

Magnetism and quadrupolar order in *f*-electron systems.

Manh Duc Le



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Department of Physics and Astronomy
University College London

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Declaration

I, Manh Duc Le, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis. The work in this thesis is based on research carried out in the Department of Physics and Astronomy, University College London, England. No part of this thesis has been submitted elsewhere for any other degree or qualification.

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Abstract

This thesis presents experimental results using bulk thermodynamic measurements and scattering techniques on compounds of *f*-electron elements in which the quadrupolar interaction is strong or dominant. In the case of PrB_6 , the exchange interaction between electric quadrupoles on neighbouring Pr sites drives a complex non-collinear magnetic order, whilst in UPd_3 , the quadrupolar interaction is strong enough to suppress magnetic order and instead a series of quadrupolar ordered phases ensues at low temperatures. In addition to these two compounds, we also investigated the transuranium compounds NpPd_3 and PuPd_3 , and the solid solution system $(\text{Pu,Lu})\text{Pd}_3$ through work carried out at the Institute for Transuranium Elements of the European Commission.

The experimental techniques used include x-ray resonant scattering, which is a direct probe of the *f*-electrons' multipolar properties, and inelastic neutron scattering which reveals the dynamics of the spins of the systems and can be an indirect probe of quadrupolar interactions. Furthermore, bulk measurements such as magnetic susceptibility, heat capacity and resistivity were used to elucidate the ground state properties of the *f*-electrons, away from the ordered phase.

In particular, we present inelastic neutron scattering data on the ordered phase excitations of PrB_6 , and the paramagnetic crystal field excitations of UPd_3 and NpPd_3 ; resonant x-ray scattering in the ordered phases of UPd_3 ; and thermodynamic bulk properties measurements, including heat capacity and magnetic susceptibility, on the $(\text{Pu,Lu})\text{Pd}_3$ system which shows evidence of heavy fermion behaviour.

Finally, this work also encompasses a program to calculate the single ion properties of actinide compounds using intermediate coupling theory, as it was found that the larger spin orbit and crystal field interactions in these systems cause a qualitative change in the magnetic susceptibility.

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Chapter 1

Introduction

Many compounds exhibit phase transitions at low temperatures driven by an ordered arrangement of the charge distribution or magnetic moments of their constituent electrons. Everyday examples are the elemental ferromagnets: Iron, Cobalt and Nickel, where the total spin of the outer shell d -electrons of each atom are aligned in parallel giving rise to a macroscopic magnetic moment and corresponding magnetic field. This magnetic field, or the electric field arising from the charge distributions, may be expressed mathematically as a power series - a *multipole* expansion - over spherical harmonic functions of increasing order which have specific angular dependences. For example, the zeroth order term, a *monopole*, is spherical and independent of angle. The first order, *dipole*, term has two distinct poles; the second order, *quadrupole*, term has four poles, and so on. These angular dependences are illustrated in figure 1.1.

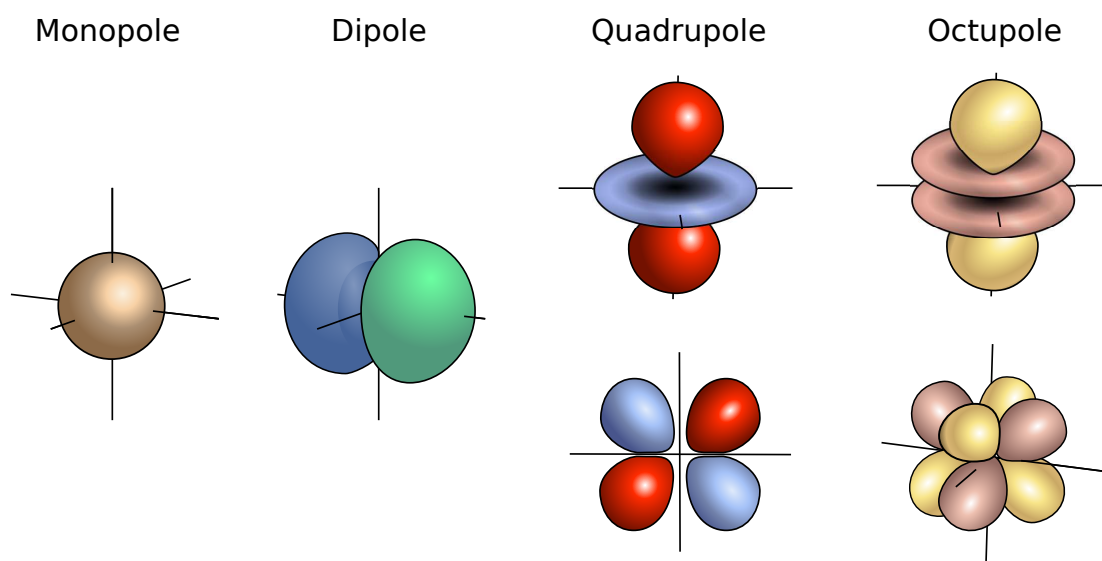


Figure 1.1: Angular dependences of low order multipoles.

The coefficients in this sum of spherical harmonic functions are the magnetic or electric *multipole moments*, which physically corresponds to the fraction of the total electric current or charge distribution which has the specific angular dependence of the associated spherical harmonic. Quantum mechanically, the multipole moment is specified as the expectation value of an operator which transforms under rotations in the same way as the spherical harmonic functions. This limits the number of terms in the multipole expansion because for a given set of $|lm\rangle$ basis states, where l is the orbital and m the azimuthal quantum number of the electrons, there are only $(2l + 1)^2$ non-zero operators with order $K = 0, \dots, 2l$ each with $Q = -K, \dots, K$ components. Thus d -electrons with $l = 2$ may support only up to $K = 4$, a *hexadecapole*, whereas f -electrons with $l = 3$ may support up to $K = 6$ ("*tetrahexacontapole*" or 64-pole).

In most compounds which show a solid state phase transition to an ordered phase below some ordering temperature, the ordering is driven by the magnetic dipole moment. This is because electrons have two angular momenta: the *orbital* momentum due to their (quantised) motion around the nucleus, and an intrinsic *spin* angular momentum, which has the value $s = \frac{1}{2}$. This means that in terms of the multipole expansion described above, the spin may only have a dipole term ($2s = 1$, and a monopole term is not allowed because the lowest spin is $\frac{1}{2}$ not 0). In most cases the interactions involving the spin is stronger than that involving the orbital angular momentum, so the magnetic dipole moment usually dominates.

However, there are some compounds where this is not the case, and higher order electric or magnetic multipole moments are important enough to drive the transition, or otherwise have significant effects on their low temperature properties. Two such compounds in particular, PrB_6 and UPd_3 , will be investigated in this work. In both cases, the outer unfilled electronic shells contain f -electrons, with orbital angular momentum $l = 3$. These electrons are spatially more compact than the d -electrons that are in the unfilled shells of the transition metals. This means that the f -electrons are subjected to a smaller crystal electric field than the d -electrons, so that their orbital moment is not "*quenched*" (that is, very much reduced¹) as in many transition metal systems. This affords greater opportunity for multipolar interaction, although there are d -electron systems which show multipolar ("*orbital*") ordering.

These types of ordering are not well understood at present, and are thus of current research interest (Santini et al., 2009). In this work we shall use inelastic neutron scattering, x-ray

¹This is due to the large crystal field which lifts the degeneracy of the $|l = 2, m = -2, \dots, 2\rangle$ states and causes the diagonal matrix elements of the orbital angular momentum operator to vanish, giving a zero orbital moment.

resonant scattering and the measurement of bulk magnetic properties, such as the magnetic susceptibility, magnetostriction, and heat capacity in order to study the quadrupolar interactions in PrB_6 , and the AnPd_3 ($\text{An}=\text{U}, \text{Np}, \text{Pu}$) series. The theoretical background is briefly described in chapter 2, where the main interactions affecting the f -electrons, and how the experimental measurements may be quantitatively modelled is discussed. Chapter 3 covers the experimental considerations for each of the main experimental techniques employed. Finally, the main experimental findings, with some numerical modelling, for each of the compounds is found in chapters 4-7.

