅₃Ti₄₇ sample together with a calculated diffractogram is shown in Fig. 2. The ND data were analyzed using GSAS Rietveld refinement with the GSH description. The analysis was based on crystal structure data described by Tadaki et al. [2] for the Ni₄Ti₃ precipitates and Hara et al. [3] for the R-phase. For T=160°C reflections of the B₂-phase and the Ni₄Ti₃ phase are present. After cooling to T=-176°C only reflections of the R-phase and of the Ni₄Ti₃ precipitates can be found. The volume fractions of the phases calculated by the Rietveld refinement are summarized in Table 1. According to this analysis, about 40% is Ni₄Ti₃. Following the lever rule and assuming a full decomposition of Ni₅₃Ti₄₇ in Ni-Ti and Ni₄Ti₃ precipitates, a volume fraction for the Ni₄Ti₃ precipitates of about 43.3% is expected. This leads to the conclusion that aging at 400°C for 10h is nearly appropriate to achieve a full decomposition. Furthermore, at T=-176°C, no traces of the martensitic B₁₉'-phase can be found. Obviously the high amount of Ni₄Ti₃ precipitates suppresses the occurrence of the B₁₉'-phase because they represent obstacles to high transformation strains and in addition stress fields around coherent Ni₄Ti₃ precipitates may trigger the martensitic transition to the R-phase.

Further evaluation of the ND-data will be necessary to determine the crystal structure of the Ni₄Ti₃ precipitates and that of the R-phase.

Tab. 1: Calculated volume fractions of the phases for the Ni₅₃Ti₄₇ sample

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Volume fractions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B₂</td>
</tr>
<tr>
<td>160</td>
<td>57.1</td>
</tr>
<tr>
<td>-176</td>
<td>60.1</td>
</tr>
</tbody>
</table>

Solid solution series are especially qualified for investigations of relationships between structures and physico-chemical properties of crystals, because their physical and chemical properties show dependencies of chemical composition, element ordering and microstructures as well as stability parameters as temperature and pressure.

In this regard structural phase transition, metal ordering and anion parameters are studied in the semiconducting system $\text{Zn}_2\text{Cu}(\text{1-x})\text{In}(\text{1-x})\text{S}_2$ ($\text{ZCIS}$), which can be used as absorber in solar cells. The system was found [1] to form an approximately complete solid solution series with a phase transition from cubic sphalerite type structure to tetragonal chalcopyrite type structure at $x \sim 0.25$. To study the distribution of the cations on the two cation sites of the chalcopyrite structure, conventional X-ray and synchrotron methods failed due to the electronic similarity of Zn and Cu and because of the chalcopyrite space group parities used respectively.

Samples were synthesized by solid state reaction of the elements in sealed evacuated silica tubes at $T=950^\circ\text{C}$. The homogeneity of the powders was checked by X-ray diffraction and microprobe.

Neutron powder diffraction experiments were carried out for samples around the phase transition composition of $\text{Zn}_2\text{Cu}(\text{1-x})\text{In}(\text{1-x})\text{S}_2$, i.e with $0.17 \leq x \leq 0.3$. We used the high resolution powder diffractometer E9 ($\lambda=1.7973\text{Å}$). Data refinements were done by the FULLPROF program[3]. The refinement of the diffraction data with $0.17 \leq x \leq 0.24$ was only possible by assuming 2 phases (see fig.1).

Additional the end components of the 2-phase field were determined by transmission electron microscopy [3].

For $x>0.1$ tetragonal domains with $x_{\text{Zn}} \sim 0.11$ in a cubic matrix with $x_{\text{Zn}} \sim 0.38$ occur. The domains decrease in size with increasing Zn content. Thus we conclude, that the structural phase transition in the solid solution 2ZnS – CuInS2 is a first order phase transition, because in the region $0.11 \leq x \leq 0.38$ two phases (tetragonal and cubic) coexist.

A disagreement between the anion displacement, resulting from the Rietveld analysis and calculated values assuming a statistic Zn distribution and no Cu-In anti site occupation (see fig. 2) gives us an evidence for Cu-In anti site occupation for $x>0.05$.

Fig. 1: Rietveld analysis with the 2-phase model (part of the diffraction pattern) for the sample with $x=0.248$. The inset shows a simulated diffraction pattern of the tetragonal phase (blue) and cubic phase (red).

Fig. 2: Lattice constants of $\text{Zn}_2\text{Cu}(\text{1-x})\text{In}(\text{1-x})\text{S}_2$ in dependence of chemical composition.

Fig. 3: Anion displacement resulting from the Rietveld analysis. Single crystal results from [4]. The triangles show calculated values according [5].

References:
The physical and chemical properties of solid solution series especially including phase transitions show dependencies of chemical composition, element ordering and microstructures as well as stability parameters as temperature and pressure.

The system Zn$_{2x}$Cu$_{(1-x)}$In$_{(1-x)}$S$_2$ (ZCIS), which is an interesting photovoltaic material, was found to form a solid solution series [1], but with an area of non-solubility for 0.11<x<0.38 (see PHY-01-113). Differential Thermo-Analyses (DTA) measurements on samples with 0 ≤ x ≤ 0.3 between room temperature and 1300°C shows a number of transition before the melting point is reached. We found in agreement to [2] 3 different phases for CuInS$_2$ (x=0), a transition from the tetragonal chalcopyrite to the cubic sphalerite structure at 980°C and a further transition to an unknown phase at 1045°C, before the melting point at 1090°C is reached.

The aim of the experiment was to study the structure of the high temperature phases of Zn$_{2x}$Cu$_{(1-x)}$In$_{(1-x)}$S$_2$ with 0 ≤ x ≤ 0.3 in the temperature region 300°C ≤ T ≤ 1250°C. The samples were prepared by solid state reaction from the pure elements in sealed evacuated silica tubes and analysed at room temperature by X-ray powder diffraction and microprobe. The neutron powder diffraction experiments were performed at the high resolution powder diffractometer E9 (λ=1.79 Å) at temperatures up to 1100°C. The samples were measure in a closed system (sealed evacuated silica tubes) to avoid sulfur evaporation during heating. For all measured samples we found in agreement with DTA results 3 different phases before the melting point is reached. With increasing temperature first a transition from chalcopyrite to sphalerite structure occurs followed by a transition to wurtzite structure (see fig.1). Thus the unknown high temperature phase is a hexagonal phase with wurtzite type structure.

Additional peaks were observed in the sphalerite type structure phase. It is possible to identify them as the (h0l) peaks with l=2n of the wurtzite type structure. Up to now there is no explanation for the occurrence of this precursor peaks. Therefore this problem has to be studied in detail in future.

Fig. 1: Powder diffraction pattern for a mixed crystal sample with x=0.05, measured at room temperature, 965°C and 1060°C (from bottom to top). The peaks are marked by their indices according to the chalcopyrite, sphalerite and wurtzite structure respectively. Peaks marked with PS result from the sample holder. The two peaks marked by an arrow are the wurtzite precursor peaks in the sphalerite structure. The background in the 965°C and 1060°C measurement results from the silica tube.

References:
In the course of our studies on the existence of diazenides in the binary system Sr – N we observed by chemical analysis a successive insertion of \([\text{N}_2^2]\)-dumb-bells into the structure of \(\text{Sr}_2\text{N}\) [1]. Former neutron diffraction experiments carried out on \(\text{SrN} \rightarrow \text{Sr}_2[\text{N}_2]\text{[N}_2]\) and \(\text{SrN}_2 \rightarrow \text{Sr[N}_2]\) led to their complete crystal structures [2].

In combination with X-ray diffraction studies the reported experiment led to the determination of the crystal structure (especially precise nitrogen positions) of an intermediate phase \(\text{Sr}_2\text{N}_3 \rightarrow \text{Sr}_4[\text{N}_4]\text{[N}_2]\). Neutron diffraction experiments were carried out at 298 K and 2 K using E9 [3]. Structure refinements (Fig. 1) were performed applying the program FULLPROF [4].

### Table: Structural parameters of \(\text{Sr}_4\text{N}_3\) [3]

<table>
<thead>
<tr>
<th></th>
<th>298 K</th>
<th>2 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of reflections</td>
<td>272</td>
<td>261</td>
</tr>
<tr>
<td>Lattice (a) (Å)</td>
<td>6.7070(4)</td>
<td>6.6868(3)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>3.8280(2)</td>
<td>3.8173(2)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>13.7625(8)</td>
<td>13.7382(6)</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>96.519(5)</td>
<td>96.447(3)</td>
</tr>
<tr>
<td>(\text{Sr1 in (4i)})</td>
<td>(x) 0.413(1)</td>
<td>0.4133(7)</td>
</tr>
<tr>
<td>(z)</td>
<td>0.1413(4)</td>
<td>0.1412(3)</td>
</tr>
<tr>
<td>(\text{Sr2 in (4i)})</td>
<td>(x) 0.127(1)</td>
<td>0.1290(7)</td>
</tr>
<tr>
<td>(z)</td>
<td>0.3406(3)</td>
<td>0.3413(3)</td>
</tr>
<tr>
<td>(\text{N1 in (4i)})</td>
<td>(x) 0.775(1)</td>
<td>0.7748(6)</td>
</tr>
<tr>
<td>(z)</td>
<td>0.2515(4)</td>
<td>0.2483(3)</td>
</tr>
<tr>
<td>(\text{N2 in (4i)})</td>
<td>(x) 0.083(1)</td>
<td>0.0850(8)</td>
</tr>
<tr>
<td>(z)</td>
<td>0.0217(6)</td>
<td>0.0234(4)</td>
</tr>
<tr>
<td>(\text{pp})</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>(R_{\text{Profil}} / R_{\text{Bragg}})</td>
<td>0.055/0.053</td>
<td>0.066/0.047</td>
</tr>
</tbody>
</table>

Fig. 1: Neutron powder diffraction pattern at 298 K (observed, calculated and difference profiles, ticks mark the Bragg positions).

The crystal structure of \(\text{Sr}_4\text{N}_3\) can be topologically deducted from \(\text{Sr}_2\text{N}\): half of the free octahedral holes between every second \(\text{Sr}_2\text{N}\)-layers are occupied by \([\text{N}_2^2]\)-dumb-bells thereby shifting the \(\text{Sr}_2\text{N}\) layers to each other (monoclinic unit cell). Neutron diffraction experiments led to a C-centered cell with an occupation of the \(\text{N}_2\)-positions of one half. The two possible limiting structures (P-cells) are shown in Fig. 2.

Fig. 2: Crystal structure of \(\text{Sr}_4\text{N}_3 \rightarrow \text{Sr}_8[\text{N}_4]\text{[N}_2]\).

### References:


Initially, Li$_7$[VN$_4$] was prepared at temperatures below 1020 K and described in the cubic space group $P\bar{4}3n$ [1]. For some time we have observed in X-ray powder patterns of Li$_7$[VN$_4$] samples obtained above 1070 K reflections not allowed in the space group $P\bar{4}3n$. Recently, we have obtained single crystals Li$_7$[VN$_4$] from Li melt at 1173 K [2]. The single crystal structure refinement supported our suspicion of a polymorph (space group $Pa\bar{3}$). These facts led us to investigate the thermal behaviour of Li$_7$[VN$_4$] above 900 K.

Li$_7$[VN$_4$] forms from Li$_3$N and VN in nitrogen atmosphere above 920 K. Depending on the preparation conditions three polymorphs are obtained as microcrystalline powders. Two polymorphs of Li$_7$[VN$_4$] have been established from X-ray powder diffraction ($\gamma$-Li$_7$[VN$_4$]: $P\bar{4}3n$, $a = 960.90(4)$ pm, $Z = 8$; $\beta$-Li$_7$[VN$_4$]: $Pa\bar{3}$, $a = 959.48(3)$ pm, $Z = 8$). For both crystal structures starting models were taken from single crystal structures of isotypic compounds. For a third polymorph $\alpha$-Li$_7$[VN$_4$] ($P4_{2}hmc$, $a = 675.90(2)$ pm, $c = 488.34(2)$ pm, $Z = 2$) the site occupation of Li could not be unambiguously extracted from X-ray powder diffraction. Therefore we have carried out neutron powder diffraction experiments (see fig 1).

The combination of X-ray and neutron powder diffraction was essential for the structure solution and refinement (program package FULLPROF [3]), because the neutron scattering length of V is close to zero, while the contribution of Li to the X-ray diffraction pattern is small.

The crystal structures of $\gamma$, $\beta$- and $\alpha$-Li$_7$[VN$_4$] are depicted in fig. 2. A comparison reveals, that all three structures are based on Li$_2$O superstructures with nitrogen on the oxygen site and ordered distributions of Li and V on the lithium position. The three polymorphs differ in the ordering scheme of Li and V atoms within the fcc arrangement of nitrogen.

References


**EXPERIMENTAL REPORT**

Localization of fluorine and deuteron atoms in the structure of (ND$_4$)$_2$ND$_4$ScF$_6$ elpasolite.

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**Proposal No:** PHY-01-1185

**Instrument:** E9

**Local Contact:** M. Tovar

**Date(s) of Experiment:** 17-23 October 2002

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Physical properties of ammonium cryolites (NH$_4$)$_2$NH$_4$M$_{III}$F$_6$ (M = Al, Ga, Cr, Fe, V, Sc, In) are significantly affected by the size of the unit cell volume. At ambient pressure crystals with large trivalent ions (M$^{3+}$: Sc, In) exhibit a succession of three ferroelastic PTs Fm$\bar{3}$m – P12$_1$/n1 – I12/m1 – P1 [1], whereas the presence in the structure of M$^{4+}$ ions with intermediate size (Fe-Ga) leads to one PT just into triclinic phase [2]. At last in Al-compound, having the least unit cell volume, there exist two structural transformations Fm$\bar{3}$m – P1 [2].

The total entropy obtained in calorimetric measurements and connected with a succession of three phase transitions in (NH$_4$)$_2$NH$_4$ScF$_6$ is compatible with the entropy of the order-disorder model. However only PTs at $T_1=331$ K and $T_2=293.5$ K can be considered as associated with the ordering process according to the values of entropy close to Rln8 and Rln2, respectively. The entropy change (Rln8) at Fm$\bar{3}$m – P2$_1$/n PT can be supposed to be connected with the ordering of ammonium tetrahedra (Rln2) and with the partial ordering of ScF$_6$-octahedra (Rln4). Final ordering of the octahedra results from the PT at $T_2$ (Rln2). PT at $T_3=243$ K is the first order one followed by great thermal hysteresis ($\Delta T=7$ K) and small entropy change ($\Delta S=0.1$ R) and so it is not an order-disorder transformation. It can be supposed that at $T_3$ there exists PT between two phases which are completely ordered variants of the initial phase Fm$\bar{3}$m. Calorimetric and pressure measurements on partially (80%) deuterated (NH$_4$)$_2$NH$_4$ScF$_6$ have shown that namely this PT is the mostly pronounced effected by deuteration ($T_1=234.5$ K, $\Delta T_3=10$ K, $\Delta S_3=0.15$ R) [3].

We must answer the questions:

1) What is the mechanism of structural distortions?

2) Is the triclinic phase P1 the finally stable one?

For this aim it is necessary to refine the sites and coordinates of fluorines and deuterons at five temperatures: at 355 K in a cubic phase, at 310 K, 265 K and 100 K in three distorted phases, and, at last, at 10 K to be sure that triclinic distortion is the final one.

![Fig.1 Neutron powder patterns at 353, 310, 265, 100 and 10K (from top to bottom).](image)

The (NH$_4$)$_2$ScF$_6$ compound was prepared by interaction of equivalent quantities of NH$_4$F and Sc$_2$O$_3$ with HF (10%) as solvent. The deuteration has been made by four-fold recrystallization of the cryolite in D$_2$O.

References


3. I. N. Flerov, M. V. Gorev, M. L. Afanasyev, T. V. Ushakova. Fizika Tverdogo Tela, accepted
Solid super-ionic conductors are important materials for technical applications, e.g. in fuel cells. Recently, a new type of oxygen ionic conductor was reported, based on perovskite-type LaGaO$_3$, allowing operating temperatures at 800 °C [1]. Oxygen vacancies in the anion lattice, necessary to enhance the ionic conduction, can be introduced by doping with aliovalent oxides like SrO and MgO. In order to understand the conduction mechanism, it is essential to determine the phase relationships as a function of temperature and composition. We have previously reported on neutron powder diffraction measurements (at D2B/ILL) of sol-gel synthesized La$_{0.9}$Sr$_{0.1}$Ga$_{1.2}$Mg$_{0.9}$O$_{2.85}$ [2]. At high temperatures (above 800 °C), the average structure is cubic $Pm\bar{3}m$ with a statistical distribution of the vacancies. However, a recent analysis of another sample with the same overall composition prepared by a solid state synthesis, using instrument E9/HMI [4], revealed that the structures could be better refined in space group $I2/a$ for temperatures up to 900 °C. Furthermore, it was found that structural parameters (e.g. lattice parameters and monoclinic angle) displayed an intriguing deviation from a “normal” linear trend with increasing temperature [4]. This might reflect the anomalies found in the electrical conductivity data [1]. In this contribution we report on detailed structural investigations of different La$_{0.9}$Sr$_{0.1}$Ga$_{1.2}$Mg$_{0.9}$O$_{3.0(0.1+y)}$ samples with various Mg-dopant concentrations (with $x = 0, 0.1,$ and 0.2) leading to different concentrations of oxygen vacancies. The samples were prepared by a novel solution combustion synthesis technique using nitrate solutions and employing urea as a complexing agent [5]. The neutron data were collected at the instrument E9 (wavelength of 1.797 Å) equipped with a high-temperature furnace. The 2T-range was up to 160° with a step width of 0.05°. Measurements were carried out between room temperature and 900 °C in intervals of 100 °C. The data were analyzed with the Rietveld program FullProf. At temperatures > 300 °C all data could be refined in the space group ($R\bar{3}c$). In the figure the evolution of the reduced pseudo-cubic lattice parameter of the rhombohedral structure with temperature for all samples is presented. The reduced lattice parameters converge with increasing temperature towards the metrically cubic value. However, the cubic aristotype $Pm\bar{3}m$ structure is not reached at 900 °C in all cases. Furthermore, it is observed that with increasing Mg-content the rhombohedral lattice is expanded and the $c/a$ ratio is reduced. At room temperature we could confirm the monoclinic space group $I2/a$ only for the sample La$_{0.9}$Sr$_{0.1}$Ga$_{0.9}$Mg$_{0.1}$O$_{2.90}$ ($a = 5.5048(1)$ Å, $b = 7.8020(2)$ Å, $c = 5.5372(1)$ Å, $\beta = 90.033(6)^\circ$) which transforms to the rhombohedral distorted $R\bar{3}c$ structure at ~ 400 °C. For the sample with the lowest amount of oxygen vacancies La$_{0.9}$Sr$_{0.1}$Ga$_{0.9}$O$_{2.95}$ an orthorhombic structure at RT ($Pnma$) is found which exhibits a phase transition to the rhombohedral structure ($R\bar{3}c$) at 200 °C. Further structural results will be presented elsewhere.

The financial support of the DFG (No. LE781/7-1) is gratefully acknowledged.

Understanding activity-composition relations in spinels is crucial in modelling phase relations in a wide variety of metamorphic and igneous rocks within the Earth. If the activity-composition relations for one phase are well known, those of others may be derived from experimentally observed phase relations. One hurdle in the effective extrapolation of data in pressure-temperature-composition space is, however, the appreciation of the influence of cation order-disorder phenomena (intracrystalline element partitioning) on the activity composition relations as a function of temperature (which determine the intercrystalline element partitioning). We are carrying out the first detailed and systematic study in which we are attempting to directly observe the role of order-disorder in spinels on the activities of their components.

This project set out to measure the temperature dependence of Co and Mn cation disordering across the tetrahedral and octahedral sites of the spinel structure, in samples of composition \((\text{Co},\text{Mn}_{1-x})_2\text{TiO}_4\). Using neutron powder diffraction the aim was to determine site occupancies directly by Rietveld refinement, enabling the composition-dependence of the high temperature enthalpies and entropies of ordering to be determined for the first time. Samples of composition \((\text{Co}_{0.85}\text{Mn}_{0.15})_2\text{TiO}_4\), \((\text{Co}_{0.7}\text{Mn}_{0.3})_2\text{TiO}_4\), \((\text{Co}_{0.5}\text{Mn}_{0.5})_2\text{TiO}_4\), and \((\text{Co}_{0.3}\text{Mn}_{0.7})_2\text{TiO}_4\) have been synthesised and the aim was to measure these to temperatures above 1000 °C.

Spinels of composition \((\text{Co}_{0.85}\text{Mn}_{0.15})_2\text{TiO}_4\), \((\text{Co}_{0.7}\text{Mn}_{0.3})_2\text{TiO}_4\), \((\text{Co}_{0.5}\text{Mn}_{0.5})_2\text{TiO}_4\), and \((\text{Co}_{0.3}\text{Mn}_{0.7})_2\text{TiO}_4\) have been measured on the powder diffractometer E9 using the high temperature furnace, achieving temperatures of up to 1400 °C. These measurements have allowed the construction of a model for cation ordering in these unique spinels, where ordering of 2+ cations between tetrahedra and octahedra dominates. Our measurements have validated earlier data for the 50:50 composition, and show that the more dilute samples develop greater degrees of order than previously anticipated. We were able to measure two samples to high temperature \([((\text{Co}_{0.7}\text{Mn}_{0.3})_2\text{TiO}_4 \text{and } (\text{Co}_{0.5}\text{Mn}_{0.5})_2\text{TiO}_4)]\) as well as carrying out careful room temperature measurements of \((\text{Co}_{0.85}\text{Mn}_{0.15})_2\text{TiO}_4\) and \((\text{Co}_{0.5}\text{Mn}_{0.5})_2\text{TiO}_4\). Problems of reaction between the vanadium sample can and the sample precluded the measurement of \((\text{Co}_{0.85}\text{Mn}_{0.15})_2\text{TiO}_4\) to high temperature, but the room temperature measurements will allow the construction of an overarching thermodynamic model for ordering in this system, which will be used to test models for activity-composition relations in solid solutions at high temperatures.

Figure: measured Co-Mn site occupancy disorder for \((\text{Co}_{0.7}\text{Mn}_{0.3})_2\text{TiO}_4\) as a function of temperature.

The results are currently being prepared as a manuscript to be submitted for publication shortly.
EXPERIMENTAL REPORT

Phase transformations caused by hydrogen in Fe-based alloys

The aim was to clarify the nature of H-induced phases and find their correlation with relaxation phenomena in the Fe-based alloys on account of studies [1-4]. Along with the relaxation peaks caused by H migration in the fcc lattice, the internal friction spectra contain some hysteretic peaks (H_4 and H_5 in Fig. 1) of unclear nature.

Fig 1. Internal friction spectra of hydrogen-charged alloys Fe_{55}Cr_{25}Ni_{20} and Fe_{50}Ni_{50}.

Studies were carried out on the alloys Fe_{55}Cr_{25}Ni_{20} and Fe_{50}Ni_{50}. Samples of 50x100x0.030 mm^3 in size were charged in 1N H_2SO_4+50 mg/l NaAsO_2 for 72 h at T=300 K and current density of 10 mA/cm^2. The instrument E9 was used for neutron diffraction measurements at 80 K with λ=0.130762 nm. The results for charged specimens (2) and after outgassing at 473 K (1) are shown in Fig. 2.

H charging causes an increase of background, shift of peaks to smaller angles, their broadening and appearance of additional peaks. The shift of main peaks corresponds to hydrogen content n_H/n_Me of about 7%. The small peak (311)_H (see Fig. 3) originates from the layers extremely saturated by hydrogen and having the lattice parameter a=0.3771 nm (5% of lattice expansion comparing with the non-charged sample). We suppose that splitting of reflections can be caused by the hydrogen-induced ferromagnetism and, hence, a large volume magnetostriction in the H-enriched regions.

Other additional peaks belong to the hcp ε-phase with a=0.2595 nm, c=4.178 nm. Reflections of alloy Fe_{50}Ni_{50} show similar behaviour, however, the ε-phase was not formed.

The comparison of the IF (Fig. 1) and neutron diffraction (Figs 2,3) data allows to conclude that hysteretic internal friction peaks H_4 and H_5 in alloy Fe_{55}Cr_{25}Ni_{20} are caused by hydrogen outgassing from the γ and ε phases respectively, whereas the single hysteretic peak in alloy Fe_{50}Ni_{50} belongs to the γ phase.

Fig 2. Neutron diffraction patterns of alloy Fe_{55}Cr_{25}Ni_{20} with and without hydrogen.

Fig 3. Enlarged part of neutron diffraction pattern of alloy Fe_{55}Cr_{25}Ni_{20}.

In recent years the preparation, structure, luminescence and magnetic properties of ALn(XO₄)₂ (A= monovalent alkali, Cu and Ag; Ln= lanthanide; X= Mo, W) have been studied. Depending on their composition, they present a wide diversity of crystal structure types. The family of copper molybdates presents the orthorhombic S.G. Pnca (n° 61) symmetry [1-5]. The whole Ln-Cu-W series shows dimorphism with either triclinic P-1 (n°2) [4,7-9] or monoclinic P12/n1 (n° 13) [6,10-12] crystal structures. Whereas Ag molybdates containing a quite larger rare earth, Sm, or the smaller Yb and the intermediates Eu,Gd and Tb are described in the tetragonal S.G. I4 (n° 82) [13-17]. In the corresponding tungstate family two structural types are found depending on the size of the considered lanthanide: AgLa(WO₄)₂ is tetragonal S.G. I4₁/a (n° 88) [14] and a more recent work [6], focused on the AgLn(WO₄)₂ (Ln=Eu, Gd, Tb, and Dy) shows that the crystal structure of these compounds can be described by a monoclinic distortion of the tetragonal scheelite cell to accommodate the smaller Ln³⁺ ions. On the other hand, excitation and emission spectra of AgLn(WO₄)₂ (Ln=Eu, Gd and Tb) show that energy transfer from the tungstate to Ln³⁺ occurs. In these compounds the tungstate group can sensitize the emission of Ln³⁺ ions. One possible application of rare earth double tungstates is using these compounds as active materials in solid state lasers. In this sense, we studied too the spectroscopic properties of AgNd(WO₄)₂. At first glance, X-ray data can be explained using the I-4 (n° 82) tetragonal scheelite structure, but due to discrepancies between experimental and calculated intensities of several reflections, we tried to explain our data using the related monoclinic distortion of the scheelite unit-cell [6]. These trials were fruitless. IR spectrum for the title compound is somewhat more complex than those for similar lantanide-containing molybdates, where the MoO₄²⁻ has S₄ site symmetry, instead of that NdAg(WO₄)₂ spectra are similar to those of the monoclinic DyAg(WO₄)₂ [6]. In this sense, the calculated energy levels scheme show much better agreement with the experimental data by considering that the Nd³⁺ occupies in this matrix a single site of C₂ (C₂) symmetry. So IR spectra suggest that this compound presents a monoclinic structure while X-rays does not allow unambiguous determination of the crystalline structure of NdAg(WO₄)₂.

The aim of the neutron diffraction study is to solve the crystal structure in combination with X-rays, taking into account the advantage of the former technique to locate the oxygen atoms. This work is now in progress.

Figure 1.- X-ray (top) and neutron (bottom) powder diffraction patterns of AgNd(WO₄)₂ at room temperature in d space. Notice the different intensity ratio.

[15] Li H, Hong G and Yue S 1990 Zhongguo Xitu Xuebao 8 37
ZnV$_2$O$_4$ exhibits a cubic to tetragonal phase transition at 50 K [1]. This can be ascribed to the Jahn-Teller Effect due to the presence of V$^{3+}$-ions with the outer electron configuration $d^2$. The crystal structures of both phases have been determined from neutron powder diffraction data collected on the instrument E9 at 1.8 K and 70 K. The powder diffraction patterns were recorded between 20 values of 5 and 150° using the neutron wavelength $\lambda = 1.7982 \text{Å}$.

At 70 K this compound crystallizes in a cubic spinel-type structure with the space group $Fd\bar{3}m$. The atoms Zn, V and O are on the Wyckoff positions 8$a$ (1/8, 1/8, 1/8), 16$d$ (1/2, 1/2, 1/2) and 32$e$ (x, x, x), respectively. At 1.8 K ZnV$_2$O$_4$ shows a tetragonal distortion along cube edges with $c/a = 0.99480(12)$. The unit cell of the tetragonal phase (space group $I\bar{4}1/amd$) is just half of the cubic one with the cell dimensions $a\sqrt{2} \times a\sqrt{2} \times a$. In this structure the Zn-, V- and O-atoms are on the positions 4$a$ (0, 3/4, 1/8), 8$d$ (0, 0, 1/2) and 16$h$ (0, x, z), respectively. The Rietveld refinements of both structures were successful resulting in residuals $R_N = 0.047$ for the cubic and $R_N = 0.032$ for the tetragonal structure, respectively. The results of the refinements are summarized in Table 1.

The central V$^{3+}$-ion has six next-nearest neighbours of oxygen atoms forming an octahedral environment. In the cubic form the bond lengths between the vanadium and oxygen atoms are the same [$d_{V-O} = 2.0168 \text{Å}$]. In the tetragonal form the distance between the vanadium and the apical O-atoms (approximately parallel to the c-axis) is shorter [$d_{V-O} = 2.0041 \text{Å}$] than in the cubic phase. On the other hand the distance to the other four O-atoms (approximately within the ab-plane) is larger [$d_{V-O} = 2.0243 \text{Å}$]. Further it is interesting to see that the cell volumes $V$ at 1.8 K and $V = 593.30(12) \text{Å}^3$ at 60 K are practically the same.

### Table 1

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>ZnV$_2$O$_4$</th>
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<tbody>
<tr>
<td>1.8</td>
<td>5.9526(4)</td>
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<td></td>
<td>8.4028(4)</td>
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<tr>
<td>70</td>
<td>8.3744(6)</td>
</tr>
<tr>
<td></td>
<td>8.4028</td>
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<tr>
<td>$a$ [Å]</td>
<td>5.9526(4)</td>
</tr>
<tr>
<td></td>
<td>8.4028(4)</td>
</tr>
<tr>
<td>$c$ [Å]</td>
<td>8.3744(6)</td>
</tr>
<tr>
<td></td>
<td>8.4028</td>
</tr>
<tr>
<td>$V$ [Å$^3$]</td>
<td>296.73(6)</td>
</tr>
<tr>
<td></td>
<td>593.30(8)</td>
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<tr>
<td>$x(\text{O})$</td>
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<tr>
<td></td>
<td>0.0200(5)</td>
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<tr>
<td>$z(\text{O})$</td>
<td>0.2604(2)</td>
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<td>0.2611(5)</td>
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<tr>
<td>$B(\text{Zn})$ [Å$^2$]</td>
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<tr>
<td></td>
<td>0.49(17)</td>
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<tr>
<td>$B(\text{V})$ [Å$^2$]</td>
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<tr>
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<td>0.2</td>
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<tr>
<td>$B(\text{O})$ [Å$^2$]</td>
<td>0.29(9)</td>
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<tr>
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<td>0.45(6)</td>
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<tr>
<td>$R_N$ (No. of $F^\prime$s)</td>
<td>0.032(51)</td>
</tr>
<tr>
<td></td>
<td>0.047(20)</td>
</tr>
</tbody>
</table>

The isotropic thermal parameter of vanadium were held at $B = 0.2 \text{Å}^2$ during the refinements $R_N$ is the residual of the nuclear structure defined as $R_N = \Sigma ||F_o|| - ||F_c||/\Sigma |F_o|$. 

### References

The \(-\text{N-H...O=C-}\) skeleton of N-methylacetamide (NMA, \(\text{CH}_3\text{NHCOCH}_3\)) is the "residue" so important in protein structure analysis. NMA is the smallest molecule whose crystal structure has this property, and it may therefore be viewed as the simplest model system for alpha-helical proteins and polypeptides. In consequence NMA has been the subject of intense interest in the dynamics of the H-bond proton, peptide group and methyl group [1,2].

NMA is highly hydroscopic, melts just above room temperature (28ºC) and undergoes a structural phase transition around room temperature \((T'=274K)\ [3, 4]\). Most recently structural results supported the idea of a glassy-type disorder [4] below \(T'\), as well as the occurrence of a second phase in the vicinity of 230-240K [3]. With the purpose of better understand very recent quasi-elastic data [5], and re-check the reported transitions in NMA, we performed differential scanning calorimetry (DSC) measurements. As shown below, we could observe that besides the first order transition that takes place around 280K, a very weak anomaly around 220K (~50ºC) indicates that a second structural transition may occur.

In this experiment we took a different approach as the one followed in reference 4. To avoid breaking of the crystal structure, instead of pulverizing the sample we quenched it down to 20K, and measured on heating up to 280K, i.e. just below the melting point. However due to the fast re-crystallization of NMA, and consequently formation of various crystallites with different preferential orientations, we have encountered few problems during the experiment. To facilitate the data collection we have taken data rotating the sample around its axis (using three different positions), and the data shown below are the result of an average. This preliminary experiment is evidence for a structural transition-taking place below 200K. Further investigations are under way.

Neutron diffraction data obtained on NMA using E9 at various temperatures.

EXPERIMENTAL REPORT

INVESTIGATION OF THE POLLUCITE TYPE COMPOUND Cs₂Cu₂Si₅O₁₂

Principal Proposer: M. Tovar, HMI Berlin
Experimental Team: M. Tovar, HMI Berlin
F. Fleischer, Universität Leipzig

Proposal EF
Instrument E9
Local Contact M. Tovar
Date(s) of Experiment 9/11-9/15, 2002
Date of Report: 30.1.2003

Experiment:

Due to the Jahn-Teller effect many transition metal compounds show a more or less strong deviation from their ideal crystal structure. Examples can be found in the spinel and the perovskite or spinel family for instance [1]. Depending on the configuration of the d-shell electrons, the Jahn-Teller effect causes local polyhedral or a macroscopic crystal structure distortion by reducing the symmetry of the whole structure.

The pollucite type compound Cs₂Cu₂Si₅O₁₂ crystallizes at room temperature in the tetragonal space group P4₁2₁2, a=b=13.5776 Å, c=13.6189 Å [2]. Hence it exhibits a distorted pollucite (zeolite-like) structure.

Cu²⁺ together with the Si⁴⁺ built a framework of MO₄ tetrahedra. Within this framework the large Cs²⁺ occupies the holes. Since Cu⁵⁺ is influenced by the Jahn-Teller effect, its local coordination sphere is distorted. Heinrich and Baerlocher [2] found an strongly distorted and in the mean elongated Cu²⁺ tetrahedron applying the Rietveld method on a X-ray powder diffractogram of Cs₂Cu₂Si₅O₁₂. This is in opposite to the theory which gives only rise for a flattening of the individual tetrahedra.

There are two possible explanation for this observation: first, the framework of the SiO₄ tetrahedra forces the CuO₄ tetrahedra to flatten, second, the X-ray data were not sufficient for an exact determination of the atomic position to tell between flattening or elongation. However, to prove this observation neutron powder diffraction was used, since the neutron sensitivity to oxygen is much higher than that of X-rays. Therefore atomic positions of much better accuracy could be expected.

Results:

Rietveld refinements of the patterns results at least in quite unstable and partly meaningless results. So constraints to the atomic bondings were introduced. Furthermore additional X-ray data were introduced to increase the number of independent observations. This lead to an increasing Bragg R value from 7.2% to 12.7% but giving much more meaningful values for distances and angles especially for Cu-O and Si-O bonds (Rietveld plot is given in fig. 1 for neutron).

Results:

Using whole powder pattern fitting the lattice constants could be determined as a=b=13.5763 Å, c=13.6251 Å, showing comparable dimension as found in literature.

Fig. 1: Rietveld plot of the neutron powder diffractogram of Cs₂Cu₂Si₅O₁₂

The combination of neutron and X-ray data could greatly improve the accuracy of the refinements results. However, the found Cu²⁺ tetrahedron shows a remarkable but not-systematic distortion which is obviously more influenced by the SiO₄ tetrahedra framework than by the Jahn-Teller effect.

Literature:

We have studied the acoustic phonon lifetimes at very small reduced scattering vector $Q$ in the icosahedral quasicrystal i-AlPdMn. Previous triple-axis inelastic neutron scattering [1] and our own inelastic x-ray scattering experiments [2] have shown that the longitudinal acoustic (LA) phonon linewidth $G$ is not measurably broadened for small $Q$, but that it becomes very large for $Q$ larger than about 0.4 nm. We found that the transverse acoustic (TA) linewidth increases quadratically with $Q$. This preliminary experiment was to investigate the possibility of using a neutron resonant spin echo (NRSE) spectrometer to study the small-$Q$ region. We used the triple-axis instrument V2 at the Hahn-Meitner Institute with NRSE option [3].

The sample used has previously been prepared at Jülich and used in the thesis of N. Shramchenko [4]. We have measured the lifetime of the TA mode at small reduced $Q$ starting from the (18,29) reflection along the 5-fold axis (see [1]) and at room temperature. This orientation was chosen to maximise coupling between the TA modes and static phason disorder [4]. We have found the following preliminary results:

1. The NRSE-determined mosaic spread of our sample at this reflection is about 4.38' ± 0.03', as shown in Figure 1 (upper). This demonstrates the very high quality of the sample.

2. The NRSE-determined correlation time at $Q = 0.025$ and 0.050 Å$^{-1}$ is shown in Figure 2 (lower) with a decay time of about 4 ps.

3. This linewidth is larger than that expected from previous INS experiments [1], and because of the sample quality it cannot be due to the mosaic spread. We are investigating the phonon-phason coupling as a reason for this extra width.

EXPERIMENTAL REPORT
Search for unusual line-widths of NH₃ rotational transitions in Hofmann clathrates

Proposal Nº EF / SF1
Instrument: V2/FLEX
Local Contact: P. Vorderwisch

Date(s) of Experiment
10-17.07.2002

Hofmann clathrates Ni(NH₃)₂Ni(CN)₄·2G with guest molecules G=C₆D₆, C₆H₆ (benzene) and C₁₂H₁₀ (biphenyl) are among the rare examples where (almost) free rotations of molecules in the solid state have been observed: the NH₃ groups perform uniaxial quantum rotations with rotational level schemes identical for all three compounds [1,2].

Rotational transitions measured so far by inelastic neutron scattering (INS) refer to those between rotational levels $E_J = B J^2$ with $J=0,1,2$ (where $B=0.71$ meV is the rotational constant). The INS spectra revealed an unexpected temperature dependence in that the $0 \rightarrow 2$ and $1 \rightarrow 2$ transitions broaden much faster than the $0 \rightarrow 1$ transition with increasing temperature. A recent theoretical analysis of these experimental findings is based on phonon-rotor coupling [3].

Also very recently, a different approach based on resonant coupling of free quantum rotors has been successfully applied [4] to describe the data measured thus far. This paper also predicts line widths for hitherto unmeasured transitions, i.e. those involving $J \geq 3$ levels (Fig. 1). Especially, it predicts - in contrast to transitions between $J=0,1,2$ levels - a finite width (of about 1.4 meV) at $T=0$ for transitions involving $J=3$ levels.

To verify this, experiments have been performed with V2/FLEX on Ni-Ni-C₆H₆ and Ni-Ni-C₁₂H₁₀ at different temperatures and momentum transfers. Typical data, taken at $T=1.5$ K, are shown in Fig. 2. Whereas the $0 \rightarrow 1$ (at 0.71 meV) and $0 \rightarrow 2$ (at 2.84 meV) transitions are clearly seen, the energy transfer region for the $0 \rightarrow 3$ transition (expected at 6.4 meV) shows a broad intensity distribution instead of a single line. This distribution is different for the two samples (with different guest molecules and crystal structures), thus probably due to lattice mode contributions.

Inelastic structure factor calculations, proven to be correct for transitions between $J=0,1,2$ levels, result for the $0 \rightarrow 3$ transition in a much too high intensity if no line broadening at $T=0$ is assumed. We therefore conclude that the $0 \rightarrow 3$ transition is indeed strongly coupled – either to resonant rotors or to resonant phonons. Further data analysis and interpretation is presently performed.

References
**EXPERIMENTAL REPORT**

**Phonon Linewidths and Lineloshits in Single Crystal Pb**

**Measured with Neutron Resonance Spin Echo (NRSE)**

**Proposal N° EF-SF1**

**Instrument V2-NRSE**

**Local Contact**

K. Habicht

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**Date(s) of Experiment**

11.06.– 14.06.2002; 16.06.– 23.06.2002

**Date of Report:** 15.01.2003

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We continued the experimental study of phonon lifetimes in Pb which can be regarded as a model system of anharmonic lattice dynamics in the fcc metals since phonon-phonon interaction dominates over electron-phonon interaction over a large q- and temperature range. Dispersive, transverse acoustic phonon modes in the low q limit (q<0.2 r.l.u.) have been investigated at temperatures between 5-300 K using the neutron resonance spin echo (NRSE) scattering technique on the cold TAS spectrometer V2 (FLEX). The TAS was operated with fixed \( k_i = 1.7 \text{ } \cdot \text{ }^{-1} \) in a configuration giving a transverse q-resolution of about 0.01 \( \cdot \text{ }^{-1} \) FWHM. A tunable PG filter was used to eliminate second order contamination. The field tilt angles have been calculated from Born-von-Kármán fits to dispersion data from the literature, typical tilt angles were \( \theta_1 = -30^\circ \) and \( \theta_2 = +25^\circ \) for [\( \xi_0 0 0 \)] TA phonons with \( \xi < 0.2 \text{ } r.l.u. \). Amplitudes of spin echo curves have been measured as a function of spin echo time \( \tau \) in order to determine phonon lifetimes. Within statistical error the lifeftime was consistent with a single exponential decay (Lorentzian lineshape).

A theoretical approach based on a Gaussian approximation of the instrumental resolution function has been developed and is used to separate intrinsic lifetimes from signal depolarization due to sample mosaicity and curvature of the dispersion surface. This formalism has been used to obtain the corrected values shown in fig. 1. [\( \xi_0 0 \)] TA phonons show a linear q-dependence in the range 0.05<\( \xi < 0.2 \text{ } r.l.u. \). Amplitudes of spin echo curves have been measured as a function of spin echo time \( \tau \) in order to determine phonon lifetimes. Within statistical error the lifeftime was consistent with a single exponential decay (Lorentzian lineshape).

The experimental results are consistent with previous, less accurate experimental results using the TOF technique [1] and disagree with calculated lifetimes obtained from a perturbative model of lattice anharmonicity based on a force constant parameterization of the interatomic potential [2]. The latter model has been used to obtain calculated lifetimes in the q-range covered by our experiments. Despite numerical disagreement the result shows the linear q-dependence experimentally observed. Ab initio calculations [4] show that electron-phonon interaction plays a less important role.

The temperature-dependent change in the real part of the phonon self-energy has been measured for two selected phonon modes (see fig. 2). Here a change in phase of the spin-echo signal is directly proportional to the phonon energy change. The linear dependence at high temperatures is due to the Bose-Einstein factors.

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**Fig.1:** Experimental and theoretical phonon linewidths of the [\( \xi 0 0 \)] TA mode at \( T = 300 \text{ } K \).

**Fig.2:** Temperature-dependent change in the real part of the self-energy of the [0.05 0.05 0] (squares) and [0.1 0.1 0] (circles) phonon modes. Lines are linear fits to the data.

An extensive theoretical literature developed over several decades treats the energy renormalization and lifetime of spin waves in Heisenberg antiferromagnets. However, to date such results remain unverifiable by any technique, outside narrow regions of temperature and wavevector. In the case of inelastic neutron scattering (INS) experiments, the restriction is the result of limitations of the instrumental resolution.

In MnF₂, one of the most intensively studied antiferromagnets, the magnon linewidth Γ has been investigated only in the critical region: therein is the linewidth sufficiently broad that INS measurements are not resolution-limited. An INS study of the low-temperature damping in the nearly isotropic antiferromagnet RbMnF₃ found partial agreement with theory [1]. However, the deconvolved linewidths were significantly smaller than the instrumental resolution: the smallest deconvolved Γ was only 2% of the lowest measured value of 195µeV [2].

In this experiment we used the cold triple-axis spectrometer V2 (FLEX) with the neutron resonance spin echo (NRSE) option to measure the magnon linewidth in MnF₂ at low temperatures. The NRSE technique is uniquely suited to such investigations, as the method of “phonon focusing” exploits the excellent resolution of the spin-echo technique over the entire Brillouin zone, permitting accurate measurement of the linewidth of narrow dispersive excitations.