Chapter 2

Theoretical Background

The aim of this chapter is to describe the theoretical basis to the calculations of the bulk properties and neutron spectra of the rare earth compounds studied in this work. We start with the basic Hamiltonian of the system of electrons in a *free ion* and from this deduce the major interactions acting on these electrons. These interactions are namely, the electron-electron *Coulomb* interaction (electrostatic repulsion), and the *spin-orbit* interaction between the intrinsic (spin) magnetic moment of an electron and the magnetic field which it feels in its rest frame due to its orbital motion around the atomic nucleus. This is discussed in section 2.1.

We shall then consider how the behaviour of the electrons changes when the atom to which they belong is embedded in a crystalline solid. Section 2.2 will describe this effect on a particular *single-ion*, which is called the *crystal field* interaction, and arises due to the effects of neighbouring atoms in a crystal on a particular atom in it. The final single-ion interaction which we discuss, described in section 2.3, is the *Zeeman* interaction which arises from the coupling of the magnetic moment of the electron and an external magnetic field.

Finally, in section 2.4 we describe the two-ion *indirect exchange* interactions between ions at different sites in the crystal, whereby electrons on one site indirectly interact with electrons on another site by, for example, polarising the conduction electron cloud around them. In this case we must resort to a *mean-field* theory to calculate the Hamiltonian.

For each of the interactions listed above, we shall use tensor operator techniques to calculate the matrix elements of the Hamiltonian matrix containing the interactions, using *Russel-Saunders*- or *LS-coupled* states as basis states. In this coupling scheme, the orbital and spin angular momenta of the electrons are summed separately, subject to the Pauli exclusion principle, and then these sums, L and S , are added to give the total angular momentum J . Thus these states are characterised by these quantum numbers and also by the z -component of J , denoted

m_J . Once the Hamiltonian matrix is calculated, we may find the eigenvalues and eigenvectors associated with it using standard mathematical techniques. The eigenvalues give the energy levels of the coupled system, and the eigenvectors are the associated state vectors, which are linear combinations of the LS-coupled basis states.

From these energy levels, E_n and state vectors, $|\psi_n\rangle$ we can calculate the bulk properties using statistical mechanics, as describe in section 2.5. In addition the difference in the energy levels is measured as excitations in inelastic neutron spectra, and the intensity of these transitions may be calculated with a knowledge of the state vectors.

The chapter is divided roughly into two parts. The first part, sections 2.2, 2.4, 2.3 and 2.5 deals exclusively with the case where LS-coupling is a good description of the system. That is, L , S and J are good quantum numbers and the interactions are such that the Hamiltonian matrix is almost completely diagonal in states characterised by these numbers. Thus the matrix elements will only vary with m_J , and for low energies and low temperatures, only the ground state multiplet need be taken into account.

The second part, section 2.6, will deal with the case when this approximation breaks down, and we have to calculate the full Hamiltonian matrix and solve the resulting eigensystem. This is called *intermediate coupling*, and we again repeat the series of steps described above for this case. That is, starting again from the equations for the major interactions in section 2.1, we describe how to calculate the matrix elements of the Coulomb, spin-orbit, Zeeman, crystal field, and exchange interactions, and finally reuse the equations of section 2.5 to calculate the physical properties in intermediate coupling.

2.1 The Hamiltonian

The non-relativistic Hamiltonian, for a system of N electrons is given by:

$$\mathcal{H} = \sum_{i=1}^N \left[\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right] + \sum_{i>j=1}^N \frac{e^2}{r_{ij}}$$

The first term in the square bracket is the kinetic energy of the electrons. The second term in the brackets is the electrostatic potential energy between the electrons and the nucleus, whilst the final term is the potential energy between any two electrons. These later two terms prevent a separation of variables to solve the Schrödinger equation, but using the *central field approximation* we may treat these two terms as part of a single radial potential $U(r_i)$. This approximate

Hamiltonian,

$$\mathcal{H}' = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + U(r_i) \right]$$

may now be solved yielding hydrogen-like wavefunctions and energy levels.

These levels are called *configurations* and are labeled by the principal and orbital angular momentum quantum numbers, $(n_1 l_1)(n_2 l_2) \dots (n_N l_N)$, of the electrons in the system. Each set of p identical nl is denoted by the shorthand nl^p and is called an *orbital* and the set of electrons with the same n is called a *shell*. By the Pauli exclusion principle, each orbital may have $2(2l + 1)$ electrons with different values of the z -component angular momentum quantum numbers, m_l and m_s . The configurations are thus degenerate with respect to m_l and m_s . When a shell has only filled (fully occupied) orbitals it is referred to as a *closed shell*. The lowest lying configuration has as many electrons in closed shells as possible. That is, the N electrons fill up each shell in turn until there is an unfilled orbital left. As a short hand, the configurations are usually denoted only by the quantum numbers nl^p of this unfilled orbital, and the number l is replaced by a letter s, p, d , and f for $l = 0, 1, 2, 3$, and followed alphabetically by g, h , etc., for $l = 4, 5$, etc. Thus the lowest energy configuration for Li with three electrons is denoted $1s^2 2s$, but in the short hand is simply $2s$. Similarly for Pr^{3+} , the lowest configuration is denoted $4f^2$.

We shall now only concern ourselves with this lowest configuration, as the energy separation between it and the next configuration in energy is very large, and the effects of the higher energy configuration on this ground state configuration, the *configuration interaction* is relatively small. We turn now to the difference between the central field Hamiltonian and our original Hamiltonian:

$$\mathcal{H} - \mathcal{H}' = \sum_{i=0}^N \left(\frac{Ze^2}{r_i} - U(r_i) \right) + \sum_{i>j=1}^N \frac{e^2}{r_{ij}}$$

The first summation shifts the energy of the configuration as a whole, and thus may be ignored as we are interested only in the energy levels within a configuration. The second summation, which we shall call the *Coulomb interaction* is then the first term of interest to us.

In addition, we also need to include relativistic corrections to the Hamiltonian $\mathcal{H}$, the most important of which is the *spin-orbit* interaction. The standard derivation of this interaction between the magnetic field generated by an electron moving around the nucleus and its intrinsic

magnetic moment due to its spin gives:

$$\mathcal{H}_{SO} = \sum_i \frac{\hbar^2}{2m^2c^2} \frac{1}{r_i} \frac{dU(r_i)}{dr_i} \mathbf{l}_i \cdot \mathbf{s}_i$$

More usually, the coefficients to the left of the dot product are taken outside of the sum and replaced by a constant ζ^1 , and the individual angular momenta replaced by the total angular momenta, $\mathcal{H}_{SO} = \zeta \sum \mathbf{l} \cdot \mathbf{s} \equiv \zeta \mathbf{L} \cdot \mathbf{S}$.

The Coulomb and spin-orbit interactions arise as a result of the forces between the electrons on a single atom or between those electrons and the nucleus. Thus they apply regardless of the environment in which the atom is located, that is whether the atom is embedded in a crystal or left free in a gas. They are thus termed *free ion* interactions. In addition to this, there is the crystal field interaction which arises due to the interaction of other atoms and their electrons in a crystal on the electrons of a particular atom.

In general, the free ion interactions are large, and for the case of the lanthanide series they are much larger than the crystal field interaction. This means that the low temperature and low energy properties of compounds containing these elements may be calculated using perturbation theory with the crystal field perturbing the free ion ground state. We refer to these cases as *LS-coupling*, because we shall use the LS-coupling ground state $|\alpha LSJ\rangle$ only and calculate only the crystal field Hamiltonian involving the $2l + 1$ degenerate m_J levels of this state whose degeneracy is lifted by the crystal field.

For the actinides however, the $5f$ radial wavefunction extends much further from the nucleus than corresponding $4f$ wavefunctions. Thus there is much greater scope for the interaction between the $5f$ electrons with neighbouring ions than for $4f$ electrons, and the crystal field interaction is correspondingly much larger. In addition, the Coulomb interaction is weaker, whilst the spin-orbit interaction is stronger in the actinides as compared to the lanthanides. It is no longer true that the configuration may be split into *terms*² of states with the same L and S , and subsequently into *multiplets* of particular J , because there is now greater mixing of states of different J due to the larger crystal field, and states of different L and S due to the larger spin-orbit interaction. We must thus calculate the full Hamiltonian, and this situation, we refer to as *intermediate coupling*.