We used a half-cylindrical crystal of volume 8.5cm³, mounted in the ac-plane. kᵢ was fixed at 1.74Å⁻¹, corresponding to a fixed transverse background TAS resolution of ~0.01Å⁻¹ FWHM. A tunable PG filter was used to reject higher-order contamination. We investigated magnons with q ranging from 0 - 0.1 r.l.u., at temperatures between 4 and 40K (0.06 - 0.6Tₘ). We focused on the antiferromagnetic Brillouin zones centered at (001) and (100), and observed qa and qc-magnons, respectively.

The coil tilt angles for NRSE were calculated using an analytical expression for the spin-wave dispersion [3] that fits previous experimental data well, in combination with values of the magnon energy measured during the experiment. Coil tilt angles were as large as (θ₁=−27°, θ₂=+0.2°) for qₓ=0.1.

With the NRSE-TAS technique, we measure the polarization of the scattered neutrons as a function of the spin-echo time τ. This polarization is the Fourier transform of the spectral lineshape. The observed polarizations decay as P(τ)=P₀ exp(-Γτ), which corresponds to a Lorentzian lineshape. From the fit we obtain the magnon linewidth Γ.

The preliminary dataset (Fig.1) allows qualitative comparison with the theory. Within fitting error, the data is not inconsistent with the expected monotonic increase in linewidth with q and T. The smallest measured linewidth was 10.8 ± 1.8µeV.

Fig.1: Experimental [001] magnon linewidths in MnF₂ at various temperatures.

EXPERIMENTAL REPORT

Molecular dynamics in solid ammonium cyanate

Proposal N° CHE-03-207
Instrument NEAT
Local Contact A. Desmedt
Date(s) of Experiment 13/05/02 – 20/05/02
Date of Report: 13/01/2003

It is traditionally believed that organic chemistry started in 1828 when Friedrich Wöhler heated solid ammonium cyanate (NH$_4^+$.NCO$^-$) to obtain solid urea. However, although this solid state transformation of ammonium cyanate has now been known for well over a century, details of the reaction in the solid state remain sparse. Indeed, even the crystal structure of ammonium cyanate was unknown until recently [1] and very little is known about the dynamic properties of this material. Recent studies by solid state $^2$H NMR [2] have shown clearly that the ammonium cation undergoes dynamics on a timescale shorter than 10 ns at temperatures above 143 K, but is unable to distinguish different dynamic models that may be proposed for this system.

In order to overcome this problem and to obtain a comprehensive understanding of the dynamic properties of this material, we have performed QENS experiments on the time-of-flight spectrometer NEAT. The spectra were recorded on a powder sample with two different energy resolutions, $\Delta E = 90\mu$eV ($\lambda_0 = 5.1\text{Å}$) and $\Delta E = 30\mu$eV ($\lambda_0 = 8.1\text{Å}$). It should be noticed that no significant quasi-elastic broadenings have been observed for $T < 240\text{K}$ with $\Delta E = 30\mu$eV and for $T < 260\text{K}$ with $\Delta E = 90\mu$eV. Full spectra have then been recorded at 293K, 282K, 267K and 253K with $\Delta E = 30\mu$eV and at 282K and 267K with $\Delta E = 90\mu$eV for probing any faster component of the cation motions.

In order to analyse qualitatively the spectra, the HWHMs (half-width at half-maximum) and the EISFs (Elastic Incoherent Structure Factor) of these broadenings have been estimated by fitting the experimental data with an elastic peak plus a Lorentzian function. In a first step of the analysis, all the angles have been fitted independently and no significant Q-dependence of the HWHMs has been observed. Thus, in the final phenomenological fitting procedure, the HWHMs have been constrained to be identical for all angles. As can be seen on the table and the figure below, the HWHMs and the EISFs exhibit a strong temperature and resolution dependence. In view of these results, it clearly appears that the quasi-elastic broadenings are not well resolved for temperatures below 293K with both resolutions.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta E = 30\mu$eV</th>
<th>$\Delta E = 90\mu$eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>253</td>
<td>63</td>
<td>-</td>
</tr>
<tr>
<td>267</td>
<td>27</td>
<td>80</td>
</tr>
<tr>
<td>282</td>
<td>12</td>
<td>80</td>
</tr>
<tr>
<td>293</td>
<td>11</td>
<td>-</td>
</tr>
</tbody>
</table>

Thus, this preliminary analysis indicates that the data recorded at 293K with $\Delta E = 30\mu$eV may be used to elaborate a model for establishing the cation dynamics. The other spectra could then be analysed to determine the activation energy. However, additional QENS experiments on a backscattering spectrometer ($\Delta E \approx 1\mu$eV) would be necessary to confirm the model and to determine the activation energy across a larger temperature domain.

References:
2 - S.J. Kitchin, K.D.M. Harris, J.D. Dunitz, R.R. Tykwinski, unpublished results
Introduction

In \( \text{In}(\text{CH}_3)_3 \) is very similar to the recently studied \( \text{Ga}(\text{CH}_3)_3 \) [1]. The four tunneling bands of \( \text{In}(\text{CH}_3)_3 \) with relative intensities 1:1:1:3 at 15.9, 8.7, 4.7 and 1.7 \( \mu \text{eV} \) are inconsistent with the tetragonal space group \( P4_2/n(Z=8) \) and 3 inequivalent \( \text{CH}_3 \) groups found at \( T=273 \text{K} \) [2]. The similarity to \( \text{Ga}(\text{CH}_3)_3 \) [3] makes us suppose that the low temperature phase is \( C2/c(Z=16) \) with 6 inequivalent \( \text{CH}_3 \) groups.

Experiment and Results

Quasielastic neutron spectra were measured in the temperature regime \( 45 < T[K] < 98 \).

![Some quasielastic spectra of In(CH3)3. Temperatures 45.0K (○), 50K (x) and 55.0K (□). Solid lines: fit.](image)

The chosen number and weights of quasielastic Lorentzians to be fitted are based on the tunneling spectra and the supposed crystal structure. The similarity of some barriers made it impossible to distinguish 6 individual contributions. A fit by a single Lorentzian was also impossible. A promising generalisation of this simplest model was obtained by combining tunnel transitions with peaks of the measured vibrational density of states: the extracted rotational potentials showed barrier heights differing by less than 8% for 5 of the 6 methyl groups. One group showed a clearly weaker rotational potential. Thus the new model contains 2 Lorentzians of an intensity ratio 5:1. The final fit (solid lines of figure 1) is very good up to about 60K. At higher temperatures \( 70 \leq T[K] \leq 98 \) a single Lorentzian describes the data rather well. This discontinuity is the fingerprint of the suggested phase transition - meanwhile confirmed by X-ray diffractometry.

![Arrhenius plots of quasielastic linewidths. Weights: \( \frac{1}{6} (\circ), \frac{5}{6} (\square), 1(\triangle) \)](image)

Arrhenius fits of linewidths yield activation energies of 210(305)K in the LT phase for the components with relative intensities 1(5), and \( \sim 210 \text{K} \) in the HT phase (fig. 2). The obtained rotational potentials deviate by no more than \( \sim 20\% \) from pure \( \cos(3\varphi) \).

Quasielastic neutron scattering measurements on the system of molecular hydrogen adsorbed on single walled carbon nanotubes were performed on the NEAT spectrometer. In these measurements, the molecular hydrogen was loaded into the SWNT’s at 1 atmosphere. A weak quasielastic component to the scattering is present at 30K and increases in width as the temperature is increased (Figure 1). We find that the quasielastic component to the scattering is well described by a liquid-like jump diffusion (Figure 1). In addition, diffusion observed in these measurements follows an Arrhenius behavior with relatively fast diffusion (Figure 2). The diffusion coefficient extracted is an order of magnitude larger than that of the bulk liquid, but much lower than the theoretically predicted value for the self diffusion coefficient of molecular hydrogen adsorbed inside the tubes of a bundle, the endohedral sites. In addition, the activation energy and diffusion coefficient measured for H₂ on SWNT’s are comparable to the values obtained for HD adsorbed on Grafoil. These initial measurements show that the adsorbed H₂ is adsorbed in the exterior grooves between individual tubes in a bundle, is promoted out of these groove sites and diffuses on the external surface of the nanotube bundles.
In the clathrate hydrate tetramethylammonium hydroxide pentahydrate, \((\text{CH}_3)_4\text{NOH} \cdot 5\text{H}_2\text{O}\) (noted TMAOH hereafter), the water molecules and the hydroxyl ions form an extensively hydrogen-bonded anionic “host” substructure within which there are inclusion cavities that contain the “guest” cations \((\text{CH}_3)_4\text{N}^+\) [1]. Because of the existence of hydroxyl ions in the aqueous matrix, this water clathrate is a very nice proton conductor [2].

TMAOH (melting point at 341K) exhibits phase transitions involving the cation dynamics. A structural phase transition has been identified at 315K between a cubic phase I above 315K and an orthorhombic phase II below 315K [1]. \(^1\text{H}\) and \(^2\text{H}\) NMR experiments have suggested that the cations undergo “pseudo isotropic reorientation” in the rapid motion regime (i.e. \(\tau_c > 10^{-8}\)s) for temperatures above 130K in phase II [3]. In the present experiment, we aim to re-investigate the cation dynamics by means of Incoherent Quasi-Elastic Neutron Scattering (QENS) technique.

On this issue, the QENS experiments have been performed on the selectively deuterated sample, \((\text{CH}_3)_4\text{NOD} \cdot 5\text{D}_2\text{O}\) (noted TMAOD hereafter), with the time-of-flight spectrometer NEAT. Three resolutions have been used:

(a) \(\Delta E \approx 90\mu\text{eV}\) \((\lambda_o = 5.1\text{Å})\) at 330K, 300K, 270K, 240K, 208K and 179K,
(b) \(\Delta E \approx 50\mu\text{eV}\) \((\lambda_o = 6.0\text{Å})\) at 208K and 179K,
(c) \(\Delta E \approx 25\mu\text{eV}\) \((\lambda_o = 8.0\text{Å})\) at 179K and 150K.

Quasi-elastic (QE) broadening has been observed for all temperatures and resolutions, except for \(T=150K\) and \(\Delta E=25\mu\text{eV}\). In order to quantify these QE broadening, the spectra have been fitted by means of an elastic peak plus a Lorentzian function. For \(T=179K\) and \(\Delta E=25\mu\text{eV}\), no significant Q-dependence of the HWHMs has been observed, so that in the final fit, the HWHMs have been constrained to be identical for all angles. The typical thermal evolution of the EISFs is presented on the figure shown below (the letters within the brackets refer to the resolution used).

As shown on this figure, an abrupt change is observed in the temperature dependence of the EISFs at 330K (phase I) and 300K (phase II). In phase II, the temperature dependence of the EISFs is due to the instrumental resolution. However, in the high temperatures of phase II, the EISFs tend towards a limit value which can be directly compared to the EISFs calculated according to the “pseudo isotropic reorientation” model proposed by Ratcliffe et al [2]: on the figure, the continuous line represents the calculated EISF for an isotropic rotation on a sphere of radius 2.1Å (corresponding to the distance NH in the tetramethylammonium). At this level of the analysis, it seems that this model cannot reproduce the experimental data.

Thus, subsequent analyses of the spectra will be performed to elaborate a more realistic model for establishing the cation dynamics in phases I and II. Such information is crucial to elucidate the phase transition and the protonic conduction mechanisms at a microscopic level [4].

**References:**
In clathrate hydrates, a host structure comprises a hydrogen bonded arrangement of water molecules and contains inclusion cavities within which a large number of guest molecules can be located. The confinement of acid or base guest molecules leads to aqueous nanoporous matrices that are cationic or anionic, respectively. Clathrate hydrates of strong acids or bases are then excellent proton conductor.

Our aim is to elucidate the proton transport mechanisms in such crystalline materials. For the acid clathrate, the investigation has been performed in the clathrate hydrate of perchloric acid by means of an original "resolution-dependent" incoherent Quasi-Elastic Neutron Scattering (QENS) study \[1,2\]. In the present QENS experiment, we aimed to analyse the basic clathrate typified by the tetramethylammonium hydroxide pentahydrate (\(\text{(CH}_3\text{)}_4\text{NOH - 5H}_2\text{O}\)) (details concerning the structural properties could be found in \[3\]).

The QENS measurements have been performed on (\(\text{(CH}_3\text{)}_4\text{NOD - 5D}_2\text{O}\)) (noted TMAOD) and (\(\text{(CH}_3\text{)}_4\text{NOH - 5H}_2\text{O}\)) (noted TMAOH). The proton dynamics within the aqueous sub-structure can then be extracted by differentiating the spectra of the two samples. In order to analyse the localised diffusive motions (reorientations of \(\text{H}_2\text{O}\) molecules and \(\text{OH}^-\) ions, for instance), the spectra have been recorded with the time-of-flight spectrometer NEAT at 300K in the orthorhombic phase I and at 330K in the cubic phase II. Four different resolutions have been used: \(\Delta E=600\text{µeV}\) with \(\lambda_0=4\text{Å}\) and \(\Delta E=300\text{µeV}\), \(90\text{µeV}\), \(30\text{µeV}\) with \(\lambda_0=5.1\text{Å}\).

For all resolutions and both phases, a range of quasi-elastic broadenings (with half-widths at half maxima ranging from \(\text{ca. 70µeV}\) to \(\text{ca. 700µeV}\)) have been observed and rationalized by fitting the spectra by means of an elastic peak plus a Lorentzian function. On the basis of these fits, the Elastic Incoherent Structure Factors associated to the host substructure (noted EISF\(_{\text{host}}\)) have been extracted as followed:

\[
EISF_{\text{host}} = \frac{23}{11}\left(\frac{EISF_{\text{TMAOH}} - \frac{12}{23}EISF_{\text{TMAOD}}}{EISF_{\text{TMAOD}} - EISF_{\text{TMAOH}}}ight)
\]

As shown on the figure below, the EISF\(_{\text{host}}\) exhibit stronger energy resolution dependence in phase II (300K) than in phase I (330K). These variations clearly indicate that the localised diffusive motions are characterised by several quasi-elastic components exhibiting different Q-dependence. The greater value of the EISF at T=300K compared to that at T=330K suggest that the proton transport mechanisms may be different in the two phases with correlation times obviously shorter at 330K than at 300K.

Thus, the crystalline structure being known (see references in \[3\]), modelling this data should provide the opportunity for understanding the elementary mechanisms of protonic conductivity in TMAOH. However, further experiments on backscattering spectrometers (\(\Delta E=\text{1µeV}\) and \(\Delta E=\text{10µeV}\)) would be crucial to analyse slower localised diffusive motions and the long-range translation of the protons.

References:
Hofmann-type clathrates are described by the general chemical formula $M(NH_3)_2M'(CN)_4G$ (and usually abbreviated as M-M'-G), where M and M' are divalent metal ions and G are guest molecules. In some of these compounds nearly free uniaxial quantum rotations of the NH$_3$-groups have been observed by inelastic neutron scattering [1-3]. Interaction of the rotors with their environment leads to a temperature dependent broadening of the transition lines between rotational levels [3].

The free rotor energy levels read as

$$E_J = B J^2 \quad (J = 0,1,2,...)$$

with the rotational constant $B=\hbar/2\Theta$, where $\Theta$ is the moment of inertia. The experimental B value for NH$_3$ groups in the Hofmann clathrates Ni-Ni-2C$_6$H$_6$ and Ni-Ni-2C$_{12}$H$_{10}$ is $B = 0.71$ meV, which is lower than the gas phase value ($B = 0.78$ meV). This difference is attributed to a coupled reverse rotation of the NH$_3$-group and its centre-of-mass [4,5]. If so, the proton density function is more extended than given by the molecular symmetry, and is described by an effective radius $r' \approx 0.99$ Å from the center of symmetry, slightly larger than the gas phase value $r_0 = 0.94$ Å.

The main aim of this experiment was to study the Q dependence of inelastic peak intensities for transitions between different rotor levels in Ni-Ni-2C$_{12}$H$_{10}$. This dependence [6] is a function of $Q r$ and sufficiently sensitive to allow for the determination of an appropriate effective radius.

Measurements were performed (with the time-of-flight spectrometer NEAT) at sample temperatures 1.8K, 10K and 20K. Incident neutron wavelengths were $\lambda_0 = 3.3$ Å (with an elastic resolution $\Delta E \sim 300$ µeV) and $\lambda_0 = 2.1$ Å ($\Delta E \sim 800$ µeV). A standard flat sample with 1 mm thickness was used, resulting in a transmission of about 93%. Multiple scattering contributions were calculated.

A good agreement of the theoretical predictions [6] with the experimental results was reached, but only using the value $r_0 = 0.94$ Å, which corresponds exactly to the projection of the N–H distance onto the plane of rotation for gas phase NH$_3$. This means that the effect of the molecular centre-of-mass motion is not observed in this experiment.

**References**


**Figure 1:** The integral intensities for the $0 \rightarrow 1$ (circles), $0 \rightarrow 2$ (squares) and $1 \rightarrow 2$ (triangles) transition lines. Solid lines – theoretical curves [6], dashed lines – multiple scattering contributions.
It was proposed:
1. to study the total reflection of neutrons with different small K on the surface of high-quality glass and/or silicon mirrors excited by the ultrasound.
2. to measure the dependences of US satellites on the power of sound oscillations fed by the generator, with the aim to define the amplitude of the ultrasound waves excited in glass.
3. to measure phonon satellites in the case of neutrons’ entering into a glass, i.e. for Q>Qc, where Qc is the critical angle, which has not been observed earlier.

For such measurements we need collimated beam, low background and good resolution of reflectometer.

The total neutron reflectivity and reflection curves for Q>Qc without and with glass sample (surface roughness less than 2Å) ultrasonic excitation were measured in 3 days experiments.

The main results are the scattered neutrons energy spectra changes upon high-power sound effects for both longitudinal (30 MHz) and transverse (50 MHz) acoustic waves. These data partly confirm previous results obtained by us in JINR (Dubna, Russia).

To our regret we can’t to complete all programme because of the source of could neutrons didn’t work and therefore the background was too high and intensity of neutron beam too low.
Aim of this proposal was the structural characterization of lyotropic mesophases formed by unsaturated nucleolipid derivatives in the low-water content region. These compounds, beside a fundamental interest concerning self-assembling issues, are potentially applicable as prodrugs-if the base on the polar head is conveniently chosen between pharmacologically active modified bases-, or as delivery agents for non-viral gene transfer.

A neutron diffraction investigation has been performed on POP-Uridine, POP-Adenosine and on their 1:1 mixture as a function of the isotopic composition of the equilibrating atmosphere (D$_2$O/H$_2$O=1/0; 1/1 and 0/1). These compounds form stable liposomes, whose spectroscopic properties indicate that bases on the polar head group interact through stacking and H-bonding modes. A UV-linear dichroism study that is currently in progress highlights a preferred orientation of bases with respect to the bilayer normal. It is therefore important to monitor the structural characteristics of such bilayers in the low water content regime.

Our goal was to infer the profile of scattering length density of the molecules in the bilayer and to monitor the structural changes in base orientation and in polar head hydration induced by base-base interaction that have already been observed by us in bilayer and monolayer self assembled structures.

The allocated beam time was sufficient to carry on most of the scheduled experiments. The quality of the collected data was particularly good for the POP-Uridine samples, for which we have collected five diffraction orders, while some problems have been encountered with the other two samples that need a careful data interpretation. In particular we have to find a compromise between the extremely long equilibration times required for POP-Adenosine and the 1:1 mixture of the two lipids and the likely possibility of chemical degradation typical of unsaturated lecithins.

For the POP-Uridine samples we have been able to obtain the density of scattering lengths of the bilayer composing the lamellar phase, while for the other samples some problems arise, probably due to the extremely long equilibration time.

Figure 1 shows a summary of the data obtained for this lipid, and a preliminary analysis of the radial density profile.
EXPERIMENTAL REPORT

Molecular dynamics in the 1,10-decanedicarboxylic acid / urea inclusion compound.

Principal Proposer: F. Guillaume, LPCM, UMR 5803 CNRS - University Bordeaux 1
Experimental Team: F. Guillaume, LPCM
A. Desmedt, HMI

Date of Experiment: 18/02/02 - 25/02/02

Date of Report: *15/01/03

1 - Scientific background

In urea inclusion compounds the urea molecules form an extensively hydrogen-bonded helical "host" substructure within which there are parallel one-dimensional channels that contain straight-chain hydrocarbon guest molecules [1]. The repeat lengths along the channel axis of the host substructure (c_h) and of the guest substructure (c_g) are incommensurate. We have undertaken since several years collaborative research studies of urea inclusion compounds containing "functionalized" guest molecules. Of particular interest is the family of inclusion compounds of $\alpha,\omega$-alkanedicarboxylic acid HO$_2$C-(CH$_2$)$_n$-CO$_2$H in urea where the guest molecules form 1-D infinite chains of hydrogen bonded diacid monomers. The dynamics of the perdeuterated 1,10-decanedicarboxylic acid guest molecules has been investigated by means of $^2$H NMR spectroscopy. At high temperatures (T > 200 K) the spectra show an axially asymmetric line-shape in the fast motion regime ($\tau$ < 10$^{-7}$ s).

Our aim in this proposal is to bring together $^2$H NMR and IQNS experiments to interpret the molecular dynamics of the 1,10-decanedicarboxylic acid guest molecules within the urea channels to be able to analyse molecular dynamics over a very large time scale ranging from the µs by means of $^2$H NMR to the ps by means of IQNS.

2 - Experiments

Selectively deuterated single crystals (needle-like) of DCO$_2$-(CH$_2$)$_n$-CO$_2$D / CO(ND$_2$)$_2$ were placed in slab type containers so that the urea channel axes were parallel to each other. Using this mosaic of aligned single crystals, two scattering geometries ($Q_\perp$ and $Q_\parallel$) were achieved allowing the rotational and translational motions of the guest molecules to be probed independently. The spectra were recorded at 4 temperatures between 300 K and 220 K for $Q_\perp$ geometry and 5 temperatures in $Q_\parallel$ geometry using resolutions of 60 µeV and 30 µeV.

3 - Results

The spectra display a very nice quasielastic broadening above 200 K for the two experimental geometries. The analysis performed by fitting one Lorentzian function plus an elastic peak to the $Q_\perp$ experimental spectra provides the resolution dependent EISFs (figure 1).

![Figure 1: Spectra recorded in the $Q_\perp$ geometry. Diamonds: runs at 223 K; Squares: runs at 253 K; Circles: run at 298K. Open symbols for resolution 60 µeV and filled symbols for resolution 30 µeV.](image)

In the $Q_\parallel$ geometry, the QENS profiles are more complex and involve rotations, translations and small amplitude oscillations (giving rise to an inelastic peak at about 1.8 meV) of the guest molecules (see figure 2).

![Figure 2: Spectra recorded in $Q_\parallel$ geometry: Symbols: experimental data; Continuous lines: theoretical spectra using a model combining 3 types of motions.](image)

Room temperature ionic liquids (RTILs) are gaining progressively larger attention as ideal reaction media for a number of clean-technology based, inorganic and organic processes. This is a consequence of the appealing chemical-physical performances of the new generation of RTILs: being composed by ionic components, with a bulky organic cation (such as 1-alkyl-3-methylimidazolium), these materials are liquid at room conditions, thus having a low viscosity, high diffusion coefficient and negligible vapor pressure. These properties make RTILs ideal for a range of synthetic applications as efficient and green alternatives to Volatile Organic Solvents (VOS), whose use is progressively raising environmental concerns. The possibility of sensibly modulating the chemical-physical parameters (such as melting point, viscosity, density, solvating power etc) by slightly changing the chemistry of RTILs also provides a useful tool to the synthetic chemist, who can accordingly optimize the reaction conditions.

One of the current limitations to a wide use of RTILs is the limited amount of knowledge existing on the chemical physical properties of these materials. Accordingly a progressively increasing number of chemical-physical characterizations are appearing in the literature providing indications on the effect of chemical details on bulk performances.

Up to now however, only limited information is available on microscopic dynamics of RTILs, which, in turn, is supposed to play a major role in determining the final properties (such as viscosity, diffusivity etc) of RTILs as a reaction medium.

We then decided to explore the fast dynamics in a representative RTIL, such as 1-butyl-3-methylimidazolium hexafluorophosphate (C₄mim-PF₆), at the NEAT, Time of Flight spectrometer. This material slowly crystallizes below 280 K and so our measurements were limited to temperatures above this limit, in order to probe the dynamics in the fully amorphous phase.

In Figure 1, the temperature dependence of the QENS patterns from C₄mim-PF₆ is reported at a selected value of momentum transfer.

We are now in the progress of rationalizing these results. In particular, we are now in the process of comparing the present experimental data with the output of recent Molecular Dynamics simulations on the same material.
The use of Quasi Elastic Neutron Scattering to probe the segmental dynamics in polymer melts is well known to provide useful information on this technologically relevant issue.

In this experiment we aimed to characterize the polymer dynamics in a synthetic polymer, such as polypropyleneoxide (PPO, \(-\text{[CH}_2\text{-CH(CH}_3\text{)-O}]_n\)), both below and above its glass transition. The effect of LiCF$_3$SO$_3$ addition to pure PPO has been studied as well, due to the technological interest of polymer electrolytes for the development of smart electric devices, such as secondary batteries and electrochromic windows.

In Figure 1, data from a high resolution backscattering instrument are reported as a function of the temperature, for pure PPO. They are useful to rationalise the observed behaviour on the medium resolution ToF instrument NEAT.

In particular, we observe that below the glass transition (approx. 150-200 K), a major relaxation occurs. This can be directly related to the methyl group relaxation. At higher temperatures, the $\alpha$ relaxation regime is also detected.

Due to the difference in instrumental resolution between the backscattering and NEAT instruments (at the chosen settings), the methyl group relaxation will be probed on NEAT at higher temperatures. Accordingly, in Figure 2, data from NEAT are reported for temperatures between 200 and 260 K, where a substantial contribution to the broadening can be related to the methyl group hopping.

In Figure 3, data corresponding to the segmental relaxation regime are also reported for pure PPO (350<T(K)<450, Q=2.0 Å$^{-1}$). In the inset a comparison between NEAT data from pure PPO and doped PPO are compared as well. A detailed data interpretation is now in progress.
**EXPERIMENTAL REPORT**

**Dynamics of poly(di-n-alkyl itaconate)s**

**Proposal No.** CHE-03-236  
**Instrument** V3  
**Local Contact** A. Desmedt  
**Date(s) of Experiment** 9–15 September 2002

<table>
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<tr>
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<th>Date of Report: 6 January 2002</th>
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**Introduction**

Poly(di-\(n\)-alkyl itaconate)s:

\[
\begin{align*}
\text{CH}_2\text{C}_2\text{O}_2\text{C}_n\text{H}_{2n+1} & \\
\uparrow \text{CH}_3\uparrow & \\
\text{CO}_2\text{C}_n\text{H}_{2n+1} & 
\end{align*}
\]

present unusual thermal properties compared to polymers with similar chemical structure as they exhibit two glass transitions for \(n=7\) to \(n=11\).

Our group initiated a program of work to investigate the relation between local ordering and the dynamic properties using poly(di-\(n\)-alkyl itaconate)s with varying alkyl side chain length. By exploiting wide and small-angle X-ray scattering, we were able to demonstrate [1] that the alkyl chains show a strong tendency to order.

In our previous quasielastic neutron scattering (QENS) experiments on IN10 and IRIS [2], we revealed the existence of various dynamic processes. However, the underlying motion in this series is characterised by a wide distribution of relaxation times that can be covered only via simultaneous measurements in a wide energy range using instruments with different resolution.

The aim of the present experiment on NEAT is to fully characterise the distribution of relaxation times by extending the time range towards short times.

**Experiment and Results**

An incident wavelength of 6.3 Å was used, yielding an energy resolution of 62 \(\mu\)eV (full width of half height). QENS measurements were successfully carried out on four different samples with side chain length \(n = 1, 5, 8\) and 10 at the same temperatures (in the range 220 – 320 K) to match the existing data collected on the IRIS spectrometer.

Analysis of the intermediate scattering function displays the existence of two relaxation processes; a fast process in the picosecond time regime and a slower process. This is shown in Figure 1 for \(n=5\) where the fast and slow processes are modelled using an exponential and a log-Gaussian distribution of relaxation times, respectively. In Figure 2, data from NEAT and IRIS spectrometers are shown to overlap well. Combined NEAT / IRIS data are being used to fully characterise the distribution of relaxation times of these materials as a function of temperature and side chain length.

![Figure 1: Intermediate scattering function of \(n=5\) obtained from NEAT at \(Q=1.57 \text{ Å}^{-1}\) for different temperatures as indicated. The lines correspond to the fits described in the text.](image1)

![Figure 2: The combined intermediate scattering function from NEAT and IRIS for \(n=5\) at \(Q=1.57 \text{ Å}^{-1}\).](image2)

**References**


Ter-butyl alcohol (TBA) and trimethyl-amino-N-oxide (TMAO), have the same large hydrophobic moiety but different polar groups and they can be used as model system to study the microdiffusivity properties of water involved in hydrophobic hydration shells.  
On these systems an experiment has already been performed at fixed solute concentration (2mol%, i.e. below the value at which a self-aggregation processes among TBA molecules occur) in the temperature range 273-320 K. The main results can be summarised as follows (see report N°PHY-03-0186):

1. In both TBA and TMAO solutions the introduction of hydrophobic molecules decreases the water self-diffusion coefficient with respect to that of pure water. In particular the microdiffusivity parameters of water in the presence of TBA coincide with those of pure water if one assigns to the solution a “structural temperature” 10K lower than the actual thermodynamic one.

2. Upon increasing temperature above 300K, i.e. in the range where hydrophobic effect should be less important, the diffusion coefficient in TMAO aqueous solutions becomes progressively smaller than that of TBA solutions. This difference could be ascribed to the presence of a different polar group with a dipole moment three times bigger in TMAO than in TBA. These results are in qualitative agreement with MD simulations suggesting that hydrophobic hydration shells are more stable in TMAO than in TBA/water solutions[1].

On increasing T above 320K one expects the “structural temperature” to approach the actual thermodynamic temperature in TBA/water solutions in agreement with the hypothesis that the hydrophobic effect progressively decreases with increasing temperature as a consequence of the weakening of H-bonds. In this respect we may note that the H-chemical shift in the water/TBA mixture approaches that of pure water at ~ 350-360K [2].

In order to verify this hypothesis in Aug 2002 we have performed an experiment in the T-range 320-360 K using the TOF NEAT spectrometer (\(\gamma=5.1\,\text{Å}\), range of momentum transfer, \(Q=0.3-2.3\,\text{Å}^{-1}\), energy resolution, \(\Delta E = 70\,\mu\text{eV (FWHM)}\). The spectra seem to confirm the expected behaviour. For the TBA/water solution at 360K the spectra appear to be very close to those of pure water at the same temperature, while for the TMAO/water solutions they are systematically narrower indicating a slower dynamics (see Fig1).

Unfortunately part of the allocated beam time (~2 days) was lost due to an unforeseen reactor shutdown. Moreover the Al cells employed proved to be not rigid enough and got progressively deformed above ~340K, while a layer of Al oxide grew on the inner walls. As a result the spectra are quite poor and noisy especially at the higher temperatures. Further experiments with cells suitable for this temperature range should be most helpful in order to properly complete the experiment and confirm these preliminary data.

Acknowledgments: This experiment was supported by the EC under the IHP II (contract HPRI-CT-2001-00138).

References
H₂ confined in randomly ordered porous silica has been studied extensively. In all randomly ordered material a suppression of the adsorbates freezing temperature, and a hysteresis upon melting has been observed. This suppression of the freezing temperature has been attributed most strongly to the pore radius, the suppression growing larger with decreasing pore radius. It has been observed in past experiments that the freezing temperature has been suppressed by almost 6K from the bulk value of 14K in the randomly ordered ~60Å pores of Vycor glass[1].

We have carried out preliminary studies of H₂ confined in MCM-48, a geometrically ordered porous silica glass with 20Å diameter pores using NEAT, the quasi-elastic neutron scattering spectrometer. Quasi-elastic scattering allows for the direct observation of the liquid -solid transition through the appearance of quasi-elastic scattering. Surprisingly, preliminary analysis of the data indicates there is little to no suppression of the freezing temperature and no hysteresis between freezing and melting. The observed scattering, shown in figure 1, clearly illustrates that the freezing is occurring at ~14K. A complete analysis is underway at present. However preliminary analysis indicates that diffusion above 14K is liquid like.

For pores of this size we would have expected, based on previous studies of porous media, freezing temperature suppression much larger than that seen for Vycor, due to the smaller pore size. In fact, extrapolating current results to our pore size suggests that freezing might be totally suppressed. Though the results are preliminary they call into question the validity of theoretical arguments that pore radius is the governing factor in the suppression of the freezing temperature. Future experiments will clarify whether pore size or geometry gives rise to these unusual results.

![Figure 1: Scattering of H₂ confined in the 20Å pores of MCM-48. The curve with filled in dots is the 14K diffusion data, which is in stark contrast to the 17.8 K (diamonds) data where the H₂ is obviously liquid.](image)

Reference List

Hydrogen bonding has an important role in structure and function of proteins. In structural biology so called "non conventional" hydrogen bonds have been shown to be significant. The aromatic hydrogen bond, more precisely the X—H...π(Ph) bond is one of the most important of the so-called "non-conventional" hydrogen bond types. Nevertheless, the dynamical properties of the aromatic hydrogen bonds have up to now hardly been investigated. Among the compounds with aromatic hydrogen bonds, a particularly interesting substance class are the tetraphenylborate salts. In the simplest member of the family, ammonium tetraphenylborate (NH₄B(C₆H₅)₄), the ammonium ion, NH₄⁺, is encapsulated between four phenyl rings of nearest tetraphenylborate ions, (C₆H₅)₄B⁻[1]. Each N-H vector of the ammonium ion points on time-average at the midpoint of a phenyl ring and creates an aromatic hydrogen bond with it [2].

Technically ammonium tetraphenylborate (ATPB) with its large amount of H-atoms is well suited for a QINS experiment. Each molecule has twentyfour H-atoms and four aromatic H-bonds. It is assumed that the ammonium ion is involved in two distinct types of local diffusive motions: whole cation rotation of the ammonium ion, and large amplitude librations of an N-H vector over the aromatic face.

Following the instruction of [3] the ATPB sample has been prepared from natriumtetraphenylborate and ammonium chloride. The dynamics of the aromatic hydrogen bond have been studied by quasielastic incoherent neutron scattering (QINS) via the behaviour of the ammonium ion and its temperature dependence. The experiments were done with resolutions ca. 200μeV, 100μeV and 50μeV and at ten different temperatures in the range from 20K to 300K. In the Fig. 1 is shown the experimental EISF at three temperatures and the theoretical EISF of three different cation rotation models. The theoretical models do not reproduce the experimental data accurately. As assumed, the whole cation rotation cannot explain alone the local diffusive motions of ammonium ion.

Figure 1. EISF as a function of Q. The dashed line represents two different theoretical models: 2 site jump model and 3 site jump model (one proton fixed). The black line represents the model for tetrahedral sites jump. Symbols represent experimental data at three different temperatures: cross-200K, triangle-250K and quadrangle-300K.

References:
Neutron-spin-echo experiments were done on SPAN in order to extend the wave vector range from earlier measurements on (deuterated) polybutadiene (dPB). This glassforming polymer was chosen as a kind of standard material where it is possible to compare the results with earlier measurements in the lower $Q$ range.

The sample was placed in a hollow cylindrical sample holder of 30 mm diameter with a sample thickness of 0.6 mm. The calculated scattering efficiency from dPB in this container is 11%.

The first test runs showed that the background scattering from the 0.4 mm thick aluminium walls of the sample holder was intolerably high. As an efficient remedy a cadmium sheet was placed behind the sample holder shielding the low angles. Because the aim of the experiment was to investigate high $Q$ this measure did not affect the performance. In retrospect, a flat sample holder put in reflection with a cadmium backplate would have performed better because the restriction to high angles is by far outweighed by the reduction of background.

With this configuration measurements were done at two incident wavelengths, 2.5 Å and 2.9 Å. For each wavelength 6 angular ranges were averaged so that in total 12 $Q$ values in the range 2.25...4.64 Å$^{-1}$ were recorded. The measured temperatures were 204 K, 220 K, 240 K, and 260 K. (The glass temperature of dPB is 181 K.) The run durations (per temperature) were 23 hours for 2.5 Å and 12 hours for 2.9 Å where the flux is higher.

The figure shows exemplarily the data obtained at 220 K. It can be seen that due to the extremely short incident wavelengths the time range is shifted to very low values, 0.3...141 ps and 0.5...219 ps. This makes–probably for the first time in the history of NSE—the fast $\beta$ relaxation visible in the NSE window.

Of course, the IN11 data reach longer times because of the wavelength of 4.2 Å used.

The data itself present a somewhat puzzling picture. The dynamics of dPB in that high $Q$ range seems to be divided into three regimes: For $76.2 \leq Q \leq 11$ Å the $S(Q,t)$ is independent of $Q$. For $Q = 11$ Å$^{-1}$ there seems to be only a weak $Q$-dependence. Then there is a strong reduction of $S(Q,t)$ in the range $2.76 \leq Q < 3.71$ Å$^{-1}$. (Unfortunately, due to the incomplete equipment with supermirrors there are only two very close $Q$s available in that range.) Finally for $Q \geq 3.71$ Å$^{-1}$ the curves are again independent of $Q$. This is by no means the behaviour expected from a Debye-Waller factor and there is currently no explanation for it.
Polymer dynamics is a complex issue. This complexity stems from the large spatial and temporal range which are characteristic of macromolecules’ behaviour. In order to unravel this complexity and rationalise the experimental behaviour in terms of theoretical approaches a wide set of experimental data is required. In particular these data sets should cover large spatial and temporal ranges. Unfortunately most of the experimental techniques access only a limited dynamic and structural window. Accordingly, it is necessary to extend the accessible ranges to provide data which can be tested with theoretical approaches. Quasi Elastic Neutron Scattering, in general and Neutron Spin Echo, in particular are well known techniques which provide useful insights into the dynamical properties of soft condensed matter. In particular polymer melts have been widely investigated with NSE and useful information has been obtained on their collective dynamics. The conventionally accessible temporal range from NSE measurements spans from $10^{-2}$ to $10^{2}$ nsec, over a momentum transfer range between approximately $10^{-2}$ to $10^{1}$ Å$^{-1}$. We have been involved in the characterization of the collective dynamics of deuterated atactic polypropylene (D-aPP) in last few years, extensively using the SPAN spectrometer. In the past we also used the unique possibility of employing the SPAN spectrometer as a Time of Flight spectrometer with Polarization Analysis, using the same analysers that are used in the NSE setup. This unique possibility of SPAN provides the possibility of expanding the accessible dynamic range in the characterization of the dynamics between $10^{-4}$ to $10^{2}$ nsec.

We then developed a set of experiments aiming to measure the collective dynamics of D-aPP above its glass transition on the short temporal range in the high momentum transfer regime ($Q>3.0$ Å$^{-1}$). In Figure 1, we report the obtained results. We compare the different patterns at different temperatures. The data are also compared with the corresponding data obtained at $Q=1.1$ Å$^{-1}$, using two experimental setup (NSE and ToF to probe the slow and the fast regimes respectively). This comparison allows to realise that the measurements at $\lambda=2.9$ Å, allow covering a dynamic range that is complementary to the temporal ranges that are accessible with more conventional NSE and ToF.

This work is developed in collaboration with Dr. V. Arrighi (Heriot-Watt University, Edinburgh, UK)
Studies of pattern formation and of dynamic phenomena occurring during phase separation in confined systems are an emerging field of research in physics and materials science. The micro-phase separation in the porous matrix can lead to a variety of structural patterns depending e.g. on pore size and shape, connectivity of the network as well as the preference of the pore walls for one of the components. However, experimentally it is difficult to obtain information about phase transitions in confined geometry since most of the available methods are strongly perturbed by the solid containing the fluid.

NSE experiments directly provide the intermediate scattering function $S(Q,t)$ and therefore allow to investigate the dynamics of fluctuations in the confined liquid mixture. The observed dynamics can be interpreted as fluctuations of partially demixed regions inside the pores.

**SANS and former NSE experiments:**
Small angle neutron scattering was used to study the structural aspects of the demixing behaviour and to get an idea about the interesting $Q$ and time range to be investigated by NSE experiments.

Former NSE experiments, performed on MESS (LLB, Saclay, France), have shown interesting dynamic behaviour at $0.2 < Q < 0.3$ nm$^{-1}$. Unfortunately only a few experiments at higher $Q$ were obtained, due to the low scattering intensity of the sample in this region. The reason for the experiment at V5 was to obtain additional information at larger $Q$.

**Experimental details:**
The intermediate scattering function was measured for $70^\circ$, $60^\circ$, $50^\circ$, $43^\circ$, normalised on $S(Q,t)$ at RT in a $Q$ range between $0.35 < Q < 1.2$ nm$^{-1}$. Fitting a single exponential decay to the intermediate scattering function (Fig. 1) was used to determine the characteristic relaxation frequency $\Gamma$. The effective diffusion coefficient was then obtained by:

$$D_{eff} = \frac{\Gamma}{Q^2}$$

**Results:**
Experimental results of the effective diffusion coefficient $D_{eff}$ as a function of $Q$ for different temperatures are shown in fig. 2. Unfortunately we have not been able to confirm the expected behaviour: the dynamics should decrease when approaching the phase separation temperature. Long relaxation times of the system (up to $\sim 100$ ns) due to very slow dynamics and a noisy exp. signal $S(Q,t)$ cf. fig.1 due to low intensities are probable reasons.

We proposed a similar experiment at IN15 (ILL, Grenoble) to obtain more reliable results.
The use of Quasi Elastic Neutron Scattering is well known to provide almost unique pieces of information on the microscopic dynamics of glass formers. This is also true for synthetic polymers, such as polypropylene, whose high degree of connectivity, induced by the molecule backbone and by the interactions between neighbour chains, further complicates the dynamics, with respect to simpler molecular materials.

The use of Neutron Spin Echo applied to fully deuterated polymers further extends the range of accessible information. In these conditions, it is possible to characterize the coherent scattering, due to the high coherent scattering cross section of Deuterium and accordingly obtain information on the collective dynamics of the material.

These measurements are highly informative, as they allow to know how the cross correlation function of D atoms relaxes in time. It has been recently shown that the relaxation probed with NSE measurements is directly related to the processes which are responsible for the viscoelastic behaviour of the material. It is then extremely useful to collect NSE data on technological relevant materials, as NSE provides dynamic information on a spatial and temporal scale generally inaccessible to other techniques.

In view of this, we have focused our attention to a fully deuterated sample of atactic polypropylene. This material, in all its tactic forms, has a high applicative impact and a detailed knowledge of its microscopic dynamics would be of relevance in optimizing the performances of this material in its life cycle.

Up to now our interest was focused to the study of the collective dynamics at relatively high values of momentum transfer (0.8<Q (Å⁻¹) <1.4). After the successful tests that have been run on SPAN in a previous experiment, it was understood that it is possible to use neutron beams with a very short wavelength (λ=2.5 Å), to successfully obtain NSE frames at very high Q values (Q>3.0 Å⁻¹).

Due to the short wavelength, the dynamic range that can be covered is limited to short times. This implies that only the fast collective dynamics can be explored, thus superimposing with the dynamic range traditionally covered by medium resolution Time of Flight.

In Figure 1, data are reported from a number of complementary experiments, highlighting on one hand the advantage of the use of different experimental conditions, and, on the other hand, the versatility of the SPAN spectrometer.

![Figure 1. Comparison between three different data sets collected on SPAN: a) NSE data (λ=2.5 Å, present experiment), black symbols; b) NSE data (λ=6.5 Å), red symbols; c) Fourier Transform of ToF data (λ=6.5 Å), blue symbols. Data refer to the same deuterated aPP sample at 300 K and Q=1.1 Å⁻¹.](image-url)

This work is developed in collaboration with Dr. V. Arrighi (Heriot-Watt University, Edinburgh, UK)
We have intended to determine the molecular structure of a self-assembling bicopper complex located in two macroscopic phases that are in contact at equilibrium (a polymer-rich phase (atactic polystyrene/trans-decalin) and a complex-rich phase (bicopper complex/trans-decalin). Two questions were be addressed:

1. does the bicopper complex still form threads within the polymer-rich phase?
2. to which extent is the thread-like structure in the complex-rich phase perturbed by the presence of the polymer-rich phase?