¹In general, $\zeta = \int R(r)\xi(r)R(r)dr$ where $R(r)$ is the radial wavefunction and $\xi(r)$ is the coefficients of the dot product. However, it is difficult to calculate $R(r)$ so ζ is normally taken as a phenomenological parameter.

²Denoted ^{2S+1}L where L is a letter corresponding to the total orbital angular momentum number.

First however, we shall explore the LS-coupling case, and proceed to discuss how the physical properties may be calculated if all other interactions are only small perturbations on the free-ion ground state.

2.2 Crystal Field Interactions

The crystal field interaction may, as a first approximation, be thought of as arising from the electric fields of neighbouring ions on a particular ion. It was initially thought that the neighbouring ions may be treated solely as sources of electric fields, and that only the magnetic properties of the ion of interest need be taken into account. These models thus discount the angular momentum properties of the open shell electrons of neighbouring ions and only deal with their charge. Thus this effect was initially termed the *crystalline electric field*. A later model, *ligand field theory* emphasised the effect of the wavefunctions of neighbouring ions and their overlap with the ion of interest, and there are also many other models dealing with these phenomena. We shall follow Newman & Ng (2000) and use the term *crystal field* for the general effect of neighbouring ions on a particular ion in a crystal, and much of the following treatment derives from there and additionally from Jensen & Mackintosh (1991).

2.2.1 The Point Charge Model

For lanthanide compounds, the single ion interactions are dominated by the electrostatic (Coulomb) interactions between electrons within the ion, $\mathcal{H}_{ee}$, and the spin-orbit interaction between the spin and orbital angular momenta of these electrons, $\mathcal{H}_{SO}$. In these cases, where $\mathcal{H}_{ee} \gg \mathcal{H}_{SO} \gg \mathcal{H}_{CF}$, then the crystal field interactions, $\mathcal{H}_{CF}$, may be modeled as a perturbation which splits a degenerate spin-orbit ground state. For example, taking the Pr^{3+} ion which has two outer shell f -electrons, we find using Hund's Rules that the spin-orbit ground state in the LS-coupling approximation is $^3\text{H}_4$. This state is nine-fold $(2J + 1)$ degenerate, and this degeneracy may be lifted by the crystal field, whose symmetry determines what new degeneracies remain.

Returning to the electrostatic model, we may introduce a simple theory which treats all ions in a crystal as point charges, and from this we may deduced expressions for the crystalline electric field potential (Hutchings, 1964). This is the *point charge model* which is still somewhat in use in modified form, despite that it gives inaccurate quantitative predictions of the strength of the crystal field splitting. The electrostatic potential at a position $\mathbf{r}$ away from a particular ion due to a charge density $\rho(\mathbf{R})$ caused by neighbouring ions at $\mathbf{R}$ is:

$$V_{CF}(\mathbf{R}) = \int \frac{\rho(\mathbf{R})}{|\mathbf{r} - \mathbf{R}|} d\mathbf{R} \quad (2.1)$$

Now, because we are assuming that the ions in the crystal behave like point charges, then the electric potential outside these points may be described by Laplace's equation, $\nabla^2 \rho(\mathbf{R}) = 0$, whose solution may be expressed as a sum of spherical harmonics:

$$V_{CF}(r, \theta, \phi) = \sum_{k,q} C_{kq} r^k Y_{kq}(\theta, \phi) \quad (2.2)$$

in spherical polar coordinates, where:

$$C_{kq} = (-1)^q \frac{4\pi}{2k+1} \int \frac{\rho(\mathbf{R})}{R^{k+1}} Y_{k,-q}(\hat{\mathbf{R}}) d\mathbf{R} \quad (2.3)$$

This is in fact a multipole expansion of the charge density. In real materials however, ions do not behave as point charges, and the overlap between the electric field of one ion on another means that Laplace's equation is not satisfied. Nonetheless, because the spherical harmonic functions form a complete orthonormal set, the expansion of the crystal field potential in them is still valid. However, the coefficients in this expansion are now not proportional to r^k and the parameters C_{kq} are not as given in equation 2.3. Instead, one common approach is to take these two terms and use them as freely varying parameters to fit experimentally observed crystal field split energy levels.

2.2.2 Phenomenological Crystal Fields and Stevens Operators

In this phenomenological model, the spherical harmonic function in equation 2.2 is replaced by a tensor operator $T_q^{(k)}$ which transforms under the operations of the rotation group R_3 ($SO(3)$ in more modern notations) in the same way as the spherical harmonic Y_{kq} . This is in order to simplify the calculation of the matrix elements of V_{CF} .

The tensor operators derived spherical harmonics are not hermitian, and thus in order to satisfy the quantum mechanical requirements that energy operators be hermitian, the crystal field parameters will, in general, be complex. However, we can form operators which are hermitian combinations of the tensor operators $T_q^{(k)}$ and hence only use real parameters. These operators transform in the same way as *tesseral harmonic* functions (Hutchings, 1964), which are formed as follows,

$$\begin{aligned}
Z_{k0} &= Y_{k0} \\
Z_{kq}^c &= \frac{1}{\sqrt{2}} (Y_{k,-|q|} + (-1)^q Y_{k,|q|}) \\
Z_{kq}^s &= \frac{i}{\sqrt{2}} (Y_{k,-|q|} - (-1)^q Y_{k,|q|})
\end{aligned} \tag{2.4}$$

Equation 2.2 may now be re-expressed in terms of the tesseral harmonics as:

$$\begin{aligned}
V_{CF}(r, \theta, \phi) &= \sum_{k,q} A_{kq} r^k Z_{kq}(\theta, \phi) \\
A_{kq} &= \frac{4\pi}{2k+1} \sum_j \frac{q_j}{R_j^{k+1}} Z_{kq}(\theta_j, \phi_j)
\end{aligned} \tag{2.5}$$

where we have explicitly replaced the charge distribution by a collection of point charges q_j in units of the electronic charge e . For positive values of q , the cosine tesseral harmonics Z_{kq}^c are used, whilst for negative ("imaginary") q , the sine tesseral harmonics Z_{kq}^s are used. These expressions, converted back into Cartesian coordinates formed the starting point for the classic work on operator equivalents by Stevens (1952).

In this work, Stevens showed that within a set of states of constant J , the matrix elements of V_{CF} are proportional (equivalent) to those of similar expressions involving the angular momentum operators J_x , J_y , and J_z . The procedure to construct these operator equivalents, $\bar{O}_{kq}(\mathbf{J})$ is to replace all instances of x , y , or z in the expression for a particular tesseral harmonic function $r^k Z_{kq}(x, y, z)$ with the equivalent J_x , J_y or J_z allowing for the non-commutation of the angular momentum operators. In addition there is also a proportionality constant θ_k , called the *Stevens operator equivalent factor*³ between the matrix elements of the $\bar{O}_{kq}$ and Z_{kq} . The relation between the tesseral harmonic and the operator thus constructed is:

$$\sum_j r^k Z_{kq}(x_j, y_j, z_j) = \theta_k \langle r^k \rangle \bar{O}_{kq}(\mathbf{J}) \tag{2.6}$$

where $\langle r^k \rangle$ denotes the radial integral. Equation 2.5 then becomes:

³Stevens denoted them α , β and γ for the case $k = 2, 4, 6$ respectively.

$$\mathcal{H}_{CF} = e \sum_{k,q} \theta_k A_{kq} \langle r^k \rangle \bar{O}_{kq}(\mathbf{J}) \quad (2.7)$$

The terms $A_{kq} \langle r^k \rangle$ are generally taken as phenomenological variables, and are termed *crystal field parameters*.