These two questions have a direct bearing upon the way the bicopper complex threads are encapsulated in polymer sheaths in the course of the physical gelation of isotactic polystyrene [1,2].

Measurements have been carried out in each phase once equilibrium is reached. Under these conditions, the complex structure have been studied in both phases by placing the scattering cell in an appropriate manner with respect to the neutron beam (see figure 1).

Figure 1: For the measurements in each phase the neutron cell has been positioned so as to have only one phase irradiated at a time.

The neutron scattering experiments have been interpreted with the scattering function for rod-like object of finite cross-section:

\[ q^2 I(q) \propto C_{\text{Cu}} \mu_x J_1(q \sigma_c) \left[ \frac{4J_1^2(q \sigma_c)}{q^2 \sigma_c^2} \right] \left[ \pi q - \frac{2}{<L>} \right] \]

The fits show that the bicopper complex still form long filaments in the polymer-rich phase and that this structure in the complex-rich phase is not perturbed by the presence of the polymer-rich phase (see figures 2 and 3).

Figure 2: Neutron scattering curves obtained for the bicopper complex in complex-rich phase plotted by means of a Kratky representation \((q^2 I / c(q) \text{ vs. } q)\). Solid line = best fit.

Figure 3: Neutron scattering curves obtained for the bicopper complex in polymer-rich phase plotted by means of a Kratky representation \((q^2 I / c(q) \text{ vs. } q)\). Solid line = best fit.

References
We have studied the molecular structure of the complexes formed between a surfactant (CTAB) and either of two types of polystyrene sulfonates: atactic polystyrene sulfonate (aPSS) and isotactic polystyrene sulfonate (iPSS) (for further reading on this type of complex see reference 1). The molecular structure has been investigated in a good solvent of the complex (n-butanol) and in a solvent wherein gelation takes place (nitrobenzene). Only the polyelectrolyte was deuterium-labelled and we used either hydrogenous solvents or deuterated solvents. Typically, in hydrogenous solvent the scattering is mainly due to the polymer while in deuterated solvent the scattering arises from the CTAB molecules.

A typical scattering curve in deuterated n-butanol is shown in figure 1. There are two important outcomes: i) there is no difference of molecular structure between aPSS/CTAB and iPSS/CTAB complexes, ii) in both cases the scattering curve can be fitted, as shown by the solid line, by considering a dual population of helices (one extended helix and one “compressed” helix, see figure 2). Conversely, in the gel state the molecular structure differ as highlighted in figure 3 for experiments carried out in hydrogenous nitrobenzene. Typically, there are still individual chains of complex in the case of iPSS/CTAB, particularly as shown by the strong upturn at large q-values (due to a negative apparent cross-sectional radius of the fibrils constituting the gel). Also, the cross-section polydispersity of the fibrils is probably low in the case of aPSS/CTAB systems as suggested by the oscillations of the scattering curve, compared to iPSS/CTAB gels.

Further details on the way the scattering curves have been fitted will be made available in a forthcoming publication.

References
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Specific aim of this proposal was the investigation of the structural properties of semi-flexible wormlike aggregates formed by di-lauroyl-phosphatidyl-uridine (DLPU) in aqueous solution as a function of the ionic strength.

The surfactant belongs to a class of amphiphilic molecules synthesized in our laboratory in Florence that merge the self-assembling properties of lecithins to the recognition properties of nucleic acids. They present enormous interest both from a fundamental point of view and from an applicative standpoint as self-assembled prodrugs and have been the subject of thorough investigation in our group. We have had already characterized DLPU aggregational properties as a function of lipid concentration in a wide volume fraction range, demonstrating the presence of wormlike aggregates.

The analysis of SANS spectra was utterly complicated by the presence of a net charge at the surface of the aggregates. In particular an electrostatic contribution to the persistence length of the aggregates, proportional to the bending modulus of the rod \( l_p = k/k_B T \), has to be expected.

We can thus write

\[
l_p = l_{p0} + l_{pel}
\]

where \( l_p \) is the observed persistence length, \( l_{p0} \) is the intrinsic persistence length and \( l_{pel} \) is the contribution arising from electrostatic repulsion that vanishes at high ionic strength.

We have investigated the micellar growth of DLPU at a fixed surfactant concentration \( q_s \) varying the ionic strength of the medium, by addition of two different electrolytes, first \( \text{NH}_4\text{Cl} \) (same cation as the surfactant counterion), and then \( \text{PyCl} \) that should display a stronger affinity for micellar surface, thanks to the presence of an aromatic ring. Penetrating counterions are strong promoter of micellar growth, in fact they affect the surfactant packing parameter and they decrease the surface charge density.

During the beam time allocated a set of experiments have been performed at three different sample-detector distances, in order to fully benefit of the potentialities of SANS analysis.

The analysis of the results presented here is semiquantitative, but we should mention that a Monte Carlo analysis, accounting also for structure factor and polydispersity contributions, is underway.
EXPERIMENTAL REPORT
Small Angle Neutron Scattering Investigation of Magnetic Nanoparticles Using Polarized Neutrons

Proposal No CHE-04-687
Instrument V4
Local Contact A. Wiedenmann

Principal Proposer: Piero Baglioni, Dep. Of Chemistry and CSGI, University of Florence
Experimental Team: Piero Baglioni, Massimo Bonini and Emiliano Fratini, University of Florence
Albrecht Wiedenmann and Martin Kammel, HMI
Date(s) of Experiment 28/02/2002-03/03/2002
10/06/2002-14/06/2002

Date of Report: 15/01/2003

This study was aimed at the investigation of magnetic nanoparticles in water. In particular, we studied dispersions of both un-coated and silica coated nanoparticles of CoFe$_2$O$_4$.

Stable colloidal suspensions of nanosized magnetic particles are a topic of great interest, since they give rise to numerous technological applications. In particular, the capability of synthesizing size-controlled cobalt-ferrite-based nanoparticles and the possibility of using radioactive $^{60}$Co to produce enriched ferrofluids (FF) opens new perspectives in the targeting of cancer cells using antibody-coated nanoparticles. Moreover, the silica coating protects the magnetic particles from possible decomposition, further aggregation, and reduces interparticle magnetic interaction.

Cobalt–ferrite nanoparticles were prepared using a modified synthetic pathway of the method proposed by Massart$^1$. The ferro-fluids nanoparticles (FF) are constituted by CoFe$_2$O$_4$ nanoclusters stabilized by the charges present at their surface. These systems have been investigated by means of Transmission Electron Microscopy and Small Angle Neutron Scattering with polarized neutrons (SANSPOL) at the instrument V4 at the BERII reactor. In both cases we obtained a distribution of spheres centred at a radius of about 5 nanometers.

In order to obtain silica-coated particles, an aliquot of the FF has been taken and applied to the well-known Stöber$^2$ process. All the parameters during this synthetic process have been controlled in a way to obtain a silica shell thickness of about 2 nanometers. Two aliquots of this ferrofluid have been used for contrast variation: one has been diluted with water and the other with deuterated water (H$_2$O/D$_2$O ratio: 30:70).

Both samples have been investigated by means of TEM and SANSPOL analysis$^3$, obtaining almost identical results. In particular we obtained a distribution of spheres with both mean radius and the polydispersity increased with respect to the un-coated ferrite nanoparticles. While it is really difficult to evaluate the silica shell thickness from TEM micrographs, SANSPOL analysis allowed the evaluation of 1.9 nm silica shell thickness. The thickness was determined using the different contrasts of magnetic particles in two polarization states.

We collected the scattering intensities for both the polarization states ($I^+(Q)$, $I^-(Q)$) and for both the solvents (water and water/heavy water mixture). All of the obtained curves have been fitted with a core/shell model, using always the same size distribution, and by changing the contrast values. The value of the silica shell thickness resulted from this multiple fitting is 1.9 nanometers. Moreover we found that the increased poly-dispersity is due to the “aggregation” of cobalt-ferrite nanoparticles during the silica shell synthesis and not to a polydisperse shell made of silica. More in detail, this means that two or more CoFe$_2$O$_4$ nanoclusters form a single aggregate during the formation of the silica coating. This important information can’t be obtained with other techniques.

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2 Stöber, W.; Fink, A.; Bohn, E. J. Colloid Interface Sci. 1968, 26, 62.
EXPERIMENTAL REPORT

Proposal N° CHE . 04 . 690

Instrument V4

Local Contact Keiderling

Structural investigation on the L64/water system in presence of anionic or non ionic surfactants

Principal Proposer: Eugenio Caponetti, Palermo University

Experimental Team: Delia Chillura Martino, Palermo University

Date(s) of Experiment 1-3 July 2002

Block copolymers are molecules composed by two or three segments differing in nature and size. These compounds show polymer and surfactant features simultaneously making them interesting from both scientific and practical viewpoint.

The nonionic triblock poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) copolymer, belongs to the class of polymeric surfactants. In the last few years, the interest of some of us has been focused on the thermodynamic properties of the water-\(\text{EO}_{13}\text{PO}_{30}\text{EO}_{13}\) (L64) and water-L64-additive systems\(^1,2\). The phase behaviour of the L64-water system has been investigated by various techniques,\(^3,4\) over a wide concentration range. Preliminary thermodynamic (volume, enthalpy and heat capacity) measurements indicate that the interactions between L64 and surfactants strongly depend on the nature of the polar head. In particular, opposite behaviour has been observed for ternary systems containing sodium octanoate (C8Na) or octyldimethylaminooxide (ODAO) surfactants.

In order to rationalise these different behaviours, SANS measurements have been performed on water-L64, water-C8Na, water-ODAO, water-L64-C8Na and water-L64-ODAO systems.

As examples, data of water-L64, water-ODAO binary systems and data of water-L64-ODAO ternary systems are shown in figures 1, 2, and 3, respectively.

The experimental trends indicate that in surfactant free low concentration solutions, the polymer exists as a random coil structure, whereas on increasing the concentration it forms globular aggregates.

The surfactant alone forms micelles that grow with concentration, as indicated by the peaks position displacement towards higher Q values. Addition of the surfactant to a polymer solution induces the formation of globular aggregates. No evidence of the existence of independent structures (random coil and micelles) is present. The same is true for the water-L64-C8Na system.

SANS data will be analysed with the same procedure previously used\(^5,6\), that will provide more detailed information about the structure of the system.

In the recent years a great deal of interest has been devoted to the formation of various structures constituted by a polymer chain containing both hydrophobic and hydrophilic segments. The grown interest is to be led back to their applications for the industrial and biomedical use[1-3]. Typical examples are amphiphilic block and graft copolymers[4,5], which, thanks to their different interactions with solvent, take those conformations able to favor solubilization. If the graft polymer is long enough, it is able to self-screen the nonsoluble segments from the contact of the solvent. This happens, for example, for poly(ethylene glycol) methacrylate (so-called PEGMA), a comb polymer composed by oligomeric PEO units grafted to an inert methacrylate chains[6].

The small size of the pPEGMA chains required a structural investigation by Small Angle Neutron Scattering. From the concentration dependence of the neutron scattered intensity at small angle it was deduced a reliable model describing the internal conformation of the polymer pPEGMA.

In the SANS spectra of pPEGMA/deuterated Ethanol solutions, the Structure Factor contribution becomes more and more evident increasing concentration above c=2.2 \times 10^{-3} g/cm^3. Figure shows the spectra resulting from the subtraction for the incoherent background (BKG) and normalization by dividing by its concentration. For Q values higher than 1 nm\(^{-1}\), where all the spectra superimpose, the Porod's region is evidenced. The constant background (due to the superimposed incoherent background of the hydrogen atoms of the polymer chains) was determined by fitting the spectra with the Porod's law in the Q region above 1 nm\(^{-1}\). The diffraction pattern of the most diluted sample allowed us to extract the gyration radius under negligible polymer-polymer interactions and to determine the conformation and the packing degree of the polymer through the R_H/R_g ratio, R_H having been determined by Dynamic Light Scattering measurements[7]. This ratio is slightly less than unity, suggesting that chains take a microgel structure rather than a homogeneous or random coil conformation. In view of these results, the most likely hypothesis about the conformation of pPEGMA is to consider the coils constituted by a hard core with a less compact shell around made of PEO units.

References
The aim of the experiment was to give us information about the internal structure of iron colloids in ferrofluids. In addition, we wanted to study the presence of aggregates in our iron ferrofluids. We used two different iron dispersions, one with oleic-acid-coated particles (radius approximately 5 nm, coded as OA) and one with polyisobutene-coated particles (radius approximately 7 nm, coded D). The solvent of both dispersions was decalin. Dispersions were kept under nitrogen atmosphere to prevent them from oxidation. Part of dispersion OA was exposed to air for a few days (dispersion code OAox) to study oxidized particles. Measurements were performed with polarized neutrons at three different detector distances (1, 4 and 12 meters), which resulted in a q-range of 0.04 - 3 nm⁻¹. Ferrofluids OA, OAox and D were measured at different contrasts (by dilution with different amounts of deuterated decalin) to determine their internal particle structure. In addition, a concentrated dispersion of all ferrofluids was measured to determine the structure factor. Finally, a concentrated and a dilute ferrofluid OA was measured at different magnetic fields.

Dispersion OA appeared to consist of single colloids, for which a straight Guinier fit could be used to determine an average iron core of 3.7 nm. The whole series of curves measured at different contrasts could be well fitted with a core-shell model consisting of polydisperse iron cores of 3.5 nm (lognormal distribution) surrounded by an oleic acid layer of 2.1 nm with partial penetration of the solvent into the oleic-acid-shell (see figure 1). The particle size, the surfactant layer thickness and the particle concentration used in the fits correspond well to the values measured by other methods. The scattering contrasts found for the core and shell are in agreement with what is expected from theory.

The structure factor of a concentrated ferrofluid of OA shows a peak at 0.61 nm⁻¹, corresponding to a characteristic particle-particle distance of 10.3 nm, which is approximately the minimal center-center distance between particles.

Scattering curves of dispersions OAox have not been fully analysed, but can probably be fitted with a core-shell-shell model (iron core, ironoxide shell and a surfactant layer of oleic acid). Measurements of OA for different magnetic fields have not been analysed yet.

Dispersion D is a more complicated sample; we know from other methods that anisotropic aggregates are present in this case, which align in a magnetic field. Measurements on these dispersions still have not been analysed. Because a structural difference is expected for different directions in the sample, the scattering patterns will be studied both parallel and perpendicular to the magnetic field.

![Figure 1](image1.png)
Scattering curves of dispersion OA for different contrasts. (+) spin up, (-) spin down. The solid curves are fits to a core-shell model with partial solvent penetration in the surfactant layer.

![Figure 2](image2.png)
Scattering curves (spin up) of dispersion OAox for different contrasts.
Aim

The aim of this study was to investigate the interfacial structure of various Pluronic triblock copolymers adsorbed onto the synthetic clay Laponite. The effect of temperature was investigated.

Sample Materials and Conditions

The Pluronic surfactants under investigation have the structure poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), or PEO-PPO-PEO. The PEO blocks are hydrophilic, while the PPO blocks are hydrophobic.

Laponite is a synthetic clay, whose particles have a disc shape and a high aspect ratio. Previous measurements found that the radius of the disc was ~150 Å and the thickness ~9 Å. These measurements also found that the scattering length density (sld) of the Laponite particles was \( \rho_p=4.18 \times 10^{-6} \text{ Å}^2 \).

In these measurements the scattering from the adsorbed Pluronic layers was isolated, by matching the sld of the solvent to that of the particle via the \( \text{H}_2\text{O/D}_2\text{O} \) ratio of the solvent.

The data was fitted using a core-shell model designed for disc shaped particles:

\[
I(Q) = \frac{V_p}{V_f} \left[ \frac{Q R_c}{\rho_f - \rho_c} \right] \sum_{i=1}^{2} \left[ \frac{1}{2} J_1(Q R_i \sin \theta) \sin(Q R_i \cos \theta) \right] \sin^2 \theta
\]

Equation 1

where \( \phi_p \) is the volume fraction of particles, \( V_i \) is the volume of the cylinder, \( R_i \) and \( H_i \) are the radius and height of the cylinder and \( \rho_i \) is the scattering length density. The subscripts p, l and solv refer to the core particle, the shell and solvent. \( J_1 \) is the 1st order Bessel function. Subtractions were made to account for the scattering contribution from unadsorbed polymer.

Figure 1 shows the variation in layer scattering for F127, F108 and P103 adsorbed on Laponite. The adsorption plateau is attained in all of the systems.

The scattering intensity increases in the order P103 < F127 < F108, indicating that the adsorbed amounts and the layer thicknesses are increasing. This is confirmed by inspection of the fit parameters.

The PPO/PEO ratio (also called the anchor fraction) is lower for the F108 and F127 polymers than the P103 polymer, as their PEO blocks are much larger in size.

The results demonstrate the influence of the PPO block in determining Pluronic adsorption behaviour. The trends are consistent with a situation where the hydrophobic PPO blocks prefer to locate at the surface, largely excluding the PEO blocks, which form freely dangling tails.

For these polymers the surface is saturated with PPO segments and their adsorbed mass remains roughly constant. Therefore, as the PEO blocks increase in size and the anchor fraction decreases, the number of PEO segments and the number of adsorbed chains, increases. This causes the increase in the adsorbed amount. At the same time, the lateral repulsion between the PEO buoy blocks causes them to stretch, increasing the layer thickness.

Figure 2. The layer scattering from F127 adsorbed on Laponite, at 2 different temperatures. The Laponite is contrast matched.
Interactions between colloidal particles are interesting with respect to many technical applications and for fundamental questions in basic research. They show a liquid-like order in aqueous solutions with an average interparticle distance. This ordering is more pronounced if the particles are charged and at low ionic strength [1]. In the present measurements soft colloids are used where the counterions are partially entrapped within the colloid. Polyelectrolytes of different degree of branching has been used to check if the molecular architecture has an influence on the ordering of the colloids. The ordering leads to a peak in the structure factor, and the position of the structure peak $q_{\text{max}}$ is related to a correlation length via the simple Bragg relation $\xi = 2\pi/q_{\text{max}}$. Branched and linear Poly ethylene imine (PEI) and star-shaped Polyacrylic acid (PAA stars) have been investigated at different pH. The polyelectrolyte chains were protonated and solved in D$_2$O. The aqueous polyelectrolyte solutions were filled in glass cells and investigated by SANS at V4. The distance between the sample and the detector was 1m, 4m and in a few cases 12m, respectively. From the data the solvent scattering intensity was substrated. Since there was no influence of the salt concentration the pure D$_2$O data were used.

For linear polyelectrolytes in semi-dilute solutions a scaling behavior as $q_{\text{max}} \sim c^{1/3}$ is predicted [2]. In the present case the contrast for the linear PEI chains was quite poor and no structure peak has been observed. In contrast to this, solutions of branched PEI or PAA stars show a pronounced structure peak The reason for this difference could be the higher monomer density within a branched polyelectrolyte , related to a better contrast in comparison to the linear chain The position of the peak is shifted to higher q values with increasing polyelectrolyte concentration. This fits well to the image that in the case of branched polyelectrolytes the structure peak is related to the distance between the polyelectrolytes like in the case of colloids. Due to geometrical aspects the $q_{\text{max}}$ should scale with $c^{1/3}$ in colloidal dispersions which is not the case for branched PEI and PAA stars. From the measurements no scaling law has been found for the distance for these systems. The measured distance between the colloids seems to be smaller than the calculated one, but it is still much longer than the Debye length which means that the intercolloidal electrostatic repulsion does not play the most important role for the ordering. The values of the Debye length have been calculated from the ionic strength (determined by the polyelectrolyte counterions) and does not take the entrapment of counterions within the polyelectrolytes into account.

References:
The orientation of phospholipid membrane systems in a magnetic field offers the possibility to receive additional information on membrane structure and properties [1]. In our previous experiment BIO-04-0656 the orientation of 500Å large unilamellar DMPC vesicles in a magnetic field was studied for a 1% (w/w) DMPC concentration (see Fig. 1).

In the present experiment we wanted to investigate the unilamellar vesicle orientation for DMPC at increased concentration of 5% (w/w). To decrease the percentage of oligolamellar vesicles in the vesicle population and to study in addition the influence of sucrose on the membrane structure aqueous sucrose solutions with sucrose concentrations of 0%, 10%, and 20% (w/w) were used [2].

Unilamellar DMPC vesicles were prepared by extrusion of multilamellar DMPC vesicles through polycarbonate filters with a pore diameter of 500 Å. Sample temperature was 10°C, 20°C and 30°C with and without magnetic field of 4T. The experimental results show no influence of the magnetic field on the scattering curves (see Fig. 3). These calculations also show a dependence of the sucrose concentration on the membrane thickness, which at 20% sucrose is about 2±1Å smaller than in the absence of sucrose for all three temperatures used (see Fig. 3.).

Fig. 1. SANS curves from unilamellar DMPC vesicles at T=30°C with and without magnetic field of 4T. DMPC concentration 1% (w/w).

Fig. 2. Structure factor of 500Å DMPC vesicles for 1% and 5% DMPC concentration. T=30°C, 40% sucrose concentration.

Fig. 3. Experimental SANS curve from DMPC vesicles in 0% and 20% aqueous sucrose solution at T=10°C (incoherent background was subtracted). DMPC concentration 5% (w/w). The curve for 20% sucrose was multiplied with a factor of 2.

References
Experimental Report: Structural transformations in bilayer systems made up from single-chain surfactants and cosurfactants

Proposal No.: CHE-04-0742
Instrument: V4
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Date(s) of Experiment: 28/08/02 – 31/08/02
Date of Report: 15/01/03

Following previous experiments with calcium dodecyl sulfate (CDS), liquid crystalline phases were also found in the systems magnesium dodecyl sulfate (MDS) / heptanol / D$_2$O, MDS / octanol / D$_2$O, and sodium dodecyl sulfate (SDS) / octanol / NaCl / D$_2$O. It was found that the phase behavior of MDS was roughly midway between that of CDS and SDS without brine, and that a behavior similar to that of MDS could be induced by adding NaCl to the SDS system. There were indications that these phases were lamellar (L$_\alpha$) and sponge (L$_3$) phases. To experimentally verify these structures, small angle neutron scattering (SANS) was used.

In both MDS systems, the lamellar phases exhibited very narrow first-order correlation peaks, accompanied at higher concentrations by second and, in some cases, even third-order maxima, thus confirming the lamellar nature of the phases. This also hints at an extremely high degree of lamellar ordering parallel to the measuring cell walls. This conclusion was corroborated by the fact that, in the two-dimensional spectra, almost all scattering occurred in one angular direction. Perpendicular to that axis, the intensity was significantly lower.

The L$_3$ phases of the MDS systems showed wider correlation peaks, as is to be expected. These peaks are shifted against the peaks of the neighboring L$_\alpha$ phase by a factor of 1.2 – 1.3, which is well in accord with theoretical predictions$^1$.

Both the L$_3$ and the L$_\alpha$ phase in the octanol and heptanol systems were investigated along a dilution path. It was found that the interlamellar distances calculated from the SANS correlation peaks scaled linearly with the reciprocal volume fraction of solute, which is an indication of ideal swelling behavior. From the equation of this curve, lamellar thicknesses can be obtained. The results were in the average range expected for C$_{12}$ surfactant double layers ($\approx$ 20 Å). Also, lamellar thicknesses were calculated by fitting the form factor for clearly delimited bilayers to the data at high $q$. The results obtained in this manner were on the average 3 to 5 Å lower than the results of the previous method. This may be because the contrast of the head group plane, due to high water content and proton exchange, to the D$_2$O medium is so low that it cannot be resolved in this manner.

Measurements of the lamellar phases obtained with SDS, octanol and salt, however, were complicated by two experimental issues: First, these phases only exist at very low surfactant content, leading to wide interlamellar spacings on the limit of the instrument’s measuring range. On the other hand, these phases, especially when prepared with D$_2$O, are extremely sensitive to changes in composition and temperature, thus being hard to maintain stable within the measuring chamber. The data obtained on these phases seem to be rather flawed and should be verified in further experiments.

To record the temperature dependence of the MDS phase structures, the L$_\alpha$ and L$_3$ phases of the MDS / heptanol system at 4% wt. of surfactant were measured between 28 and 32 °C in 1 degree intervals. No significant change in correlation peak shape and position was found in this experiment, which leads to the conclusion that the effect of increased membrane fluctuations due to heightened temperature does not induce significant structural changes in the samples.

Mesoporous silica gels are a class of compounds that are subject of intensive investigations because of their interesting properties for a wide variety of technical applications. For many desired applications, however, normal silica gels are not useful because their pore size distribution can not be controlled.

The use of surfactants for structuring silica gels is quite common. A certain time after preparation (depending on the composition of the sample) the gel starts to shrink and retreats form the wall of the glass vessel. This phenomena called syneresis can be prevented in systems without surfactant by using small amounts of a cationic additive (1). The aim of our recent studies was to investigate the influence of the nonionic surfactant Genapol PF20 on silica gels modified by a cationic additive.

Figure 1 shows the scattering curve of a gel containing 50wt.% Si-precursor and 0.5wt.% cationic additive in H$_2$O. The correlation peak is a consequence of the repulsive forces between the charged clusters. The mean distance of the clusters calculated from $q_{\text{max}}$ ($d=2\pi q_{\text{max}}$) is about 21nm.

In figure 2 the scattering curves of three samples with increasing amounts of surfactant (without cationic additive) are plotted. At low surfactant concentrations no correlation peak due to micelles can be observed. With increasing amounts of surfactant the calculated distance between the micelles decreases from about 9.9nm to 8.8nm. This is simply caused by an rising number of micelles as the concentration is increased.

The influence of the cationic additive on the structure of the surfactant/SiO$_2$-gel is seen in figure 3. Although the addition of cationic additive does not prevent syneresis it is unlikely that the additive is incorporated in surfactant micelles. A possible explanation for this is that the correlation peak is shifted to a smaller q-value by the additive that means the middle distance of micelles is elevated from 8.8nm (without additive) to 10.3 nm may be due to repulsive forces. Further experiments with changing the contrast by the ratio of D$_2$O/H$_2$O can provide more detailed informations.

EXPERIMENTAL REPORT

Structure Characterization of mixed micelles of polybutadiene-b-poly(ethylene)oxide and the ionic surfactant SDS in water

Proposal N° CHE-04-0744 und CHE-04-0697
Instrument V4
Local Contact André Heinemann
Date(s) of Experiment 16.-21.07. 2002

Principal Proposer: Anette Nordskog, G. Findenegg, T. Hellweg
Experimental Team: Anette Nordskog, Sarah Höfl
Date of Report: 15.01.2003

The block copolymer PB₄₀PEO₆₂ mainly forms cylindrical micelles in aqueous solutions[1]. Addition of a surfactant of low molecular weight to the block copolymer micelles should lead to a higher natural curvature in the internal interface and so a change in the structure. This has been shown using the ionic surfactant C₁₂TAB for the polymer PB₄₀PEO₆₂ [1] and for PB₃₇PEO₅₃ [2], where the cylindrical aggregates of the pure BCP-solution transform into spherical aggregates. Investigations with SDS as surfactant was done so far only with the longer BCP PB₁₂₅PEO₁₅₅ [3]. In contrast to the systems with C₁₂TAB, no transformation into spherical aggregates could be observed.

In the present case we have investigated the addition of SDS to PB₄₀PEO₆₂ at different amounts of surfactant. We prepared seven samples with constant polymer concentration and rₘₙ = n(polymer)/n(surfactant) = 1-15.

The resulting scattering curves can be seen in Fig. 1. We see a decrease of the scattering intensity at low q-values with increasing surfactant amount. At higher q-values a shift of the local minimum to slightly higher q-values takes place with increasing amount of surfactant. The inset shows the pair distance distribution function p(r) resulting from the analyses with the method of indirect fourier transformation (ITP) by Glatter. As we can see the maximal dimension r of the aggregates decreases with increasing amount of surfactant.

In figure 2 a dilution series at constant polymer/surfactant ratio of rₘₙ = 5 is shown. The scattering curves loose intensity at lower concentrations, but the shape of the curves remains the same. Hence, one can say that the aggregates do not change upon dilution. From the p(r)-function in the inset one can also see that the maximal dimension of the aggregates remains the same although the intensity decreases.

To screen the charge of the surfactant, NaCl was added in different amounts. Figure 3 shows some scattering curves with constant amount and concentration of polymer/surfactant and different amounts of NaCl, namely 0.8, 1.3 and 2.0 times the molar amount of surfactant. As we can see this does not lead to any change of the scattering curves. Also the maximal dimension remains unchanged.

References
SANS spectra were measured from emulsions in which hexadecane droplets were contrast-matched to the aqueous continuous phase by selective deuteration. Droplets were sterically stabilised using poly(oxyethylene) nonylphenol nonionic surfactants containing 40 and 100 ethylene oxide (EO) units (N40 & N100, respectively). The resulting film scattering patterns are shown below.

These yielded surfactant film rms thicknesses of 1.5nm for N40 and 2.2 nm for N100, showing good consistency with the 1.9nm determined by Washington and King for triblock copolymer stabilised emulsions with 76 EO units.[1]

Work is in progress to invert the entire spectra to yield segment density profiles, and to fit it to model results based on the electroacoustic spectra of polymer-coated emulsions and particles.[2]

References:
**EXPERIMENTAL REPORT**

**Structure of Phospholipid Vesicles**

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<tr>
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<tr>
<td>Experimental Team:</td>
<td>Mikhail Kiselev, JINR, Dubna, Russia</td>
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<td>Siegfried Wartewig, MLU, Halle, Germany</td>
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<td>Thomas Gutberlet, PSI, Switzerland</td>
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<td>A. Hoell, HMI, Berlin</td>
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<th>Date(s) of Experiment</th>
<th>10.12.02-11.12.02</th>
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## Introduction

The possibility to determine the membrane structure of unilamellar vesicles is important for the characterization of vesicular based drug delivery systems. The macroscopic cross section of the vesicle population can be written as [1]

\[
\frac{d\Sigma}{d\Omega}(q) = n \cdot F_s(q,R) \cdot F_b(q,d)
\]

where \(F_s(q,R)\) is the form factor of a infinitely thin sphere with radius \(R\),

\[
F_s(q,R) = \left(4\pi \cdot \frac{R^2}{qR} \cdot \sin(qR)\right)^2
\]

and \(F_b(q,d)\) is the form factor of the symmetrical lipid bilayer, which for the case of \(\rho(x) = \Delta\rho = \text{const}\) can be presented as

\[
F_b(q,d) = \left(2\frac{\Delta\rho}{q} \cdot \sin\left(\frac{qd}{2}\right)\right)^2
\]

The purpose of the present experiment was to study the influence of trehalose on the DMPC membrane via measurements of SANS curves from vesicles in a wide range of scattering vectors.

Unilamellar DMPC vesicles were prepared by extrusion of a 1% (w/w) DMPC multilamellar vesicle suspension through polycarbonate filters with a pore diameter of 500Å. Trehalose concentrations were 0, 5, 10, 20, and 30% (w/w). Temperature was 10°C (gel phase of DMPC) and 30°C (liquid crystalline phase of DMPC).

## Results and Discussions

Fig. 1 presents the scattering curve recorded from the unilamellar vesicle population in D₂O at 30°C without incoherent background. The incoherent background was subtracted from the measured value of the macroscopic cross-section. The obtained value of the average vesicle radius of about 270Å and a polydispersity of 30% are in good agreement with previous results [2].

The value of membrane thickness can be calculated from the position of the minima at \(q_{\text{min}}=0.195\text{Å}^{-1}\) in the form-factor of the lipid bilayer (3) as

\[
d = \frac{2\pi}{q_{\text{min}}} = 32.3\text{Å}
\]

At addition of trehalose, the position of \(q_{\text{min}}\) shifts to the value of 0.205Å⁻¹ at 10% trehalose, and 0.215 Å⁻¹ at 20% trehalose, which corresponds to a decrease of the membrane thickness \(d\) to a value of 30.7Å and 29.2Å, respectively. A similar decrease in the DMPC membrane thickness in the presence of trehalose was detected for the gel phase (T=10°C). A more detailed analysis of the internal membrane structure in the presence of trehalose is in progress [2].

![Experimental SANS curve from DMPC vesicles in D₂O at 30°C without incoherent background.](image)

**Fig.1.** Experimental SANS curve from DMPC vesicles in D₂O at 30°C without incoherent background.

## Conclusions

The precise measurements of the scattering curve from vesicles in the range of the scattering vector \(q\) from 0.15 Å⁻¹ to 0.3Å⁻¹ give more detailed information about the influence of sugars on the membrane structure [3]. As shown in the present experiment, the membrane structure factor (3) can be evaluated and directly analysed from obtained SANS data.

## References

EXPERIMENTAL REPORT

Assembly of Myelin Model Membranes on a Soft Polymer Cushion

Principal Proposer: Paolo Riccio, University of Basiliata, Potenza
Experimental Team: Paolo Riccio, University of Basiliata, Potenza, Heinrich Haas, University of Campinas, Roland Steitz, TU Berlin / HMI Berlin/ MPI-KGF Golm

Proposal N° BIO-04-668
Instrument V6
Local Contact Roland Steitz
Date(s) of Experiment 10.-16. Dec. 2001
Date of Report: 18.03.2002

Myelin basic protein (MBP) is the predominant protein component of the myelin sheath. This encephalitogenic protein is thought to play a fundamental role for the formation, stabilization and degradation of myelin membrane. The foundation for these structural and functional coherencies still needs to be clarified.

The aim of this project is to get insight into the correlation between the interactions among the myelin components and structural & functional features of the myelin sheath. To this end, the self-assembly of myelin basic protein (MBP) in the presence of lipids and detergent at a soft polymer cushion at the solid-liquid interface was studied by neutron reflectivity measurements.

In the present experiment, particularly the characteristics of lipid-bound (LB) and lipid free (LF) MBP were directly correlated. LB-MBP was extracted from the myelin sheath by an alternative technique, together with its environmental lipids, and therefore it is expected to be in a more native-like conformation than the LF-MBP, for which unfolding to a certain extent has to be taken into account.

In our previous experiments, well-defined supported bilayers from pure lipids (DMPA) were made up through vesicle fusion to the polyelectrolyte precursor. By subsequent binding of LF-MBP and further vesicle fusion to these supported membranes, a lipid/MBP/lipid assembly was achieved, similar to the fundamental structural unit within the myelin sheath. The membranes were formed stepwise, in a layer-by-layer approach. In the current measurements, the membranes were formed in a single step, where lipids as extracted from the myelin sheath and detergent were present together with the protein in the aqueous medium. The molecular assemblies as achieved from the lipid-bound and the lipid-free varieties of MBP were directly compared. In each case, as a hydrophilic precursor, 5 double layers of PSS/PAH were deposited at the silicon block before the experiment. Thus a soft polymer cushion with positive surface potential was provided for the adsorption.

In fig. 1, for the two sets of experiments, the reflectivity curves before and after adsorption of protein are shown. As can be seen from the shift of the first minimum positions (indicated by the vertical lines), in both cases adsorption occurred, but for LB-MBP a much larger thickness increase was observed (Tab. 1). The thickness of the molecular associate with LB-MBP was similar to the one as achieved through layer-by-layer deposition with pure lipids and LF-MBP, where a lipid/protein/lipid assembly was achieved. For the LF-MBP, on the contrary, the observed thickness increase corresponds to that of a pure lipid bilayer (Tab. 1), i.e., the data indicate that the protein was not inserted into the bilayer in that case.

In fig. 1, for the two sets of experiments, the reflectivity curves before and after adsorption of protein are shown. As can be seen from the shift of the first minimum positions (indicated by the vertical lines), in both cases adsorption occurred, but for LB-MBP a much larger thickness increase was observed (Tab. 1). The thickness of the molecular associate with LB-MBP was similar to the one as achieved through layer-by-layer deposition with pure lipids and LF-MBP, where a lipid/protein/lipid assembly was achieved. For the LF-MBP, on the contrary, the observed thickness increase corresponds to that of a pure lipid bilayer (Tab. 1), i.e., the data indicate that the protein was not inserted into the bilayer in that case.

<table>
<thead>
<tr>
<th>Layer</th>
<th>LB-MBP (Å)</th>
<th>LF-MBP (Å)</th>
</tr>
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<tbody>
<tr>
<td>Precursor</td>
<td>287</td>
<td>269</td>
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<td>Protein-lipid membrane</td>
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Tab. 1 Preliminary results from fitting of the experimental curves
**Introduction**

We continued extensive previous work on critical adsorption and wetting at binary liquid mixture/spectator solid interfaces. The mixture was CD$_3$OD + c-C$_6$H$_{12}$, rather than CH$_3$OH + c-C$_6$D$_{12}$, as before and the spectator phase was the strongly hydrophilic SiO$_2$ surface of a RCA-cleaned Si block. Such a surface tends to preferentially absorb and be wetted by the methanolic component in both mixtures. The objectives were: (i) to determine the detailed form of the critical adsorption profile in terms of the Dietrich and Schack procedure [1] with particular reference to the unexpected results found previously for CH$_3$OH + c-C$_6$D$_{12}$; (ii) to compare wetting and adsorption for these mixtures with those obtained earlier for the free liquid surface by Zhao et al.[2]; and (iii) to compare the application of the D&S procedure to an *upper* critical temperature $T_{\text{asc}}$ mixture with that of our previous study on a *lower* $T_c$ mixture, 2-butoxy-ethanol + D$_2$O [3].

**Results and discussion**

Our earlier studies (CHE-04-520) on CH$_3$OH + c-C$_6$D$_{12}$ were conducted largely in the one-phase region above $T_{\text{asc}}$ = 43ºC and were concerned with the detailed shape of the reflectivity profile near the total reflection edge (TRE) that the preponderance of perdeuterated material yielded. The variety of unexpected structures found in the reflectivity-momentum transfer (R-Q) profiles was hard to interpret in terms of the predicted straightforward shift in the TRE to higher Q as the temperature approached $T_{\text{asc}}$. This pattern made it hard to analyse the data in terms of the D&S treatment. Recently, others have offered partial explanations of related complex observations. In the current study, the upper phase and the critical mixture are perdeutero-component weak and there is thus no expectation of a TRE either in the supercritical mixture or in the upper unwetted phase. The simple absence of the TRE in the supercritical mixture made the D&S test difficult to apply. A more general exploration of the R-temperature profile at a fixed Q=0.108 nm$^{-1}$ revealed unexpectedly that on cooling from $T>T_{\text{asc}}$ with no TRE, there appeared sharply at $T=T_{\text{asc}}$ a large rise in R (Figure) that persisted, although lessening, till its disappearance at a much lower temperature.

It did not reappear on heating $T>T_{\text{asc}}$ but did return reversibly on repeating the cooling/heating cycle. We postulate that the rise in R is due to a CD$_3$OD wetting layer that disappeared at what we identify as a dewetting temperature $T_d$. Slow diffusion accounts for its absence during heating but at $T=T_{\text{asc}}$, and above, the wide interfacial area and the thinness of the two coexisting liquid phases promoted mixing with no mechanical stirring. Full (R-Q) determinations were made at temperatures both (a) above and below the wetting region-and (b) as close as possible to the top of the enhanced R region but these remain to be analysed. However, the large magnitude of the reflectivity in (b) compared to those at higher and lower temperatures is strongly indicative of a wetting layer rich in CD$_3$OD- so supporting the hypothesis just laid out. We believe that this portrayal of wetting and dewetting is novel, that it confirms the theoretically predicted pattern of events, and, in particular, that our results confirm that wetting and mixing equilibration can proceed rapidly in the specific geometry of our sample environment-contrary to what has often hitherto been believed. This will ease our analysis of our CH$_3$OH + c-C$_6$D$_{12}$ results.

The polymer-polymer interfacial width for immiscible polymers is given by two contributions: the mean field component, as predicted by self-consistent field theory, and an additional contribution given by thermally excited capillary waves, controlled by dispersive forces. If a more polar film is on a less polar substrate the Hamaker constant is negative, and the Van der Waals forces tend to destabilise the system: the capillary waves at the interface are amplified resulting in the so-called “spinodal dewetting”. This process depends on the viscosity of the films and therefore could be used to probe thin films viscosity.

The aim of our experiment was to investigate with neutron reflectivity the kinetics of the spinodal dewetting for a liquid/liquid polymer system, with the goal to probe the viscosity of thin films as the annealing temperature approached the glass transition.

We measured with the reflectometer V6 specular neutron reflectivity of by-layers of PMMA and PS on silicon substrates. The Mw of the lower layer PS was 1.9M, while the Mw of the top thin d-PMMA layer was 120k. In this situation, we are in a solid regime: the process is then controlled by the viscosity of the top layer.

We followed the dynamic of the dewetting process measuring the reflectivity as a function of the annealing time for sample with different thickness of the PMMA layer, from 95Å up to 125Å, and keeping fixed the thickness of the bottom layer of PS at about 1800Å. To investigate the viscosity in thin films approaching the glass transition, where we expected differences between bulk and surface properties to become more pronounced, we used temperatures of annealing around and below 135°C, to be close to the glass transition temperature for PMMA.

Following the development of the roughness at PS/PMMA interface and PMMA surface (fig.2), we extracted characteristic growth times for the dewetting process, that is connected to the viscosity by the relation
\[ 3\eta_{\text{PMMA}} = 2e^{-3\gamma_{\text{PMMA}}} q^4 \tau \]

We have observed approaching the T_g a deviation of the viscosity for the thin film from the Vogel-Fulcher prediction.

Our results show also a strong dependence of the dewetting time from the film thickness as expected from the theory.

References:
4. F. Brochard-Wyart et al., Lang. 9, 3683 (1993)
Thermosensitive polymers often show a very fast response to external stimuli. In particular, the swelling/de-swelling behavior in solvents is of major interest for potential applications in engineering and biotechnology. The design of devices often requires the implementation of the sensing material in coatings, adsorbed to solid substrates. Here, one of the most promising candidates is Poly-N-Isopropylacrylamide (PNIPA), which as PNIPA macro- and microgel, shows a temperature induced de-swelling in water at 35°C [1].

We report on experiments that focused on confinement and composition effects on the swelling behavior of PNIPA. Therefore, we assembled ultrathin multilayers by alternate adsorption of cationic and anionic thermosensitive poly-electrolytes from aqueous solution on silicon single crystals (80 x 50 x 15 mm³), precoated with a layer of branched polyethyleneimine. The structure of the solvent-swollen films was investigated by neutron reflectometry as a function of sample temperature. Five films were prepared: films 31 and 32, [PSS/PAH]₅/PSS-b-PNIPA, composed of multi-layers of polystyrene-sulfonate (PSS) and poly-allylhydrochloride (PAH) with top layers of PSS-b-PNIPA, prepared at 5°C and 25°C, respectively; film 33, [PSS-b-PNIPA/PDEAEM-b-PNIPA]₈.₅, assembled from two block copolymers of opposite charge, both of which contained PNIPA; film 34, [PSS-b-PNIPA/poly-(SS-NIPA)]₅.₅, composed of PSS-b-PNIPA and a statistical copolymer, poly-(SS-NIPA); and film 35, [PSS-b-PNIPA/PDEAEM – b – PNIPA]/[PSS – b – PNIPA / poly-(DADMAC-stat-NIPA)]₃.₅, with two building blocks containing PNIPA. The multilayer-coated substrates served as top of a flow cell filled with D₂O. The cell was water-thermostated to the respective temperature. The incident neutron beam impinged on the solid/liquid interface from the solid side.

Figure 1 shows two typical sets of reflectivity curves obtained from the solvent-swollen films. A strong correlation was found between the chemical structure of the polymers used and the quality of the assembled films as attested by the occurrence of Kiessig fringes in the reflectivity patterns. The ability of film formation (++) dropped with the total amount of statistical copolymer incorporated in the multilayers with film 31 (++) > film 32 (++) > film 33 (+) > film 35 (-) > film 34 (--). All films responded to elevated temperature as verified by the corresponding changes of their reflectivity (see also Fig. 1).

<table>
<thead>
<tr>
<th>Tab. 1: Results from box model fits to films 31-33</th>
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<tbody>
<tr>
<td>d [Å]</td>
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<tr>
<td>---</td>
</tr>
<tr>
<td>Film 31</td>
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<tr>
<td>Film 32</td>
</tr>
<tr>
<td>Film 33</td>
</tr>
<tr>
<td>Film 33</td>
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<td>Film 33</td>
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</table>

In a series of experiments, we (B.K., Thomas Gutberlet, Roland Steitz, Irina Estrela-Lopis, R. K.) investigated the deposition of lipid (bi) layers onto solid supports under several modifications associated with the support surface. The final goal is to develop a protocol for model membrane formation to serve for the investigation of basic biophysical processes, and also as a starting point for self assembled nanostructuring up to controlled patterning of interfaces using biopolymers.