Stevens and subsequent authors listed the operator equivalents $\bar{O}_{kq}$ in terms of J_x , J_y and J_z for many values of k and q and tabulated the corresponding matrix elements (see Hutchings (1964) for a collated tabulation). These were by no means exhaustive, though, and have become superseded as computers became more powerful by the tensor operator methods of Racah (1949)⁴ which may be used to calculate the matrix elements of any k and q . In this work the later methods have been used to calculate the matrix elements in a Matlab computer program, but the formalism of the former has been retained because of its prevalence in the literature.

2.2.3 The Wigner-Eckart Theorem

To calculate the matrix elements by tensor operator techniques we return to the tensor operators $T_q^{(k)}$ which transform in the same way as spherical harmonics. We can use the Wigner-Eckart theorem to factorise the matrix elements into a part dependent on the total orbital momentum quantum number's $\mathbf{J}^2$ component, J , and a part dependent on the J_z component, m_J .

If an operator h_j transforms in the same way as a set of functions ψ_j under the operations of a group $\mathcal{G}$, and further if ϕ_i , ψ_j and θ_k are sets of functions that each form a basis for the *irreducible representations* (IR) Γ_I , Γ_J and Γ_K of $\mathcal{G}$, then the Wigner-Eckart theorem states that the matrix element of h_j between ϕ_i and θ_k ,

$$\int \phi_i^\dagger h_j \theta_k d\tau = \sum_{\beta} A_{\beta}(\Gamma_I i \beta | \Gamma_J j; \Gamma_K k) \quad (2.8)$$

is related to the vector coupling (VC) coefficient $(\Gamma_I i \beta | \Gamma_J j; \Gamma_K k)$ between the three sets of functions. A derivation of the theorem may be found in Judd (1963), but in outline it follows from the expression of the direct product of two IR of $\mathcal{G}$ as a linear combination of other IR of $\mathcal{G}$, $\Gamma_J \times \Gamma_K = \sum_L c_L \Gamma_L$, such that the product $h_j \theta_k$ may also be expressed as a linear combination of another set of functions λ_l that form the basis for the IR Γ_L of $\mathcal{G}$,

$$h_j \theta_k = \sum_{\beta, L, l} (\Gamma_L l \beta | \Gamma_J j; \Gamma_K k) \lambda_l(\beta) \quad (2.9)$$

⁴ And previous papers in the series. For a review see Judd (1963)

As the bases are orthonormal, left multiplying $h_j\theta_k$ by ϕ_i and integrating yields terms in the sum over λ_l with $l = i$ and $\Gamma_L = \Gamma_I$ non-zero, and results in equation 2.8. The constant $A_\beta = \int \phi_i^\dagger \lambda_i(\beta) d\tau$ is called the reduced matrix element, and β distinguishes between equivalent IR. In the case of the group R_3 , there is only ever one term in the sum over β .

For lanthanide ions where there is a great separation between the spin-orbit states with different values of J , we need only calculate the crystal field as a perturbation acting on the lowest J state. Thus we need to calculate the matrix elements of $\mathcal{H}_{CF}$ only between the $2J+1$ states $|J, m_J = -J\rangle, \dots, |J, m_J = J\rangle$. We can now make the identification $\phi_i = |J, m_J\rangle$, $\theta_k = |J, m'_J\rangle$, and $\psi_j = \sqrt{4\pi/2k+1}Y_{kq}$, so it follows that $h_j = T_q^{(k)}$.

From the theory of angular momentum in quantum mechanics⁵ the wavefunction, ψ_{jm} , of a compound system of two angular momenta, with wavefunctions ψ_{j_1, m_1} and ψ_{j_2, m_2} may be expressed as a linear combination:

$$\psi_{jm} = \sum_{m_1, m_2} (j_1 m_1 j_2 m_2 | jm) \psi_{j_1, m_1} \psi_{j_2, m_2}$$

where $(j_1 m_1 j_2 m_2 | jm)$ are the Clebsch-Gordan or Wigner coefficients, which comparing to equation 2.9, we can identify as the coefficients $(\Gamma_J j; \Gamma_K k | \Gamma_L l \beta)$ in the case of the group R_3 . In more modern notations, we replace the Wigner coefficients with a 3- j symbol which shows the symmetry between the different quantum numbers more clearly, and the Wigner-Eckart theorem, equation 2.8, as applied to R_3 gives:

$$\langle J m_J | T_q^{(k)} | J m'_J \rangle = (-1)^{J-m_J} \begin{pmatrix} J & k & J \\ -m_J & q & m'_J \end{pmatrix} \langle J || T^{(k)} || J \rangle \quad (2.10)$$

The *reduced matrix element* $\langle J || T^{(k)} || J' \rangle$ is the constant A_β in equation 2.8 and contains all the information on the J and k dependent part of the matrix elements, which for a particular operator $T_q^{(k)}$ in a particular J spin-orbit level is constant. This reduced matrix element is given by the expression (Smith & Thornley, 1966):

$$\langle J || T^{(k)} || J \rangle = \frac{1}{2^k} \left(\frac{(2J+k+1)!}{(2J-k)!} \right)^{1/2} \quad (2.11)$$

The tensor operators whose matrix elements we calculate with this reduced matrix element transform in the same way as spherical harmonic functions with the normalisation

⁵See for example, Rose (1957), chapter III.

k	$ q $						
	0	1	2	3	4	5	6
2	$\frac{1}{2}$	$-\sqrt{6}$	$\frac{1}{2}\sqrt{6}$				
4	$\frac{1}{8}$	$-\frac{1}{2}\sqrt{5}$	$\frac{1}{4}\sqrt{10}$	$-\frac{1}{2}\sqrt{35}$	$\frac{1}{8}\sqrt{70}$		
6	$\frac{1}{16}$	$-\frac{1}{8}\sqrt{42}$	$\frac{1}{16}\sqrt{105}$	$\frac{1}{8}\sqrt{105}$	$-\frac{3}{16}\sqrt{14}$	$-\frac{3}{8}\sqrt{77}$	$\frac{1}{16}\sqrt{231}$

Table 2.1: Ratios of the Stevens to the Wybourne parameters. $\lambda_{kq} = A_{kq}\langle r^k \rangle / L_{kq}$.

$$\left(\frac{4\pi}{2k+1} \right)^{1/2} Y_{kq}(\theta, \phi)$$

which is called the *Wybourne* normalisation. In order to obtain the Stevens operators which we shall use to calculate the angular part of the crystal field Hamiltonian matrix, we sum the negative and positive q -component operators for each k rank and multiply by a k - and q dependent factor which is given in table 2.1:

$$\begin{aligned} \bar{O}_{k,0} &= \lambda_{k0} \left(T_0^{(k)} \right) \\ \bar{O}_{k,\pm q} &= \lambda_{kq} \sqrt{\pm 1} \left(T_{|q|}^{(k)} \pm (-1)^q T_{-|q|}^{(k)} \right) \end{aligned} \quad (2.12)$$

Finally, the phenomenological crystal field Hamiltonian is:

$$\mathcal{H}_{CF} = e \sum_{k=2,4,6} \sum_{q=-k}^k \theta_k A_{kq} \langle r^n \rangle \bar{O}_{k,q} \quad (2.13)$$

It is conventional to write the Stevens crystal field parameters $A_{kq}\langle r^n \rangle$ as B_q^k . In addition, there is a convention in the neutron scattering literature to set the Stevens operator equivalent factors θ_k to unity, or absorb it into the parameter as well. These parameters will thus produce the same spectra for ions with the same J , but different L or S . For example, the ground state of Pr^{3+} , $4f^2$ with $^3H_4$, and Np^{4+} , $5f^4$ with $^5I_4$ both have $J = 4$.

However, parameters derived from inelastic neutron spectra are usually quoted in meV or Kelvin, whereas crystal field parameters in early optical spectroscopy are Stevens parameters quoted in wavenumbers (cm^{-1}), but with the Stevens factor. Later optical spectroscopy work used the Wybourne normalisation, also in wavenumbers. A complication is that sometimes authors used the non-hermitian operators $T_q^{(k)}$, so the parameters for negative q are imaginary,

but more often, the hermitian operator which we denoted $\bar{O}_{kq}$ were used. In this work, where we deal only with LS -coupling, we shall follow the neutron scattering convention and identify the crystal field parameters as $B_q^k \equiv |e|\theta_k A_{kq}\langle r^n \rangle$. In the case of intermediate coupling, though, the Stevens factor is meaningless because it is absorbed into the values of the reduced matrix elements, and we shall use the full notation $A_{kq}\langle r^n \rangle$, rather than B_q^k .