Our protocol involves the subsequent sandwich built-up of a layered system starting with a bare solid (Si) support, possibly a polymer layer thereupon, the deposition of lipids by interfacial vesicle rupture, and the monitoring of the resulting structure step by step.

For hydrophobic surfaces we observed the fast deposition of an inner lipid monolayer and the subsequent formation of a bilayer, both with almost 100% coverage. This result was essentially the same for a polymer (PS) grafted Si surface as for the bare one. However, two major and independent reasons can be given in favor of preparing model membranes on soft cushions: first, the experimental range of a reflectivity experiment can be shifted by use of a sufficiently thick (~400Å) cushion towards a higher structural resolution. Second, a planar model membrane deposited onto a soft unstructured cushion will more probably exhibit similar characteristics as a vesicular, cell-like membrane than one associated to a solid crystalline support. One intriguing result as yet is the unexpected absence of a water gap between the mono- and the bilayer even when deposited onto polymer grafted supports. This suggests the absence of membrane fluctuations (1). Nevertheless, the lipid layer that is in contact with the aqueous subphase easily interacts with membrane active molecules up to the complete breakdown of a layered structure. This indicates that the outermost layer is rather fluid-like than solid.

Bare hydrophilic Si surfaces reveal the instantaneous deposition of a single bilayer as far as that can be reliably analyzed in the absence of a cushion spacer. We still miss the results from a hydrophobic cushion that we tried to obtain during the last beamtime. As a polymer cushion we were using a multilayer sequence of polymer consisting of PEI(PSS-PAH)_8. Though we could appropriately measure the thickness of the polymer cushion and also successfully matched the polymer-subphase contrast in order to increase the perception of lipid when deposited onto the hydrophilic multilayered polymer, we did not find the distinct double-layer lipid structure that we expected. The observed pattern could not be interpreted in terms of layers at all. Therefore, the experiment needs to be repeated.

An important side effect of the investigations so far is the recognition of incomplete wetting in water in the case of hydrophobic interfacial surfaces. Experimental evidence was given by reflectivity patterns that could not be attributed to intentionally deposited layers but rather to the presence of interface associated gaseous inclusions (2). The interpretation was supported in AFM experiments that depicted nanobubbles at the polymer-water interface.

References:

Sample preparation. Monolayers of alkanethiol-terminated poly(ethylene glycol) with different morphology were prepared on polycrystalline thin Au films evaporated on Si wafers with 1 nm Ti as adhesion promoter. Amorphous films with a layer thickness between 20 and 40 Å were prepared by immersion of the substrates into 50 µM dimethylformamide (DMF) solution. Dense-packed, quasicrystalline films with a layer thickness in the range of 100 to 120 Å were prepared by immersing the samples overnight. After removal from the solution, the samples were rinsed with ethanol p.a., sonicated for 5 minutes, and blown dry with argon.

Set-up. Si wafers freshly coated with a thin Au film were cut into half and then mounted into an Al sample chamber. To save machine time one half was measured in vacuum before film preparation, while the second half was directly immersed into DMF solution. The Al chamber could be sealed and evacuated down to a base pressure of 1 mbar by means of a membrane pump. For venting it was connected to a nitrogen line. For measurements in a saturated D2O/N2 atmosphere, the samples were first evacuated to remove physisorbed H2O and then vented with D2O saturated N2. Then, a flange on top of the sample chamber was opened and a small amount of D2O (~1.5 ml) was placed into the chamber in counter current flow of nitrogen.

Measurements. A total of four samples were measured (1) without polymer film, (2) with a PEG film in vacuum, (3) with a PEG film in D2O saturated N2, and finally (4) again in vacuum. To check on equilibrium conditions in case of exposure to the D2O saturated atmosphere, at a selected incidence angle the signal was monitored over a period of ~ 15 min until it didn’t change any more. To check on long scale effects the scan in D2O/N2 environment was repeated directly after the first scan was obtained.

Results. The figures display some of the results obtained. Figure 1 compares the neutron reflectometry data of a film with a layer thickness of 100 Å in contact with the D2O/N2 atmosphere as well as in vacuum. Particularly in the range between 0.02 < Qz < 0.04 Å⁻¹ a significant difference can be seen in the spectra. Most important, the water-uptake has proved to be completely reversible, as demonstrated by the third spectrum in fig. 1 that was taken after the second evacuation of the chamber. In this case, equilibrium seemed to be achieved instantly and the measurement was launched immediately. One crucial point was that the second measurement in D2O/N2 environment showed some deviations from the first one for the first ~3 hours of the scan. We interpreted this as a long scale effect that was not observable in our test experiments for equilibrium, where only a fast drop of intensity could be seen on the time scale of ~ 10 min. To gain information on the time scale of the slow change, we performed time scans up to 3 hours at selected Qz. Figure 2 shows such a scan on a sample with a polymer layer thickness of 120 Å. From that measurement we estimated 5 hours for the sample to reach equilibrium.

![Figure 1](image1.png)

**Figure 1:** Comparison of neutron reflectometry data for a PEG layer of 100 Å in vacuum and exposed to a saturated D2O/N2 atmosphere.

![Figure 2](image2.png)

**Figure 2:** Long term change of reflected intensity at Qz = 0.08 due to interaction between PEG and water.
Neutron reflectivity data were recorded from the interface between a Si-single crystal and suspensions of colloidal particles in D$_2$O. The particles were (i) charge stabilised polystyrene latex spheres with a diameter of $d=64$ nm and (ii) polybutadiene-b-poly(ethylenoxide) blockcopolymer micelles with a cross sectional diameter of 19 nm.

**Polystyrene spheres**

Reflectivity curves were recorded for six different volume fractions $\phi$ of the solute. The corresponding normalised scattering length density profiles along the interface normal $z$ are displayed in Figure 1. At the lowest concentration the reflectivity is only insignificantly different from the Fresnel-reflectivity, while at the higher concentrations undulations occur. This is also reflected in the scattering length density curves where the curve is almost flat for the lowest concentration and oscillations occur at all higher concentrations. However we could not yet identify a clear trend with concentration and do not have an understanding of the underlying physics yet.

**Blockcopolymer micelles.**

Reflectivity curves were measured for three polymer concentrations in D$_2$O. The corresponding normalised scattering length density profiles are displayed in Figure 2.

For all concentrations distinct undulations occur in the reflectivity curves the amplitudes of which increase with increasing polymer concentration, while their positions are concentration independent. The corresponding scattering length density profiles are in accordance with a layer of micelles at small $z$, which is aligned parallel to the interface. The micelle number density of the layer increases with increasing bulk concentration, which is in qualitative agreement with theoretical predictions for the isotropic to nematic pretransition of rods close to a hard wall. However, the effect might also be caused by monolayer adsorption due to attractive interaction between the rods and the wall. On the basis of the limited number of profiles available it is not yet possible to distinguish between the two mechanisms.

![Figure 1](image1.png)  
**Figure 1** Scattering length density profiles along the surface normal normalised to the bulk value as obtained from reflectivity measurements on solutions of polystyrene latex spheres.  

![Figure 2](image2.png)  
**Figure 2** Scattering length density profiles normalised to the bulk value obtained from reflectivity measurements on blockcopolymer micelles.
PEO-PPO-PEO triblock copolymers of ethylene oxide (EO) and propylene oxide (PO) are commercially available and popular in many applications since their molecular weight and EO/PO ratio can be widely varied. In aqueous solutions they behave as polymeric surfactants (the PPO block is hydrophobic) whose molecules can be tailored to meet specific requirements. Their adsorption at the solid/liquid interface is relevant to the wetting and spreading of surfactant solutions, steric stabilization of suspended particles or emulsion droplets, modification of the solid surface affinity for protein adsorption, etc.

The aim of this project is to explore the influence of the surface energetics on the adsorption of such triblock copolymers: Synperonic L101, P104, and F108 (Uniqema). Two coatings with different degree of hydrophobicity were used: amorphous Teflon and polystyrene PS (critical surface tension 12.5 and 33 mN/m, resp.). A layer of amorphous Teflon AF1600 (DuPont) was spin coated on a suitably sized silicon block and then heat-treated as recommended by the manufacturer. The neutron reflectivity of the fluoropolymer layer was measured in air. The layer thickness was 33 nm and the SLD very close to the value calculated on the basis of chemical composition. The roughness of the silicon/polymer interface was rather high (~ 3.5 nm) - probably due to the use of an adhesion promoter (a perfluorosilane). The PS layers were also deposited by spin-coating and have been characterized previously.

The adsorption of block copolymers from aqueous solutions on the polymer surfaces was carried out as follows. Initially the reflectivity of the polymer/D$_2$O interface was recorded. Then the cell was emptied, washed with ethanol (5 times) and D$_2$O (twice), filled with a sample solution (0.1 wt% Synperonic copolymer; 0.5 wt% NaCl) and the reflectivity of the polymer/solution interface was monitored again. Repeated measurements were made in order to confirm that the system has had reached equilibrium.

The reflectivity curves of AF1600/D$_2$O recorded before and after washing the adsorbed copolymer away with ethanol were practically identical thus proving the fluoropolymer layer was essentially unchanged. It is also important for some applications that L101, P104, and F108 adsorbed on Teflon can be easily and completely removed (washing with water decreases the layer thickness to some extent).

The reflectivity curves for the three Synperonic copolymers are shown in the Figure below. In all cases the copolymer concentration was 0.1 wt% (which is above their CMCs).

The results were assessed with an independent layer model, which included separate polymer (AF1600 or PS), PPO, and PEO layers, sandwiched between bulk silicon and D$_2$O. Some preliminary estimates are listed in the following Table:

<table>
<thead>
<tr>
<th>PEO-PPO-PEO</th>
<th>$d_{PPO}$ [Å]</th>
<th>$d_{PEO}$ [Å]</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L101</td>
<td>32</td>
<td>38</td>
<td>0.4</td>
</tr>
<tr>
<td>P104</td>
<td>34</td>
<td>38</td>
<td>1.5</td>
</tr>
<tr>
<td>F108</td>
<td>32</td>
<td>72</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The thickness of the hydrophobic block, $d_{PPO}$, is practically constant. The thickness of the hydrophilic PEO block (hence the total thickness of the adsorption layer) increases with the asymmetry of the molecule (the asymmetry ratio, $\beta$, is the ratio of the radii of gyration of the PEO and PPO blocks).

A similar trend was observed on the PS samples. The PS coating however, was somewhat influenced by the sequential adsorption/desorption: its thickness decreased (although by less than 1 nm in total) and its roughness dropped from about 2 to 1 nm during the course of the experiments.
The permeability of water in ultrathin polyelectrolyte multilayers (~30 nm) by coating them with charged wax particles was studied. We expect that the presence of a hydrophobic layer atop the films leads to a reduction of their sensitivity to water. A model of water-sensitive multilayer was prepared by electrostatic self-assembly of poly(allylamine) (PAH) and poly(styrene sulfonate) (PSS) on silicon wafer. The successful deposition of the wax particles on the top of this film was evidenced by ellipsometry, AFM and contact angle measurements. We showed that the wax particles deposited on the film melt to form a continuous hydrophobic layer after annealing at 60°C. We expect that this layer provides a barrier to prevent the diffusion of water molecules in the films. To quantify the swelling behavior of the films neutron ray reflectivity (NRR) was used.

Two samples were prepared: [Si/(PAH+PSS)_{9.5 bilayers}] (= reference sample) and [Si/(PAH+PSS)_{9.5 bilayers} + wax particles]. For each of them, the NRR measurements were performed at room temperature according to the following steps: (i) measurement in dried state against air; (ii) measurement in closed solid/liquid exp. cell against D_2O; (iii) removal of D_2O, drying with nitrogen gas and annealing of the at 60°C for 45 min; (iv) measurement in dried state against air; (v) measurement against D_2O.

The reflectivity curves for each experiments were fitted by a model-free routine which discretises the scattering length density (SLD) profiles into boxes of adjustable height and constant thickness (fixed by the largest scattering vector of the experiment). To avoid noise amplification, a Thikonov’s regularization procedure was applied(1). The SLD profiles obtained before and after annealing against air and D_2O are depicted in the Fig.1. The results show that against air the annealing process does not modify the structure of [Si/(PAH+PSS)_{9.5}] film. Moreover, the similar curves obtained for the films with and without wax particles is explained by the poor contrast between SLD of wax particles and SLD of air. In presence of D_2O, we observe a strong swelling of the [Si/(PAH+PSS)_{9.5}] film. The amount of D_2O in the film is estimated around 50%. By contrast, the amount of D_2O in [Si/(PAH+PSS)_{9.5}+wax] sample is lower and tends to strongly decrease with the distance from the Si substrate. After annealing, the external roughness and the swelling behaviour of the film strongly decrease in agreement with the formation of a continuous barrier layer of wax.

The comparison of the swelling behaviour of [(PAH+PSS)_n ] and [(PAH+PSS)_{n+wax} ] samples clearly reveals that the presence of wax particles on the top of the films prevents the diffusion of water molecules. The melting of the wax particles strongly increases the barrier properties of the wax layer. These first results are particularly stimulating. Future experiments involving the incorporation of wax particles directly in the polyelectrolyte films are planned.

(1) The analysis program was kindly provided by A.M. Jonas (Univ. Louvain, Belgium).
The primary goal of this project is chemical "switching" of the interaction between water-soluble proteins and ultrathin polymer films. The polymer used here is poly(2-(dimethylamino) ethyl methacrylate-block-methyl methacrylate) (poly-(DMAEMA-b-MMA)) with 50 % MMA (Diblock 50, Mn = 9.3 kD). It was synthesized by the group of S. P. Arms (Univ. Sussex). pH titration of the subphase induces changes in surface charge density and chain conformation (i.e. viscoelasticity) of the polymer.

Monolayers of Diblock 50 at air/water interface were transferred by Langmuir-Schäfer deposition onto Si blocks with spin-coated films of deuterated (d) and protonated (h) -PMMA. The thickness of the PMMA precursor film was measured by ellipsometry in air, yielding ~280 Å, while that of the Diblock 50 layer (transferred at 25 mN/m) was ~ 40 Å, respectively. Prior to the first beamtime, the stability of the transferred films were checked against prolonged immersion in different buffer solutions and intensive rinsing with water, while the swelling of the DMAEMA was measured by self-developed ellipsometry under controlled humidity.

Firstly, we measured specular neutron reflectivity of a Diblock 50 monolayer transferred at 25 mN/m on a d-PMMA film (sample D3) in air. This measurement was most sensitive to the d-PMMA support film. As the top (diblock) layer was protonated, the contrast at the interface of the Diblock 50 film and air was poor. The situation changed drastically upon exchange of air by D₂O. In the latter case maximum sensitivity was achieved for the protonated Diblock 50 layer. For the measurements in the presence of bulk solvent (D₂O), the coated blocks were mounted on the top of a flow cell. As silicon is transparent to neutrons (for 4.66 Å neutrons), the neutrons accessed the solid/liquid interface from the solid backside. Each scan took about 10 h of beamtime, and another short scan (θ = 0.5 – 1.1) of 2 h was added to confirm the stability of the film. For the film transferred at 25 mN/m (area per chain: 410 Å²), we observed a clear change between pH = 8.5 and 5.5 in terms of thickness, scattering length density, and roughness of the DMAEMA layer (see Fig. 1 and Table 1). Throughout the experiments, the film remained stable against intensive rinsing with buffer as well as multiple pH titration cycles. pH dependent structural changes were also seen for a Diblock50 monolayer deposited on an h-PMMA support film (not shown). The conducted neutron reflectivity experiments confirm a pH dependent structure of the polyelectrolyte films (Diblock50) at the solid/liquid interface. Future experiments will focus on the pH dependence and thus the chemical switching of the interactions of the diblock50 films with proteins in the liquid phase.

![Reflectivity and scattering length density profiles of the Diblock 50 in D₂O at different pH subphase conditions (red triangles pH = 5.5, black circles pH 8.5).](image)

**Figure 1.** Reflectivity and scattering length density profiles of the Diblock 50 in D₂O at different pH subphase conditions (red triangles pH = 5.5, black circles pH 8.5).

<table>
<thead>
<tr>
<th>Sample D3</th>
<th>pH 8.5</th>
<th>pH 5.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>d_{PMMA} [Å]</td>
<td>282</td>
<td>279</td>
</tr>
<tr>
<td>σ_{PMMA, Si} [Å]</td>
<td>19.2</td>
<td>21.8</td>
</tr>
<tr>
<td>d_{diblock50} [Å]</td>
<td>34</td>
<td>41</td>
</tr>
<tr>
<td>10^6 x N_{diblock50} [Å²]</td>
<td>2.95</td>
<td>3.65</td>
</tr>
<tr>
<td>σ_{diblock50,subphase} [Å]</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>10^6 x N_{subphase} [Å²]</td>
<td>5.97</td>
<td>5.87</td>
</tr>
<tr>
<td>φ_{D₂O in diblock50}</td>
<td>0.40</td>
<td>0.55</td>
</tr>
</tbody>
</table>

**Table 1.** Best-Fit parameters of the 2-box model of substrate D3 against buffer solutions with different pH $N_{\text{PMMA}} = 6.796 \times 10^6$ Å² (fixed). $\phi_{D₂O \text{ in diblock50}}$ denotes the volume fraction of D₂O inside the adsorbed Diblock50 monolayer.
Recently we have shown that the conductivity of self-assembled Au-nanoparticle/dendrimer films is strongly affected by the presence of solvent vapours [1, 2]. This property makes such materials promising candidates for chemical sensor applications. Currently we assume that the chemical sensitivity is mainly due to analyte-induced film swelling, a process that requires the diffusion of analyte molecules into the film material. Since molecular diffusion in such novel materials is only poorly understood we decided to use Neutron Reflectometry (NR) as a unique tool for delivering quantitative information about the diffusion and distribution of analyte molecules within these very thin (<50 nm) nanostructured films.

The Au-nanoparticle/dendrimer film used in this study was prepared via layer-by-layer self-assembly on a glass substrate [2]. As film components we used alkylamine-stabilized Au-particles (ca. 4 nm diameter) and poly(propylene imine) (PPI) dendrimers of 4th generation. The measurements were performed in a newly developed gas-tight chamber, which allowed working at well-defined gas concentration and temperature. A first measurement was carried out under dry \( N_2 \) to obtain reference data. Then, the sample was exposed to saturated vapours of \( D_2O \), \( d_8 \)-toluene or \( d_4 \)-methanol and the specular reflectivity was measured in the Q-range up to ca. 0.12 \( \text{Å}^{-1} \).

The reflectivity curve from the film under dry \( N_2 \) is shown in Fig. 1 (curve 1). A single layer model with a constant scattering length density \( \rho_{\text{film}} \) across the film was found to give the best fit of the experimental data. The obtained profile is shown in Fig. 2. The value of \( \rho_{\text{film}} \) derived from the fit is \( 1.26 \times 10^{-6} \text{Å}^{-2} \), which corresponds to an approx. 22% volume fraction of gold.

The reflectivity curves of the film measured in the presence of saturated vapours are shown in Fig. 1 (curves 2–4). The reflectivity of the sample changed as a result of vapour/film interactions. In contrast to the reflectivity curve of the “dry” film, the curves measured in the presence of analytes could only be fitted with more sophisticated models (e.g. multiple layer models). This result suggests a complex distribution of vapour molecules within the film, as illustrated by the scattering length density profile of the film dosed with \( d_4 \)-methanol (Fig. 2). A significant increase in \( \rho_{\text{film}} \) is observed due to diffusion of the vapour molecules into the film interior. Additionally, a thin layer with greater scattering length density is formed on the top of the film, which is probably due to condensation of vapour at the gas/film interface. We note, however, that this preliminary interpretation requires further verification by more detailed investigations. In accordance with the electrical responses of the film our preliminary data analysis suggests that the analyte distribution profiles are mainly controlled by the solubility properties of the dendrimer component.

Our results highlight that NR is a powerful tool for studying sorption processes in thin composite films in-situ. The method delivers information about the uptake and the distribution of analyte molecules within the film. Combining NR with other complementary methods (e.g. X-ray reflectivity, microgravimetry and resistance measurements) will enable a deeper understanding of the mechanism of vapour sensing with such novel materials.

References:
Sample preparation. Monolayers of alkanethiol-terminated poly(ethylene glycol) (PEG) with different morphology were prepared on polycrystalline thin Au films (70 nm) evaporated on Si wafers with 1 nm Ti as adhesion promoter. Amorphous PEG films with a layer thickness between 20 and 40 Å were prepared by immersion of the substrates into 50 µM dimethylformamide (DMF) solution for ∼10 min. Dense-packed, quasi-crystalline PEG films with a layer thickness in the range of 100 to 120 Å were prepared by immersing the samples overnight. After removal from the solution, the samples were rinsed with ethanol p.a., sonicated for 5 minutes, and blown dry with argon.

Set-up. After preparation, the wafers were mounted into an Al chamber, which could be evacuated down to 1 mbar. For measurements in a saturated D_2O/N_2 atmosphere, the samples were evacuated to remove physisorbed H_2O and vented with D_2O saturated N_2. Then, the sample chamber was opened to place a small amount of D_2O (~1.5 ml) into it in counter current flow. The Al chamber could be heated by an electrical heater up to 80° C. To save machine time, two Al chambers were used alternatively. That way, one sample was allowed to equilibrate before measurement, while a second sample was measured.

Measurements. A total of five PEG films of different morphology were measured (1) in vacuum and (2) in D_2O saturated N_2 at three different temperatures: RT, 55° C, and 80° C. To check on equilibrium conditions, the scans in D_2O/N_2 environment were repeated for several times.

Results. Figure 1 shows the changes induced in the neutron reflectivity spectra of amorphous and crystalline PEG layers due to exposure to the D_2O/N_2 mixture at different temperatures as compared to the measurements under vacuum conditions. For amorphous films changes are most prominent for Q_z > 0.03 Å⁻¹. For crystalline films a significant difference can be observed in the range between 0.02 Å⁻¹ < Q_z < 0.055 Å⁻¹. Interestingly, the amorphous films show no change in reflectivity up to temperatures of 55° C, suggesting that the films alter only at elevated temperature above that value. In contrast, the crystalline films show an immediate change in reflectivity if exposed to the D_2O/N_2 mixture even at RT. While in our last experiments (MAT-04-729) at RT, the swelling of the films turned out to be completely reversible, we now found a significant degradation at elevated temperature even for the crystalline films. Figure 2 demonstrates the long term changes for a crystalline layer exposed to the D_2O/N_2 mixture at 55° C with increasing time. Also the spectra taken at RT before and after heating of the sample differ significantly (not shown). From that we conclude that morphology of the film has changed irreversibly.
The surface coverage $\Gamma$ of Langmuir films at the air-water-surface can be determined by several techniques: Spread amount, ellipsometry, LB-transfer, x-ray and neutron reflection. All methods sometimes fail: Spreading errors, no information about the refractive index in the surface layer, ambiguities in interpretation of reflectivity data, or adsorption from solution. Neutron reflection on air-contrast matched water (zero water) is a direct approach to determine $\Gamma$. Reflectivities up to $R=10^{-2}$ can be calculated within the Born approximation [1].

$$R(q_z) = \frac{16\pi^2}{q_z^2} \left| \int_0^\infty \rho(z) e^{i q_z z} dz \right|^2$$

with $\rho(z)=\Sigma_n B_n$ as the scattering length density of the monolayer. The contrast matched subphase does not contribute to the reflectivity. For small values of $q_z$ we can expand that equation [2]:

$$\int_0^\infty \rho(z)(1+i q_z z^2/2) dz = \Gamma^2 + (\Gamma(z)^{1/n} - q_z^2 \Gamma'(z)$$

with $\Gamma$ the scattering length per area and $\langle z^n \rangle$ the n-th moment of the density profile

$$\Gamma = \int_0^\infty \rho(z) dz \quad \langle z^n \rangle = \int_0^\infty \rho(z) z^n dz$$

For small film thickness and low $q_z$, $R(q_z) q_z^2$ is linear in $q_z^2$, and $\Gamma$ can be directly determined.

Fig. 1 shows $R(q_z) q_z^2$ of a PEE$_{20}$PEO$_{160}$ block copolymer surface layer at different surface pressures with linear fits in the small $q_z^2$ regime. The obtained surface coverage is shown in the inset (broken line). For comparison, the value calculated from chemical composition (scattering length per molecule: $818\times10^{-2}$ Å) and deposited amount is also shown (straight line).

$$\sigma^2 = \langle z^2 \rangle - \langle z \rangle^2$$

is negative, prohibiting a logarithmic approximation [2]. Due to these problems, our measured surface coverage exhibits a large error bar, which hopefully will be reduced in the future. Yet already, we find reasonable agreement between the expected and measured surface coverage, and can conclude that even such structured profiles as shown in Fig. 2 are due to a monolayer, not a multilayer.

Fig. 2 shows calculated density profiles, using reflectivity data from [3] measured on D$_2$O at different surface pressures (cf. Fig. 1). Apparently, the monolayer consists of two vertically separated blocks, air adjacent PEE ($\rho_{PEE}=3.11\times10^{-2}$ Å$^2$) and a (swollen) PEO brush ($\rho_{PEO}<6.808\times10^{-2}$ Å$^2$). The PEE/PEO interface is set at $z=0$, where an additional PEO-monolayer is found, a finding supported by X-ray reflectivity[4].

The positive and negative contributions of the blocks to $\Gamma$ nearly cancel each other, leading to a very small value of $\Gamma$. Furthermore, the mean square deviation $\sigma^2 = \langle z^2 \rangle - \langle z \rangle^2$ is negative, prohibiting a logarithmic approximation [2]. Due to these problems, our measured surface coverage exhibits a large error bar, which hopefully will be reduced in the future. Yet already, we find reasonable agreement between the expected and measured surface coverage, and can conclude that even such structured profiles as shown in Fig. 2 are due to a monolayer, not a multilayer.

Literature
In aqueous solution blockcoplymers (BCP) of the type polybutadiene-b-poly(ethyleneoxide) (PBPEO) form cylindrical micelles, if the respective block lengths are about balanced. Solutions of this kind show an isotropic to nematic (I/N) phase transition at sufficiently high volume fractions of the polymer[1]. Using neutron reflectivity, we have investigated the influence of the flat interface between a silicon single crystal and solutions of the proteated polymer PB_{1.5}PEO_{1.5} in H$_2$O and of the deuterated polymer d-PB$_{1.7}$d-PEO$_{1.8}$ in non reflecting water (NRW) on the solutions' I/N phase transition. The subscripts indicate the blocks' molar mass in kg/mol. The bulk phase transition occurs at a volume fraction of $\phi_{\text{I/N}}=0.078$ in the case of the proteated polymer in H$_2$O and at $\phi_{\text{I/N}}=0.066$ for solutions of the deuterated polymer in NRW.

The amplitude of these undulations increases with increasing $\phi$, while its period is constant. Qualitatively this can be interpreted as the formation of an interfacial layer, the density of which increases with volume fraction while its thickness remains unchanged. The qualitative analysis by using either the so called box-model approach[2] or the model independent groove tracking algorithm[3] shows that the thickness of the layer matches quite well with the cross-section diameter of the micelles, which has been determined by SANS beforehand[4]. This is strong evidence for a biaxial to uniaxial transition at $\phi=0.85\times\phi_{\text{I/N}}$, i.e. the formation of nematicaly ordered micellar monolayer followed by incomplete wetting. A paper giving details of the analysis and the model has been submitted to Macromolecules.

The transduction of biological signals in cells involves a large number of enzymatic reactions in an enzymatic cascade. One of them concerns a minor components of cell membranes, called phosphoinositols and consisting of a phosphatidic lipid linked to a inositol head group via a P-O bond. The phosphorylation of the inositol unit is one of the step of the signal transduction process in cells. To analyse the interaction of the enzyme phosphatidylinositol-3-Kinase (PI3K) which catalyses the phosphorylation, the adsorption of this enzyme onto a phospholipid having the same interfacial properties as phosphoinositols has been followed by Neutron Reflectivity.

The measurements were performed on a silicone wafer modified by a (PAH/PSS)$_{9.5}$ cushion (PSS PolyStyreneSulfonate and PAH PolyAllylamine Hydrochloride). The wafer was prepared and dried several days before measurements for storage. Just before the measurement, the Hepes buffer (Hepes 10mM, KCl 130mM, NaCl 10mM, pH 7.2 in D$_2$O) was introduced under the polymer cushion.

The polymer cushion is characterized by a thickness of 355Å and a roughness of 44Å (Fig. 1, squares). The 2-arachidonoyl-1-stearoyl-phosphatidic acid (ASPA) is an unsaturated phospholipid, proved previously in our lab to be the best candidate to replace phosphorylated phosphoinositols as a unique defined component. It carries a negatively charged head group presumably required for the interaction of the enzyme to membranes. It forms a milky suspension of multilamellar vesicles which spread onto the PAH-terminated polymer cushion by forming a bilayer. After adsorption of the amphiphiles (for 40 minutes), the cell was rinsed to remove non adsorbed amphiphile molecules and refilled by the Hepes buffer in D$_2$O. The profile is recorded in these conditions (Fig.1, open symbols). While DMPC (dimyristoyl phosphatidylcholine) forms a perfect bilayer on a similar PSS-terminated polymer cushion, ASPA vesicles do not form a homogeneous bilayer (Table 1).

The introduction of the PI3K enzyme beneath the ASPA layer (250µg in 15mL of D$_2$O buffer) leads to a slight modification of the reflectivity curves corresponding to the formation of a thin adsorbed layer after 1h (Fig.1, triangles and Table 1).

![Figure 1. Neutron Reflectivity curves of a (PAH/PSS)$_{9.5}$ polymer cushion on a silicone wafer against (squares) D$_2$O and after adsorption of (circles) ASPA and (triangles) PI3K enzyme.](image)

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness, Å</th>
<th>Roughness, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASPA</td>
<td>74</td>
<td>18</td>
</tr>
<tr>
<td>PI3K</td>
<td>37</td>
<td>5</td>
</tr>
<tr>
<td>DMPC</td>
<td>51</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 1. Parameters of the lipid layers and the adsorbed enzyme layer after adsorption at the lipid layer.
Interactions between surfactants and polymers is a large field of interest since polymers contribute to modulate the interfacial properties of solutions. To understand this behaviour with natural polymers, we have analysed the adsorption of a pectin onto an amphiphilic layer by Neutron Reflectivity.

The measurements were performed on a silicone wafer modified by a PEI/(PSS/PAH)_{6.5} cushion (PolyEthyleneImine PEI, PolyStyreneSulfonate PSS and PolyAllylamine Hydrochloride PAH). The wafer was prepared and dried several days before measurements. We have considered a pectin made up of mainly galacturonic acid units partially methylated (37%). The adsorption of the pectin has been analysed on two amphiphilic substrates : cetyl trimethyl ammonium bromide CTAB that forms micelles in a salty solution at \( C = 5 \times 10^{-4} \text{M} \) and dimyristoyl phosphatidylcholine DMPC that forms multilamellar vesicles (C=1mg/ml). The temperature was fixed to 30°C over the Krafft temperature of CTAB and over the melting point temperature of DMPC.

The polymer cushions are characterised by a thickness of about 260Å and a roughness of 20Å (Figs. 1 and 2, squares). After adsorption of the amphiphiles (40 minutes), the cell is rinsed to remove non adsorbed molecules and the pectin solution is introduced. In the case of CTAB (Fig. 1, circles), the reflectivity profile is strongly modified. The introduction of the pectin kept in the cell during the measurements has the same effect. In the case of DMPC (vesicles sonicated in a bath at 30°C for 50min before introduction), the phospholipid fixes to the polymer cushion in one single perfect bilayer of thickness 57Å (with hydration) and roughness 5Å (Fig 2, circles). The adsorption of the pectin for 40 minutes was followed by a rinsing of the cell to remove free pectin macromolecules. The change in reflectivity (Fig.2, triangles) reveals the presence of a thin pectin layer stacked to the DMPC bilayer in agreement with previous results from other physico-chemical methods.
Several independent neutron reflectivity measurements on deuterated polystyrene (d-PS) coatings on silicon blocks against liquid D$_2$O conducted in 2000 and 2001 showed non-vanishing scattering contrast at the polymer/liquid interface although the two materials (d-PS and D$_2$O) have closely similar scattering length densities (SLDs). A protonated contamination layer adsorbed at the polymer surface from the bulk D$_2$O can explain some of data [1]. On the other hand non-vanishing contrast might also be achieved whenever gas bubbles are trapped at the polymer/liquid interface. Nanobubbles at hydrophobic surfaces against water were reported recently [2]. But, also macroscopic gas bubbles can be trapped during the filling process of the sample cell. To experimentally crosscheck on the mechanism of contrast formation we conducted neutron reflectivity experiments on thin d-PS films on silicon supports against air, H$_2$O and D$_2$O under various experimental conditions.

Figure 1 shows a typical reflectivity curve obtained from the interface of a 28 nm thick d-PS film on silicon support against liquid D$_2$O. Opposed to expectation, there are pronounced oscillations in the reflectivity pattern. They stem from a 3 nm thick layer of reduced SLD (5.67·10$^{-6}$ Å$^{-2}$), sandwiched between the d-PS coating (NbdPS = 6.42·10$^{-6}$ Å$^{-2}$) and the bulk liquid phase (NbD$_2$O = 6.37·10$^{-6}$ Å$^{-2}$)

To investigate the effect of macroscopic gas bubbles on the reflectivity, part of the liquid volume of the sample cell (~10 ml) was displaced by air, which is forming macroscopic bubbles at the d-PS/D$_2$O interface in the present experimental geometry. The changes of the reflectivity brought about by two displacement steps are shown in Figure 2. On increasing the fraction of the interface covered by air bubbles (i) the reflectivity R(θ) at θ<θ$_c$ falls below unity; (ii) the edge of total external reflection (TRE) becomes smeared out; (iii) the amplitude of the Kiessig oscillations at θ>θ$_c$ increases. This is very different from what is observed at the pristine d-PS/D$_2$O interface. Hence, macroscopic air bubbles can be ruled out as source of the non-vanishing contrast. From measurements of the thickness of the d-PS films by neutron and x-ray reflectometry before and after exposure to liquid D$_2$O, we can also rule out that the interfacial layer of reduced SLD is primarily due to the adsorption of a (non-deuterated) organic contaminant. Therefore we conclude that the observed contrast is caused by a depletion of the liquid in the boundary layer against the hydrophobic substrate.

Figure 1. Neutron reflectivity curve obtained from a typical d-PS coating against D$_2$O (symbols) and calculated reflectivity (red line) based on the exp. findings at the polymer/H$_2$O interface. Blue line: Best fit to the data. For details see text.

Figure 2. Neutron reflectivity from the d-PS coating against D$_2$O before and after partial displacement of D$_2$O by air. The inset shows the behavior near the TRE on an enlarged scale.

EXPERIMENTAL REPORT

Does the chemical nature of the substrate trigger net adsorption of pluronic F127?

Principal Proposer: R. Steitz\(^1,2\), G.H. Findenegg\(^1\)
Experimental Team: S. Zhang\(^1,4\), S. Schemmel\(^1\), R. Steitz\(^1,2\)

\(^1\)TU Berlin, \(^2\)HMI, \(^4\)currently at Cambridge, UK

In conclusion, the conducted experiments proof a strong dependence of the F127 net adsorption on the chemical nature of the substrate surface.

We are investigating the structure of adsorbed films of triblock copolymers BAB at the interface of their aqueous solutions against solid substrates, to elucidate the way in which the adsorbate affects the wettability of the substrate surface. Well-defined model substrates of different hydrophilicity and surface energy were prepared by immersion of silicon wafers (50 × 80 × 15 mm\(^3\)) in Piranha solution (½vol H\(_2\)O\(_2\) + ½vol H\(_2\)SO\(_4\)) or coating silicon wafers with thin films of deuterated polystyrene (d-PS). The net adsorbate structure of triblock copolymer F127 (EO\(_{100}\)-PO\(_{65}\)-EO\(_{100}\)) at the two chemically different substrate surfaces in contact with the diluted aqueous solutions of the polymer was studied by neutron reflectometry.

Figure 1 shows a typical reflectivity curve obtained from the hydrophilic Si/SiO\(_2\)/liquid interface against the aqueous liquid phase. No pronounced change in the reflectivity of the interface occurred upon displacement of D\(_2\)O by solutions of F127 in D\(_2\)O. However, close inspection shows that there was F127 net adsorption at the interface below the cmc (1.26 wt-% F127). Omitting the F127 adsorption layer in corresponding model 1 does change the quality of the fit considerably for c < cmc.

The situation at the hydrophobic substrate surface was found quite different from that observed at the hydrophilic substrate surface. After displacement of the D\(_2\)O subphase by a very diluted solution of F127 in D\(_2\)O (0.1 wt-% F127) the reflectivity of the hydrophobic d-PS/liquid interface changed drastically. The enhanced amplitude of Kiessig fringes can be taken as direct proof of the F127 adsorption layer that developed further in time (see Fig. 2). Stepwise increase of the bulk F127 concentration led to additional changes of the reflectivity with a very minor time dependence for c ~ cmc (1 wt-%) and no time dependence for c > cmc (5 wt-%). No simple model could be found to describe the adsorption layer at first glance. A detailed analysis of the data is in progress.

\[ \text{Tab.1: F127 net adsorption to the Si/SiO}_2/\text{liquid interface} \]

<table>
<thead>
<tr>
<th>Subphase [wt-% F127]</th>
<th>(d_\text{ad} [\text{Å}])</th>
<th>(N_\text{Bd,ad} [10^{-6} \text{ Å}^2])</th>
<th>(N_\text{Bd,sub} [10^{-6} \text{ Å}^2])</th>
<th>(\Gamma [\text{mg/m}^2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>39 ± 6</td>
<td>6.09 ± 0.05</td>
<td>6.36 ± 0.09</td>
<td>0.18 ± 0.09</td>
</tr>
<tr>
<td>1.0</td>
<td>106 ± 6</td>
<td>6.16 ± 0.06</td>
<td>6.30 ± 0.16</td>
<td>0.26 ± 0.16</td>
</tr>
<tr>
<td>5.0</td>
<td>48 ± 48</td>
<td>6.07 ± 0.15</td>
<td>6.05 ± 0.18</td>
<td>-0.02 ± 0.14</td>
</tr>
</tbody>
</table>

\[ \text{Figure 1. Comparison of model 1 with and without F127 adsorption layer for 1 wt-% F127 in D}_2\text{O against the hydrophilic Si/SiO}_2\text{ surface. Although hardly visible by eye the fit improves by a factor of 2 on the presumption of a net F127 adsorption layer (see Table 1 for details).} \]

\[ \text{Figure 2. Neutron reflectivity of the Si/d-PS/liquid interface after successive, stepwise increase of the bulk F127 concentration as stated in the legend. For details see text.} \]
Absorption of vapours in thin self-assembled composite films

Self-assembled films of organically encapsulated metal nanoparticles have gained considerable attention due to their optical and electronic properties. These films change their properties upon exposure to vapours of organic and inorganic solvents. Previous studies have shown that the interplay between the film swelling, the diffusion of the analyte in the film and the interaction of the analyte with active sites in the film interior determine the film response. Neutron reflectivity (NR) is a suitable method for investigating such films because it can provide information about these contributions to the response process in a single experiment. The aim of the investigation was to demonstrate the ability of the NR method to get information about the change of the properties of the film exposed to different analytes.

Two Au-nanoparticle/organic composite films prepared via layer-by-layer self-assembly on glass substrates were studied. As organic components hydrophilic poly(amidoamine) (PAMAM) and hydrophobic hexadecane dithiol (HDT) were used. The measurements were carried out in dry N2 and in saturated vapours of D2O and d8-toluene. The reflectivity curves for the PAMAM sample are presented in Fig.1. Upon exposure to analyte vapours the reflectivity from the film increases, indicating penetration of the analyte in the film. Preliminary fits show that the swelling of the film is only minor. The curve in dry N2 is fitted with a single box model, while the curves in presence of D2O and d8-toluene could be fitted with three-box model, showing complex distribution of the analyte in the film. The differences between the runs show slow kinetics of analyte uptake. The kinetic experiments were conducted with D2O (Fig.2) and show that constant reflectivity (we attribute this to equilibrium absorption) is reached after 4 hours.

Because of the time limit less experiments were performed with the Au/HDT sample. The reflectivity curves for this film obtained in lab air and d8-toluene are shown in Fig. 3. It is seen that the analyte absorbs in the film, which leads to effect similar to that of the Au/PAMAM sample. Here, however, the effect is less pronounced. Possible explanation is that the film was not dried before the experiment.
EXPERIMENTAL REPORT

Self-assembly of fullerene-containing in solutions.

Principal Proposer: V.T. Lebedev, Petersburg Nuclear Physics Institute, Gatchina, St. Petersburg dist., Russia
Experimental Team: Gy. Torok, Research Institute for Solid State Physics, Budapest
A. Len, Research Institute for Solid State Physics, Budapest
E. Yu. Melenevskaya, L. V. Vinogradova, V. N. Zgonnik, Institute of Macromolecular Compounds, St. Petersburg

Date(s) of Experiment: 3.06 - 15.06.2002

Date of Report: 30.10.2002

The hydration of novel Poly(N-vinylpyrrolidone)-Tetraphenylporphyrin-C60-complexes [1] has been studied. The dry complexes contained the PVP (mass M=10^4), and a constant amount of TPP (C TPP=2%wt.). Doping the PVP+TPP-complexes with C60, we recognised the evolution of their structures in D2O (20°C, content C P=1%wt.) from mass fractals, dimension D M~2.3 at C=0 % wt., to other fractals (surface dimension D S~2.8 at C≈2 % wt.), and again to mass fractals, D M(C)~2.8 at C≈5%wt.(Fig.1). At C60 amounts, C F< C*~1% wt., the triple complex does not show any qualitative difference from a double compound forming chain-like structures. Above the threshold C>C*, the complexes are associated in compact clusters ~40nm. This shrinking of associates (~1000 nm) resembles a collapse of polymers. The over doped complex (C~5%wt.), behaves like a compound below C' (the influence of C60 on water).

Polymer-fullerene interaction leads to structural peculiarities in solutions of stars (PS)6C60 with poly(styrene) arms (PS), dimers (PS)kC60-Si-(CH3)3-C60/PS)k and hybrids with six paired arms of PS and PTBMA (poly(tertbutylmethacrylate))[2]. At q=1-5 nm^-1 the stars showed the scattering law I(q)~q^-D1 where D1=1.35±0.03 in (PS)6C60, D p =1.26±0.04 in hybrids, and D h=1.07±0.04 in dimers. Such twin core effect testifies the donor-acceptor fullerene-polymer interaction. The strained arms provide a strong dimers' clustering in toluene (q=0.001-0.1 nm^-3, fractals, dimension D~2.7-2.9, size~300nm, ~10^8 molecules). At concentrations 1-6 % wt. the single-core stars are only slightly associated (~10-80 molecules). The stars' self-assembly is mainly dependent on C60 nor the number and arms' length.

Phosphocholine cytidylyltransferase (CT) is regulated by binding to lipid membranes, but the precise structural details of CT’s interaction with different lipid membranes are not known. The depth of insertion and orientation of the amphipathic helical membrane-binding domain (domain M) of CT within a membrane appears to be crucial to CT activation. For this reason, our aim was to measure the interactions of full-length domain M peptides, each containing a specific deuterated amino acid, with bilayers containing known lipid regulators of CT. This information would be vital to our understanding of the mechanism of lipid activation of CT, and may also provide more general insight into the regulation of amphitropic proteins by membrane binding.

Having already completed measurements on undeuterated domain M peptide with stacked bilayers in December 2000, we used the same protocols to study the bilayer location of deuterium label on specifically domain M peptide in bilayers comprising pure DOPC, or DOPC/DOPG at equimolar ratios. The peptide, CTd285, was deuterated at the position corresponding to residue number 285 in the intact protein.

Data analysis involved phasing the observed structure factors, using a combined isomorphous replacement and swelling series method, previously developed by us for neutron studies. The difference method was then used to locate the label sites with Å resolution. The figure shows the results of this process. Future studies with peptides deuterated at other sites will enable us to determine the exact location and orientation of domain M of CT, using a protocol previously developed by us (Bradshaw et al., 2000).