The sum over k in equation 2.13, being a multipolar expansion, is over all positive integers $\leq 2l$. However, the potential function must be invariant under the operations of the point group of the ion which the crystal field affects. This limits the allowed harmonics and hence the nonzero crystal field parameters, but the particular allowed set k and q for an ion is affected by the axes chosen. In general, if there is a centre of inversion, there will be no odd- k term, and if the z -axis is a q -fold rotation axis, then the B_q^k will be nonzero (Hutchings, 1964). The lowest number of crystal field parameters are obtained for high symmetry point groups where the calculation axes coincide with the symmetry axes, and it is possible to rotate sets of crystal field parameters between one set of axes and another using rotation matrices for each Euler angle (Rudowicz, 1985).

2.3 Zeeman Interaction

In an applied magnetic field, the electrons gain an energy $-\boldsymbol{\mu} \cdot \mathbf{H}$ due to the Zeeman interaction between its magnetic moment and the field. The electron magnetic moment of the i -th electron is a sum of the contributions due to the orbital angular momentum and spin, $\mu_B(\mathbf{l}_i + g_s \mathbf{s}_i)$, where μ_B is the Bohr magneton, and $g_s \approx 2$ is the spin gyromagnetic ratio. Thus, in a magnetic field we need to add the Zeeman term to the Hamiltonian:

$$\mathcal{H}_Z = -\mu_B H \cdot \sum_{i=1}^N (\mathbf{l}_i + g_s \mathbf{s}_i)$$

Because we shall be using LS -coupling basis states and restricting ourselves to a single configuration of the unfilled shell, we can take the summation separately for the $\mathbf{l}$ and $\mathbf{s}$ terms and replace the above equation by:

$$\mathcal{H}_Z = -\mu_B H \cdot (\mathbf{L} + g_s \mathbf{S}) \quad (2.14)$$

where the capitals indicate a vectorial sum of the individual electronic angular momentum.

In the case of LS -coupling, it is more convenient to use the total angular momentum $\mathbf{J}$, which using a simple vector coupling argument is related to the sum $\mathbf{L} + 2\mathbf{S} = g_J \mathbf{J}$ by the *Landé*

g-factor,

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \quad (2.15)$$

The matrix elements of $\mathbf{J}$ are by definition the same as those of the Stevens operators $\bar{O}_{1q}$ of rank-1⁶, without the operator equivalent factors.

Thus the matrix elements of the Zeeman interaction may be calculated by equations 2.10, 2.11 and 2.12 with the conversion factor $\lambda_{10} = \lambda_{11} = 1$,

$$\langle J, m_J | \mathcal{H}_Z | J, m_J' \rangle = \mu_B \langle J, m_J | H_x \bar{O}_{11} + H_y \bar{O}_{1,-1} + H_z \bar{O}_{10} | J, m_J \rangle$$

2.4 Two Ion Interactions

The Pauli exclusion principle means that electrons with the same spins cannot be at the same position, because then their spatial wavefunction must be antisymmetric. In contrast, if the electrons had opposite spins, their spatial wavefunction must now be symmetric and there is a greater probability that their wavefunctions may overlap. In this case their electrostatic repulsion will be higher than in the first case. The energy difference between the two states, with spins parallel or antiparallel, is called the *exchange energy*,

$$-2I\mathbf{S}_i \cdot \mathbf{S}_j$$

I is the *exchange integral* which is related to the overlap of the wavefunctions of electrons i and j . For ions in a crystal, a similar interaction arises, but in this case, it is not through the direct overlap between the wavefunctions of electrons on one ion and that on another, but rather through the indirect polarisation of conduction electrons. In this *indirect exchange* interaction, we replace the second spin $\mathbf{S}_j$ with the spin density of the conduction electrons $\mathbf{s}(\mathbf{r})$ (Jensen & Mackintosh, 1991),

$$- \int 2I(\mathbf{r} - \mathbf{R}_i) \mathbf{S}_i \cdot \mathbf{s}(\mathbf{r}) d\mathbf{r}$$

This interaction energy may be thought of as arising from the action of a magnetic field, $\mu_B \mathbf{H}_i(\mathbf{r}) = I(\mathbf{r} - \mathbf{R}_i) \mathbf{S}_i$, due to the magnetic moments of the electrons on one ion at $\mathbf{R}_i$, act-

⁶We identify $J_x \equiv \bar{O}_{11}$, $J_y \equiv \bar{O}_{1,-1}$, and $J_z \equiv \bar{O}_{10}$.

ing on the conduction-electron moment density, $\mu(\mathbf{r}) = 2\mu_B \mathbf{S}(\mathbf{r})$, at $\mathbf{r}$,

$$\mathcal{H}(i) = - \int \mathbf{H}_i(\mathbf{r}) \cdot \mu(\mathbf{r}) d\mathbf{r} \quad (2.16)$$

The moment generated at $\mathbf{r}$ then interacts via the reverse process $\mathcal{H}(j)$ with the spins, $\mathbf{S}_j$, of electrons around the ion at $\mathbf{R}_j$, leading to the indirect coupling. We can express the induced moment of the conduction electrons due to the electrons of ion i as the product of the field $\mathbf{H}_i$ and the nonlocal susceptibility of the conduction electrons $\bar{\bar{\chi}}$,

$$\mu(\mathbf{r}) = \int \bar{\bar{\chi}}(\mathbf{r} - \mathbf{r}') \mathbf{H}_i(\mathbf{r}') d\mathbf{r}' \quad (2.17)$$

Substituting 2.17 into 2.16, the two ion indirect exchange interaction is:

$$\mathcal{H}(ij) = \iint \bar{\bar{\chi}}(\mathbf{r} - \mathbf{r}') \mathbf{H}_j(\mathbf{r}) \cdot \mathbf{H}_i(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (2.18)$$

However, we can regain the familiar Heisenberg form for the interaction by substituting back the expression for the magnetic field $\mathbf{H}_i$ into equation 2.18 and subsuming all the coefficients into an exchange coefficient $\mathcal{J}(ij)$. Finally we sum over all sites and count each interaction only once, to get the Hamiltonian

$$\mathcal{H}_{\text{ex}} = \sum_{ij} \mathcal{H}(ij) = -\frac{1}{2} \sum_{ij} \mathcal{J}(ij) \mathbf{J}_i \cdot \mathbf{J}_j \quad (2.19)$$

where $\mathcal{J}(ij) = \frac{1}{\mu_B^2} \iint |\mathbf{I}|^2 \bar{\bar{\chi}}$. We have replaced the spins $\mathbf{S}$ by the total angular momentum $\mathbf{J}$ in this equation as this is more convenient in the case of f -electrons and LS-coupling.

2.4.1 Mean Field Theory

The *Heisenberg* form of equation 2.19 is general for many two ion interactions, not just the exchange interactions discussed above. In addition to the magnetic indirect exchange interaction, we shall also look at the quadrupolar exchange interaction and the two ion magneto-elastic coupling.

Although we may write the exchange Hamiltonian and solve the eigenvalue equations associated with it, in order to calculate the most stable arrangement of the spins given a particular set of $\mathcal{J}(ij)$ (that is, the ordered magnetic structure), we need to calculate the nonlocal susceptibility, $\bar{\bar{\chi}}$. However, to calculate this from the Hamiltonian which includes all the free-ion,

single-ion and exchange terms we must use some approximation.

The most general approximation amenable to numerical calculation is the *mean field approximation*, in which we neglect the correlations of the spins around their equilibrium orientations, which is only important very close to a phase transition. The mean field theory would thus fail in these cases, but is adequate away from T_N on either side of the transition. We introduce the expectation value of the spins through

$$\mathbf{J}_i \cdot \mathbf{J}_j = (\mathbf{J}_i - \langle \mathbf{J}_i \rangle) \cdot (\mathbf{J}_j - \langle \mathbf{J}_j \rangle) + \mathbf{J}_i \cdot \langle \mathbf{J}_j \rangle + \mathbf{J}_j \cdot \langle \mathbf{J}_i \rangle - \langle \mathbf{J}_i \rangle \cdot \langle \mathbf{J}_j \rangle$$

We make the mean field approximation by neglecting the first term in brackets on the right hand side. The sum over both i and j in equation 2.19 now becomes a sum over single sites i because we can pool together the second and third terms in the expansion of $\mathbf{J}_i \cdot \mathbf{J}_j$:

$$\mathcal{H}_{\text{ex,mf}}(i) = -\frac{1}{2} (2\mathbf{J}_i - \langle \mathbf{J}_i \rangle) \cdot \sum_j \mathcal{J}(ij) \langle \mathbf{J}_j \rangle \quad (2.20)$$

We can now include the single ion and Zeeman terms as discussed above and introduce an effective field,

$$\mathbf{H}_i^{\text{eff}} = \mathbf{H}_i + \sum_j \frac{\mathcal{J}(ij)}{gJ\mu_B} \mathbf{J}_j \quad (2.21)$$

to give the full mean field Hamiltonian,

$$\mathcal{H}_{\text{mf}}(i) = \mathcal{H}_{\text{si}}(i) - \mathbf{J}_i \cdot \mathbf{H}_i^{\text{eff}} + \frac{1}{2} \langle \mathbf{J}_i \rangle \cdot (\mathbf{H}_i^{\text{eff}} - \mathbf{H}_i) \quad (2.22)$$

where $\mathcal{H}_{\text{si}}(i)$ is the single ion term, and is in the case of LS-coupling just the crystal field term, but will also include the Coulomb and spin-orbit interactions more generally. The final term is constant for a particular configuration $\langle \mathbf{J}_i \rangle$ and is called the *correlation energy*, E_{corr} .

We have thus re-expressed the exchange interaction in terms of a constant energy and an effective magnetic field. Starting from some initial magnetic structure we find the expectation values of the moments in this structure $\langle \mathbf{J}_i \rangle$, and from this calculate the effective field. We then use this to calculate the mean-field Hamiltonian 2.22. Then we solve the eigenvalue system of this to get the energy levels E_n and wavefunctions $|\psi_n\rangle$ for this effective field. We then calculate $\langle \mathbf{J}_i \rangle$ again using these energy levels and wavefunctions through,

$$\langle \mathbf{J}_i \rangle = \frac{1}{Z} \sum_n \langle \psi_n | \mathbf{J}_i | \psi_n \rangle \exp(-E_n/k_B T) \quad (2.23)$$

Then this again is used to calculate a new effective field and the process is repeated until the effective field calculated from $\langle \mathbf{J}_i \rangle$ generates a Hamiltonian whose eigenvalues and eigenvectors produce the same $\langle \mathbf{J}_i \rangle$, that is until *self-consistency*. This self-consistent solution may give non-zero $\langle \mathbf{J}_i \rangle$ in zero applied field, describing spontaneous magnetic ordering.

2.4.2 Quadrupolar and Magneto-Elastic Interactions

For the quadrupolar two-ion interaction, we generalise the exchange interaction 2.19 to include Stevens operators of rank-2,

$$\mathcal{H}_Q = -\frac{1}{2} \sum_{ij} \sum_q \mathcal{K}^q(ij) \bar{O}_{2q}(i) \cdot \bar{O}_{2q}(j)$$

Again we use the mean field approximation and re-express the above equation as,

$$\mathcal{H}_Q(i) = -\sum_q \left[\left(\bar{O}_{2q}(i) + \frac{1}{2} \langle \bar{O}_{2q}(i) \rangle \right) \cdot \sum_j \mathcal{K}^q(ij) \langle \bar{O}_{2q}(j) \rangle \right] \quad (2.24)$$

Like the crystal field, the allowed combinations of these operators must be invariant to the space symmetry operations of the ions. For example, for cubic symmetry there are two modes which involve the quadrupolar operators, the γ and ϵ modes. Considering only the on-site terms ($i = j$) and dropping the site indices, the mean field quadrupolar Hamiltonian in this case is (Morin & Schmitt, 1990),

$$\begin{aligned} \mathcal{H}_Q &= -\mathcal{K}^\gamma (\langle \bar{O}_{20} \rangle \bar{O}_{20} + 3 \langle \bar{O}_{22} \rangle \bar{O}_{22}) - \mathcal{K}^\epsilon \left(\langle \bar{O}_{21} \rangle \bar{O}_{21} + \langle \bar{O}_{2,-1} \rangle \bar{O}_{2,-1} + \frac{1}{4} \langle \bar{O}_{2,-2} \rangle \bar{O}_{2,-2} \right) + E_Q \\ E_Q &= \frac{1}{2} \mathcal{K}^\gamma (\langle \bar{O}_{20} \rangle^2 + 3 \langle \bar{O}_{22} \rangle^2) + \frac{1}{2} \mathcal{K}^\epsilon \left(\langle \bar{O}_{21} \rangle^2 + \langle \bar{O}_{2,-1} \rangle^2 + \frac{1}{4} \langle \bar{O}_{2,-2} \rangle^2 \right) \end{aligned}$$

The two symmetry modes, γ and ϵ , are related to the two anisotropic normal strain modes in cubic symmetry, namely the tetragonal (γ) and trigonal (ϵ) modes.

2.5 Calculating Physical Properties

We can derive expressions for thermodynamic quantities such as the magnetisation and heat capacity from the partition function of the system, which is,

$$Z = \sum_n \exp(-E_n/k_B T) \quad (2.25)$$

which we can find once we know the energies of the system, E_n , by solving the eigensystem

associated with the Hamiltonian matrix, $\mathcal{H}$.

2.5.1 Magnetisation

The magnetisation is the thermal expectation value of the magnetic moment operator, $\hat{\mu} = \mathbf{L} + g_s \mathbf{S}$, of the system in a magnetic field,

$$M(H, T) = \frac{1}{Z} \sum_n \langle \psi_n(H) | \hat{\mu} | \psi_n(H) \rangle \exp \left(\frac{-E_n(H)}{k_B T} \right) \quad (2.26)$$

where the wavefunctions $|\psi_n(H)\rangle$ and energies $-E_n(H)$ are obtained by solving for the eigenvectors and eigenvalues of the full Hamiltonian of the system with a Zeeman term at a particular applied magnetic field, H ,

$$\mathcal{H} = \mathcal{H}_{\text{cf}} + \mathcal{H}_{\text{ex}} + \dots - \mu_B \hat{\mu} \cdot \mathbf{H}$$

2.5.2 Heat Capacity

The heat capacity is the derivative of the internal energy U with respect to temperature,

$$C_v = \left. \frac{\partial U}{\partial T} \right|_{N, V}$$

and the internal energy is

$$U = - \left. \frac{\partial \ln Z}{\partial \beta} \right|_{N, V} = \frac{1}{Z} \sum_n E_n \exp \left(\frac{-E_n}{k_B T} \right) \quad (2.27)$$

where $\beta = 1/k_B T$. Rearranging the expression for the heat capacity above in terms of β rather than T , we obtain,

$$\begin{aligned} C_v &= \frac{1}{k_B T^2} \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) \\ &= \frac{1}{k_B T^2} \left\{ - \left(\frac{1}{Z} \sum_n E_n \exp(-\beta E_n) \right)^2 + \frac{1}{Z} \sum_n E_n^2 \exp(-\beta E_n) \right\} \end{aligned} \quad (2.28)$$