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The initially proposed microparticle polymer system was omitted in the course of the investigations and instead, another potential porous drug release system was chosen that consist of a cubic lipid phase. Different from the amorphous polymer system, the cubic one forms spontaneously by self assembly of the lipid monoolein in water. It consists of a liquid bilayer phase and two unconnected water channels, at least in the defect/free ideal cubic conformation. By the way it may serve to as a diffusion controlled release system for hydrophilic and also for hydrophobic drugs which is an advantage as compared to the polymer system: here, the drug had to be water soluble. Moreover, the test experiments (see proposal, e.g.) gave evidence of only small pores, maybe unconnected. This is most inconvenient for the intended purpose. This is different for the newly chosen system that may even allow the combined administration of two well established anti-cancer drugs, namely the water soluble carboplatin (Cp) and also the membrane soluble taxol (Tx). The lipid drug container is formed off-corporal and then implanted in large mm size volumes directly into the cancerous tissue (breast) or placed nearby a tumor (brain).

For the experiments, a mixed lipid system consisting of MO and 5% MPEG-DSPPE is used. X-ray diffraction (PhD thesis R. Schlüter, Univ. Dortmund) showed that the use of up to 5% MPEG-DSPPE causes a shift into the cubic Im3m structure whereas the PEG free system of MO only exhibits Pn3m. At these low concentrations, the headgroup-PEGylated lipids (known already from “stealth” liposomes) shield the particle surfaces from immune system attacks without a breakdown of the inner cubic structure of the particles.

In the neutron diffraction experiments, the water (D2O) channel system structure, and the effect of the drugs thereupon, was investigated at 30°C in about mm size droplets of lipid cubic phase. The result (fig.1) reveals a slight 4% increase of the cubic lattice parameter a in the presence of both taxol and carboplatin from ~96Å to ~100Å. The simultaneous presence of equal amounts (2.5mg) of Tx and also Cp had no further effect. The details of the phase diagram must be further investigated, but as yet the MO cubic seems to be a promising drug carrier for a diffusion limited slow release system.

![Fig. 1 : effect of drug molecules (Cp, Tx) admixture to the cubic phase of MO (monoolein) – MPEG-DSPPE( monitor normalized intensity )](image-url)
Two large membrane protein complexes the photosystems I (PS I) and II (PS II) catalyse the conversion of light energy from the sun into chemical energy. They capture light and transform the solar energy to a charge separated state. Knowledge of the structure and function of these native biological systems will be the basis of development of stable artificial photosystems, which could provide a powerful tool for solving the energy problems of civilization.

Photosystem I is present in the membranes as a trimer, with a molar mass of more than 1000 kDa. Trimeric PSI from the thermophilic cyanobacterium Synechococcus elongatus is crystallized by dialysis against low ionic strength. Crystals are dark green hexagonal needles with a diameter of 0.5-0.8 mm and a length of 1-2 mm.

To study the structure of water and detergent within the crystals we are conducting a series of low resolution neutron diffraction experiments with the DB21 facility at ILL and the Membrane Diffractometer V1 at HMI. We rotated the crystals parallel or perpendicular to the c-axis at different H2O/D2O contrast. Due to limitations of the experimental set-up in Grenoble at the four circle diffractometer DB21 we extended the measurements of the data sets to 0 < 2θ < 20° in the parallel orientation using the Membrane Diffractometer at HMI. For this purpose we constructed a special small quarz container to be able to orient the crystal with its c-axis parallel to the primary neutron beam. With a quarz capillary usually used, this orientation cannot be achieved. The beam time was used to complete a data set at a contrast of 100% D2O with a stepwidth in 2θ of 0.25°.

Combination of the data collected at HMI and ILL allows us now to start structure determination of the detergent phase within the PS I crystals. A program written by Judith Peters (HMI) is used to determine the angular position and the integrated intensity of a Bragg peak measured with the area detector of the Membrane Diffractometer.

Fig 1: Diffraction pattern of PS1 crystals at 0° between c-axis and neutron beam.
The Influence of NK-2 on the Lamellar Structure of POPE and POPG

In 1999 the Director of the National Center for Infectious Diseases (NCID) J.M. Hughes stated that: 'Infectious diseases are the leading cause of world-wide and third leading cause of death in the United States'. This is due to the fact that bacteria develop an increasing resistance against antibiotics. Therefore either new antibiotics working on the classical principle of receptor induced reaction/destruction of the bacteria have to be developed. The other possible way is to think of new antibiotics which act directly on the pathogen cell membrane without involving protein receptors. To this class peptide antibiotics belong. They destroy the target membrane within minutes by physically reacting with the lipids. Their mode of action so far is not understood.

In previous measurements we localized the peptide NK-2 in multilamellar layers of POPE and POPG (80:20). The peptide NK-2 was derived from NK-lysin, an antibacterial and cytotoxic protein, which was isolated from porcine NK-cells.

During the data analysis it became obvious that the buffer conditions (either water or 10 mM sodium-phosphate buffer, pH 7.4) do influence the formation of the multilamellar layers. Furthermore we detected diffraction peaks which were doubled (see Report: Investigation of the Demixing of POPE and POPG multilamellar layers). Therefore we started to investigate the influence of the peptide on single lipid membranes composed of POPE or POPG. In each case a molar ratio of 1:100 (peptide:l lipid) was prepared. The samples were measured at three different contrast condition (100% D$_2$O, 50% D$_2$O, 100% H$_2$O, 98% humidity). The peptide was used in its native protonated form (results not shown here) and with partially deuterated amino acids at the position isoleucine-2 [I$_2$d] and leucine-23 [L$_{23}$d].

As can be seen in figure 1 the peptide does not change the repeat distance of the POPE membrane stack.

This is different for POPG membranes were a small decrease of the repeat distance can be found (figure 2).

In comparison with a mixed membrane of POPE-POPG(80:20) we see a small decrease upon addition of NK-2 also for the POPE contribution of the diffraction pattern (See HMI User-report 2001, BIO-01-998).
Membrane binding of a doubly lipid-modified heptapeptide from the C-terminus of the human N-ras protein was studied by Fourier transformed infrared, solid-state NMR, and neutron diffraction spectroscopy. The 16:0 peptide chains insert well into the DMPC phospholipid matrix. This is indicated by a common main phase transition temperature of 21.5°C for both the lipid and peptide chains as revealed by FTIR measurements. Further, 2H NMR indicates that peptide and lipid chains have approximately the same chain length in the liquid crystalline state. This is achieved by a much lower order parameter of the 16:0 peptide chains compared to the 14:0 phospholipid chains. Finally, proton/deuterium contrast variation of neutron diffraction experiments indicate that peptide chains are localized in the membrane interior analogous to the phospholipid chains.

In agreement with this model of peptide chain insertion, the peptide part is localized at the lipid-water interface of the membrane. This is supported by 1H nuclear Overhauser enhancement spectra recorded under magic angle spinning conditions. Quantitative crosspeak analysis allows the examination of the average location of the peptide backbone and side chains with respect to the membrane. While the backbone shows the strongest cross-relaxation rates with the phospholipid glycerol, the hydrophobic side chains of the peptide insert deeper into the membrane interior. This is supported by neutron experiments that reveal a peptide distribution in the lipid water interface of the membrane. Concurring with these experimental findings, the amide protons of the peptide show strong water exchange as seen in NMR and FTIR measurements. No indications for a hydrogen bonded secondary structure of the peptide backbone are found.

Therefore, membrane binding of the C-terminus of the N-ras protein is mainly due to lipid chain insertion but also supported by interactions between hydrophobic side chains and the lipid membrane. The peptide assumes a mobile and disordered conformation in the membrane. Since the C-terminus of the soluble part of the ras protein is also disordered, we hypothesize that our model for membrane binding of the ras peptide realistically describes the membrane binding of the lipidated C-terminus of the active ras protein.

Abstract from:

Membrane Insertion of a Lipidated ras Peptide Studied by FTIR, Solidstate NMR, and Neutron Diffraction Spectroscopy

Daniel Huster, Alexander Vogel, Catherine Katzka, Holger A. Scheidt, Hans Binder, Silvia Dante, Thomas Gutberlet, Olaf Zschörnig, Herbert Waldmann, and Klaus Arnold

**Introduction**

Bioenergetic cellular membranes maintain proton gradients for energy transduction. A leakage of protons through these membranes are only balanced by additional energetic costs. Isoprenes, such as squalene, are known to function as proton leakage inhibitors, but localizing these groups in lipid membranes by different physical methods has not been trivial and led to contradictory results. We employed neutron diffraction on lipid bilayers with protonated and deuterated squalane (the saturated isomer of squalene) to find an unambiguous answer to this question.

**Experiment and Results**

Perdeuterated squalane (2,6,10,15,19,23-hexamethyltetrasacane-d$_{62}$) was purchased from CDN Isotopes. Protonated squalane was obtained from Aldrich. 1,2-dioleoylphosphatidylcholine (DPC) and the net negatively charged lipid 1,2-dioleoylphosphatidylglycerol (DPG) were products of Avanti Polar Lipid. Two chloroform solutions containing DPC/DPG 90:10 w/w and 10% molar squalane, either protonated or deuterated, were prepared. The total lipid weight was 20 mg.

Oriented samples were obtained by spraying the solutions on quartz slides (5 mm x 15 mm x 0.3 mm). Traces of the solvent were removed by placing the slides in a vacuum dessicator for 12 h (p < 1 mbar). Samples were then rehydrated for 24 h at room temperature in an atmosphere of 98% relative humidity, maintained with a saturated K$_2$SO$_4$ solution. Neutron diffraction measurements were carried out on the membrane diffractometer 1. The samples containing protonated and deuterated squalane were placed in thermostated aluminum cans, in which the humidity was controlled by aqueous saturated solutions of K$_2$SO$_4$ kept in Te on reservoirs. Contrast variation was achieved by adjusting the atmosphere in the sample can to three different compositions of D$_2$ :H$_2$ (i.e., 50:50, 20:80 and 8:92). Diffraction intensities were measured at T = 27 C with rocking scans. Up to 6 orders were detected for each sample. A mosaicity inferior to 0.5 degrees was a proof of the excellent quality of the samples. Di ffraction patterns of DPC/DPG bilayers containing 10% (mol) of deuterated and protonated squalane were measured (Fig.1) at a neutron wavelength of 4.53 Å.

![Figure 1: Measured diffraction patterns of DPC/DPG lipid membranes with protonated (solid line) and deuterated (dotted line) squalane at different D$_2$ :H$_2$ ratios.](image-url)
Investigation of the Demixing of POPE and POPG multilamellar layers

The development of new antibiotics will become a very important field of research in the near future since the increasing resistance of pathogenic bacteria against antibiotics is a severe problem in health care. A possible approach is the use of natural antimicrobial peptides and derivatives thereof. In contrast to classical antibiotics where a protein receptor is needed, these peptides act by direct physical destabilization of the target cell membrane. Nevertheless, they exhibit a high specificity for bacteria over mammalian cells. However, the precise mechanism of action and the molecular basis for membrane selectivity still is a matter of debate.

In this work we investigate the interaction with the new peptide antibiotic, termed NK-2, with model membranes. During our work with lipid mixtures of POPE (palmitoyl-oleoyl-phosphatidyl-ethanolamine) and POPG (palmitoyl-oleoyl-phosphatidyl-glycerol) in a molar ratio of 80:20 we detected two lamellar phases (figure 1).

In order to understand if the lipid mixture forms simply demix during film preparation we measured model membranes with different molar ratios of the two lipids. The assumption is that the left peak is correlated with POPE and the right peak to POPG which can clearly be concluded from the diffraction pattern (figure 2).

![Diffraction pattern from a POPE:POPG (80:20) model membrane. Small shoulders can be seen on the right hand side of each peak.](image1)

![Comparison of the model membranes consisting of two phospholipids at different concentrations. It can clearly be seen that the peaks are caused by POPE or POPG indicating a demixing of the two lipids.](image2)
The diffusion barrier for most compounds deposited on skin surface is located in the superficial epidermal layer, the stratum corneum (SC), which exhibits a unique architecture similar to a brick-and-mortar assembly with a staggered corneocyte arrangement in a lipid continuum. One of the key elements for SC barrier function is its hydration state. Despite its great importance, the actual mechanism of water-SC interaction is yet unresolved. In this context, the membrane neutron diffraction method has been employed to reveal important SC structural changes that emanate upon water uptake, and provide an insight on the relevant process.

Earlier results that we obtained from V1 (BIO-01-938, November 2000) showed that compared to vapour hydrated samples, upon excess hydration the main diffraction peak was shifted to lower Q values and finally after prolonged exposure the lamellar structure completely vanished. In a next step (BIO-01-1077, November 2001) it was proved that this behaviour is a general trend and not a result of biological variability.

It was the primary aim of the current experiment to further investigate the above observations. A series of measurements on fully hydrated skin samples were performed. The biological variability of SC was again tackled by using several both porcine and human epidermis samples prepared with different methods. 5 in total human and 4 porcine samples, all originating from different donors, were measured. All samples were initially exposed to D$_2$O vapours for different time periods up to 26 h. A special cell which could accommodate a stack of two or three SC layers was used. Each sample was aligned parallel to the beam, and 2? scans were performed, at a wavelength of 0.45 nm.

All samples equilibrated in vapours, exhibited a diffraction peak at Q=0.11Å$^{-1}$, as expected. For one of the human samples this peak was really pronounced, while a weak second order reflection was also observed (curve a in the attached figure).

After the completion of each measurement, liquid D$_2$O was added in situ in the sample cell and a new run was performed with exactly the same as before experimental set-up. Again the behaviour of all specimens was consistent: excess hydration resulted in a smooth diffraction pattern (curve b). In contrast to our previous experiment (BIO-01-1077) where it was possible to monitor the kinetics of the hydration process (the main peak was progressively shifted towards lower Q with exposure time), the quenching of the main peak was now really fast. Nevertheless, the above results prove that the increased SC water content leads indeed to the disruption of the highly ordered lipid configuration and the formation therefore of more fluid and permeable membrane domains, explaining the generally accepted function of water as a very effective natural transdermal penetration enhancer.

Each sample after being removed from the beam was left for sufficient time to reequilibrate in D$_2$O vapours and subsequently was measured again, to reveal that the disappearance of the main peak, and therefore the disruption of the lipid organisation due to excess hydration, is a reversible process. Indeed, the corresponding diffraction patterns (curve c) showed that the main peak was regenerated, although less pronounced and shifted to lower Q values. This remarkable observation is in accordance with the tendency of native skin to restore its mechanical/physicochemical properties after its prolonged exposure to water (during bathing, swimming etc.).
The original experiment proposed was the interaction of phosphocholine cytidylyltransferase (CT) with lipid membranes. However, due to technical difficulties in the synthesis of deuterated CT, it was not possible to perform the allocated experiment so, with the agreement of Dr Hauß, we performed preliminary measurements on mono-methyl dioleoyl phosphatidylcholine (DOPE-me) in the HII phase, as a first step towards resolving a complete 3D structure of this phospholipid. In excess water conditions, the HII phase occurs at temperatures higher than 65°C. To the best of our knowledge, no such study has been performed before. The resolved three dimensional structure of DOPE-me in the HII phase will give insights into the mechanisms of fusion peptides (such as that from HIV) that act upon biological membranes, thereby providing further knowledge of the fusion process. This type of study has only recently become possible, thanks to the efforts of HMI staff in developing and building an "excess-water" sample cell.

Twenty milligrams of DOPE-me were dissolved in chloroform and sprayed onto a rectangular glass slide, using an artist's airbrush. A pre determined amount (147 μl) of H2O/D2O mixture was pipetted onto an excess water cell sample holder, prior to the placement of the glass slide containing the DOPE-me. Four different D2O concentrations (100, 67, 33 & 0 %) were used in order to resolve the structure. The experiment took advantage of the flexibility of the V1 instrument’s detector, such that the detector can be programmed to move in both horizontal and vertical directions. This allowed us to sample a far wider range of reciprocal space than would have been possible with a detector fixed in the vertical direction.

Each sample was run for a total of approximately four days. The first 36 hours were run at 25°C with the detector horizontally in line with the sample. The next 60 hours were combined low and high runs. Low runs were completely aligned along the horizontal axis with the sample. High runs were set-up by performing another θ – 2θ scan, this time adjusting the DECL parameter to raise and tilt the detector. A few (vertical) degrees of overlap between the low and high scans were designed to facilitate the task of scaling the data. For the high scans, the detector had a DECL value of 8.5. High runs were carried out only when the HII phase was attained by increasing the water bath temperature to 67°C. Low runs were also carried out on HII phase, in an alternate pattern with high runs. The wavelength utilised was 4.5208 Å and the detector length was 101.78 cms.

The experiments were intended as a pilot study. Once the data have been fully analysed, it should provide a partial three-dimensional structure of the inverted hexagonal phase. Further studies/beam time applications will focus on gathering further data utilizing a similar protocol, in order to build a more complete 3D picture. When a fully resolved 3D structure of the HII phase is obtained, the interaction of fusion peptides on the HII phase will be studied. A similar protocol will be utilised for these studies.
Introduction

Proton gradients across bioenergetic membranes are ubiquitous, as is bilayer proton leakage. A recently proposed model suggested that isoprenes specifically in the center of the lipid bilayer inhibit proton leakage. We have already shown by neutron diffraction [1] that squalane, a polyisoprene with 6 isoprene units, lies predominantly in the bilayer center, parallel to the plane of the membrane. Ubiquinone (CoQ) is the dominant isoprene in the mitochondria and it is known to participate in electron and proton transport. We are exploring the possibility that it also acts as proton leak inhibitor. We have therefore used protonated CoQ and deuterated lipids, in order to localize the isoprenic chains in stacked lipid bilayers by neutron diffraction.

Experiment and Results

Perdeuterated 1,2-dimyristoyl-phosphatidylcholine (DMPC) and 1,2-dimyristoyl-phosphatidylserine (DMPS) were products of Avanti Polar Lipids; coenzyme Q was obtained from Sigma. Chloroform solutions containing perdeuterated DMPC/DMPS 90:10 w/w with and without 10% molar CoQ were sprayed on quartz glass, resulting in oriented stacked lipid layers. A third sample containing protonated DMPC and 10% molar CoQ was also prepared. The total lipid weight was 20 mg. Traces of the solvent were removed by overnight dessication at p < 1 mbar. The samples were then placed in thermostated aluminum cans in which the humidity was controlled by aqueous saturated solutions of K2SO4 (98 % rel. humidity) kept in Teflon resevoirs. The measuring temperature was T=25C. The diffraction measurements were performed at different isotopic ratios of the atmosphere, namely 0.5:0.5, 0.2:0.8, 0.08:0.92, 0.1 D2O/H2O. Diffraction patterns were obtained by rocking the samples around the expected Bragg positions. Due to restricted measuring time diffractograms up to the 6th order for each sample were recorded, the total time for each scan being 24 h. Significant differences between the relative integral intensities of the peaks of the samples with and without CoQ were detected. An example is reported in Fig. 1. The reconstruction of the membrane profile via Fourier synthesis of the spectra is currently carried on. As a continuation of this experiment, we plan to investigate samples containing protonated lipids and selectively deuterated CoQ. For this purpose an n-decyl derivative of ubiquinone with 6 deuterons on the quinone moiety will be synthesized and will be available by the end of 2002.


Figure 1: Diffraction patterns of a pure lipid membrane (top) and of a lipid membrane containing 10% molar CoQ (bottom), in atmosphere of 100% D2O
**Introduction**

In previous neutron diffraction investigations, we were able to locate a selectively deuterated β-amyloid peptide in membranes of different lipid composition [1]. We had also started to investigate samples with a high amount of cholesterol (40% molar). In the current measurements, we have extended our study to membranes with different cholesterol content, i.e. 10% and 1% molar.

**Experiment and Results**

1-palmitoyl-2-oleoyl-phosphatidylcholine (POPC) and 1-palmitoyl-2-oleoyl-phosphatidylserine (POPS) were products of Avanti Polar Lipids; cholesterol was obtained from Sigma. As previously described (February and August 2000), two Aβ(25-35) peptides were synthesized, one with protonated and one with deuterated leucine (10 deuterons) in position 24. A choloform solution of palmitoyloleyl phosphatidylcholine (POPC), palmitoyloleyl phosphatidyserine (POPS) and cholesterol was sprayed on quartz slides and then equilibrated at 98% relative humidity. The total lipid amount was 20 mg. Two samples containing 3% (molar) of the peptide, either protonated or deuterated, were prepared as well. In the measurements performed in February 2002, the samples contained 10% molar cholesterol, while in November 2002 the cholesterol content was lowered to 1%. Traces of the solvents were removed by overnight dessication at p < 1 mbar. The samples were then placed in thermostated aluminum cans in which the humidity was controlled by aqueous saturated solutions of K₂SO₄ kept in Teflon reserevoirs. This procedure adjusts the relative humidity to 98%. The measuring temperature was T=25°C. In the presence of cholesterol the samples showed a mosaicity of about 0.2°. The diffraction measurements were performed at different isotopic ratios of the atmosphere, namely 0,5:0,5, 0,2:0,8, 0,08:0,92, 0:1 D₂O/H₂O. Diffraction patterns were obtained by rocking the samples around the expected Bragg positions. The total time for each scan was 24 h. Neutron diffraction spectra showed up to the 6 diffraction orders. The data evaluation to obtain the scattering density profile of the membrane and the localization of the label in the lipid bilayers are currently in progress.


![Figure 1: Diffraction patterns of a lipid membrane containing 1% molar cholesterol with protonated Aβ(25-35), in atmosphere of 98% H₂O](image)
We performed an inelastic and quasielastic neutron scattering investigation on lysozyme solvated with both deuterated glycerol and heavy water. The experiment was performed at the V3 spectrometer with an incident neutron wavelength of 6 Å and an energy resolution of 98µeV. We measured the following lysozyme +deuterated glycerol + heavy water mixtures, as a function of the hydration degree (numbers refer to the relative weight of lysozyme-glycerol-water): 1:1:0, 1:1:0.1, 1:1:0.2, 1:1:0.3, 1:1:0.4, 1:1:0.8. All the samples have been measured at room temperature. The anhydrous sample, 1:1:0, was measured also at 100K to estimate the vibrational contribution. This has been subtracted from the room temperature intensity after a Bose rescaling in order to properly evaluate the only quasielastic signal.

Fig. 1 shows the dynamical structure factor $S(Q,E)$ (in arbitrary units) of the sample 1:1:0 at an average $Q$ value of 1Å⁻¹, after the subtraction of the vibrational contribution. Two quasielastic components are well visible, with widths 0.13 meV and 1.9 meV (HWFM).

The quasielastic intensity increases as a function of the hydration degree. In fact, Fig. 2 shows that the quasielastic signal of the sample 1:1:0.4 is enhanced, but it can be well fitted with two components with the same linewidths as the 1:1:0 sample, i.e. the same characteristic times. These results suggest that hydration promotes protein internal diffusive motions on the picosecond timescales.

The analysis as a function of $Q$ of the spectra indicates that such motions are confined. The interpretation of the data as a function of both $Q$ and hydration is still under progress. We remark that, due to a reactor shutdown of 36 hours, we could not measure at all samples at high energy resolution.
The method of elastic resolution spectroscopy was tested using alanine dipeptide and dehydrated lactalbumin with and without Calcium bound. The dipeptide crystals served as a test system to determine the rotation of the methyl groups, which were measured previously using the conventional method. These results were compared to similar motions in dehydrated lactalbumin. The energy resolution was varied between 4 and 450 micro eV. The very important technical result was that the different frames corresponding to different experimental parameters (chopper speed and wavelength) could be superimposed without contamination of background artefacts. Changing the chopper speed between 1000 and 15000 rpm did not give rise to major problems, the system was stable and worked very well. With the peptide we observe a fast initial decay in the intermediate scattering function due to methyl group rotation and a slower process due to a new structural transition in the crystal. This is consistent with previous results of the conventional method. The sample holder needs to be improved. It was not suitable for hydrated or liquid samples (leakage) and an ill positioned Cadmium mask cut out a significant fraction of the Q-range. These deficiencies were not anticipated and can be removed in the next attempt.
Photosynthetic water cleavage takes place in a multimeric membrane-bound protein complex referred to as photosystem II (PS II). The overall reaction pattern comprises three reaction sequences: (i) light-induced generation of a radical ion pair of high oxidizing and moderate reducing power; (ii) water oxidation to molecular oxygen along with proton release, and (iii) plastoquinone reduction to plastoquinol (for a review see ref. 1).

The reaction pattern of PS II is characterized by a high degree of specific coupling between structural dynamics and function. Among the different modes of coupling, hydrogen-bond networks play a key role in controlled electron and proton transfer reactions. In addition to specific amino acid residues, bound-water molecules are of central relevance for the substrate pathway of water oxidation itself and also for other reactions. It is therefore understandable that e.g. dehydration of the sample may cause marked changes in the reaction pattern. Recent findings revealed that below a certain degree of sample hydration, PS II redox reactions become progressively blocked (2,3).

As a consequence of the above mentioned results the question arises whether the change in functionality of PS II with hydration degree can be correlated with the microscopic dynamical properties of the hydration water molecules. Due to the large incoherent scattering cross section of hydrogen, quasielastic incoherent neutron scattering (QENS) experiments are perfectly suited to study diffusive motions of hydration water in biological membranes (see e.g. ref. 4).

In the present study, PS II membrane fragments were equilibrated using H2O vapors of several well-defined relative humidity (r.h.) values between 22 and 95 %. Quasielastic neutron scattering (QENS) experiments were carried out using an incident neutron wavelength of 5.1 Å (~3.2 meV) and two elastic energy resolutions of 65 and 93 µeV, respectively.

As shown in Fig. 1, the QENS spectra reveal a clear broadening with increasing hydration degree. A detailed analysis of the latter effect is currently in progress (5).

Figure 1
QENS spectra of PS II obtained with an incident neutron wavelength of 5.1 Å and an elastic energy resolution of 93 µeV at 300 K.

References:
5. Pieper, J.; Renger, G.; Lechner, R.E., to be published
Photosynthesis is the fundamental physiological process in nature that permits the transformation of solar radiation into storable chemical energy. In most general form, this photochemical process of all oxygen evolving photoautotrophic organisms (cyanobacteria, algae and green plants) can be described by the equation:

\[
\text{nH}_2\text{O} + \text{nCO}_2 \rightarrow (\text{CH}_2\text{O})_n + \text{nO}_2.
\]

It represents the overall reaction of the light-induced cleavage of water and fixation of carbon by formation of a carbohydrate \((\text{CH}_2\text{O})_n\) under the release of oxygen. The key steps in photosynthetic water cleavage take place in a multimeric membrane-bound protein complex referred to as Photosystem II (PS II) (for a review see ref. 1). The reaction pattern of PS II is characterized by a high degree of specific coupling between structural dynamics and function. Correlations between protein flexibility and electron transfer in PSII have already been observed in a study combining Mössbauer spectroscopy and measurements of flash-induced changes of fluorescence quantum yield as a function of temperature (2). Recent time-resolved absorption studies revealed that PS II redox reactions exhibit a pronounced dependence on the relative humidity of the sample (3).

The aim of the present study was to investigate the protein flexibility in PSII as a function of hydration degree. Thus, PS II membrane fragments were hydrated with D\(_2\)O and equilibrated using D\(_2\)O vapors of several well-defined relative humidity values (r.h.) between 22 and 75 %. Quasielastic neutron scattering (QENS) experiments were carried out using an incident neutron wavelength of 5.1 Å (~3.2 meV) and two elastic energy resolutions of 65 and 93 µeV, respectively.

In order to phenomenologically account for protein flexibility, the low-resolution data were fit with a model for an isotropic rotation on a sphere. Here, the rotational diffusion coefficient was the only free parameter while the radius of rotation was kept constant for all r.h. values. As shown in Fig. 1, the rotational diffusion coefficient (full line) clearly increases with increasing water content of PSII (full squares). Thus, there seems to be a clear correlation between protein flexibility and hydration degree of PSII (4).

![Figure 1](image)

**Figure 1**
The normalized rotational diffusion coefficient \(D_{\text{rot}}\) (full line) and the normalized weight increase of PSII samples (full squares) are shown as a function of r.h.. See text for details on QENS experiments and fit procedure.

**References:**
4. Pieper, J.; Renger, G.; Lechner, R.E., to be published
The pigment-protein complex LHC II is the major antenna complex of green plants. Its function is to absorb light in a broad spectral range as well as to efficiently transfer excitation energy to reaction center complexes, where the photochemical processes of photosynthesis take place. The coupling of purely electronic transitions of pigments to low-frequency vibrational modes of the protein matrix is of great importance for light absorption and excitation energy transfer in antenna complexes. So far, electron-vibrational coupling has been primarily studied by optical spectroscopy. In the case of LHC II, however, hole-burning (HB) and fluorescence line-narrowing (FLN) experiments yielded contradictory results [1].

In the present experiment solubilized LHC II was studied at temperatures of 40 and 80 K by inelastic neutron scattering (INS). According to [2], two different incident neutron wavelengths of 2.0 (~20 meV) and 5.1 Å (~3.2 meV) were chosen in order to measure INS spectra for energy gain and energy loss of the neutron at each temperature. The corresponding elastic energy resolutions were 921 and 93 µeV, respectively.

LHC II complexes were solubilized in a D₂O-containing buffer solution, so that the contribution of the solvent had to be determined by separate experiments. Figure 1 shows INS spectra of solubilized LHC II (upper full line) and buffer solution (dashed line) obtained with an incident neutron wavelength of 2Å at 80 K. The former and latter spectra exhibit apparently different shapes with maxima at about 2.5 and 6 meV, respectively. Complementary data for an incident neutron wavelength of 5.1 Å and 80 K are shown in Fig. 2. The density of vibrational states of LHCII will be calculated from the Q- and T-dependence of the acquired INS data and compared to results of optical spectroscopy [3].

References:
3. Pieper, J.; Irrgang, K.-D.; Renger, G.; Lechner, R.E., to be published
EXPERIMENTAL REPORT
Geometric and hydration parameters of unilamellar Vesicles composed of lipid/detergent mixture (POPC/C\(_{12}\)E\(_5\))

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Date(s) of Experiment
2002-7-8 to 2002-7-12

Date of Report: 2003-01-15

Vesicles of lipid/detergent mixtures orient under the influence of sufficiently strong magnetic fields where the original spherical shape of vesicles is deformed according to NMR [1]. The authors also derive indirectly the vesicle shape and the orientation of the deformed vesicles with respect to the applied field from NMR line shape.

Our work aims to determine the structural parameters of the vesicle shape such as size and half axes as well as of the vesicle forming membrane (thickness of the water-free core and of the outer water-accessible parts) and simultaneously of the hydration applying a recently developed new method of evaluating SANS curves [2]. It uses a multi-strip model with only three independent parameters.

Three different D\(_2\)O dispersions of C\(_{12}\)E\(_5\)/POPC (molar ratio 0.6) vesicles (concentration 10 mg/ml) with mean vesicle diameters of 100, 200, and 400 nm as well as three D\(_2\)O dispersions of pure POPC vesicles with the same diameters as references were prepared by extrusion procedure (30 extrusions) and their small angle neutron scattering was measured under different magnetic fields (0, 1.5, 2.24, and 5 T) at 25° C. Two mean scattering curves of 400 nm vesicles measured under B = 0 and 5 T are represented in Fig 1 as examples.

The measurements performed can be considered only as a first attempt. Firstly, we had to use the circular aluminium cuvettes instead of the quartz cuvettes because the latter cracked during inserting the sample holder with the sample into the magnet due to freezing of the water dispersions. Secondly, the influence of the magnetic field seems to be much smaller as expected according to [3]. Before repeating the measurements the construction of the sample holder must be changed for a better temperature control and it must be clarified why we found only a small influence of the magnetic field onto the scattering in contrast to [3].

Reference:
Introduction
MEs are of special interest because a variety of reactants can be introduced into the nanometer-sized aqueous domains, leading to materials with controlled size and shape [1]. In the past few years, significant research has been conducted in the reverse ME-mediated synthesis of organic nanoparticles [2]. In this study, a W/O ME medium was employed for the synthesis of lidocaine. The interest of these organic nanoparticles lies in their pharmaceutical application as model drug delivery system. SANS is good technique to elucidate the structure and particle size as well as the location of nanoparticles in the ME droplet [3].

Experiments
The W/O MEs was prepared containing H₂O or D₂O (5 wt%), Isopropylpalmitat (IPP, 75 wt%), and a blend of high HLB Tween80 and low HLB Span80 surfactant (20%). Different wt% of organic molecule of lidocaine hydrochloride are added to the W/O MEs.

Results and Discussion
The maximum amount of the active organic compound that can be added to the W/O MEs is 1 wt%. The W/O ME is destabilized (phase separation occurs), when the concentration increases more than 1 wt%. In this study, we investigated three samples, basic W/O ME, MEs with 0.25 wt% and 0.75 wt% of active organic compound. Fig. 1 shows the obtained SANS curve from basic W/O ME and W/O MEs with different concentration of active organic compound. Scattering curves indicate that organic compound form the nanoparticles in aqueous core. Since, with increasing lidocaine concentration, the scattering intensity decreases due to direct precipitation of organic compound into the heavy water core.

![Fig. 1 Measured SANS curves for different MEs.](image)

The nanoparticle size does not significantly change as a function of the concentration of active organic compound, \( R = \sqrt[3]{5} R_g = 5.8 \) nm, in the agreement with results published in [2]. More detailed data analyses are in progress now.

References
Many neurodegenerative diseases are characterized by presence of amyloid plaque consisting of insoluble fibrils. The major component of Amyloid plaque found in the brain of patients with Alzheimer disease is a 39 to 43-amino-acid residues β-amyloid peptide (Aβ) derived from trans membrane amyloid precursor protein (APP). Normally this peptide exists in monomeric or dimeric form in cerebrospinal fluid. During aging the peptide aggregates into β-sheet containing fibrils. Since Aβ has a trans membrane and an extra cellular part of APP, interactions with phospholipid membranes could play an important role for Aβ folding and toxicity [1].

Neutron reflectometry was used to provide more information about thickness of adsorbed peptide layer and possible changes in lipid bilayer upon adsorption. To improve the reflectivity signal we used adsorption of amyloid on polymer cushioned lipid bilayers. Polyelectrolyte (PE) films was used as a support for lipid membranes [2,3,4]. The PE films consist of PEI and 6 bilayers PSS/PAH deposited on the silicon wafer by self-assembly technique. The thickness of PE layer against D2O is 300 Å. The successful deposition of a lipid bilayer from vesicle solutions was shown previously [Estrela-Lopis at al Experimental Report, HMI, 2001].

In the present work we studied the adsorption of the negatively charged lipid POPS onto PE cushion. The reflectivity curves for bare cushion and after the deposition of the lipid are shown in Fig. 1. The shift of the minimum position of the Kiessig fringes in the reflectivity spectra shows an increasing thickness. The results were fitted using the Parratt program and a thickness of 53 Å was obtained for the adsorbed lipid layer. This indicates formation of hydrated bilayer at the PE support with a similar scattering length density of 4.2*10^-6 Å^-2 against D2O. We performed measurements in the present of lipid vesicles and after flushing with D2O. A small difference is observed. We suppose is due to addition weak bounding of vesicles to the bilayer. Further addition of amyloid almost does not change the reflectivity signal (Fig. 2). However the small shift of the position of the Kissing fringes can be explained by peptide adsorption. Unfortunately the layer of the peptide is too thin (∼10 Å) and this increasing of thickness is in the range of the error of the fitting procedure. Either the peptide forms a very thin layer or concentration of peptide is too low.

![Image of reflectivity curves](image1.png)

**Fig. 1:** Neutron reflectivity curves of PE layers in D2O and with adsorbed d31-POPS bilayer in the presence of vesicle and after rinsing.

![Image of reflectivity curves](image2.png)

**Fig. 2:** Neutron reflectivity curves of d31-POPS bilayer adsorbed on PE layers in pure D2O and the presence of Aβ.

### Literature


The adsorption of a protein at an aqueous-solid interface is a frequently observed phenomenon that can be explained by both enthalpic and entropic driving forces. While enthalpic contributions include electrostatic interactions between the protein and the substrate, entropic contributions may arise from conformational changes of the protein molecules or the release of water from hydrophobic surface areas. For example, the adsorption of hen egg white lysozyme at the silica-water interface has been found to be favoured at elevated temperatures, i.e., the adsorption process appears to be entropy-driven [1].

In order to get a deeper understanding of the relative weight of entropic and enthalpic driving forces for the adsorption of proteins at aqueous-solid interfaces, we have performed a neutron reflectivity study of the adsorption of staphylococcal nuclease (SNase) on a poly(styrenesulfonate) (PSS) surface. The substrate was prepared by coating a silicon wafer with layers of poly(ethylenimine) (PEI), poly(allylamine hydrochlorid) (PAH) and PSS as described by Decher [2]. The experiments were performed at different pH-values, temperatures and scattering length densities of the protein solution. Since SNase has an isoelectric point of about 9.5, attractive electrostatic interactions between SNase and the PSS surface are enhanced as the pH-value is lowered. Temperature was varied to find out, if the adsorption process is governed by an enthalpy or entropy increase. The scattering length density of the protein solution was varied by using either pure D$_2$O or a 3:1 D$_2$O/H$_2$O mixture for the preparation of the solution.

In Fig. 1, typical neutron reflectivity curves are shown as obtained in the experiments. In a detailed analysis of the data, global fits of an appropriate structure model to pairs of reflectivity curves differing in contrast will be performed. Here, we present a preliminary analysis of the reflectivity curves with D$_2$O as the solvent using a simple four-layer structure model, Si-polymer-protein-solution. In the following table the amount of SNase adsorbed to the PSS-water interface is given in mg m$^{-2}$ (the solution concentration was 0.05 mg mL$^{-1}$):

<table>
<thead>
<tr>
<th>pH</th>
<th>23 °C</th>
<th>43 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>1.1</td>
<td>1.9</td>
</tr>
<tr>
<td>7.1</td>
<td>2.3</td>
<td>4.1</td>
</tr>
</tbody>
</table>

From the surface concentrations given in the table the following conclusions may be drawn: 1. The degree of protein adsorption is strongly increased with increasing temperature at both pH-values studied, which indicates entropy-driven adsorption processes. 2. The degree of adsorption is strongly decreased with decreasing pH-value at both temperatures studied, although the electrostatic attraction between the protein and the substrate is higher at lower pH-values. This finding indicates that there is a significant protein-protein repulsion within the adsorbate. However, a more detailed data analysis is needed for further interpretations.

Fig. 1. Neutron reflectivity curves of an Si-PEI-PSS-(PAH-PSS)$_n$-D$_2$O interface without (black) and with adsorbed SNase at 23 °C (blue) and 43 °C (orange).

Sugars have a wide occurrence in living organisms. Soluble sugars stabilise cells against desiccation and fusion caused by freezing or freeze-drying. Their action is believed to result from specific interactions between the membrane phospholipids and the polar sugar molecules in the surrounding phase. Results from certain investigations [1-3] show that the addition of sugar leads to an increase in the interlayer distance. At comparatively small concentrations this effect is explained by moderate hydration repulsion between the layers. On further increase of the sugar concentration an enormous increase in the lamellar spacing is obtained which is attributed to double layer electrostatic or swelling effects. The aim of our present study was to investigate the strength of interaction between lipid bilayers and Si substrates in the absence and presence of sucrose. These experiments could show the active centres where the binding of sugars occurs.

The measurements were performed using the solid/liquid experimental cell for neutron reflectivity [4] at V6. Protonated DMPC was used as model lipid. It was deposited at the surface of the Si blocks by self-assembling from suspensions of DMPC in D$_2$O with concentration 1 mg/ml. Two different Si blocks were used. The first one was exposed to the lipid suspension in D$_2$O. The second Si block was exposed to the same lipid suspension but in presence of 0.5 M sucrose. After 20 min the suspensions were washed out from the cell (H$_2$O, Milli-Q water). Reflectivity curves were collected against pure D$_2$O. The temperature was kept constant at 30 °C, which is above the temperature of the main phase transition of the lipid.

In Fig. 1 the reflectivity curves obtained from the experiments are presented. In case of the DMPC suspension in D$_2$O the curve was successfully fitted using a two layer model. This shows formation of a lipid layer with a thickness of ~45 Å separated from the Si substrate by a layer of D$_2$O with a thickness of ~13 Å. The obtained thickness of the lipid layer proofs the formation of a single lipid bilayer.

In the presence of 0.5 M sucrose the reflectivity curve changed. The obtained curve was successfully fitted with a two layer model. Here the thickness of the lipid bilayer remained constant, but a small increase of the thickness of the D$_2$O layer, which separates the lipid from the Si substrate, from ~13 Å to ~17 Å was observed. This increase is in a line with literature results [1,3] which show increase in inter-lamellar distances in concentrated lipid suspensions although the increase is much smaller than that reported. An interesting point is the maximum present in the reflectivity curve at Q around 0.09 Å$^{-2}$. It may indicate the presence of adsorbed multi-lamellar vesicles at the Si substrate in co-existence with the deposited single lipid bilayer. To evaluate the complete reflectivity curves of the deposited lipid structures further studies at enlarged Q range are necessary.

From neutron diffraction studies on the interaction of the neurotoxic β-amyloid peptide Aβ (25-35) with stacked lipid multilayers we were able to locate the C-terminus of the peptide in the core of the phospholipid bilayers [1]. To gain further information on the adsorption of Aβ in/on lipid membranes, we conducted also neutron reflectivity experiments on lipid layers obtained via fusion of small unilamellar vesicles to a polymer-coated substrate. This method seemed to be particularly appealing, because under optimum conditions, a hybrid biomembrane, consisting of a polymer adsorbed lipid monolayer, resembling a soft membrane surface with an aqueous interface, and a single free floating lipid bilayer in the fluid state should be obtained. While a first lipid monolayer (d-DMPC) formed spontaneously, the additional free floating bilayer could not be established [2]. When exposed to Aβ in D₂O the peptide adsorbed rather than penetrated the lipid layer. The discrepancy to the results as obtained from the multilayer stacks demanded clarification. Therefore, we performed further neutron reflectivity experiments on polymer supported lipid layers where the emphasis was put on the preparation of supported lipid layers with different surface densities.

As a model system we chose d-DMPC (d67) spread from diluted solution in CHCl₃ on the aqueous subphase of the Teflon trough of the flow cell for neutron reflectivity investigations. Different surface densities of the lipid layers were achieved by spreading different total amounts of lipid to different surface pressures of the films (10 mN/m; 30 mN/m and 42 mN/m). The monolayers were then transferred to pre-prepared thin films of deuterated polystyrene (d-PS) on silicon blocks by Langmuir-Schaefer deposition (LS). The LS transfer was also the final step of the assembly of the flow cell for the neutron reflectivity experiments. Sets of 4 measurements, Si/d-PS/air, Si/d-PS/d-DMPC/ D₂O, ..d-DMPC/H₂O, ..d-DMPC/air were conducted to characterise the deposited lipid layers.

Figure 1 shows the neutron reflectivity curves recorded from two lipid layers with different surface densities σ₁ < σ₂ (corresponding to 10 mN/m and 42 mN/m respectively) at the polymer/liquid interface. There is a pronounced left-shift of the Kiessig fringe positions in case of the lipid layer with higher surface density and therefore larger surface pressure. This shift proofs that differences in packing density of the free-floating lipid layers are conserved after transfer to the polymer support. The analysis of the complete data sets revealed that in all cases the lipid layer thickness at the interface against D₂O exceeded monolayer thickness by a factor of 1.6-2. Against H₂O the layer thickness matched monolayer thickness (22 Å). The observations at the polymer/D₂O interface can be linked to current findings at the pure d-PS/D₂O interface where a reduced water density was observed in the liquid boundary layer of 20-50 Å thickness [3]. Presuming this concordance one has to conjecture that the transferred lipid layer does not uniformly cover the underlying polymer support. It seems likely that the lipid layer condenses on the support thus forming a patchwork of lipid covered and free polymer surface. Further experiments are necessary to clarify this point.

First binding studies of Aβ in D₂O to the lipid monolayer transferred at 30 mN/m to the polymer support revealed no peptide adsorption or penetration at all.

Figure 1. Neutron reflectivity curves obtained from the solid/liquid interface of transferred lipid monolayers as indicated in the legend.