2.5.3 Magnetostriction

Magnetostriction is the change of length of a sample under an applied magnetic field. One distinguishes between the *spontaneous magnetostriction* which occurs on changing temperature across a magnetic transition, and the *forced magnetostriction* which occurs due to and is a

function of an externally applied magnetic field. It is the latter case which we shall measure. The magnetoelastic strain is related to the derivative of the free energy (Doerr et al., 2005),

$$\epsilon^\mu(T, \mathbf{H}) = - \sum_{\nu} \frac{s^{\mu\nu}}{V} \frac{\partial F}{\partial \epsilon^\nu} \quad (2.29)$$

where the indices μ and ν are abbreviated such that $\mu=1,2,3,4,5,6$ corresponds to the Cartesian indices 11, 22, 33, 12, 13, 23. V is the volume, T the temperature and $\mathbf{H}$ the applied magnetic field. The elastic compliances $s^{\mu\nu}$ are related to the elastic constants by

$$\sum_{\gamma} c_{\mu\gamma} s^{\gamma\nu} = \delta_{\mu\nu}$$

the free energy F may be written as a sum of separate contributions due to the magnetic interactions, phonons, and conduction electrons, and thus the magnetoelastic strain may also be separated into these components,

$$\epsilon^\mu(T, \mathbf{H}) = \epsilon_{\text{mag}}^\mu(T, \mathbf{H}) + \epsilon_{\text{ph}}^\mu(T) + \epsilon_{\text{el}}^\mu(T)$$

As a function of temperature, the phonon and electronic contributions to the thermal expansion may be separated by either measuring the thermal expansion of a non-magnetic isostructural analogue, or by calculations using models such as the Debye model. As a function of applied magnetic field however, these terms only contribute an additive constant. In this work we shall deal only with the field dependence and shall ignore the temperature-dependent phonon and electronic terms.

In context of the Hamiltonian developed in the previous sections, there are two main contributions to the magnetoelastic strain. These arise from the crystal field and magnetic exchange interactions, both of which depends on the position of the ions, and are hence coupled to any change in the lattice. These two interactions give rise to *crystal field striction* (Morin & Schmitt, 1990) and *exchange striction* (Doerr et al., 2005), respectively. In order to calculate the effects of these interactions on the strain, we expand them in a Taylor series in ϵ^μ , making the *harmonic approximation* by keeping only the first order terms,

$$\mathcal{H}_{\text{cf}} = \sum_{kq,i} B_q^k(i, \epsilon) \bar{O}_{kq} \approx \sum_{kq,i} B_q^k(i, \epsilon = 0) \bar{O}_{kq} + \epsilon^\mu \frac{\partial B_q^k}{\partial \epsilon^\nu} \bar{O}_{kq} \quad (2.30)$$

$$\mathcal{H}_{\text{ex}} = -\frac{1}{2} \sum_{ij} \mathcal{J}(ij, \epsilon) \mathbf{J}_i \cdot \mathbf{J}_j \approx -\frac{1}{2} \sum_{ij} \mathcal{J}(ij, \epsilon = 0) \mathbf{J}_i \cdot \mathbf{J}_j + \epsilon^\mu \frac{\partial \mathcal{J}}{\partial \epsilon^\nu} \mathbf{J}_i \cdot \mathbf{J}_j \quad (2.31)$$

The energy as a function of strain may now be calculated using first order perturbation theory, giving

$$\begin{aligned} E_n(\epsilon) \approx E_n(\epsilon = 0) + \epsilon^\mu \sum_{kq} \frac{\partial B_q^k}{\partial \epsilon^\nu} \langle \Psi_n(\epsilon = 0) | \bar{O}_{kq} | \Psi_n(\epsilon = 0) \rangle \\ - \epsilon^\mu \frac{1}{2} \sum_{ij} \frac{\partial \mathcal{J}}{\partial \epsilon^\nu} \langle \Psi_n(\epsilon = 0) | \mathbf{J}_i \cdot \mathbf{J}_j | \Psi_n(\epsilon = 0) \rangle \end{aligned}$$

Now, the free energy is given by

$$F = -k_B T \ln Z$$

Using equation 2.25 we find the derivative with respects to the strain to be

$$\frac{\partial F}{\partial \epsilon} = -\frac{1}{Z} \sum_n \frac{\partial E_n}{\partial \epsilon} \exp\left(\frac{-E_n}{k_B T}\right) = \left\langle \frac{\partial E_n}{\partial \epsilon} \right\rangle \quad (2.32)$$

So the magnetoelastic strain, from equation 2.29, is given by,

$$\epsilon_{\text{cf}}^\mu = - \sum_{\nu, kq, i} \frac{s^{\mu\nu}}{V} \frac{\partial B_q^k}{\partial \epsilon^\nu} \langle \bar{O}_{kq} \rangle \quad (2.33)$$

$$\epsilon_{\text{ex}}^\mu = \frac{1}{2} \sum_{\nu, ij} \frac{s^{\mu\nu}}{V} \frac{\partial \mathcal{J}}{\partial \epsilon^\nu} \langle \mathbf{J}_i \cdot \mathbf{J}_j \rangle \quad (2.34)$$

The angled brackets denote the thermal expectation values of the matrix elements of the operators within, and the prefactors may be taken to be constant. These constants may be fitted to experimental data, as we show for UPd₃, once a satisfactory mean field model has been constructed so that the thermal expectation values $\langle \bar{O}_{kq} \rangle$ and $\langle \mathbf{J}_i \cdot \mathbf{J}_j \rangle$ can be calculated.

2.5.4 Neutron scattering

In a typical scattering experiment, we measure the energy, $E_{i,f}$, and momentum $\mathbf{k}_{i,f} = \mathbf{p}_{i,f}/\hbar$ of the incident and scattered particle (neutron or photon), and from this derive the energy, $\hbar\omega = E_i - E_f$, and momentum $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$ transferred to the sample. We can select the incident and scattered energies and momentum of the probe particle, which is a neutron in the case of this section, and measure the rate at which they are scattered from a sample. This rate is proportional to the product of the flux Φ of neutrons incident on the sample and the double differential cross-section, $\frac{d^2\sigma}{d\Omega dE}$, where $d\Omega$ is the element of solid angle into which neutrons with energy between E and $E + dE$ are scattered. Furthermore, using Fermi's Golden Rule and the Born approximation where the incident and scattered neutrons are treated as plane waves, it may be shown that (Squires, 1978),

$$\frac{d^2\sigma}{d\Omega dE} = N \frac{k_f}{k_i} \left[S_{\text{nuc}}(\mathbf{Q}, \omega) + \left(\frac{2\mu_N e^2}{mc^2} \right)^2 \sum_{\alpha\beta} (\delta_{\alpha\beta} - \mathbf{k}_\alpha \mathbf{k}_\beta) S_{\text{mag}}(\mathbf{Q}, \omega) \right] \quad (2.35)$$

$$\begin{aligned} S_{\text{nuc}}(\mathbf{Q}, \omega) &= \frac{1}{2\pi\hbar N} \sum_{jj'} b_j b_{j'} \int_{-\infty}^{\infty} \langle \exp\{-i\mathbf{Q} \cdot \mathbf{R}_{j'}(0)\} \exp\{-i\mathbf{Q} \cdot \mathbf{R}_j(t)\} \rangle \exp(-i\omega t) dt \\ S_{\text{mag}}^{\alpha\beta}(\mathbf{Q}, \omega) &= \frac{1}{2\pi\hbar N} \sum_{jj'} \int_{-\infty}^{\infty} \langle \mathbf{J}_j^\alpha \exp\{-i\mathbf{Q} \cdot \mathbf{R}_{j'}(0)\} \mathbf{J}_{j'}^\beta \exp\{-i\mathbf{Q} \cdot \mathbf{R}_j(t)\} \rangle \exp(-i\omega t) dt \end{aligned} \quad (2.36)$$

where $S_{\text{nuc}}(\mathbf{Q}, \omega)$ is the nuclear, and $S_{\text{mag}}^{\alpha\beta}(\mathbf{Q}, \omega)$ the magnetic scattering function, introduced by van Hove (1954); b_j and $\mathbf{R}_j(t)$ are the scattering length and position at time t of the j^{th} atom respectively. α and β label the Cartesian directions. We shall now consider only the magnetic scattering part, and concentrate on $S_{\text{mag}}^{\alpha\beta}(\mathbf{Q}, \omega)$, which is related to the absorptive part of the dynamical susceptibility due to the fluctuation-dissipation theorem (Lovesey, 1984),

$$S_{\text{mag}}^{\alpha\beta}(\mathbf{Q}, \omega) = \frac{\chi''_{\alpha\beta}(\mathbf{Q}, \omega)}{1 - \exp\left\{-\frac{\hbar\omega}{k_B T}\right\}} \quad (2.37)$$

and obeys the principle of detailed balance,

$$S_{\text{mag}}^{\alpha\beta}(-\mathbf{Q}, -\omega) = \exp\left\{-\frac{\hbar\omega}{k_B T}\right\} S_{\text{mag}}^{\alpha\beta}(\mathbf{Q}, \omega) \quad (2.38)$$

because the probability of a transition depends on the thermal population of the initial state.