BENSC EXPERIMENTAL REPORTS 2001, 170
EXPERIMENTAL REPORT

Proposal N° MAT-01-1098

Instrument E2

Local Contact S.Danilkin

Date(s) of Experiment 14.03-18.03.2002

07.08.2002

The redistribution of twin martensitic domains under constant magnetic field was studied on Ni_{1.99}Mn_{1.14}Ga_{0.87} alloy single crystal. This magnetic-shape memory alloy shows more than 5% strain in magnetic field of 1 T at room temperature. The Curie and phase transformation temperatures in Ni_{1.99}Mn_{1.14}Ga_{0.87} are: $T_C = 368$ K, $A_s = 303.8$ K, $A_f = 305.8$ K, $M_s = 300$ K, $M_f = 298$ K. The unit cell of martensite was determined as orthorhombic 5-layered with $a'=0.421$ nm, $b=0.562$ nm, $c'=2.105$ nm at 296 K [1].

In the experiments we studied the modification of martensitic domain structure by applied magnetic field at temperature from 290 K to 98 K and kinetics of the domain redistribution.

**Experiment.** Measurements were performed with E2 diffractometer at $\lambda = 0.1218$ nm with the single crystalline sample aligned to have (001) plane coinciding with scattering plane. Measurements under magnetic field (0.2-2.5 T) were carried out with vertical cryomagnet.

**Results.** The magnetic field of 0.9 T causes the reversible change in the intensity of martensitic peaks at room temperature. This effect becomes partly non-reversible at temperature 206 K under the magnetic field of 0.7 T. The magnetic field $H=0.5$ T applied at 249K affects markedly the ratio in the peaks intensity. The field value 0.9T causes redistribution in the intensity of (105) and (020) peaks almost completely (Fig. 1a). (Fig. 1a). The magnetic field of 0.2 T applied at temperature 290 K (Fig1b) causes the change in the martensite structure, which is comparable with the effect of applied field of 0.5 T at 249 K. This decrease of the magnetic field needed for the redistribution of the martensitic variants can be explained by enhancement of the twin boundaries mobility at higher temperatures.

The redistribution of martensitic domains with time was observed under the constant magnetic field of 0.5 T (Fig.2). The temperature affects this process strongly. A mechanism of kinetics requires additional study.

**Fig.1** Effect of temperature and magnetic field on the redistribution of the martensitic variants.

**Fig.2** Dependence of intensity of martensite peaks under the constant magnetic field on the time of exposure

References:
Composites with 70 vol.% reinforcement of silicon carbide particles in a cast AlSi metal matrix show high stiffness and strength, low density and low thermal expansion in addition to high thermal conductivity. Problem of this material with respect to its use as base plate material in electronic packaging are residual stresses and inhomogeneities of the microstructure (distribution of silicon carbide particles, porosity) leading to base plate deformation during joining process and/or during ageing of the modules (relaxation processes). This can have influence on lifetime and reliability. For a non-destructive in-situ characterisation of the volume high temperature stress measurements were carried out on differently fabricated samples of different manufacturers and with different thermal histories (Tab.1) using neutron diffraction. Measurements were carried out with a focusing flat Cu(220) monochromator, wavelength 1.3 Å and for shorter measuring times only with a primary collimation of 40°. The cylindrical sample geometry of Ø 4.5 mm x 20 mm defined the gauge volume together with a primary slit system (mask aperture 1.5 x 15 mm² parallel cylinder axis) for good grain statistics. The instrument is equipped with a two-dimensional position sensitive multi wire proportional $^3$He counter (MWPC) (128 x 128 pixel) with a grid distance of 1 mm. It was possible to view an angle range of 8° (2θ) for simultaneous measurements of SiC(202) = 62° and Al(311) = 68° (2θ). Additional equipment for in-situ high temperature measurements was an ellipsoidally focusing mirror oven device. Temperature cycling was carried out from room temperature to 325°C in steps of 25 - 50°C. The strainfree reference material for the Al phase was the AlSi7Mg0.25 matrix alloy and for the SiC phase loose SiC was used.

Fig.1. shows one example of thermal phase stresses as a function of temperature of differently heat treated samples: (a) quenched into liquid nitrogen, (b) slowly cooled in the oven, both after heating for 5 hours at solutionizing temperature. Stress compensation due to the condition of stress balance is given and stresses decrease with increasing temperature. The absolute values of the phase specific stresses do not differ greatly, but at 50°C the stress in the matrix of specimen (a) is higher (stress relation between matrix and SiC = 2:1) than that in (b), where the absolute values of stresses are equal in both components. Obviously no plastic stress relaxation during the temperature cycles of the measurements can be observed. The conditions of both pre-treatments seem to be reproduced. The influence of cooling pre-treatment seems to be not evident for this example.

Table 1. Investigated samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal history</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate P1</td>
<td>500°C/30min/quenched in liq. N₂/150°C/5h</td>
</tr>
<tr>
<td>Plate P1</td>
<td>500°C/30min/slowly cooled</td>
</tr>
<tr>
<td>Plate P1</td>
<td>500°C/30min/quenched in liq. N₂</td>
</tr>
<tr>
<td>Plate P2</td>
<td>535°C/8h/quenching in H₂O/154°C/8h</td>
</tr>
<tr>
<td>Plate P1</td>
<td>as fabricated</td>
</tr>
<tr>
<td>Plate P1</td>
<td>in-situ hardening</td>
</tr>
<tr>
<td>Plate P3</td>
<td>(500°C/30min/quenched in liq. N2/275°C/5h)</td>
</tr>
<tr>
<td>Plate P3</td>
<td>500°C/30min/quenched in liq. N₂</td>
</tr>
<tr>
<td>Plate P3</td>
<td>500°C/30min/slowly cooled</td>
</tr>
</tbody>
</table>

EXPERIMENTAL REPORT

“Residual stress states in a quenched cylinder, -
comparison of calculation, Neutron and X-ray diffraction measurements.”

Principal Proposer: Thomas Hirsch, IWT
Experimental Team: Alexandre da Silva Rocha and T. Hirsch, IWT
Adrian Manescu and T. Poeste, HMI
Rainer Schneider, HMI

Date(s) of Experiment
March 11-14
July 29-August 02, 2002.

Date of Report: January 14, 2003

1 Aims
The present investigation was carried out to compare predicted with experimental values of residual stresses which are generated in an austenitic cylinder by means of a controlled gas-quenching process.

2 Experimental Description
As shown in Figure 1, the residual stress measurements were executed at the middle plane of the cylinder. The lattice distances were measured by means of neutron diffraction for the three main directions (axial, radial and tangential).

The $a_0$ value necessary for the calculations of the lattice strains was determined using three different types of samples: an annealed fine powder from the quenched cylinder, a thin plate (produced by electro-discharge machining and electro-polishing) and the cylinder itself. X-ray diffraction with two different radiations (Cu and Cr-radiation) was employed when measuring the $a_0$ value at the stress-free direction of the cylinder and thin plate and for powder. Besides that the $a_0$ was measured with neutrons in the specific set-up using powder and annealed cubes (3X3X3mm$^3$) manufactured from the cylinder. Finally, the accurately determination of $a_0$ followed the procedure described in [1].

3 Results and Discussion
The $a_0$ found by X-ray diffraction (0.35926nm) was in excellent agreement with the $a_0$ measured in the actual measuring set-up with neutrons (0.35921nm). $a_0$ indicated in reference [2] for austenitic steel with 18%Cr and 12%Ni is 0.35909nm.

Based upon these $a_0$ measurements, figure 2 presents the residual stresses obtained by means of neutron diffraction in comparison with the FEM calculated values. Values of RS measured in the surface by means of X-ray diffraction are also shown.

4 Consequences
The simulation led to lower hoop stresses than measured in deeper sections of the sample. If this “hoop stress effect” can be explained in the near future there seems to be a good agreement of Neutron- and X-ray diffraction measurements and calculation. The proposers will try to optimize the set-up of the sample on the neutron diffractometer by manufacturing a special sample holder.

5 Literature:
EXPERIMENTAL REPORT

Residual stresses analysis on tensile MMC specimens after loading/unloading tests in several conditions.

Proposal N° MAT-01-1167
Instrument E3
Local Contact R. Schneider

Date of Experiment: 25 August-05 September 2002 (E3).
Date of Report: 15 January 2003

Since the 1980s, the automotive and aeronautical industries have shown the feasibility of using particulate reinforced MMC structural components such as rear wheel hubs (automotive application) and stringers and shafts (aeronautical application). The experiment here described have been carried out in a more general research, aiming to develop a set of complementary models to optimise the forming process of these MMC components.

12 specimens were produced from extruded bars of 6061 + 22% Al₂O₃ (fig. 7.1). They were produced with a ZWICK Z100/TL3S machine, following the norm EN10002-1, with speed of 0.033 mm/s and extensiometry. The longitudinal initial dimension is of 20 mm, with a 4 mm thick diameter. For each MMC, tensile tests have been carried out at 2mm/minute loading rate and at different temperatures, typical of those encountered during the forming process. They are listed in the Table 1.

The gauge volume was 4x4x4 mm³ determined by the slit system: 4x4 mm² on the incoming beam and 4x40 mm² on the diffracted beam.

The gauge volume was centred in the geometrical centre of each sample so that the radial and hoop strain were coincident. Thus measurements in only two directions (radial and axial) have been requested (as shown in figure 1).

The unstrained interplanar distance (d₀) of the AA6061 matrix was determined by using a powder obtained from a grinded ingot. The original powder obtained from the supplier was used for the Al₂O₃ reinforcement.

The elastic constants for Al and Al₂O₃ have been taken from the library of the XEC Program (Al: E = 67GPa, ν = 0.35; Al₂O₃: E = 384 GPa, ν = 0.25).

In any case, by centring the gauge volume in the geometrical centre of each sample, the following condition holds:

$$\langle \sigma_{macro} \rangle = \frac{1}{V} \int_{V} \sigma_{macro} dV = 0$$

$$\sigma_{macro} = f\sigma_{tot}^{Al_2O_3} + (1 - f)\sigma_{tot}^{Al}$$

$$\downarrow$$

$$f\langle \sigma_{tot}^{Al_2O_3} \rangle + (1 - f)\langle \sigma_{tot}^{Al} \rangle = 0$$

We assumed the above hypotheses because the specimen section was fully immersed in the beam. This condition was used to check the validity of the obtained results.

<table>
<thead>
<tr>
<th>Sample n.</th>
<th>Temperature for the tensile test</th>
<th>Imposed strain levels (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Room Temperature</td>
<td>0.0%</td>
</tr>
<tr>
<td>2</td>
<td>Room Temperature</td>
<td>0.2%</td>
</tr>
<tr>
<td>3</td>
<td>Room Temperature</td>
<td>0.5%</td>
</tr>
<tr>
<td>4</td>
<td>Room Temperature</td>
<td>0.8%</td>
</tr>
<tr>
<td>5</td>
<td>450°C</td>
<td>0.0%</td>
</tr>
<tr>
<td>6</td>
<td>450°C</td>
<td>0.2%</td>
</tr>
<tr>
<td>7</td>
<td>450°C</td>
<td>0.5%</td>
</tr>
<tr>
<td>8</td>
<td>450°C</td>
<td>0.8%</td>
</tr>
<tr>
<td>9</td>
<td>500°C</td>
<td>0.0%</td>
</tr>
<tr>
<td>10</td>
<td>500°C</td>
<td>0.2%</td>
</tr>
<tr>
<td>11</td>
<td>500°C</td>
<td>0.5%</td>
</tr>
<tr>
<td>12</td>
<td>500°C</td>
<td>0.8%</td>
</tr>
</tbody>
</table>

Table 1. List of the specimens.

The gauge volume was 4x4x4 mm³ determined by the slit system: 4x4 mm² on the incoming beam and 4x40 mm² on the diffracted beam.

The gauge volume was centred in the geometrical centre of each sample so that the radial and hoop strain were coincident. Thus measurements in only two directions (radial and axial) have been requested (as shown in figure 1).

The unstrained interplanar distance (d₀) of the AA6061 matrix was determined by using a powder obtained from a grinded ingot. The original powder obtained from the supplier was used for the Al₂O₃ reinforcement.

The elastic constants for Al and Al₂O₃ have been taken from the library of the XEC Program (Al: E = 67GPa, ν = 0.35; Al₂O₃: E = 384 GPa, ν = 0.25).

In any case, by centring the gauge volume in the geometrical centre of each sample, the following condition holds:

$$\langle \sigma_{macro} \rangle = \frac{1}{V} \int_{V} \sigma_{macro} dV = 0$$

$$\sigma_{macro} = f\sigma_{tot}^{Al_2O_3} + (1 - f)\sigma_{tot}^{Al}$$

$$\downarrow$$

$$f\langle \sigma_{tot}^{Al_2O_3} \rangle + (1 - f)\langle \sigma_{tot}^{Al} \rangle = 0$$

We assumed the above hypotheses because the specimen section was fully immersed in the beam. This condition was used to check the validity of the obtained results.
Through micrographic examination of the 6061 + 22% Al₂O₃ material, a strong texture of both the Al and Al₂O₃ phases in the longitudinal direction (axial direction) was noticed. This is confirmed by data reported in figures 2. In fact fig. 2.a reports the Bragg peak of the (444) reflection of Al₂O₃ in the radial direction after a counting of 90 minutes. Figure 2.b is the Bragg peak of the same reflection in the axial direction after the same counting time: the difference in peak intensity is evident. The same behaviour was detected for some Al peaks.

Thus, the Bragg peaks (400) for Al and (214) for Al₂O₃ were chosen because they were verified to be the much less affected by texture, supplying a good reflection in both the directions (axial and radial).

Fig. 1. Specimens measurement conditions.

Fig. 2.a: Al₂O₃ (444) Bragg Peak, radial direction.

Fig. 2.b. Al₂O₃ (444) Bragg Peak, axial direction.
Experimental Report

Residual stresses analysis by X-ray diffraction measurements in MMC shaft for aerospace application.

Proposal N° MAT-01-1171
Instrument X1
Local Contact A.Pyzalla

Date of Report: 15 January 2003

Since the 1980s, the automotive and aeronautical industries have shown the feasibility of using particulate reinforced MMC structural components such as rear wheel hubs (automotive application) and stringers and shafts (aeronautical application). The experiment here described have been carried out in a more general research, aiming to develop a set of complementary models to optimise the forming process of these MMC components.

Residual stress measurements have been performed on a AA2009+25%SiCp MMC tube by X-ray diffraction technique.

Experimental conditions

Fig.1: Specimen positioning a) Measurement in the axial direction; b) Measurement in the tangential direction.

Used slits: 1x3.14 mm
Wavelength: 1.54 Å;
Diffracting plans: Aluminium phase (422)\text{Al},
Silicon carbide phase: (511)\text{SiC}
Measurements were performed in two corrispondent points on the inner and outer surface of the cut tube.

Results

Experimental stresses measured by X-ray diffraction are shown in the following table:

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial direction (inner point)</td>
<td>13 MPa</td>
<td>-360 MPa</td>
</tr>
<tr>
<td>Tangential direction (inner point)</td>
<td>190 MPa</td>
<td>-120 MPa</td>
</tr>
<tr>
<td>Axial direction (outer point)</td>
<td>27 MPa</td>
<td>-360 MPa</td>
</tr>
<tr>
<td>Tangential direction (outer point)</td>
<td>176 MPa</td>
<td>-180 MPa</td>
</tr>
</tbody>
</table>

\(d = 0.824 \text{ Å};\)

For both phases, the errors are not higher than ± 50 MPa.

Separation of macro- and microstresses using the model developed by FITZPATRICK and coworkers(*):
<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Macrostress</strong></td>
<td>Axial (inner pt.): -80 MPa</td>
<td>Tang (inner pt.): 112 MPa</td>
</tr>
<tr>
<td></td>
<td>Axial (outer pt.): -70 MPa</td>
<td>Tang (outer pt.): 87 MPa</td>
</tr>
<tr>
<td><strong>Elastic</strong></td>
<td>Axial (inner pt): 8 Mpa</td>
<td>Axial (inner pt): -39 Mpa</td>
</tr>
<tr>
<td><strong>microstress</strong></td>
<td>Axial (outer pt): 7 Mpa</td>
<td>Axial (outer pt): -33 Mpa</td>
</tr>
<tr>
<td></td>
<td>Tangential (inner pt): -11 Mpa</td>
<td>Tangential (inner pt): 54 Mpa</td>
</tr>
<tr>
<td></td>
<td>Tangential (outer pt): -9 Mpa</td>
<td>Tangential (outer pt): 42 Mpa</td>
</tr>
<tr>
<td><strong>Thermal</strong></td>
<td>Axial (inner pt): 85 MPa</td>
<td>Axial (inner pt): -240 MPa</td>
</tr>
<tr>
<td><strong>microstress</strong></td>
<td>Tangential (inner pt): 88 Mpa</td>
<td>Tangential (inner pt): -287 Mpa</td>
</tr>
<tr>
<td></td>
<td>Axial (outer pt): 89 MPa</td>
<td>Axial (outer pt): -256 MPa</td>
</tr>
<tr>
<td></td>
<td>Tangential (outer pt): 97 Mpa</td>
<td>Tangential (outer pt): -309 Mpa</td>
</tr>
</tbody>
</table>

Measurements on Al phase (axial direction) were also performed on outer surface of the not-cut tube in order to check if, cutting the tube (with the aim of measuring the inner surface too), new residual stresses were introduced. The behaviour of the graph was the same.

(*) M. E. FITZPATRICK, M. T. HUTCHINGS, P. J. WITHERS
Separation of macroscopic, elastic mismatch and thermal expansion misfit stresses in metal matrix composite quenched plates from neutron diffraction measurements.
In a hot curing adhesive joint the shrinkage of the adhesive on cure will lead to stresses in the adherends. In addition as the joint cools to its operating temperature differential thermal expansion between the adhesive and the metal adherend will lead to further stresses. Although some modelling and finite element calculations of these stresses have been made there are very few direct measurements of the stresses induced in the adherend by this process. This experiment was designed to measure these stresses as a function of position along a single shear lap joint consisting of 3 mm thick steel plates fixed using FM3002 adhesive cured at 120 °C over a 40 x 25 mm area.

In this experiment axial and transverse stresses were measured at points 0.6, 1.5 and 2.5 mm from the glueline along the edge of the adherend. The initial analysis of the axial results is illustrated in Figure 1.

It can be seen that there is considerable disagreement between the calculated longitudinal (FE) results and the experimentally measured values (ND). Similar disagreement is found in the transverse results. It is important to note that the disagreement is not only in the magnitude of the stresses but also in their symmetry.

Differences in magnitude could arise if the pre-adhesion annealing of the samples was not sufficient to relieve stresses introduced during manufacture of the steel pieces but would not explain the symmetry differences. Refinement of the FE calculations and further experiments are planned in order to clarify this disagreement.

Aged samples of the joint (immersed in water at 60 °C for two weeks before the experiment) were also measured in order to access the effect of water ingress on the shrinkage stresses. This models environmental effects on joints in service. Two competing effects occur. (i) Water softens the polymer and thus deformation of the adhesive can take place causing stress relief in the adherend, (ii) Water ingress swells the polymer which can put the adherend under increased stress. The experimental results indicate that the latter effect is more important for this system. Increased (compressive) stresses were recorded close to the interface in aged compared to unaged samples. These should be balanced by decreased stresses in the centre of the sample (away from the edges) but further measurements will be required to confirm this.

Figure 1: Single lap joint (Adherened Steel)
Longitudinal Component of Stress

![Graph showing longitudinal component of stress](image-url)
IN706, which has a more complex microstructure than the modern single crystal superalloys is a wrought Ni-Fe base polycrystalline alloy which is widely used in gas turbine disc application [1]. The main strengthening phase in IN706 alloy is not $\gamma'$ precipitates (like in the cast superalloys) but the so-called $\gamma''$ phase (Ni$_3$Nb), having a DO$_{22}$ body-centered tetragonal structure. The $\gamma''$ phase forms as fine platelets or as co-precipitates together with $\gamma'$ (Ni$_3$Al) phase, i.e. $\gamma'$ is at the core and $\gamma''$ as a mantel over it (Fig. 1). Typically, IN706 alloy has about 15 to 20% $\gamma''$ and the co-precipitates are extremely fine, having sizes smaller than 50 nm. The alloy however suffers from microstructural instability at temperatures above 650°C due to transformation of the metastable $\gamma''$ precipitates (the strengthening phase). The $\gamma$ and the $\gamma'$ phases can also transform to a Ni$_3$Ti based phase called $\eta$, [2,3]. Though the details of these transformation process is not clear, there is a general agreement on the important role played in this mechanism by the lattice misfit of $\gamma'$ and $\gamma''$ phases [4]. In order to optimize the mechanical behavior of IN706, especially, creep crack growth resistance, controlling the $\gamma''$ to $\eta$ transformation is essential. However, because of its complex microstructure (more than one coherent precipitate phases present) misfit measurement in IN706 and similar alloys is not an easy task. The high resolution E9 instrument gives an opportunity for such a measurement.

Due to the weak signal of peak to background the sample holder was shielded and a test measurement without sample was carried out. Standard reference material Y$_2$O$_3$ were used for zero calibration. The solid sample was mounted by taking the maximum value of intensity after a oscillation scan of the sample. As an example Fig. 2 exhibits a typical diffraction pattern of IN706 (after direct ageing) with three phases ($\gamma$, $\gamma'$ and $\gamma''$ in five strong reflections) and nine additionally marked peaks (not seen in X-ray), most probably from a superlattice structure. Misfit evaluation will be done in comparison to the X-ray results.

Fig. 1: Different orientation variant of $\gamma'$ – $\gamma''$ co-precipitates in a single $\gamma$ grain.

Fig. 2: $\gamma$, $\gamma'$ and $\gamma''$ phases of IN706-DA together with nine small reflections. Inset: full pattern with fcc reflections.

References:
EXPERIMENTAL REPORT
Crystal Structure Determination of Ni<sub>4</sub>Ti<sub>4</sub> Precipitates and R-Phase in SM Alloys

Proposal No: MAT-01-1190
Instrument: E9
Local Contact: Dr. D. Többens

Date of Report: 20/01/2003

Principal Proposer: Prof. Dr. W. Schmahl, RU Bochum
Experimental Team: Dr. C. Somsen, RU Bochum
Dr. C. Deroche, RU Bochum

Ni rich NiTi alloys are well known for their shape memory effect and superelasticity and are of special interest because the phase transition temperatures scale with Ni content. Phase coexistence as well as pre-existing and developing texture during the stress- or temperature-induced austenite to martensite transformation in NiTi are crucial issues in the quantitative understanding of shape-memory and superelasticity effects of the material.

R-phase:
The metrically rhombohedral R-phase occurs in the presence of dislocations or Ni<sub>4</sub>Ti<sub>3</sub> precipitates between the cubic austenite and the monoclinic B19' martensite. The R-phase is useful for shape memory applications which rely on a small thermal hysteresis.

To clear uncertainties about the symmetry and crystal structure of the R-phase, we produced this phase state by cold rolling a commercial Ni<sub>50.7</sub>Ti<sub>49.3</sub> sample and we took neutron diffractograms in 36 directions to allow refinements of texture as well as structural parameters.

Fig. 1 shows the Rietveld-fit for the sum of all 36 diffractograms using the generalized spherical harmonic texture model [1, 2]. The refinement was performed in the space group P-3 with residual values $R_{wp} = 0.0364$, $R_p = 0.0277$.and $\chi^2 = 2.367$ respectively. Cell parameters at 263 K are $a = 7.33742(11)$ Å and $c = 5.27799(16)$ Å.

Fig. 2 shows all 36 diffractograms to indicate the texture of the sample due to the cold rolling treatment.

Fig. 1: Result of the Rietveld refinement of the R-phase at 263K.

Fig. 2: 36 diffractograms of the R-phase indicate the texture of the cold rolled sample.

This investigations are still in progress.

References:
In the frame of investigations on hydrogen-induced phase transformations in austenitic stainless steels, a variety of studies based on cathodic hydrogen charging and X-ray diffraction have been published. However, controversy exists about the structures of the phases and the mechanisms of their formation. The difficulties in the phase analysis are related to the exceedingly non-uniform hydrogen distribution resulting from the technique of cathodic charging. Furthermore, the gradients in the hydrogen distribution lead to high stresses. Therefore it remains unclear, to which extent the observed phase transformations are caused by stresses and the presence of hydrogen itself.

In this report, we would like to summarise the results obtained in two experiments on AISI-type 304 (Fe-18Cr-10Ni) and AISI-type 310 (Fe-25Cr-20Ni) steels. Samples were hydrogenated in a high-pressure cell in order to obtain quite uniform hydrogen distributions in the bulk of the samples. Thus, the effects of hydrogen in a low-stress state can be studied.

Steels loaded with various hydrogen contents up to hydrogen-to-metal atomic ratios (H/Me) ≈1 have been investigated. The data were collected at diffractometer E9 at 80 K using neutrons with a wavelength of 1.307 Å. Rietveld refinement revealed the structures of the phases, the phase compositions as well as the sites and occupancies of the hydrogen atoms.

In both steels the hydrogen atoms are located exclusively in the octahedral interstitial sites. In 304 steel with H/Me = 0.56 the formation of ε-martensite was observed, whereas in case of 310 steel, no ε-martensite was detected even for H/Me = 0.94. Our results differ from those of electrolytically charged steels, where high amounts of ε-martensite were observed after the hydrogen charging at comparable hydrogen contents. The observed differences in the phase transformation behaviour are supposedly related to the different stress states resulting from electrolytic and high-pressure hydrogenation, respectively.

Fig. 1: Measured and calculated diffraction patterns and difference plot for 310 steel hydrogenated at 3.0 GPa.

<table>
<thead>
<tr>
<th>Charging pressure, GPa</th>
<th>Mass, g</th>
<th>Phases, weight fractions</th>
<th>Lattice constant at 80 K, Å</th>
<th>H-occupancy, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncharged</td>
<td>0.6</td>
<td>Fm3m</td>
<td>3.5826(1)</td>
<td>-</td>
</tr>
<tr>
<td>2.3</td>
<td>0.6</td>
<td>Fm3m</td>
<td>3.6586(1)</td>
<td>35(2)</td>
</tr>
<tr>
<td>3.0</td>
<td>0.6</td>
<td>Fm3m</td>
<td>3.7261(2)</td>
<td>66(3)</td>
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<tr>
<td>7.0</td>
<td>0.3</td>
<td>Fm3m</td>
<td>3.7798(2)</td>
<td>94(5)</td>
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<tr>
<td>deuterium</td>
<td>0.3</td>
<td>Fm3m</td>
<td>3.6236(1)</td>
<td>13(1)</td>
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</tbody>
</table>

Tab. 1: Rietveld analyses of hydrogenated 310 steel.

<table>
<thead>
<tr>
<th>Charging pressure, GPa</th>
<th>Mass, g</th>
<th>Phases, weight fractions</th>
<th>Lattice constant at 80 K, Å</th>
<th>H-occupancy, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncharged</td>
<td>0.6</td>
<td>Fm3m</td>
<td>3.5800(1)</td>
<td>-</td>
</tr>
<tr>
<td>2.3</td>
<td>0.6</td>
<td>Fm3m, 84%</td>
<td>3.6537(1)</td>
<td>30(2)</td>
</tr>
<tr>
<td>3.0</td>
<td>0.6</td>
<td>Fm3m, 84%</td>
<td>3.6988(2)</td>
<td>56(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P63/mmc, 16%</td>
<td>a=2.617(2)</td>
<td>71(9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c=4.254(3)</td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>0.3</td>
<td>fractions uncertain</td>
<td>f.c.c.: 3.7757(3)</td>
<td>103(9)</td>
</tr>
</tbody>
</table>

Tab. 2: Rietveld analyses of hydrogenated 304 steel.

* This sample has been studied at BT1, NIST
Martensitic phases induced in shape memory alloys (SMA) (as NiTi or CuAlNi) contain large number of internal interfaces. The easiness with which these and also austenite/martensite interfaces move under external stress or thermal changes is responsible for unique thermomechanical properties of these materials. As the interfaces move, the martensite crystal orientations (texture) in polycrystalline SMAs changes as well. Neutron powder diffraction is an excellent tool for studying these texture changes.

In the present experiment, three NiTi polycrystalline bars existing in the B19' monoclinic martensitic phase at room temperature: – 1) NiTi-AR-cooled from 100°C, 2) NiTi-T-cooled under tensile stress applied, and 3) NiTi-C-cooled under compression stress applied) were studied by neutron powder diffractometer E9 under variable omega angle conditions(Fig.1). The orientation of diffracting lattice planes with respect to load (bar) axis (angle \( \delta \)) is defined by angles \( \Theta \) and \( \Omega \) (inset in Fig 2). The variation of integral intensities of individual reflections is due to the very strong martensite texture partially inherited from that of the parent austenite but additionally affected by the preferential martensite variant formation under applied stress. The integral intensity variations of individual martensite reflections with the angle \( \omega \) were analyzed. Let us demonstrate the results on the behavior of \( 011_M \) and \( 100_M \) reflections (Fig. 2). Even if both the integral intensities vary drastically with \( \Omega \), their ratio \( I_{011}/I_{100} \) for the NiTi-AR specimen (Fig. 2) remains practically independent on \( \Omega \) (and hence on \( \delta \)). This is because both the \( 011 \) and \( 100 \) planes correspond to the \( 100 \) austenite planes and the martensite texture has only been inherited from that of the parent austenite. The \( I_{011}/I_{100} \) ratio, however, behaves quite differently (Fig. 2) for the martensites induced under the tension (NiTi-T) and compression (NiTi-C) stresses. The martensite variants providing tensile strain along the \( 011 \) lattice plane normal \( 011_M \) reflection) form preferentially aligned with the load axis \( \delta=0^\circ \) under tension and perpendicularly to it \( \delta=90^\circ \) under compression stress. The contrary applies for variants providing compression strain along the \( 100 \) lattice plane normals \( 100_M \) reflection). The experiment thus demonstrates how the martensite variant microstructures in SMAs strongly depend on history, particularly on the sense of the applied stress.
Portland cement clinkers and cements are important materials manufactured in hundreds of millions tons worldwide. Quality of clinkers/cements strongly depends on their phase composition, mostly on the amounts of alite (Ca$_2$SiO$_5$ or C$_3$S), belite (Ca$_2$SiO$_4$, C$_2$S), ferrite (Ca$_2$(Al,Fe)O$_5$, C$_2$AF) and aluminate (Ca$_2$Al$_2$O$_6$, C$_4$A). Except for the older methods for phase composition determination (Bogue, optical microscopy) diffractions methods are also employed [1]. Unfortunately, X-ray diffraction patterns of clinkers (cements) are very complex, mostly due to heavy overlap of the diffractions of the dominant phases, C$_3$S and C$_2$S. Diffraction patterns of C$_4$AF are affected by Al/Fe distribution and patterns of C$_3$A are typical for few strong diffractions outgrowing from a plethora of low-intensity peaks. Moreover, clinker phases can crystallize in several polymorph forms, which can occur in a sample simultaneously. Even though Rietveld refinement looks like an obvious remedy to the problem, large complexity of the patterns led to rather controversial results [2, 3]. However, complexity of the patterns can be reduced by chemical treatment of clinkers leading to two residues, here referred to as KOSH and SAM[4]. A KOSH residue contains calcium silicates, while in a SAM residue calcium aluminates/ferrites are concentrated. Some minor phases like MgO may however appear in both residues. The aim of this experiment was to collect the data suitable for quantitative phase analysis of clinkers and residues obtained by chemical treatment of clinkers. The data were collected at room temperature in high-intensity mode using the wavelength of 1.797168Å, samples were put to vanadium containers with Ø 14 and 8mm, respectively. Using a preset monitor count/step strategy diffraction patterns of three clinkers and the residues obtained from two of them were collected. Here we present some results of analyses of KOSH and SAM residues of two types of clinkers – a standard “grey” and a so called “white”, i.e. with almost zero % of Fe.

**White clinker.** The SAM residue contained only cubic C$_3$A and MgO. In contrast to previous X-ray refinements it was possible to refine profile parameters of both phases and to determine w(C$_3$A): w(MgO) = 92%:8%. No traces of other phases, like e.g. orthorhombic C$_3$A were found. The pattern of the KOSH residue was more complex and except for two polymorphs of C$_2$S (monoclinic and triclinic), C$_2$S and MgO were identified. To analyse a combination of standard Rietveld refinement with LeBail technique was used.

**Grey clinker.** In the SAM residue cubic C$_3$A, C$_4$AF and MgO were readily identified. In contrast to X-ray data traces of anhydrous CaSO$_4$ were detected. This refinement was hampered by smaller number of counts collected during the scan. The KOSH residue contained ~62% (weight) of C$_3$S(mon.), 37% of C$_2$S and ~ 1% of MgO; triclinic C$_3$S was not identified. Due to the short interval between the experiment and report time we cannot present more detailed data analysis. In the next step we will proceed with phase analysis of complete clinkers and will try to asses the accuracy using the results from both neutron and X-ray diffraction data.

The investigation of strain/stress behaviour of rocks is of great importance for a better understanding of deformation processes under conditions of the upper Earth’s crust [1,2]. Furthermore, residual stresses in rocks may influence the characteristics of their reaction in case of superimposed deformation.

The aim of the experiments on V2 was to investigate the residual stresses on rocks with high accuracy by using the neutron spin-echo instrument in the diffraction mode. In this mode changes in diffraction line position can be measured to very high accuracy in the phase of the Larmor precession angle in the spin-echo set-up [3].

Residual strain experiments were carried out on two samples: a metamorphic, monomineralic quartzite, characterized by a very strong crystallographic preferred orientation (Fig. 1: (11-20)-quartz pole figure, measured by neutron-TOF-diffraction) and a sediment rock, containing two different minerals: quartz and dolomite, with no or even a soft preferred crystallographic orientation.

Residual strain of the quartzite sample was determined using the quartz-(11-20) Bragg reflection \( (d = 2.4550 \text{ Å}) \). It was measured in 7 directions in the (yz)-plane in angular steps of 15° and in 4 directions in the (xz)-plane in angular steps of 30°. No residual strain was found in the [x]-direction, but the strain in the [z]-direction is in the order of \( \frac{d}{d_0} = 1 \) to \( 2 \cdot 10^{-4} \). The large error of the strain value measured in the [y]-direction (Fig. 2) is due to the strong texture and consequently low diffraction intensity.

The dolomite-(11-23) Bragg reflection \( (d = 2.1895 \text{ Å}) \) was measured in 6 sample directions of the sedimentary rock, containing mainly dolomite and quartz. Compressive residual strain in the order of \( 2.5 \cdot 10^{-4} \) was detected in the [x]- as well [z]-direction, but the [y]-direction is free of residual strain (Fig. 3).

**Fig. 1:** Quartz-(11-20) pole figure of the quartzite.

**Fig. 2:** Residual strain: quartz-(11-20) of the metamorphic, monomineralic quartzite.

**Fig. 3:** Residual strain: dolomite-(11-23) of the sedimentary dolomite-quartz-rock.

Cement has been used for centuries as a cost-effective construction material. However much of the materials science of cement hydration including the bonding and interaction of water with the cement hydration product (called C-S-H) still remains to be discovered. Researchers have estimated the extent of cement hydration from the amount of bound water - determined by measuring the amount of water held under defined conditions (generally specified temperatures). (Taylor [Taylor H. F. W. Cement Chemistry. 2nd edition ed. London: Thomas Telford; 1997.] has a much fuller discussion of these issues). This project used Quasi-Elastic Neutron Scattering (QENS) to monitor the amount and state of bound and unbound water in cement pastes. QENS has already been used to monitor the hydration of tricalcium silicate during the first 28 days of hydration as a function of water to cement ratio. Tricalcium silicate hydration does model cement hydration and shows that significant information about the bound and free water can be obtained from hydrated cement paste.

Cement sample description (see text)

<table>
<thead>
<tr>
<th>Sample</th>
<th>W/C</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(RT)</td>
<td>0.42</td>
<td>0.87</td>
</tr>
<tr>
<td>A(40°)</td>
<td>0.60</td>
<td>0.87</td>
</tr>
<tr>
<td>B(40°)</td>
<td>0.42</td>
<td>0.90</td>
</tr>
<tr>
<td>C(40°)</td>
<td>0.32</td>
<td>0.91</td>
</tr>
<tr>
<td>C(40°)2</td>
<td>0.60</td>
<td>0.77</td>
</tr>
<tr>
<td>C(40°)2</td>
<td>0.32</td>
<td>0.63</td>
</tr>
<tr>
<td>C(40°)2</td>
<td>0.60</td>
<td>0.5</td>
</tr>
</tbody>
</table>

In this preliminary study we examined pastes of Ordinary Portland Cement (denoted by A, B and C on the table above), "as is", dried and after rehydration (Rehydrated pastes have “2” after the brackets), prepared with different levels of hydration (noted W/C on the table) at either room temperature or 40°C (indicated within the brackets of the first column of the table) for up to 28 days. Slices of less than 2mm thick were examined. As far as we are aware our recent QENS studies are the first to use commercially available cement materials. Our investigation used the time-of-flight spectrometer NEAT (ΔE=30μeV and ΔE=98μeV) and a range of quasi-elastic (QE) broadening was observed (see example on the figure hereafter). In a first approximation the spectra of the "as is" cement can be explained in terms of unbounded and bound water (the parameter p in the table refers to the ratio of bound to total water).

After the QENS spectra were recorded the slices of paste were heated at 105°C and the QENS spectra measured. Here the QE broadening could only be explained in terms of bound water. Indeed, within the instrumental resolution no QE broadening was observed (see figure).

The pastes were then re-hydrated and the QENS spectra were measured (sample denoted C(40°)2 on the table). Once again to a first approximation the spectra (see figure) can be explained in terms of unbounded and bound water. As can be seen on the table, the ratio of bound water has decreased in the re-hydrated sample compared to the original one.

Example of spectra for sample C(40°) with W/C=0.6

Thus, subsequent analysis of the QE component may provide a much more accurate value for the hydration level and new information concerning the nature of the interactions of water molecules with the cement hydrated product.
Graphite oxide (GO) has been known and used since the 19th century. Recent interest grew due to proposed application as material for battery electrodes, owing to the possibility of intercalation. Various hydration levels are observed giving rise to different spacing of the carbon layers in the range from 6 Å to 12 Å. Information about the mobility of the water molecules is not yet complete but crucial for the understanding of the structure of the C layers as well as the intercalation process.

With time-of-flight (TOF) neutron scattering at the spectrometer V3/NEAT diffusion processes for the rotation and translation have been investigated. Three different hydration levels, characterised by the 10%, 50%, and 80% mass of water added per mass (usually 1 g) of dry GO powder, were examined. Both H₂O and D₂O samples were produced. This way contributions from GO and intercalated water can be separated.

Spectra of the six samples were recorded at room temperature with two different energy resolutions of 66 µeV and 100 µeV, and measurement times of 8 to 15 hours, taking advantage of the full available beam time. A preliminary data correction for detector efficiency and sample geometry as well as conversion to S(q,ω) could be done on site.

The position of the structural Bragg peak depends on hydration and is consistent with x-ray Debye-Scherrer patterns, also taken at HMI. The latter finding proves that the samples can be related to the above mentioned well-defined hydration degrees and that the hydration level of the corresponding H₂O and D₂O samples was comparable. We found that the layer separation increases nonlinearly with water content.

Quasielastic scattering was observed over the whole angle range with clear peaks centred on zero energy transfer. The absolute intensity of the quasielastic contribution to the spectra clearly increases with hydration degree, as expected. Therefore, the spectra promise to be an excellent base for developing models of the water motion.

Figure 1 shows normalised spectra for all six samples at a scattering angle of 52°. Clearly, the lower water contents (10% and 50%) show similar peak shapes. This means that water added up to 50% has the same properties as water in the almost dry sample. This changes with the 80% sample, where the lower part of the peak broadens substantially. The central part, however, still appears similar to the less hydrated samples. Therefore, an new component of motion must be present for the added water molecules. This component has a shorter time constant, leading to a broader energy distribution.

This experiment was supported by the European Union under contract HPRI-CT-2001-02138
Stents are devices used in interventional surgery to support arterial walls once blocked by the excessive deposition of fatty substances (Plaques). When the plaque depositions reach a certain critical amount, they may disturb the blood flow or even stop it completely, causing a local collapse of the circulation system. Specially critical is such a collapse of the blood supply in the coronary region (heart region). If the necessary amount of blood for the heart can not be supplied, the entire circulation system may collapse (heart attack). A new sort of nickel-free stainless steel (P2000) was developed specially for the manufacture of implants, to avoid allergic reactions caused by nickel. In order to understand the possible interactions of the system blood / steel, the microstructure and specially the inhomogeneities of this new material should be investigated. Deposition of biological components are specially expected to occur the in inhomogeneities of the surface stent / blood and stent / artery wall. As a complementary investigation to light microscope, SEM (Scanning electron microscope) and TEM (transmission electron microscope), SANS measurements on the instrument V4 were carried out. Fig. 1 shows a SEM and a TEM-image of a coronary stent made of P2000.

The SANS (small angle neutron scattering) of the P2000 steel revealed a very poor scattering behaviour for this alloy, which made a reasonable calculation / interpretation of the scattering curves not possible. This behaviour is caused either by a very poor scattering contrast between the matrix and the precipitates or by a high homogeneity of the alloy. In agreement with the TEM-images, no particle population could be observed. For future SAS measurements one alternative to that would be ASAXS measurements in Synchrotron facilities, which possesses much higher intensities and the possibility of adjusting the primary beam wavelength to produce anomalous scattering, allowing an increase of contrast between the metal matrix and the precipitates.

<table>
<thead>
<tr>
<th>Principal Proposer:</th>
<th>A. Pyzalla, Technische Universität Berlin, Metallphysik</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument V4</td>
<td></td>
</tr>
<tr>
<td>Local Contact</td>
<td>E. Garcia-Matres</td>
</tr>
<tr>
<td>Date(s) of Experiment</td>
<td>09 – 11.08.2002</td>
</tr>
<tr>
<td>Date of Report:</td>
<td>14.01.2003</td>
</tr>
</tbody>
</table>

Fig. 1: (a) SEM-image of stent surface showing slip bands in different crystals. (b) TEM-image of dislocation structures.
In-situ monitoring of the morphological changes in iron rich Ni-superalloy IN706

Nickel–iron base superalloy, Inconel 706, is used as disc material in gas turbines because of its good mechanical properties up to intermediate temperatures (~650°C). The predominate source of strengthening, is the precipitation of coherent, ordered Ni₃Al based γ′ phase and the Ni₃Nb based γ'' phase. A third phase, η (Ni₃Ti base) with an ordered hcp structure can also form in IN706.

Modifying heat treatment to improve microstructural stability and mechanical properties in Fe-Ni-superalloys is a significant research goal for many years. However, the earlier studies of phase transformation relied mostly on investigation on samples cooled down to room temperature after the high temperature exposure. Since the kinetics of γ' and γ'' precipitation is very fast, it is likely that the high temperature microstructure is altered during the cooling. In the present experiment, the microstructural changes were studied at the elevated temperature by in-situ SANS.

Our previous off-situ experiment with IN706 (MAT-04-638) followed by TEM observations gave rise to the question, what type of precipitates mainly contributes to the scattering in the Q range 0.01 - 0.04 nm⁻¹. The present in situ experiment was performed for the identical samples at different η-stabilization temperatures (820°C, H2-sample, or 865°C, H3-sample, directly cooled down from the 996°C solution temperature - i.e. the initial phase of the so called MST procedure). It determined that the scattering comes mainly from η phase as scattering is still present at the elevated temperature of 865°C which is above the solvus temperature of γ' and γ''. The figure displays the measured data of H2 and H3 samples taken at the end of the η-stabilization step.

The table lists the results of the fit to some of the measured data. The detailed description of the results will be presented in [1].

The in-situ experiment with the last sample (H4) was aimed to bring information about the influence of cooling down to low temperature after the solution treatment on the subsequent η-stabilization (i.e. the initial phase of the ST procedure). Integrated intensity of the scattering showed that the maximum rate of the precipitate creation is around 750°C what corresponds to the creation of γ'-γ'' co-precipitates. After cooling down (4K/min) to 270°C (following the the solution treatment), an interference peak is observed at Q=0.2 nm⁻¹. It is clearly caused by the precipitation of a dense population (distance ≈30 nm) of γ' and γ'' precipitates during the slow cooling.

Electron beam physical vapor deposition (EB-PVD) is an industrially applied technique for surface coating of superalloys. The temperature in the combustion chamber of turbines can be increased by more than 100°C when employing such ceramic thermal barrier coating (TBC) on a turbine blade (Fig. 1).

Volumetric BET measurements have shown that isochronal heat treatment results in a strong decrease of the inner surface area of pores. This decrease in porosity is expected to reduce the thermal isolation and to increase the in-plane elasticity. Time resolved SANS measurements performed at high temperature could provide a more detailed picture on the pore microstructure and its relation to the sintering process.

This in-situ experiment was joined together with the experiment MAT-04-702 and it was ascribed altogether 2 days of beam time what was insufficient for carrying out both experimental programs with high temperature furnace. The experimenters thus focused mainly (80% of the time) on the MAT-04-702 experiment, which was a continuation of the previous off-situ measurement having certain opened questions. For the EBPVD measurement, only a very limited beam-time remained. Therefore, only short tests of the sample layer connected to the superalloy substrate on one side and of the substrate itself on the other side were performed.

The selected scattering curves are displayed in Fig. 2. The γ precipitates in substrate (thickness 1.4 mm) cause relatively low scattering, which - however - can influence the total scattering curve of the sandwich "superalloy substrate - TBC" at room temperature (see the scattering maximum in the substrate scattering curve measured at RT). Nevertheless, the performed test proved, that the small γ' precipitates in substrate are already dissolved at 1000°C and their scattering practically does not influence the scattering from pores in TBC layer (layer thickness ~0.2 mm) in the measured Q-range. Investigation of the TBC nanopore microstructure is thus possible without decoupling the coating from the superaloy substrate at such an elevated temperature. This is an important fact because the investigation of the pore microstructure at real conditions (i.e. connected with the superalloy) is then possible. The option to investigate one component of a sandwich sample without being influenced by its other part extends the already known advantages of in-situ SANS experiments at high temperatures.

The scattering curves measured at the begin and at the end of the holding at 999°C (see Fig. 2) confirmed qualitatively the decrease of the specific surface of pores after such high-temperature exposition (the decrease of the asymptotic scattering).

Fig. 1. EB-PVD coating on the turbine blade.

Fig. 2. Selected measured curves (the substrate scattering is already subtracted from the coating-on-substrate scattering).
Ceramic thermal barrier coatings (TBC) allow for an increase of temperature in the combustion chamber of turbines employing Ni-base superalloys by more than 100°C. Air plasma-sprayed (APS) deposits generally contain a large number of cracks and pores which determine their thermal and mechanical properties. Contrary to most standard techniques, small angle neutron scattering (SANS) enables in-situ studies of porosity at high temperatures and can provide size distributions of pores even on the nanometer scale. The presented SANS experiment was therefore focused on the in-situ study of the pore microstructure in APS TBCs at high temperature.

The in-situ measurements were performed supplementary to earlier room temperature measurements [1] which contained some uncertainties (the measured scattering curve from the as-sprayed sample was largely influenced by incoherent scattering, most probably from the adsorbed molecules containing hydrogen; the extraction of information about nanometric small pores was thus rather ambiguous).

The heat treatment chosen in the present study was intended to remove the hydrogen and thus to reduce huge incoherent scattering. The in-situ experiments were performed with three samples in different temperature regimes using a high-temperature furnace. The selected scattering curves together with their fits (using the SASFIT program) for one of the heating cycles are displayed in Fig. 1.

It can be seen from Fig. 1, that the incoherent scattering is already negligible at 410°C, i.e. hydrogen is fully removed. Apart from a very low volume fraction of nanosized pores, the scattering originates practically only from large cracks at this temperature.

The measurements with slowly increased temperature also revealed an additional interesting feature: at about 800°C, a population of nanometer sized pores is created (see Fig. 2). Between 800°C and 1200°C, this population is practically unchanged. During one-hour holding at 1200°C, however, the size of nanosized pores increases and their volume slightly decreases. On subsequent cooling, no significant change occurs.

The experiment confirmed the hypothesis of strong influence of incoherent scattering on the as-sprayed-sample scattering curve. It has also been shown that in-situ measurements at high temperatures provide valuable data on structural changes of pore microstructure in TBCs.


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**Fig. 1.** Selected scattering curves with subtracted diffuse (temperature dependent) scattering part.

**Fig. 2.** The fit results (volume fraction, size) for 2F sample. The temperature profile is displayed as well.
Rheological investigations of ferrofluids under shear flow and magnetic field have shown an increase of the viscosity with increasing magnetic field strength (magnetoviscous effect) and a decrease of the viscosity with increasing shear rates. These results seem to be an effect of structure formation in the ferrofluid with increasing magnetic field strength and a breakage of these structures for high shear rates. For the investigation of these microstructural changes we use a specially designed rheometer that allows SANS measurements in the same experimental conditions as for rheological ones.

Fig. 1 Schematic sketch of the arrangement for SANS

Two commercial ferrofluids-Ferrotec APG513A from two different production lines and an experimental ferrofluid TOA (UT Timisoara) were investigated, all three magnetite based. The experiments were carried out in a magnetic field range from 0 - 160 kA/m, parallel to the neutron beam, and with shear rates from 0 - 200 s\(^{-1}\). The three samples have a different content of large particles and thus different magnitudes of the magnetoviscous effect. For each investigated fluid we compared the scattering patterns obtained varying the magnetic field strength and the shear rate. We use, as a reference, the situation with high shear rate (\(\dot{\gamma} = 200\) s\(^{-1}\)) when it is supposed that the particles are homogeneously distributed in the fluid (no structures). We built, for example (Fig.2), the difference between the scattering patterns for shear rate 1 s\(^{-1}\) and the reference one (APG513A [1]). With increasing shear rate (Fig. 3) a clearer difference can be observed due to the fact that the projection of the chains, detected by the beam, increases. For higher shear rate (Fig. 4) the difference becomes smaller due to the breakage of the structures.

Fig. 2 Difference between scattering patterns for \(\dot{\gamma} = 1\) s\(^{-1}\) and \(\dot{\gamma} = 200\) s\(^{-1}\) for H = 160 kA/m

Fig. 3 Difference between scattering patterns for \(\dot{\gamma} = 10\) s\(^{-1}\) and \(\dot{\gamma} = 200\) s\(^{-1}\) for H = 160 kA/m

Fig. 4 Difference between scattering patterns for \(\dot{\gamma} = 60\) s\(^{-1}\) and \(\dot{\gamma} = 200\) s\(^{-1}\) for H = 160 kA/m

The analysis of the scattering patterns and scattering curves for all magnetic fields strength’s and shear rates is in progress.
EXPERIMENTAL REPORT

Synergism effects of hydrogen and radiation defects in steel

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There is a hypothesis which postulates the microstructural radiation defects as effective traps for hydrogen and this deposited hydrogen as a stabilizer of these features. Thus, the higher the content of hydrogen the stronger is the embrittlement. The H-trap hypothesis should be examined by a SANS-experiment.

The radiation defects have a lower nuclear scattering length density as the matrix. A deposition of \( ^1\text{H} \) reduces this density and so the nuclear scattering contrast is increased whereas the magnetic scattering contrast remains unchanged. The same samples (10x10x0.8 mm\(^3\)) of irradiated steels which have high contents of radiation defects (> 0.3 vol.-%) estimated in former experiments [1] and their unirradiated reference samples were H-precharged by electrolysis. The measurements were carried out under a saturating magnetic field perpendicular to the neutron beam direction in order to separate magnetic and nuclear scattering.

Fig. 1 shows the results for one material. No differences occur in the magnetic contribution (Fig. 1a) as expected. An increase of the nuclear scattering intensity is observed for both un- and irradiated states after H-precharging (Fig. 1b). If we consider the nuclear scattering of the irradiation induced defects (Fig. 1c) the differences between the H-precharged and uncharged state disappear. Thus, it seems that the radiation defects do not effect as H-traps in this material. Obviously H-deposition occurs mainly on other inhomogeneities, e.g. carbides, which are not influenced by irradiation.

However, this result does not refuse the above-mentioned hypothesis in principle. The material selected has a high Cu content. In this case the radiation effects are Cu-rich precipitates. As the Cu-H affinity is low, the trap effectivity of such precipitates can be low as well. Therefore, in a following step the effect should be checked in Cu-poor steels, in which preferentially vacancy-rich foreign atom clusters are formed.

The measurement has shown that we can detect H-deposition (\( > 1\times10^{-4} \) wt.-%) by SANS. The incoherent scattering of H plays a subordinated role by this low content in comparison with the incoherent scattering of the different iron isotopes.

As a second result this experiment has shown that the SANS measurements are excellent reproducible when we additionally investigate another sample from the same irradiated material state. This is an important result for comparisons of susceptibilities of different materials by measurement only one sample in every condition.

Fig. 1: SANS cross sections a) magnetic, b) and c) nuclear scattering contribution of different states of a reactor pressure vessel steel.

**EXPERIMENTAL REPORT**

**Magnetic configuration in core-shell Fe/Fe oxide nanocomposites**

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**Date(s) of Experiment:** 22/10/02 - 25/10/02

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Nanostructured magnetic materials exhibit phase modulation on a length scale of the order of 1-10 nm, thus making neutrons an appealing probe for their structural and magnetic characterisation. The samples investigated in this experiment have been obtained by cold-compaction of Fe nanoparticles surrounded by an oxide surface layer [1]. This procedure yields bulk-like materials constituted by an oxide matrix with dispersed Fe cores. Three samples with different Fe core diameters (6, 10 and 14 nm) and hence oxide volume fraction (0.2, 0.4 and 0.6 respectively) have been measured.

SANSPOL (Small Angle Neutron Scattering with POLarized neutrons) experiments have been carried out on the V4 spectrometer, using a vertical cryomagnet to explore the $T=5$-300 K range with a maximum magnetic field $H=2$ T. Three sample-detector distances of 1.2, 4 and 12 m with $\lambda=6$ Å were employed, covering the $0.03<Q<2$ nm$^{-1}$ range. The analysis of the nuclear scattering contribution according to a model of core-shell particles yields a core size in agreement with x-ray diffraction and electron microscopy results.

The scattering intensities in the direction $Q\perp H$ for the two polarization states (neutron spin parallel to $H$, $I^-$; neutron spin antiparallel to $H$, $I^+$) are reported in Fig. 1. The curves $I^-$ and $I^+$ exhibit two crossovers for all measured samples. This structure suggests the presence of an intermixing region between the magnetic metallic core and the non magnetic oxide shell.

Fig. 2 and 3 display $I^-$, $I^+$ and the full radial average of 2-D patterns at $H=0$, respectively, as a function of temperature for the 6 nm sample. No significant temperature dependence was observed in the scattering profiles. This finding somewhat contrasts with the magnetic properties, which show a transition to a low-temperature frozen state [1]. SANSPOL data indicate that the distribution of magnetic scattering lengths in individual scattering particles does not appreciably change with temperature, even if their collective behaviour exhibit dramatic temperature and field dependence.

Data analysis according to a model of composite core-shell particles with different magnetic and nuclear scattering lengths is currently underway.

Fig. 1: SANSPOL intensities ($Q\perp H$) at $T=250$ K and $H=2$ Tesla for samples with different Fe core size. $\uparrow$: $I^-$; $\downarrow$: $I^+$.

Fig. 2: SANSPOL intensities ($Q\perp H$) at $H=2$ Tesla and different temperatures on the 6 nm sample. $\uparrow$: $I^-$; $\downarrow$: $I^+$.

Fig. 3: Full radial average of SANS intensities, at $H=0$ and different temperatures on the 6 nm sample.

Hyperbranched polymers are presently extensively investigated for a wide range of potential applications. Their degree of branching is one of their most prominent feature, determining, together with the chemical nature of the branches, most of the micro- and macroscopic properties of these material both in bulk and in solution. These materials show different properties as compared to their linear homologues, as they are characterized by a lower degree of chain entanglement, a lower glass transition and larger fraction of cavities which might host guest molecules.

An hyperbranched polyglycidol (HPG) has been recently synthesised [X. Wang et al., J. Polym. Sci.: Polym. Phys. 39, 2225 (2001)] and is characterized by a molecular weight of approx. 2000 and a rather narrow distribution. While these material can find useful application in the field of polymer electrolytes, when properly doped with an inorganic salt, up to now no information is available on the solution behaviour of these macromolecules.

In order to obtain information on the structural details of these solutions and minimise the incoherent contribution from the solvent, heavy water has been used as a solvent, while fully hydrogenated HPG has been used.

HPG turned out to be miscible with water and a range of concentrations have then been investigated. In particular, we explored the concentration range between 0.08 an 10.4 % (w/w).

In Figure 2 the SANS patterns arising from the different solutions are reported at 25 °C.

Figure 1. Schematic representation of the Hyperbranched PolyGlycidol, whose aqueous solutions have been investigated by SANS.

Figure 2. Concentration dependence of the SANS pattern from aqueous solutions of HPG.

The temperature dependence of the SANS pattern has also been investigated aiming to characterize the effect of the change of affinity of the glycidol moieties towards water on the macromolecule morphology in solution.

Data are now in the progress of being evaluated with quantitative structural models.
Recently, much interest in steel research has focussed on materials with an enhanced formability caused by the so-called transformation-induced plasticity (TRIP) effect. The enhanced plasticity is caused by a martensitic transformation of retained austenite (fcc phase) into ferrite (bcc phase) when stress is applied, and strongly depends on the dimension of the austenite grains (about 2 µm). The addition of niobium leads to NbC precipitates with dimensions of 5-10 nm and generally causes a significant reduction of the grain size.

In order to study the influence of the NbC precipitates on the microstructure of these steels we performed SANS measurements on two sets of TRIP steels (0.2 wt% C, 1.5 wt% Mn, 0.25 wt% Si) with (Nb) and without (LSi) added 0.05 wt% niobium. Two different heat treatments were applied to the samples: (TRIP1) heating to 1200 °C, annealing at 750 (or 825) °C, holding at 400 °C for 1 min, and cooling to room temperature. (TRIP2) heating to 740 °C, holding at 400 °C for 0.5, 1, 2, 5, and 10 min, and cooling to room temperature.

The SANS measurements were performed at room temperature in a transverse applied magnetic field of 1.15 T in order to saturate the magnetisation of the matrix to allow for a separation of dominant anisotropic magnetic contribution and the isotropic nuclear contribution. The magnetic scattering closely resembled the Porod law characteristic for relatively large non-magnetic inhomogeneities in an saturated magnetic matrix with \((\Delta \varepsilon / d\Omega)(Q) = K_M Q^{-4} + B\). The Porod constant \(K_M = 2\pi (\Delta \rho_{mag})^2 S\) is characteristic for the specific surface \(S\) between the magnetic and non magnetic phases of the sample for the contrast in magnetic scattering length density for iron \(\Delta \rho_{mag} = 4.8 \times 10^{10} \text{ cm}^{-2}\). The specific surface of the samples without niobium (LSi) amounts to about \(S_L = 0.46 \text{ m}^2/\text{cm}^3\) for the TRIP1 and \(S_L = 0.89 \text{ m}^2/\text{cm}^3\) for the TRIP2 samples.

In Fig. 1 the difference in magnetic SANS scattering between the samples with and without Nb is shown for the TRIP1 samples with two different annealing temperatures. For the annealing temperature of 825 °C a deviation from the Porod law is observed which may be ascibed to an additional contribution from the NbC precipitates.

In Fig. 2 the difference in magnetic SANS scattering between the samples with and without Nb is shown for the TRIP2 samples with two different holding times at 400 °C. The observed difference is small compared to the total signal of samples with and without Nb. The data can roughly be described by assuming spherical precipitates with a radius of 3 nm and a volume fraction of half the maximum \(f_{max} = 0.055\%\) as indicated by the solid line.
The goal of the experiments is the determination of changes in microstructure in a Sn-15\% Pb alloy (area of melting temperatures 182 - 212\(^{\circ}\)C) exposed to shear stress. Within first measurements in 2001 the experimental set up was tested using aqueous polymer suspensions with a known particle diameter and solid fractions \(f_s\) of around 35\%.

The used test cell consists of two concentric cylinders implemented into a rheometer. The resulting coaxial slit is 1.5 mm wide. The inner cylinder is rotating impressing a mechanical load to the material in the slit. Both cylinders are composed of synthetic quartz. To perform experiments with the metal alloy the sample environment was inertized with \(N_2\) and the cell was heated from the bottom.

At the beginning of the first measurement period in 2002 the empty cell was investigated in terms of transmission and scattering. After this the scattering of the alloy was analyzed in the liquid and the semi solid state. The alloy was first cooled down from 225\(^{\circ}\)C (\(f_s = 0\)) to 197\(^{\circ}\)C (\(f_s = \) ) without shear stress and reheated again. The neutron scattering was detected for varying detector distances (1 - 16 m). No scattering effects could be observed. Afterwards the alloy was cooled down to 199\(^{\circ}\)C (\(f_s = 42.5\%\)) and reheated with a shear rate of 100\(s^{-1}\). The viscosity of the alloy increased after reaching the semi solid state up to a stationary value indicating solid matter and a certain structure in the material. After heating up again the viscosity reached its initial value. A correlation between the progress of the viscosity and the scattering intensity is expected. The intensity should increase due to the solid matter and the structure. After heating up it should lead to its initial value again. Unfortunately no relationship could be figured out yet. The scattering intensities are randomized.

It is assumed that inhomogeneous temperature in the slit due to a heating from the bottom of the cell and oxidization of the alloy influenced the scattering of the solid matter.

Therefore the cell was optimized concerning heating and oxidizing conditions. The cell was surrounded by a heating chamber to insure a more homogeneous temperature. Additionally \(H_2\) was used for inertization.

Within the second measurement period this setup was used. The alloy was cooled down to the solid state and reheated again; firstly without a shear strain secondly with a shear rate of 100\(s^{-1}\). A detector distance of 4 and 16 m was used to check out the scattering area. As expected the intensity increased after reaching the semi solid state and reached the highest value in the solid state. This effect is reversible. Comparing the results with and without shear rate it can be stated that a mechanical load during cooling leads to smaller particles and a more isotropic structure (Figure below).

Afterwards the alloy was cooled down to the semi solid state (\(f_s = \) ) applying different shear rates (100\(s^{-1}\), 200\(s^{-1}\)). The integral intensity increased after achieving the semi solid state, but was not completely reversible. The irreversibility might still be a result of a small rate of oxidization, but can not be explained exactly Nevertheless a change in structure occurs when the alloy is sheared while cooling and this structure disappears after heating up (figure below, 100\(s^{-1}\)).

Different shear rates result in a change of particle diameter; the higher the shear rate the higher the diameter.
The dynamic sintering behavior of nanocrystalline zirconia ceramics doped with 12 mol-% yttria was investigated with small angle neutron scattering (SANS). The nanocrystalline powder was produced by Chemical Vapor Synthesis (CVS) and pressed into greenbodies. The samples were heated in the in-situ furnace HTF-1 from room temperature to 1000°C - 1300°C, by fast firing with more than 250 K/min, reaching the target temperature within a very short time of approximately 4 minutes. Two different time-temperature profiles were applied: In profile (A), the samples were directly heated from room temperature to a final temperature of 1000°C or 1200°C, and then sintered at this temperature for 3 hours. In profile (B), the samples were first overheated to a higher peak temperature of 1200°C or 1300°C. Immediately after reaching this temperature, the furnace heating was switched off, causing the sample temperature to decrease quickly. As soon as the sample reached 1000°C, the heating was switched on again with reduced power, to hold the sample at 1000°C for 3 hours, just like in profile (A). Therefore, the only difference between profiles (A) and (B) was the addition of a very short overheating (less than 1 min) at the beginning of the sintering process, as shown in Fig.1. The aim of these experiments was to determine the influence of this overheating peak on the long-time development of the sample structure during the subsequent standard sintering at a constant temperature. During the 3 hours at this constant temperature, SANS spectra were measured with a very good time resolution of only 2 min, yielding approximately 90 snapshots of the structure evolution. However, the duration of the overheating peak itself was too short for a time-resolved analysis with sufficient raw data statistics. Therefore, in profile (B) the zero-point of the time axis had to be located at the end of the overheating peak, where the speed of the structure development in the samples became slower. The measurements covered a wide range of the scattering vector Q between 0.035 nm⁻¹ and 3 nm⁻¹. This was achieved by using a new sample greenbody (all from the same powder batch) for each sample-detector distance of 1.1 m, 4 m, and 15.8 m, respectively. The size distributions of grains and pores as a function of sintering time were determined from the corrected scattering curves, using a direct model fitting with sets of lognormal size distributions. A special data processing technique was applied to compensate the effect of the very short data collection time per snapshot on the measurement statistics. This allowed a full preservation of the high experimental time resolution in the final results. Fig. 2 shows the differences in the evolution of grain and pore sizes for a final temperature of 1000°C, caused by the addition of a short overheating to 1200°C. It can be clearly seen that the overheating significantly reduces grain and pore sizes, and slows down subsequent grain growth. More results for other peak and constant temperatures, and for the influence on the relative density of the sample, will be published in an upcoming paper.
In advanced ceramic processing, ultrafine powders are employed to reduce sintering temperature and time to obtain a fine-grained structure. The most limiting factor for sintering of many ultrafine powders to full density is the presence of agglomeration. The aim of the experiments was to investigate, which sizes of agglomerates can be found in suspensions of ultrafine powders of silica, and in which way these agglomerate sizes are influenced by impact of high-power ultrasound at different pH-values of the dispersion. The agglomerate sizes of ultrafine silica dispersions, and the way to minimize them, play an important role both in industrial and in the academic field, since many properties of the dispersions are related to the size, e.g. polishing performance or rheological behavior.

For the present study, ultrafine silica powders were produced by Chemical Vapor Synthesis (CVS). The powders were dispersed both in pure distilled water and in a 0.01 molar NaOH aqueous solution with a solid concentration of 3wt%. The pure water dispersions had a pH of 4 and the 0.01 molar NaOH dispersions a pH of 9.5.

For the SANS measurements, a Starna flow cell with a thickness of 1 mm was placed in the neutron beam. This flow cell was connected to a closed tube circuit in which the dispersion circulated, driven by a flexible-tube pump. Outside the sample position of the SANS instrument, the dispersion passed a cooled double wall glass cell, in which an ultrasonic sonode with a diameter of 14 mm and a power of 200 W acted on the dispersion. After switching on the pump, first the scattering without ultrasonic agitation was measured as a reference, followed by a series of SANS spectra with a very good time resolution of only 2 min over a period of approximately 80 min, yielding 40 snapshots of the structure evolution. One final measurement was performed a few minutes after switching off the ultrasonic sonode, in order to determine whether there was any relaxation towards the agglomerate sizes before ultrasonic agitation.

The measurements covered a wide range of the scattering vector Q between 0.035 nm⁻¹ and 3.2 nm⁻¹. This was achieved by repeating the experiment three times for each sample at sample-detector distances of 1.0 m, 4.0 m and 15.8 m, respectively, each time using a fresh amount of sample liquid. The data reduction was performed using the HMI-standard 'BerSANS' software package. The two-dimensional data revealed a perfect circular symmetry, and were radially averaged to produce the scattering curves dΩ/dΩ. The related size distributions were calculated from these scattering curves by direct model fitting of lognormal distributions of spheres.

Fig. 1 shows volume-weighted size distributions for silica with a specific surface area of 350 m²/g, dispersed in pure water (top) and in 0.01 molar NaOH aqueous solution (bottom), for some selected agitation times. With increasing time, in the 0.01 molar NaOH dispersion a significant amount of large agglomerates is formed. This could be due to sintering of the particles caused by the high power ultrasonic impact. On the other hand, the effect of agitation in pure water is only minor. A possible explanation for this pH dependence of the agglomerate growth are solution effects and enhanced condensation reactions at high pH-value. To study this effect in more detail, further experiments should be made at different and higher pH-values.

Fig. 1: Size distributions from SANS data.
We are currently performing a comprehensive investigation of new Ferrofluids (FF) by means of small angle scattering using polarized neutrons (SANSPOP) [1]. In very diluted Co-Ferrofluids we were able to evaluate precisely the core-shell structure and size distribution of the nanoparticles. In a more concentrated Co-FF a previous study revealed the set-up of ordering effects in an external magnetic field [2]. In order to clarify the nature of the field induced correlations we investigated samples of different particle concentrations in variable external magnetic fields applied in different directions parallel and perpendicular to the incident beam. Anisotropic structure factors can be extracted by using the results of the scattering of individual particles previously obtained from SANSPOP in very diluted samples. Samples of Co-Ferrofluids of 1%, 2%, 3%, 4% and 6 vol. % in deuterated toluene have been prepared by Berlin Heart AG followed by its subsequent magnetic separation.

Two dimensional SANS pattern for non-polarised neutrons measured in a horizontal magnetic field of 1.1 T perpendicular to the incident beam are shown in Fig. 1. All samples pronounced peaks at low Q, which disappeared in zero field. As a typical example the 2D SANSPOP intensities I(-) and I(+) for neutron spin parallel and antiparallel respectively, are shown in Fig. 2 for the 2% Co-FF. The average [I(+)+I(-)]/2 corresponds to the scattering pattern of non-polarised neutrons while the difference pattern I(+)-I(-) of Fig. 2 reflects the nuclear-magnetic cross term resulting solely from one and the same particle. From Fig. 1 and Fig. 2 four peaks are clearly distinguished at scattering vectors with constant lengths corresponding to $Q_1 = 0.33 \text{ nm}^{-1}$ and forming angles of $\pm 30^\circ$ with the horizontal direction of the applied magnetic field. Two additional peaks appear at $Q_2 = 0.57 \text{ nm}^{-1}$ in the horizontal direction which results solely from nuclear contrast and disappears completely in the cross-term. $Q_1$ and $Q_2$ describe the pseudo-crystalline ordering of the Co particles in an external field. A second type of texture described by the scattering vector $Q_3 = 0.24 \text{ nm}^{-1}$ was found to be present simultaneously [2].

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[1] A. Wiedenmann
SANSPOL measurements have been combined with small angle synchrotron X-ray scattering (SAXS) study performed on the ID01 beamline at ESRF, Grenoble. The same samples with Co concentration 1%, 2%, 3%, 4% and 6 vol. % have been measured in thin tubes using a horizontal magnetic field applied perpendicular to the incident beam.

As with the neutrons, four well-resolved peaks correspond to reflections at $Q_1$ of texture type I and two reflections in vertical direction to type II. The cut along the vertical direction, plotted in Fig. 1b, show clearly the strong peak at $Q_3$, as well as a shoulder corresponding to a scattering vector $Q_1$. SAXS and SANSPOL intensities averaged over azimuth angles of 15° in the four sectors (Fig. 2) are in perfect agreement. Below $Q_3$ the intensity in the sector $\alpha=90^\circ$ is found to increase continuously according to $Q^{-1}$ which confirm the presence of chain segments aligned along $H$. The position of the SAXS peak at $Q_3=0.324\text{nm}^{-1}$ was found to be nearly independent of the concentration while the peak width decreases and the position for $Q_3$ varies from 0.22 to 0.27 nm$^{-1}$ in the concentration range between 2% to 6%.

Work supported by the project DFG Wi 1151/2-2
In order to investigate the structural arrangement perpendicular to the basal planes, two samples with 3 vol% Co ("D3a") and 5 vol% Co ("D5a") were mounted in a horizontal cryomagnet where the field up to 4 T was aligned parallel to the incoming neutrons. Since in this configuration $\sin^2 \alpha$ is unity for all values of $Q$, fully isotropic patterns are expected for SANS and SANSPOL as long as $S(Q, \alpha = 90^\circ)$ is isotropic. In Fig. 1a) the SANS pattern of the D3a (3%) sample averaged in sectors of 10° width are plotted for the sectors $\phi = 0^\circ$ and 90°, respectively. When the magnetic field is switched to 1T a diffuse ring is observed at $Q_3 = 0.08-0.1$ nm$^{-1}$ for D3a (3%) which is assigned to a “powder” reflection. The maximum of intensity is slightly enhanced in vertical direction $\phi = 90^\circ$ with respect to $\phi = 0^\circ$ which proofs the presence of some texture with a slight preference of type II. The radial averaged SANSPOL intensities, shown in Fig. 1b) confirmed this results. No further peak is detected, indicating that the correlations perpendicular to the magnetic field are less pronounced. In the 5%-Co sample the peak appeared at a much higher value of $Q_3 = 0.21 - 0.23$ nm$^{-1}$. This indicates that with increasing particle concentration the average distance between layers decreases from $c(D3a) = 78$ nm to $c(D5a) = 31$ nm which is much larger than the (concentration independent) in-plane distance of $a = 21.34$ as reported in [1].

When the sample D3a was cooled in an external field of 1T applied parallel to the incident neutrons, the total scattering intensity showed an abrupt increase around $T_f = 185 K$ together with an increase of the anisotropy (i.e. increasing texture), indicating freezing of the matrix. The process was found to be fully reversible. The freezing transition was followed on the 2 vol% DS2 sample when the magnetic field was applied perpendicular to the incident neutrons. The differences $I(+) - I(-)$ plotted in Fig. 2 for the sectors at 90° and 30° reveal again maxima at $Q_3 = 0.27$ nm$^{-1}$ and $Q_1 = 0.34$ respectively. The peak positions were not changed at $T_f$ but the intensity of the $Q_3$ peak (type II texture) increased at the expense of the $Q_1$ peak (type I texture). An additional contribution with the characteristic $Q^{-1}$ dependency occurs below $T_f = 185 K$ which implies in fact the freezing-in of uncorrelated chains aligned along the magnetic field (which is perpendicular to the incident neutrons).

FIG. 1: 3% Co FF sample in a magnetic field applied parallel to the incident neutrons. a) The SANS signals at $H = 0$ and $H = 1T$, averaged over sectors of $10^\circ$ in horizontal (open symbols) and vertical directions (solid symbols). b) Radial averaged SANSPOL-intensities $I_+$ and $I_-$ at $H = 0.3T$. The solid lines correspond to non-interacting core-shell particles.

FIG.2: SANSPOL difference intensities $I_+ - I_-$ for DS2 sample (2vol%) measured at $H = 1T$ applied perpendicular to the incident neutrons

We acknowledge Dr. Gansau and Dr. Buske from Berlin heart company for supplying samples.

Work supported by the project DFG Wi 1151/2-2.
A variety of samples were submitted by various research groups from South African institutions for analysis using the SANS technique at beam-line V4. The aim of these investigations was to determine the feasibility of SANS related research in the South African context. The outcome of such experiments were essential towards an IAEA Technical Cooperation proposal of setting up a SANS facility at the South African research reactor, SAFARI-1.

The raw data was processed using the procedures outlined in the BERSANS manual. Samples of bolaamphiphile fibres, which could play an important role in future anti-microbial matrices and biosensor development, were investigated, but did not yield any SANS scattering. Maintaining the fibres in suspension in solution, instead of sinking to the bottom of the vial and out of the beam line of sight, could not be overcome.

Two samples of metal oxide coatings on a Ti substrate revealed positive SANS results (fig. 1). Further analysis of the $Q^{2.5}$ scattering is pending further input from the supplier of the samples (i.e. TEM/SEM images, PIXE analysis, WAX results, etc.) Polybutyl acrylate mini-emulsions of particle sizes 20-50nm and 100-120nm yielded unexpected SANS results (fig. 2). Scattering from the sample consisting of smaller particles was typical of that of larger particles (prominent $Q^4$ like behaviour). The reason for this was probably due to interference effects of the particles in this sample.

A 20%methacrylate/80%methyl-methacrylate copolymer sample (fig. 3) showed a significant SANS peak at 1.9nm$^{-1}$ that corresponds to a lamellar spacing of 3.3nm$^{-1}$. This peak was not present in the pure methacrylate polymer sample.

Eleven foil samples of electrospun fibres made of PAN powder (MW 85k) under various conditions were investigated for nanostructural differences using the SANS technique. From the spectra (fig. 4) no differences in curve shape can be distinguished, hence it may be deduced that there are no nano-structural differences.

PAN fibres of MW=210 were aligned almost vertically in the beam, and an anisotropic SANS pattern recorded (fig. 5). The anisotropic scattering perpendicular to the fibre orientation was typical of the $Q^2$ behaviour expected from polymers.

**Fig. 1 – SnO$_2$, RuO$_2$ and IrO$_2$ nano-composite embedded on a Ti substrate.**

**Fig. 2 – 100nm (circles) and 20nm (squares) particle SANS scattering curves.**

**Fig. 3 – MET20PMMA (circles) and MET (squares) showing peak.**

**Fig. 4 – Scattering curves of PAN foil samples showing similar shape.**

**Fig. 5 – Anisotropic scattering pattern observed at SD=12m for fibres aligned almost vertically.**

**Experimental Report:**

- **IAEA Technical Application:**

  - **Proposal Nº:**
    - Instrument: V4
    - Local Contact: Dr. A. Wiedenmann
    - Date(s) of Experiment: 3-11/09/2002

  - **Date of Report:** 15/01/2003
EXPERIMENTAL REPORT  
SANSPOL investigations of a citric acid based magnetite ferrofluid

<table>
<thead>
<tr>
<th>Principal Proposer:</th>
<th>A. Wiedenmann, HMI Berlin</th>
<th>Date(s) of Experiment</th>
<th>25.03 - 26.03. 2002 06.09 - 07.09. 2002</th>
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<td>Experimental Team:</td>
<td>M. Kammel, HMI Berlin</td>
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<td></td>
<td>E. García-Matres, HMI Berlin</td>
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<td>A. Hoell, HMI Berlin</td>
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Ferrofluids are magnetic liquids with a great potential for medical applications. Therefore it is necessary to develop new ferrofluids, which are bio-compatible. The stabilisation of the magnetic cores with citric acid is one possible way. However, the nanostructure of such a ferrofluid is still unknown. This is the reason for our SANSPOL[1] investigation of ferrofluids based on a stabilisation with citric acid. The Berlin Heart AG prepared four different samples for the investigation. All samples contain magnetite from the same preparation and water as solvent. For the chemical contrast variation we have been analysing samples with different H/D ratios of the solvent. Additionally the use of polarised neutrons allows a magnetic contrast variation.

All measurements were performed on the Instrument V4 of the BERII reactor at the Hahn Meitner Institute Berlin, using polarised neutrons with a wavelength of $\lambda=0.6\text{nm}$.

The results for the case of a highly deuterated sample shows Figure 1. In previous investigations [2,3] we observed a crossover of the scattering curves $I^{-}$ and $I^{+}$ for the scattering intensities of polarised neutrons. In the case of citric acid this crossover phenomenon did not occur. This is a hint for a very small shell thickness or a small contrast between the shell and the matrix. In fact, a fist analysis revealed the presence of two sorts of magnetic particles namely nanosized core - shell particles and large aggregates. In the next steps of data analysis we analyse all scattering curves of the contrast variation simultaneously to get a reliable result for the shell thickness and the composition of the aggregates.

Work supported by DFG project Wi 1151/2-2 in the frame of priority program SPP1104.

References:
EXPERIMENTAL REPORT

Structural and magnetic properties of Nd$_{60}$Fe$_{20}$Co$_{10}$Al$_{10}$ bulk amorphous alloy

<table>
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<th>Principal Proposer:</th>
<th>García-Matres E. HMI</th>
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<tr>
<td>Experimental Team:</td>
<td>Kumar G. IFW-Dresden</td>
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<td></td>
<td>García-Matres E. HMI</td>
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<td>Heinemann A. HMI</td>
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</table>

Date(s) of Experiment: 25.10.- 27.10.2002
                  11.11.- 13.11.2002

Date of Report: *6.01.2003

Amorphous rare-earth-transition-metal alloys can be produced in the as-cast state exhibiting hard magnetic properties. It has been reported that the coercivity of amorphous ferromagnetic materials is sensitively dependent on the microstructure[1].

The structural and magnetic properties of Nd$_{60}$Fe$_{20}$Co$_{10}$Al$_{10}$ bulk amorphous rods were investigated in a previous work by X-rays diffraction and scanning electron microscopy[2]. It has been found that all these samples exhibit two-phase microstructure comprising of Nd-rich and Fe-rich regions. Additionally, the TEM examinations revealed that the nominally amorphous phase consists of an amorphous Nd-rich matrix with small grains of Nd-crystallites[3].

From the magnetic point of view, the thermomagnetic curves reveal two Curie Temperatures $T_{C1}$=32-52K and $T_{C2}$= 470-500K suggesting the presence of two magnetic phases[3].

The aim of this work is to clarify the correlation between the structure of the sample and the magnetic properties. Small-angle-scattering is a sensitive technique which allows to determine the presence of the nanoscaled crystallites, characterize their size and the volume fraction and also to investigate the magnetic structure.

The measurements were performed on the instrument V4, using the polarisation option, SANSPOL. For the experiments at low temperatures (from 6K to 250K) the vertical cryo-magnet VM3 was mounted as sample environment, and the electromagnet with furnace for the high temperatures (from 300K-470K).

It is important to point out the use of the polarized neutrons in these measurements in order to separate accurately the nuclear and magnetic scattering contribution due to the expected weak magnetic effect. Measurements where performed in 1 Tesla magnetic field at different temperatures following the two magnetic phase transitions at $T_{C1}$ and $T_{C2}$ . Field variation has been also investigated at some fixed temperatures.

The scattering curves in fig 1 show a variation of the magnetic scattering length density at different temperatures. These curves corroborate the weak effect as predicted. However we can clearly observe that at low temperature the scattering curve denoted by “on” is below the “off” one, but it reverts around the $T_{C1}$, suggesting a change in the magnetic moment of the particles. Data analysis is underway.

Fig 1: SANS scattering curves at different temperatures. The polarisation of the incoming neutrons are denoted by on and off

This job is supported by DFG-Wi-1153/3-1

References:
   L. Schultz.
   J. of Alloys and Compounds (in press)
   L. Schultz, S.Ram
   Acta Materialia (in press)
Ferrofluids are a mixture of different constituents. In a surfactant stabilized ferrofluid core-shell particles, aggregates and free surfactant material coexists. The SANSPOL method combined with H/D isotope variation of solvents allows an accurate determination of the structural parameters. We will report on our investigations of two identical Magnetit ferrofluids with oleoylsarcosine as surfactant in different solvents (toluene and water). To clarify the question, how oleoylsarcosine is bonded to the magnetic particle surface, we performed a SANSPOL measurement at the instrument V4 of the BERII reactor at the Hahn Meitner Institute Berlin. For this purpose the thickness of the surfactant layer in different solvents had to be determined precisely.

The SANSPOL intensities perpendicular to the applied field are given for the two polarization states by $I_{\perp}(Q \perp H) \propto [F_N \pm F_M]^2$ when the magnetic moments and neutron polarization are fully aligned along the external field. The difference $I_{\perp}(Q \perp H) - I_{\parallel}(Q \perp H) \propto F_N \cdot F_M$ represents a nuclear magnetic cross term which is linear in the nuclear and magnetic amplitudes and contains only particles with magnetic form factor $F_M$. The detailed equations of the scattering cross sections and form-factors for the non-fully aligned case are also given in [4]. By calculating the magnetic-nuclear cross term, as shown by the symbols in Fig. 1a, the scattering parts of free non-magnetic structures were eliminated. It turned out that two different magnetic structures are present in this ferrofluid. Besides the main component of separated magnetic core-shell particles a definite amount of larger magnetic aggregates was identified. These aggregates consist of a mixture of magnetic cores and a higher amount of surfactants with a broader size distribution. The averaged core radii $\langle R \rangle$ are 5nm and identical for both the water and toluene based ferrofluids. This is the direct evidence that the core size distributions remain unchanged during the slightly different ferrofluid preparations when water or toluene is used as solvents.

Using these results derived from the cross term the reconstruction of the direct measured curves for the two polarization directions, $I_{\parallel}$ and $I_{\perp}$, yield at low Q to good agreement of the data but not at high Q. This is the direct evidence that the sample must contain additional non-magnetic free nano-structures besides the two identified magnetic ones.

Three structural parts, core-shell particles, aggregates and excess surfactants were found in both ferrofluids. As a main result the shell thickness of the surfactant, oleoylsarcosine, is found to be clearly different in water (2.3nm $\pm$ 0.1nm) and toluene (1.9nm $\pm$ 0.1nm) based ferrofluids. From that we conclude to have a bilayer formation in water and a monolayer in toluene. This indicate that bonding of the surfactants to the magnetic core is mediated via the hydrophilic acid group.

![Figure 1](image)

**Figure 1**  
(a) magnetic-nuclear cross term as calculated by $I_{\perp}(Q \perp H) - I_{\parallel}(Q \perp H)$ the water based ferrofluid with the model fit (line)  
(b) SANSPOL intensities calculated with the fit results

Work supported by DFG project Wi 1151/2-2 in the frame of priority program SPP1104.

**References:**
A new preparation method of ferrofluids [1] opens the access to ferrofluids with a small size distribution. This method works with a thermal decomposition Co-Carbonyl compound in the presence of Trialkylaluminium. The magnetic cores are stabilized against coagulation with oleoylsarkosine. A ferrofluid with a small size distribution is interesting for some biomedical applications, e.g. hyperthermia [2]. We perform SANSPOL measurements, in order to evaluate their unknown nanostructure. For this structure investigation 3 different samples with different H/D-ratios of the solvent (toluene) was prepared.

Measurements were performed on the instrument, V4, using the polarisation option, SANSPOL [3]. The SANSPOL intensities for two polarisation states \(I(Q;\perp H)\) and \(I(Q;\perp H)\) and the nuclear and magnetic scattering are presented in Fig.1 for the high deuterated sample. At high Q values we observe no dependence of the intensities from the polarisation of the neutrons. This is a hint for a fraction of non-magnetic particles. The nuclear-magnetic interference term \(I-I'\) allows the analysis without non-magnetic particles and we obtain a core-shell particle with a lognormal distribution with a mean radius of 3 nm and a small width of 0.8nm.

The mixture of the high deuterated sample and the non deuterated sample shows an arrangement effect, similar to that observed in another type of Co - ferrofluid. [4] The data analysis is in progress.

Work supported by DFG project Wi 1151/2-2 in the frame of priority program SPP1104.

References:
Recent interest in cellular metals [1] generate questions about the size and structure of the porous within the foam. USANS measurements performed at the GKSS were used to extract information about the typical porous sizes and the foaming time dependency [2]. The available q-range in the USANS experiment is perfect for the expected pore-sizes in the range of 1-100 µm but can’t give some information about the pore-surface constitution. In [2] a porod behaviour of the scattering curve for the q-range greater than 2*10⁻³ nm⁻¹ was expected. SANS measurements were performed on the instrument V4 to check this hypothesis. In Figure 1 the results of the USANS and SANS experiments are shown. For all samples, the unfoamed and foamed one find a clear deviation from the porod law I(q) ~ q⁻⁴. This is a hint of a possible coarse pore-surface. As expected, the growth of the pores with foaming time leads to a decreasing number of small structures. This can be deduced from the intensity difference between the black and the blue curve in Figure 1 for the different q-ranges. Both the q-ranges for the USANS and SANS experiments can be expanded to surmount the existing gap. This was a possible task for further experiments.

Figure 1:
The USANS and SANS data from a foamable precursor material (unfoamed) and two different foamed states. In the USANS q-range the upper (blue) curve comes from the 120 s foamed sample. The lowest intensity shows the red curve from the unfoamed sample and the black curve between them is from the for 80 s foamed sample.

References:
The nano crystalline materials have excellent mechanical and electrical property compared to conventional materials. These advantages mainly come from their nano-sized grain structure. Usually the nano crystalline materials are fabricated using nano powder. The optimum consolidation process is essential to obtain fully densified structure. The quantitative characterization on remaining pores is important to study the consolidation process. SANS is the best technique to characterize the nano sized inhomogeneities in bulk samples.

Al nano powder was synthesized by Pulsed Wire Evaporation (PWE) method in KAERI. The nano-powder compacts were fabricated by Magnetic Pulse Compaction (MPC) method. The fabrication conditions of Al nano compacts are listed in Table 1. The relative densities of Al nano powder compacts are also shown in Table 1. The relative densities were measured using Archimedes’ method. The Aluminum Oxide was observed by TEM (Transmission Electron Microscopy) at the surface of Al nano powder. The small angle neutron scattering experiments were performed both at the instrument V4 in HMI and at the SANS facility in KAERI.

The Fig. 1 shows the comparison the SANS result of Al275z compact measured in HMI with the SANS result obtained in KAERI. The light water used for absolute calibration of HMI SANS data and the porous silica used for absolute calibration of KAERI data. The two results show the excellent agreement in the overlapping Q range. Because maximum sample to detector distance of KAERI SANS facility is only 4.5m, minimum Q value of KAERI data reveals 0.1nm⁻¹.

Fig. 2 shows the SANS results of Al271z, Al270z, Al273z and Al272z compacts. The scattering intensity at high Q region increases with decreasing relative density, while the intensity at low Q region increases with increasing relative density. The scattering intensity depends on the content of residual pores and Al oxide particles. The volume fraction of Al oxide particle increases with relative density due to the fragmentation of Al oxide layer. The extra scattering at low Q region results from the presence of Al oxide particles.

<table>
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<td>275z</td>
<td>0.7</td>
<td>300</td>
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Fig. 1 Comparison of HMI SANS result and KAERI SANS result of Al275z compact.

Fig. 2 SANS results of Al nano powder compacts.
The ability of magnetotactic bacteria to orient and migrate along geomagnetic field lines is based on intracellular magnetic structures, the magnetosomes, which consist of nano-sized, membrane bound crystals of magnetic iron materials [1-3]. The formation of magnetosomes is achieved by a biological mechanism that controls the accumulation of iron and the biomineralization of magnetic crystals (in most cases magnetite) with a characteristic size and morphology within membrane vesicles.

Nowadays, there are a lot of efforts to cultivate these magnetotactic bacteria to produce and extract the magnetosomes particles, which has proven to be difficult. The mechanisms of magnetosome formation might be relevant for the synthesis of ferrofluids (FFs) with designed properties, useable in magnetic drug targeting, cell separation and hyperthermia. Chemical prepared FF’s have magnetite core diameters up to 15 nm or larger than 70 nm. The medical most interesting size range is excluded. Therefore, magnetosomes with sizes of about 40 nm can fill that size gap.

This report focuses on SANSPOL investigations of magnetite magnetosomes samples extracted from cultivated bacteria (Magnetospirillum gryphiswaldense) and soluted in H\textsubscript{2}O/D\textsubscript{2}O. Measurements were done on the instrument V4 using the polarisation option SANSPOL [4] and applying a horizontal magnetic field of 1 T to the samples perpendicular to the neutron beam.

In Fig. 1 the SANSPOL scattering curves and the derived nuclear scattering are shown. The simultaneous fits of these three curves (solid lines) revealed the existence of core-shell particles (magnetite surrounded by an organic membrane) and also few aggregates were found. The volume size distribution of core radii as shown in Fig. 2 corresponds to an averaged core radius of 21.8 nm and a shell thickness of 3.4 nm. These sizes are larger than those values of a former measurement (R_{core} = 15.6 nm, d_{shell} = 4 nm). This is evidence that the sizes can be controlled by biological environment conditions, because the magnetotactic bacteria were grown under different conditions.

The two dimensional SANS pattern of a comparable but higher concentrated fluid measured in a horizontal magnetic field for neutron spin parallel is shown in Fig. 3. The pattern is non-radial symmetric and exhibit pronounced peaks at low Q values that disappeared in zero field. The iso-intensity regions are found to be also non-radial symmetric in case of neutron spin antiparallel and also for non-polarised neutrons. The regular arrangement of the peaks indicate a pseudo-crystalline field induced ordering of the magnetite cores, as observed in case of Co-FFs [5].

The work was supported in parts by DFG priority program “Ferrofluids”. Dr. D. Schüler, MPI Bremen, provides the samples kindly.

The magnetization of barium hexaferrite nanocrystals used as cores in ferrofluids was found to be about 43% comparing with the bulk value [3,5]. This effect can be caused by non-stochiometry leading to a homogeneously distributed reduced magnetization or by a crystal surface region with reduced magnetization. On the other hand the different ferrofluid preparation steps could have an influence. To clarify this we measured by SANS-POL (V4 with polarization option, HMI) glass ceramics in which the nano-crystals were grown during annealing at 580 °C [1]. A first set of different samples annealed for different durations in air yields SANS results that won’t follow a growth series. The scattering of the as quenched samples differ slightly, which is direct evidence that the fast cooled glassy flakes contain different amounts of athermal nuclei and some particles, too. Therefore, one and the same sample was annealed stepwise starting with short annealing durations (2min) and prolonging the duration. By SANS was found a very fast formation and growth of magnetic particles during the early annealing states followed by slight increases. The invariant \( \text{Inv} = \int I(Q) Q^2 dQ = f (1-f) (\Delta\eta)^2 \), whose value increase with the volume fraction \( f \), are shown in cases of nuclear and magnetic scattering in Fig. 1. The increasing invariants reveal a fast particle formation that is followed by a slower growth of magnetic nano-crystals.

**Fig.1:** Invariants calculated from SANS as function of annealing time.

It is known, that beside the formation and growth of barium hexaferrite other non-magnetic phases are formed during the glass crystallisation, too [4]. Therefore, the calculation of the nuclear-magnetic cross-term from the measured curves of the two polarization states (ON-OFF) yields the scattering cross section of magnetic nano-structures only, and excludes all pure non-magnetic inhomogeneities.
The relaxation processes in an elongated linear polymer melt were studied using SANS. The polyisoprene sample was stretched to a ratio of 2 and quenched immediately afterwards in order to stop the kinetics of the molecules. We observed the elongated sample before relaxation as well as relaxed states obtained later on by warming the sample, creating thereby a series of „snapshots” on the relaxation time axis. This technique enables us to decouple the measuring time from the microscopic time and thus observe even extremely fast motions with SANS.

The aim of this work is to shed light on the retraction processes in a polymer melt. In their theory of polymer dynamics, Doi and Edwards\(^1\) described the relaxation dynamics in a polymer network but stopped in the case of a melt after a few assumptions. Experimentally, a study on a melt is extremely delicate since the sample flows after elongation. This study is a follow-up of a former work done by F. Boué\(^2\) on one side, who studied elongated polystyrene samples which were poorly entangled and therefore had a broad tube diameter, and the work done by M. Heinrich\(^3\) on the other side, who realized a study on H-shaped polymers using the same home-built extensional rheometer as reported here. We were able for the first time to observe the relaxation in both directions (parallel to the stretch and perpendicular to it) of linear chains.

The experimental setup consists of two clamps holding the sample, located in a thermo box which regulates the temperature with a precision of \(\pm 1\)°C using gaseous nitrogen. A step motor realizes a stretch with a constant strain rate. The sample was stretched within one second to a ratio of 2 in the length at a temperature of \(-35\)°C, so that nearly no retraction happened during the elongation itself (the WLF coefficients were determined in a preliminary linear rheology study). We chose this temperature as low as possible in order to minimize the relaxation during elongation, but maximize the viscosity during the stretch. The sample was quenched immediately after the stretch within one second to a temperature of \(-85\)°C, which is below the glass transition temperature \((T_g)\) of the sample and therefore stops the molecular dynamics. All the SANS measurements were realized at \(-85\)°C. The relaxed states were obtained by warming the sample slightly above \(T_g\). We calculated online the equivalent time it represents at room temperature by using the WLF coefficients. With this technique we can decouple completely the measuring time from the microscopic time and thus observe - quenched- extremely fast motions with SANS.

The results plotted here represent the scattering function at 5m in 2D. The left plot is the isotropic state of the sample, whereas the elongated -but not yet relaxed- one is represented on the right. Along the parallel axis to the stretch the molecules have the highest radius of gyration \((R_g)\), which is responsible for the fastest decay in intensity (the intensity goes to smaller Qs, short ellipse axis) and along the perpendicular axis the other way around (large axis).

The first elongated state (before relaxation) was fitted in 2D as well as along the axes according to newly developed concepts. This experimental technique has therefore proven its valuability: using the full Q range of the SANS we were able to observe the relaxation, the limit being solely the quality of the sample. The investigation will be carried out to other relaxation times as well as other elongation times and elongation factors in order to cover the full dynamic range of Rouse to reptation processes. We will also be working with other molecular masses and the rheometer will soon be implemented with a load cell located below the lowest clamp.

**EXPERIMENTAL REPORT**

The optimum composition for ceramic neutron image plates based on BaFBr:Eu$^{2+}$ and GdF$_3$

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Principal Proposer: J. Zimmermann, R. Kolb, TU-Darmstadt
Experimental Team: R. Kolb, J. Zimmermann, TU-Darmstadt
J. Klenke, S. Danilkin, HMI

**Date of Experiment:**
February 2002

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**Introduction:**
In commercial neutron image plates a powder mixture of neutron converter (Gd$_2$O$_3$) and storage phosphor (BaFBr:Eu$^{2+}$) is embedded in an organic binder. The storage center generation due to neutron irradiation is initiated by the absorption of neutrons in the converter material and subsequent emission of conversion electrons produced during the isotope decay. The electrons penetrate the storage phosphor and generate defects which are able to store the neutron information as a latent image. The readout of this information is performed by optical stimulation of defects resulting in the so called photostimulated luminescence (PSL). The intensity of the PSL signal reflects the efficiency of the NIP. The organic binder phase is used only for mechanical stabilization and is coupled with a loss of efficiency caused by its volume fraction giving no contribution to the detected luminescence and also by absorbing electrons from the converter material on their way to the storage phosphor. Ceramic NIPs without binder phase are alternatives for improving the efficiency, where overall efficiency of the NIP is mainly dependent on the volume fraction of the neutron converter.

**Experimental:**
Investigations on the influence of the volume fraction of converter material were carried out at samples consisting of BaFBr:Eu$^{2+}$ as storage phosphor and GdF$_3$ as converter material whereby the later was varied in a range between 0 and 40 Vol%. All samples were irradiated for 1 minute with neutrons in the experimental hall at the E1 using a cold neutron beam with a wavelength of $\lambda = 2.42$ Å and a flux of $2.6 \times 10^6$ cm$^{-2}$s$^{-1}$. PSL was measured using a setup developed at TU-Darmstadt stimulating in a range from 750 to 450nm.

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**Results and Discussion:**
The correlation between the measured PSL-intensity and the volume fraction of converter material is plotted in figure 1. A maximum in PSL output was found for a content between 4 and 5 Vol% converter material. A mathematical discussion of this result is made in the following: Since the storage mechanism is initiated by conversion electrons as a result of neutron absorption, the PSL intensity has to be proportional to the number of absorbed neutrons which is given by:

$$N_{\text{neutron}} = 1 - \exp \left( -x \sum a_i \cdot \sigma_i \right) \left[ 1 \right]$$

Whereby $x$ is the penetration depth of neutrons, $\rho$ is the relative achieved density taken from equation [2], $\sigma_i$ is the absorption coefficient of the component $i$ (0,124 cm$^{-1}$ for BaFBr and 1200 cm$^{-1}$ for GdF$_3$) and

$$I_{\text{PSL}} = a \cdot \left( 1 - \exp \left[ -x \sum a_i \cdot \sigma_i \right] \right) \cdot a_{\text{phosphor}} \left[ 3 \right]$$

Vol$_i$ is the volume fraction of the component $i$. The linear correlation of the density as a function of the volume fraction GdF$_3$ was obtained by fitting the experimentally determined values leading to:

$$\rho = -0.66 \cdot V_{\text{GdF}_3} + 0.92 \left[ 2 \right]$$

Only neutrons captured by the converter material give a contribution to the PSL, making it reasonable to multiply equation [1] with the volume fraction of converter material. This results in equation [3] which was finally used describe the PSL intensity:

The fitted curve is plotted in figure 1, the obtained fitting parameters were found to be 211µm for the penetration depth of neutrons, a background of $a=1.8$ and a factor of $b=252$ with a maximum at 4.4 Vol% GdF$_3$. According to calculations by Thoms [Applied Optics, 1996, Vol.35 No.19] it should be mentioned that the above made calculations where done with the assumption that the penetration depth of the readout light is in the same range as the penetration depth of neutrons so that the whole volume of created color centers was read out.

**Summary:**
A model is presented giving the correlation between volume fraction of converter material and PSL-intensity showing an optimum at 4.4 Vol% GdF$_3$, which is in good agreement with the experiments.
**EXPERIMENTAL REPORT**

**Photostimulated Luminescence in fluoroaluminate glass after neutron irradiation**

<table>
<thead>
<tr>
<th>Principal Proposer:</th>
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<th>Proposal N° * EF</th>
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<td>Experimental Team:</td>
<td>J. Zimmermann, R. Kolb, TU Darmstadt</td>
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<td>J. Klenke, S. Danilkin, HMI</td>
<td>Local Contact J. Klenke</td>
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<td>Date(s) of Experiment</td>
<td>18.03.-24.03.2002</td>
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**Introduction**

Commercial neutron image plates (NIPs) usually consists of a mixture of crystalline powders of the neutron converter Gd\(_2\)O\(_3\) and the Europium doped BaFBr as the active storage phosphor embedded in an organic binder. Such a NIP possesses the disadvantage of a limited spatial resolution which is caused by the scattering of the readout light at the interface of grain boundaries and the organic binder due to differences in the refractive index. In this study we tested new storage phosphors which are based on an amorphous fluoroaluminate glass with the potential advantage of enhanced spatial resolution due to reduced light scattering of the photo-stimulating laser beam. The focus of investigations was placed on the occurrence of photostimulated luminescence (PSL) after neutron and x-ray irradiation. For Europium doped aluminate glass it is shown that an amorphous material with a high amount of the converter Gd forms stable F-centers when irradiated with ionising radiation.

**Experimental**

Two compositions were investigated: 30AlF\(_3\)-14BaF\(_2\)-6BaCl\(_2\)-20CaF\(_2\)-19,GdF\(_3\)-0,1EuF\(_2\) (comp. 1) and 28AlF\(_3\)-13BaF\(_2\)-6BaCl\(_2\)-5CaF\(_2\)-15MgF\(_2\)-5NaF-29,GdF\(_3\)-0,1EuF\(_2\) (comp. 2) in mol-%.

The fluoroaluminate glass samples, covered in a light-tight aluminium box, were irradiated for several hours using a monochromated neutron beam (2,42 Å) with a flux of 2,6*10\(^6\) cm\(^{-2}\)s\(^{-1}\) to produce electron and hole traps within the material. Subsequently, the glasses were transferred in a setup developed at TU Darmstadt whereby PSL-spectra were measured with a stimulation light within a range from 455 to 700nm while the characteristic emission of the Eu\(^{2+}\) ions at 400 nm was recorded. After the PSL measurement the samples were erased in the environmental light of the experimental hall. A second PSL spectrum was recorded from the erased sample to verify the authenticity of the measured maxima.

**Results and discussion**

For both compositions PSL could be measured after neutron irradiation. However the PSL-intensity for comp. 1 was extremely weak and could not be separated successfully from the background noise. The PSL intensity of comp. 2 was at least 5 times higher and showed two maxima. [Fig. 1, curve 1] After erasing the sample in the environmental light only background were measured. [Fig. 1, curve 2]. By subtracting the background from the measured PSL curve of the irradiated sample the pure PSL spectrum was determined. [Fig. 1, curve 3]. The components of this PSL spectrum was analyzed using curve fitting based on a gaussian model. [Fig. 2]

In accordance with PSL-spectra measured after x-ray irradiation with higher dose to enhance the signal intensity two maxima were observed at 2,48 eV and 1,85 eV. Hence we suppose the existing of a short-range ordering where traps were formed. Sodium, well known as glass former, was expected to modify the bond-energies within the short-range ordering and thus facilitate the formation of two traps in comp. 2.

**Conclusion**

We have shown that PSL is observed after neutron irradiation in Eu-doped fluoroaluminate glass with an amount of Gd. In addition we observe specific PSL-maxima which were expected to be due to a trap formation within a short-range ordering in the glass. By modifying the composition the PSL intensity can be enhanced.
A new compact graphite (PG) monochromator was built with a variable vertical focussing device. This device is not much larger than a holder for a flat monochromator and fits into the 3-monochromator changer (Cu, Ge, PG) of the Flat-cone diffractometer E2. The monochromator consists of 15 PG crystals (50 x 25 x 2 mm) mounted on 15 separate plates which are adjustable manually. Three crystals are fixed together on a horizontal stripe also manually adjustable. Then we have 5 horizontal stripes as shown in Fig. 1. These stripes are fixed on an upper and lower triangular aluminium sheet which can be curved by 2 step motors.

All 15 crystals were adjusted to there zero position (flat) on the E2a instrument. There we tested also the precision of the curvature for different radii of curvature. The deviation from theory was not more than about ±0.1 degree. The monochromator was installed and tested at the E2 instrument. The intensity increase as a function of curvature is shown in Fig. 2. The increase by a factor 2 is due to the increase of the vertical divergence from 0.9 (flat) to about 1.8 degree for maximum curvature. One has to be aware that the higher divergence reduces the vertical resolution and neighbouring layers in the Flat-cone technique have than to be more separated.

We acknowledge helpful discussions with Dr. K. Knorr and Prof. W. Prandl from Tübingen. Most parts of the bending device have been manufactured in the workshop of the University Tübingen by Mr Schilling. We thank Mr Tauchelt and Mr Harm from the HMI for support in electronics.
Pressure represents besides the temperature and magnetic field one of the three principal thermodynamic variables. Physical properties of solids depend naturally on the thermodynamic conditions of the surroundings. Although is Hahn-Meitner-Institute at the forefront of the sample environment development, especially what is the high magnetic field concerned, its position is not strong in having possibilities to produce high pressure (in excess of 10 kbar) in volumes that are large enough to accommodate sample for powder diffraction. It is relatively straightforward to produce clamp type pressure cells. Problematic is, however, security a reliability of the pressure cell performance on one side and relatively thick walls that impose absorption of neutrons on the other. In combination with problems of 1, additional background signal due to incoherent scattering on the pressure-cell and the transmitting medium (FC77/77 or oil), 2, pressure drop upon cooling and 3, question how to measure the pressure in situ it appears that tests are indispensable in order to select suitable cell for user-oriented program. Two years ago a small CuBe pressure cell (from the Czech Academy of Sciences) suitable for single crystal studies that is capable to generate at room temperature 10 kbar (7 kbar at low temperatures) and fits to the 15T cryomagnet has been successfully tested and can be used. However, it proved to be not suitable for powder neutron diffraction because of too small volume.

In December we have tested pressure cell that has large enough volume and can generate pressures up to 20 kbar at room temperature. In Fig.1 temperature dependence of the pressure inside the Ti/Zr cell with Ni-Cr-Al insert as measured by the lattice parameters of NaCl is shown. The room temperature pressure was about 16 kbar. As can be seen, the pressure drops upon cooling by 2.5 kbar (see Fig. 1). This is because of larger thermal contraction of the FC77/FC70 transmitting medium.

![Fig. 1: Drop of the pressure inside the tested clamp-type CuBe pressure cell as determined from the shift of lattice constant of NaCl single crystal.](image)

Nevertheless, this pressure cell proved itself to be suitable for powder neutron diffraction. (cylindrical space for the sample has 4.5 mm in diameter and 25 mm length). HMI has ordered these cells and it is expected that from autumn 2003 it will be possible at HMI routinely measure substances at low temperatures/high magnetic fields/high pressures in combination.
Experimental Report

Integration of single-crystal area detector data of YTiO$_3$ using the “seed-skewness” method

Principal Proposer: J. Peters, W. Jauch, HMI Berlin
M. Reehuis, Universität Augsburg
C. Ulrich, B. Keimer, MPI Stuttgart
Experimental Team: M. Reehuis, C. Ulrich

Table 1.
Results of the structure refinements of YTiO$_3$. The anisotropic thermal parameters $U_{ij}$ are given in $10^2$ Å$^2$.

<table>
<thead>
<tr>
<th>SEED</th>
<th>RACER</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$ (Y)</td>
<td>-0.02067(13) -0.02049(15)</td>
</tr>
<tr>
<td>$y$ (Y)</td>
<td>0.07260(12) 0.07270(17)</td>
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<tr>
<td>$x$ (O1)</td>
<td>0.11908(18) 0.11886(19)</td>
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<tr>
<td>$y$ (O1)</td>
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<tr>
<td>$x$ (O2)</td>
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<tr>
<td>$y$ (O2)</td>
<td>0.30869(11) 0.30878(15)</td>
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<td>$z$ (O2)</td>
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<td>$\sigma_{(Ti)}$</td>
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<tr>
<td>$\sigma_{(O1)}$</td>
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<td>$\sigma_{(O2)}$</td>
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</tr>
<tr>
<td>$g$ [rad$^{-1}$]</td>
<td>107(5) 122(6)</td>
</tr>
</tbody>
</table>

References

R. Pynn pointed out more than two decades ago that the direction changes of neutron trajectories can be marked by a Larmor phase by using spin echo setups with inclined field boundaries. This allows to decouple the instrumental resolution from the neutron beam collimation and mono-chromatisation, which means that high resolution and high intensity are obtained simultaneously.

A series of novel high resolution diffraction techniques based on this idea propose to use Larmor labelling in small angle scattering (SESANS) [2], diffraction (Larmor Diffraction) [3] and reflectometry [4]. Felcher pointed out [5] that especially the analysis of the off plane scattering (out of the specular plane) by using spin echo (SERGIS) allows a simple and direct simple analysis of surface structures up to the µm range. Most of these proposals were first tested at the NRSE setup at V2, BENSC.

A limitation common to all spin echo techniques is that depolarisation effects due to ferromagnetic samples destroy the spin echo signal. This can be recovered at the cost of signal intensity by using additional polarizers [6], or, without further intensity losses, by the application of the MIEZE technique [7].

In MIEZE (fig. 1), the RF flippers C1 and C2 are operated at different frequencies \( w_{1,2} \), thus the Larmor phase is modulated with \( \omega_D = 2 \omega \). This phase modulation is converted to an intensity modulation after the analyzer. The intensity modulation is only visible, if the detector is placed at a distance \( L_2 \) from C2:

\[
L_2 = L_1 \frac{\omega_1}{\omega_2 - \omega_1},
\]

where \( L_1 \) is the distance between C1 and C2. If the sample is placed behind the analyzer, spin flips have no influence on the intensity modulated signal. A momentum transfer \( q \) in the sample changes the phase of the intensity modulation by \( \Delta \phi = \delta \cdot q \), with

\[
\delta = \frac{2 \pi n_m}{h} \omega_D L_2 \tan(\theta)/k^2,
\]

where \( L_2 \) is the distance sample-detector.

In the present experiment as first step we aimed to achieve the intensity modulation without using a sample. The coils and the detector were set parallel at an inclination angle \( \theta = 38^\circ \). Both coils were supplied with the same frequency \( \omega \), but C2 was a bootstrap coil (effective precession frequency \( \omega_{2,eff} = 4 \times \omega \), \( \omega_1 \) a single coil (\( \omega_{1,eff} = 2 \times \omega \)), thus the modulation frequency corresponds to a spin echo length \( \delta = 0.38 \mu m \).

The signal was recorded with a FAST 7886 multichannel card. The neutron wavelength was 5.92Å. The measured modulation contrast (Fig.2) is near the maximum value (solid line in fig. 2), which is given by the finite thickness (1mm) of the szintillator. The maximum modulation frequency corresponds to a spin echo length \( \delta = 0.38 \mu m \).

![Fig. 1: MIEZE setup. C1, C2 are NRSE RF spinflippers operated with frequencies \( w_{1,2} \). P polarizer, A analyzer, D szintillation detector (Li6 doped glass, 1mm thick).](image)

![Fig. 2 MIEZE modulation contrast for \( \theta = 38^\circ \).](image)
The proposal. The object is to determine by SERGIS the mean distance of a collage of droplets, formed by dewetting thin films of deuterated polystyrene dPS on top of silicon surfaces. The experiment is a test of the power of SERGIS. The experiment is an almost exact replica of a published experiment [P. Müller-Buschbaum, J.S.Gutmann, M. Stamm, R. Cubitt, S. Cunis, G. von Krosigk, R. Gehrke and W. Petry, Physica B283, 53 (2000)]. In that work the sample was examined by AFM (that gave the size of the droplets and their correlation in real space), GISAXS and GISANS, run at the D22 facility at ILL, Grenoble. We substitute GISANS with SERGIS, whose results can thus be compared with those obtained in real (AFM) and reciprocal (GISAXS) space. The most direct comparison should be obtained by plotting the height-height correlation function in real space, as a function of the coordinate y, an axis parallel to the sample surface and perpendicular to the plane of specular reflectivity. The experiment is to be run at the Hahn-Meitner-Institut in Berlin, at the triple axis FLEX conformed as a reflectometer in which the sample as horizontal surface. FLEX is equipped with neutron resonance spin echo circuits, with a maximal spin-echo length of 10⁶ Å.

The sample is to be set at grazing incidence, at an angle close to that of total reflection of the silicon substrate, and the scattering off the specular plane is to be sorted out by spin-echo. A one-dimensional detector would be quite convenient, because it would separate the specular beam from the neutrons diffused in the specular plane. The spin-echo length can be probed by changing the magnetic field, the length of the second precession coil and the tilt angle of the precession coils, according to a procedure that has to be defined. Possibly the sample will be set at other angles with the incident beam, although in this case the transmission function may have a more complex form.

The experiment. FLEX was reconfigured as a reflectometer, with the sample almost horizontal and tilted rotation around an horizontal axis (this motion was not automated). The detector was of a 2-D type. Its size (4 cm dia.) covered the reflected beam and the diffused intensities. The detector was at 2 meters from the sample. The neutron wavelength was ~ 6 Å.

The measurements were done on a sample of deuterated polystyrene on silicon, prepared and previously tested by Müller-Buschbaum, and on a silicon standard. The sample consisted of droplets of deuterated polymer on silicon, with average distance between the droplets of 5600 Å and an average droplet height of 100 Å. The sample and the standard had lateral dimensions of 3 cm x 5 cm, and were set with the long axis along the beam direction. Measurements were taken with an angle of incidence θ, at 0.8 θ, (the critical angle of silicon) and at 1.2θc.

The intensities measured for a silicon standard as a function of the angle of scattering, for θ, = 0.8θc indicated that:
- the shape of the reflected peak depended very much from its positioning. In its final setting, its FWHM was ~0.1θc. However, the peak was asymmetric, with a much longer tail (Δθ~0.4θc) at the higher angle side.
- With the spin-echo circuit non energized, the polarization of the reflected beam was 0.8.
- A background was present, equal to 0.01 of the intensity of the reflected beam. The background was not polarized.
- With the spin-echo circuit energized, the polarization of the reflected beam decreased with the effective applied field, from 0.8 (H=0) to 0.5 (H=1800 Oe).

The measurements on the sample of deuterated polystyrene gave similar results, except for the width (~0.2 θc) and the shape (less skewed) of the reflected beam. In comparison with the Si standard, no difference was detected in the diffuse scattering, and no difference in the polarization was detected when the spin-echo mode was energized.

Although the experiment did not conduces to a direct physical result, the tests made were useful for defining the conditions under which to conduct a more successful experiment. The consensus is that this would require an instrument, that is pre-configured as a reflectometer.
The aim of the present experiment was the extension of the ‘proof of principle’ experiments [1] of the SERGIS method by the observation of the second polarization order.

The same optical grating sample has been used as in the previous experiments reported earlier [2]. This sample [3] possesses a highly coherent, nominally sinusoidal corrugation. The SERGIS set-up was similar to that used in [1], i.e. the V2 triple-axis spectrometer equipped with the Neutron Resonance Spin Echo (NRSE) extension was used as a reflectometer (\(\lambda=5.92\AA\)). The horizontal sample was irradiated with a vertically collimated neutron beam under a sub-degree grazing incidence angle and the reflected neutrons were detected without any angular resolution. Due to the inclined borders of the NRSE magnetic fields upstream and downstream of the sample [4, 5], the experiment could resolve the in-plane scattering angles in the absence of any corresponding beam-defining elements such as slits or position sensitive detectors.

The applied SERGIS geometry resolved the in-plane structure of the sample surface along the direction perpendicular to the mean neutron direction; the propagation vector of the grating was pointed in this direction. The detected quantity in the SERGIS experiment, the polarization of the neutrons, is shown in Fig. 1 as a function of the spin-echo length [4, 5], a quantity, which is proportional to the frequency and the magnetic fields in the NRSE [6].

In the present experiments, in contrast to the first one [1], we could achieve spin-echo length of 7000 Å. This large range allowed us to detect the second SERGIS polarization order.

The profile shown in Fig. 1 should reveal the in-plane real-space scattering profile of the sample. That this is at least qualitatively the case, is demonstrated by an atomic force microscope (AFM) picture [7] as obtained from the sample (cf. Fig. 2).

![Figure 2. The AFM profile of the sample.](image)

The transverse lateral correlation length corresponding to the observed corrugation profile is much longer than expected from an experiment with a transversally uncollimated beam like in the present set-up. This fact is one of the main advantages of the SERGIS principle.

[3] Gold-coated holographic optical grating, 3600 lines/mm, size: 52 mm x 52 mm, type: 8306BK-520H (Thermo RGL, Rochester, NY)
[7] Explorer Scanning Probe Microscope (Veeco/TM Microscopes, Cunnyvale, CA)
3He neutron spin filters are wideband-applicable devices to produce highly polarised neutron beams. In particular at long wavelengths where the spin-selective absorption cross section for neutrons becomes rather large, they provide the possibility to make use of short cells and to work at convenient 3He pressures.

One aim of the measurements was to test new 3He filter equipment which has been developed to achieve a better adaptation to SANS requirements, following the experiences already made during an experiment at V4 last year [1,2]. In particular shortening of the device should allow the filter to be used in an extended angular divergence. The second aim was to prove the feasibility of the technique for temporally more extended SANS investigations, requiring to refill the filter cell(s) periodically due to the limited lifetime of the 3He nuclear spin polarisation.

The group of Prof. Heil at the University of Mainz supplied us with polarised 3He which was filled at a pressure of 1.8 bar to a storage cell of volume V = 370 ml. Over the whole time it has been situated in a very homogeneous guide field with a relative field gradient of \( \frac{\partial (\mathbf{B} \cdot \mathbf{r})}{\partial \mathbf{r}} / B_0 \lesssim 10^{-5} \text{cm}^{-1} \), serving as a reservoir to refill the filter cells which were made out of quartz glass with an inside-coating out of Cs to suppress wall relaxation of the 3He polarisation. The length of the both cells used was only 3.5 cm, allowing to apply a novel, more compact magnetic cavity (18 cm in length, 20 cm in diameter) in which always one of the cells was placed during the experiment. The cavity consists of a solenoid with a correction coil at each end to create a homogeneous guide field, enclosed by a double-layered mu-metal-shielding to screen external stray fields. Its size is sufficiently small to find enough space behind the electromagnet in the sample chamber of V4, enabling to use the 3He filter as an neutron spin analyser.

Five series of SANS measurements have been performed by refilling both cells with polarised 3He. Polarized neutrons with a wavelength of 0.6 nm and \( \Delta \lambda/\lambda = 10\% \) have been used in the SANSPOL set-up of the instrument [3]. Always starting with 3He polarisation degrees around 10%, a rather poor decay time constant of about 2.5 hours has been observed from transmission measurements in both cells. It was not clear whether this fast decay of the He polarisation was mainly due to wall relaxation or an insufficient field homogeneity inside the magnetic cavity. Overcoming this lack must be the object of further investigations.

The 2vol.% Co-ferrofluid sample was placed in a vertical magnetic field of about 300Gs which is enough to align partly the magnetic moments along the magnetic field. Previous detailed investigations of this system [4,5] revealed a field induced ordering of the particles. Spin analysis of the scattered neutrons allows to distinguish between spin-non flip scattering (snf) in the form-factor and structure factors, and spin-flip scattering from non-perfect alignments of the particle moments; incoherent scattering resulting from hydrogen contained in the nonmagnetic organic shell is clearly separated from snf SANS scattering resulting from small particles.

Acknowledgement

We are very grateful to Prof. Heil and his group at the University of Mainz who supplied us with polarised 3He. The work has been supported in parts by the European Union through the RTD-IHP project HPRI-CT-1999-50016 (ENPI) and by the DFG project Wi 1151/2-2.

References

This experiment was a continuation of our tests of the neutron spin echo technique as a way of encoding the scattering angle of individual neutrons. A picture of the apparatus we installed for this purpose on the V-6 spectrometer is shown below. A diagram of the essential components is shown to the right.

The method we are developing involves the use of thin (~30 micron) magnetizable films of permalloy deposited on silicon wafers as "precession fields" that encode the direction of travel of the neutron in the number of Larmor precessions experienced by a neutron within the magnetic film. The films are clearly seen in the above picture, mounted on goniometers attached to the two optic rails (one on either side of the reflecting sample).

The figure at the bottom of the left column shows the polarization of the direct beam (i.e. not reflected from a sample) as a function of the tilt angle of the second precession film. The damping of the signal results from the beam divergence (rather than wavelength spread, which is the usual cause of such damping in traditional NSE experiments). Beam polarization is reduced from its peak value to zero when the second precession film is rotated through ~0.05º so this represents, approximately, the sensitivity with which we have been able to encode the trajectory of each neutron. Below is a plot of echo polarization for a beam reflected from a Si wafer coated with a polymer film with a columnar microstructure. The reduction of echo polarization with Qz probably results from diffuse reflection from the film.
**EXPERIMENTAL REPORT**

Test of a $^3$He spin filter cell setup for reflectometry

<table>
<thead>
<tr>
<th>Principal Proposer:</th>
<th>H. Fritzsche</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental Team:</td>
<td>H. Fritzsche, A. Gorzel, A. Rupp</td>
</tr>
</tbody>
</table>

Date of Report: 26.04.02

$^3$He spin filter cells have been developed, tested and improved since 1989 [1] whereas the first test experiment in neutron reflectometry was reported only in 2001 [2]. The reason for that delay is simply that supermirrors have a much better flipping ratio and produce a neutron beam with a higher degree of polarization. The $^3$He spin filter can only compete with the supermirrors in experiments where a spin analysis is needed for the off-specularly reflected intensity. In these experiments the $^3$He cell benefits from the fact that the process of spin analysis does not depend on the angle of incidence. Hence, with the $^3$He cell a large angular range can be spin-analyzed whereas with a spin-analyzing supermirror time-consuming scans have to be performed [3].

Our aim is to use the $^3$He spin filter cell in the future as a spin-analyzer in off-specular reflectivity experiments. In a first test we mounted all components except the $^3$He gas cell to check the influence of all guide fields and flippers on the polarization of the direct beam. This testing is essential because at the V6 we work with a transverse polarization and transverse guide fields whereas the $^3$He spin filter cell developed at the HMI works with longitudinal guide fields and a longitudinal neutron polarization. In order to check whether we can realize an adiabatic rotation of the neutron spin, $^3$He gas is not needed and therefore we mounted only the guide field of the gas cell.

In a first experiment we used the setup as depicted in Fig. 1. As a polarizer we used our standard Fe/Co-Si supermirror along with a transverse $\pi$-flipper (T. Flip). After the sample position an adiabatic spin-rotation (ASR 1) is induced by a smooth change from a transverse to a longitudinal guide field. In order to investigate spin-flip and non-spin flip processes another spin flipper (L. Flip) is needed. After the $^3$He cell the spin has to be rotated back to the transverse direction with another adiabatic spin rotator (ASR 2) in order to analyze the polarization of the direct beam with our standard supermirror-analyzer.

With the setup as shown in Fig. 1 we achieved only a flipping ratio of about 6 when using the longitudinal spin flipper. The reason for that is the non-perfect compensation field. Therefore we changed the setup in such a way that we could use a transverse instead of a longitudinal spin flipper. After the sample position we introduced now first the spin flipper followed by the adiabatic rotation. That setup is shown in Fig. 2.

![Fig. 2 Second setup using a transverse flipper (T. Flip 2) after the sample position.](image)

With that setup we achieved flipping ratios of 54 with the second flipper (T. Flip 2) and 30 with the first flipper (T. Flip 1).

As a conclusion, that first test experiment was very useful and very successful. So, in the future we want to apply the $^3$He spin filter cell as a spin-analyzer for off-specular reflectivity.

**References**


Introduction

The experimental method of using the bent crystal type double crystal diffractometer (DCD) V12a for refraction contrast tomographic imaging [1,2] offers also another tomographic possibility. An additional parameter can be deduced from the measured data and can be used as image information as well. The data were - as reported - recorded in a scanning mode in which every measured point of a projection provides a whole scattering curve over a certain q – range. Each of these curves includes scattering information about the penetrated sample volume. It will be shown that such information can give contrast for tomographic reconstruction.

Experimental

After the data acquisition the absorption and refraction parameters are calculated as described before in [1]. However a third parameter can be calculated by regarding the full width of the scattering curves. Thereby the width is defined as the minimum q–range which includes a certain percentage of the whole integral intensity. Useful percentages were found to be of the order of 95 to 98 percent. This widths can be interpreted as a rough measure of the ultra small angle neutron scattering (USANS) of the penetrated volume. Using this width parameter for reconstruction by filtered back projection (FBP) one yields images including entirely new image information. This new contrast method enables to distinguish sample volumes which normally would give no contrast. These are volumes which are equal or similar concerning absorption and refraction but differ in their small angle scattering behaviour.

Results

For testing and demonstration purposes a rectangular Al matrix similar to former samples (20 x 20 mm$^2$ cross-section) with six holes (d = 4 mm) was scanned and imaged. Some of these holes were filled with solutions. See the results in the fig. 1 – 3.

Fig. 1 Refraction contrast image of Al matrix with holes partly filled with different concentrations of β-carotine in D$_2$O (compare fig.3)

Fig. 2 Scattering curves of different concentrations of β-carotine in D$_2$O

Fig. 3a New contrast method (different concentrations) b Combination of 3a with refraction contrast

References

EXPERIMENTAL REPORT

SUSANS (Super USANS) with polarized neutrons

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Date(s) of Experiment: 19–24 Nov & 3–17 Dec 2002
Date of Report: 15 Jan 2003

With 7 Ewald reflections each at channel-cut monochromator and analyzer crystals, each including a silicon wedge, the instrument yields ~ 2 arcsec wide rocking curve for 5.4 Å neutrons.

Placing a magnetic prism of 90° apex angle (vertical field ~ 3.7 kOe in air between poles of a permanent magnet) between the monochromator and analyzer, we achieved ~ 10 arcsec splitting between up- and down-spin neutrons (Fig.1).

An as–cast Fe$_{73}$Al$_5$Ga$_5$P$_2$C$_6$B$_4$Si$_3$ ribbon produces significant Super–Ultrasmall angle scattering of up–spin neutrons, but very little scattering of down–spin neutrons (Fig.2).

Without the silicon wedges and the magnetic prism, ~ 6 arcsec wide rocking curve is obtained for unpolarized neutrons. A stainless steel grating of ~ 110 µm period placed at the sample position, produces a pair of additional peaks (Fig.3) which change in intensity and position as the angle between the grating and the beam is varied.

We thank S.C. Ojha's team at BARC Workshop for magnet fabrication, T. Nierhaus and A. Hilger for experimental assistance and Gerald Badurek and Reiko Sato (Technical University of Wien) for supplying magnetic alloy samples.
**EXPERIMENTAL REPORT**

A Special Set-up for Refraction Contrast Tomography

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<th>Principal Proposer:</th>
<th>W. Treimer, HMI Berlin, TFH Berlin</th>
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<td>A. Hilger, HMI Berlin, TFH Berlin</td>
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<td>M. Strobl, HMI Berlin, TFH Berlin</td>
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Proposal No. *

Instrument V12b

Local Contact W. Treimer, M. Strobl

Date(s) of Experiment

May – Aug. 2002

Date of Report: Jan. 2003

**Introduction**

Additionally to the refraction contrast tomographies performed at the V12a bent crystal type DCD [1,2] similar measurements were done at the V12b DCD. In contrast to the V12a measurements where a whole spectrum within a certain q-range is recorded just two neuralgic points of the curve are used to gain the refraction information. The advantage of this method is that no scanning would be necessary anymore if three beams could be detected at least 2 – dimensionally. For this purpose a very special DCD-like set-up is necessary.

**Experimental**

This set-up is built up by a seven bounce perfect Si [111] crystal as monochromator [3] and a special cut analyser crystal [111]. This second crystal consists of two slabs one behind the other in beam direction with tuneable angle (in the demonstrated measurements 24.3 arcsec) to each other. It was aligned as a “double” analyser followed by three detectors (mention: not yet PSD!) for the two reflected parts of the beam and the transmitted one. The instrumental rocking curve of this device is shown in Fig. 1.

![Fig. 1 V12b DCD instrumental rocking curve in the 3 detectors](image1.png)

An Al sample of invariant cross-section in vertical direction (see Fig. 2) was scanned by a slit of 0.8 mm and steps of 0.5 mm. 60 projections of 33 steps each were recorded with the analyser crystal in the central position of 0° (Fig.1). From the three values of the detectors in each point the refraction was calculated. (The transmitted intensity is important to correct absorption effects.)

**Results**

The reconstruction of the data by the in another report here mentioned technique can be seen in Fig. 2. The first is not yet satisfying.

![Fig. 2 Refraction contrast image Al-cylinder (d=10mm holes 1 – 4mm)](image2.png)

The reason can be given by the too small angular width of the reflection profile of the monochromator. Refraction angles bigger than the total reflection width of 5.8 arcsec can not be resolved properly. This leads to artefacts of the borderlines. This can be improved by using an asymmetric reflecting monochromator.

**References**

**Introduction**

The coherent illumination of phase gratings and the measurement of the fringe patterns yield information about the lateral coherence of a neutron wave. Doing this with a tuneable double crystal diffractometer the question arises about the correlation between Darwin width and coherence width: Does $\Delta k_p/k_p$ depend on the Darwin width?

**Experimental**

The diffraction pattern of Si phase gratings can be calculated by

$$I(\theta) = \int k(x, \Lambda) \cdot e^{-i \Delta \Phi(x)} \cdot e^{-2\pi i \sin(\theta)/\lambda} \cdot dx \quad (1)$$

where $\Delta \Phi(x)$ is the phase change by the grating and $k(x, \Lambda)$ is a model Gaussian with the FWHM of $\Lambda$ for the lateral coherent wave field. One measures an intensity pattern which is the convolution of $I(\theta)$ with the instrumental rocking curve $I_i(\theta)$

$$I_m(\theta) = \int I(\theta') \cdot I_i(\theta - \theta') \cdot d\theta' \quad (2)$$

The first measurements were performed with a slit with precisely variable slit width. Then the diffraction patterns of two edged Si phase gratings ($d = 32 \mu m$ & $16 \mu m$) [1] have been measured. Both Si phase gratings were measured each with the tuned and untuned DCD (i.e. FWHM of instrumental curve 5.8 arcsec and 1.6 arcsec) [2]. Theoretical curves have been fitted providing values for all relevant grating parameters and the FWHM $\Lambda$ of the Gaussian $k(x, \Lambda)$ in (1).

**Results**

Figure 1 shows examples of the measured curves and calculated fits.

![Figure 1](image1)

The correlation between measurements and calculations becomes best at a value of $\Lambda = 50 \mu m$ which means for lateral coherence length $2 \Lambda = 100 \mu m$ (Fig. 2). This is in good accordance with the first approximations from the slit measurements (Fig. 1). Additionally as can be seen there is no hint for a dependence of the FWHM of the instrumental curve.

![Figure 2](image2)

**References**


EXPERIMENTAL REPORT
Search for scission neutrons using measurement of angular correlations

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Date of Report: 10.02.03

The angular correlations of interest was:
\[ W = C \cdot (1 + B s_{n}[n_{in}, n_{out}]), \]
where \( s_{n} \) is a neutron beam polarization, \( n_{in} \) and \( n_{out} \) are momenta of the incident and outgoing neutron, correspondingly. All vectors are normalised to unit. The origin of such a correlation is the interference between s- and p-neutron waves in the entrance channel of reaction[1]. Since the prompt fission neutrons are emitted from the outgoing particles (fragments), they cannot be responsible for the effect. It could arise only from, so called, scission neutrons emitted from the neck[2]. The background of fragment’s neutrons decreases the measured value of asymmetry and the strength of suppression is angular dependent due to difference in angular distributions of scission and fragment’s neutrons. Thus the asymmetry coefficients measured at 90° and 45° relative to fission axis can be used to evaluate quantitatively the fraction of scission neutrons.

In our previous experiment [3] (carried out with thermal neutrons on the small research reactor in Moscow) we found \( B = \frac{3.8 \pm 0.45}{10^5} \) in fission fragments count rate. The corrected average value of neutron asymmetry measured during 11 days was found to be equal to: \( B = \frac{3.8 \pm 0.45}{10^5} \). This means, at first, that at present geometry our count rate is about 10 times less than it was expected and, at second, that \( B \) value could be probably also smaller because of differences in neutron wave length compare with the Moscow reactor. Further data taking in January cycle allowed us to eliminate the systematic effect (the result is \(-0.63(82)\times10^5\) when high magnetic field is off) and to work out suggestions how to improve the count rate, to minimise the effect of the strong magnet and increase the value of the measured effect.

Part II

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