Thus, for a neutron energy gain (defined as $\omega < 0$) transition, the initial state of the sample is an excited state, and has a thermal occupation given by the Boltzmann factor. The dynamical susceptibility may be calculated by many theoretical techniques, and is directly measured by a neutron scattering experiment.

We shall make use of the mean field theory outlined in section 2.4.1 in order to calculate the dynamical susceptibility and hence the scattering function. We may then compare this to the neutron intensities measured in experiments, particularly the case of PrB_6 as discussed in chapter 4.

Recalling equation 2.22 for the mean field Hamiltonian, we reintroduce the small fluctuations which we discounted in the mean field approximation:

$$\mathcal{H}_i = \mathcal{H}_{\text{mf}}(i) - \frac{1}{2} \sum_{j \neq i} \mathcal{J}(ij) (\mathbf{J}_i - \langle \mathbf{J}_i \rangle) \cdot (\mathbf{J}_j - \langle \mathbf{J}_j \rangle)$$

and furthermore introduce a small time-dependent perturbative field $\mathbf{h}_i(t) = g\mu_B \mathbf{H}_i(t)$, and transform to the Heisenberg picture in which operators are time-dependent and wavefunctions are stationary,

$$\mathcal{H}_i(t) = \mathcal{H}_{\text{mf}}(i, t) - (\mathbf{J}_i(t) - \langle \mathbf{J}_i \rangle) \cdot \left(\sum_j \mathcal{J}(ij) (\mathbf{J}_j(t) - \langle \mathbf{J}_j \rangle) + \mathbf{h}_i(t) \right) \quad (2.39)$$

Finally, we apply the *random phase approximation* by replacing $\mathbf{J}_j(t)$ by $\langle \mathbf{J}_j(t) \rangle$ (Jensen & Mackintosh, 1991), and express the term in large brackets on the right as an effective field, $\mathbf{h}_i^{\text{eff}}(t)$.

The dynamical susceptibility is the Fourier transform of the response function $\phi(t - t')$ which relates the expectation of an observable $\langle J_{i\alpha} \rangle$ at a time t due to a perturbation $h_{i\beta}(t')$ applied from time t' ,

$$\begin{aligned} \langle J_{i\alpha}(t) \rangle - \langle J_{i\alpha} \rangle &= \int_{-\infty}^t \phi_{\alpha\beta}(t - t') h_{i\beta}(t') dt' \\ \chi_{\alpha\beta}(\omega) &= \int_{-\infty}^{\infty} \phi_{\alpha\beta}(t) e^{i\omega t} dt \end{aligned} \quad (2.40)$$

where α and β label the component directions x , y , and z . Defining the Fourier transform of the expectation of the observable as,

$$\langle J_{i\alpha}(\omega) \rangle = \int_{-\infty}^{\infty} (\langle J_{i\alpha}(t) \rangle - \langle J_{i\alpha} \rangle) e^{i\omega t} dt$$

we transform equation 2.40 to:

$$\langle J_{i\alpha}(\omega) \rangle = \chi_{\alpha\beta}(\omega) h_{i\beta}(\omega) \quad (2.41)$$

Returning to equation 2.39, we find that in the random phase approximation, for the i^{th} ion,

$$\langle J_{i\alpha}(\omega) \rangle = \chi_{\alpha\beta}^0(\omega) h_{i\beta}^{\text{eff}}(\omega)$$

where the superscripted χ^0 indicates the single ion susceptibility. However, the response due to the two ion susceptibility and the perturbative field must also be equal,

$$\langle J_{i\alpha}(\omega) \rangle = \sum_j \chi_{\alpha\beta}(ij, \omega) h_{j\beta}(\omega)$$

which implies that (Jensen & Mackintosh, 1991),

$$\chi_{\alpha\beta}(ij, \omega) = \chi_{\alpha\beta}^0(\omega) \left(\delta_{ij} + \sum_{j'} \mathcal{J}(ij') \chi_{\alpha\beta}(jj', \omega) \right) \quad (2.42)$$

which follows from the Fourier transform of the effective field,

$$h_{i\alpha}^{\text{eff}}(\omega) = h_{i\alpha}(\omega) + \sum_j \mathcal{J}(ij) \langle J_{i\alpha}(\omega) \rangle$$

To find an expression for the single ion susceptibility, we use the *Kubo formula* for the response function (Kubo, 1966; Jensen & Mackintosh, 1991),

$$\phi(t-t') = \frac{i}{\hbar} H(t-t') \langle [J_{i\alpha}(t), J_{i\beta}(t')] \rangle \quad (2.43)$$

where $H(t) = 0$ or 1 for $t < 0$ or $t > 0$ is the Heaviside step function, and the operators are expressed in the Heisenberg picture

$$\begin{aligned} J_{i\alpha}(t) &= e^{i\mathcal{H}t/\hbar} J_{i\alpha} e^{-i\mathcal{H}t/\hbar} \\ \langle J_{i\alpha}(t) \rangle &= \frac{1}{Z} \sum_{n,m} \left(e^{iE_n t/\hbar} \langle n | J_{i\alpha} | m \rangle e^{-iE_m t/\hbar} \right) e^{-\beta E_n} \end{aligned}$$

where $|n\rangle$ and E_n are the wavefunctions and energies of the mean field Hamiltonian. Substituting this into the commutator in equation 2.43 and subsequently into the expression for the dynamical susceptibility in 2.40, we get

$$\chi_{\alpha\beta}^0(\omega) = \frac{1}{Z} \sum_{n,m} \frac{\langle n|J_{i\alpha}|m\rangle \langle m|J_{i\beta}|n\rangle}{E_m - E_n - \hbar\omega} \left(e^{-\beta E_n} - e^{-\beta E_m} \right) \quad (2.44)$$

for the single ion susceptibility. Equation 2.42 may be rearranged to give $\chi_{\alpha\beta} = \frac{\chi_0}{1 - \mathcal{J}(\mathbf{Q})\chi_0}$, so that the dynamical susceptibility may be calculated at each energy ω of interest by inverting the single ion susceptibility $\chi_{\alpha\beta}^0(\omega)$. Finally, the absorptive part of the dynamical susceptibility may be obtained via

$$\chi''_{\alpha\beta} = \frac{1}{2i} (\chi_{\alpha\beta} - \chi_{\alpha\beta}^\dagger) \quad (2.45)$$

2.5.5 X-ray scattering

The effect of the electric and magnetic fields of an incident photon on a system of electrons can be taken into account by including the vector potential $\mathbf{A}$ in the Hamiltonian which otherwise includes the purely electronic and photonic interactions. The vector potential may be expanded as a linear sum of creation and annihilation operators $a^\dagger$ and a that operate on photon states $|\mathbf{k}, \omega, \epsilon\rangle$. From this we see that processes which result in the absorption or emission of photons may be explained by terms that are linear in $\mathbf{A}$, whereas scattering which involves the destruction of the incident photon and creation of the scattered photon requires terms which are quadratic in the vector potential.

The interaction between the photon and electron in terms of $\mathbf{A}$ can be treated as a perturbation on the purely electronic and photonic Hamiltonian, and Fermi's golden rule used to calculate the transition probabilities for the various absorption, emission and scattering processes,

$$W = \frac{2\pi}{\hbar} \left| \langle i|\mathcal{H}'|i\rangle + \sum_n \frac{\langle i|\mathcal{H}'|n\rangle \langle n|\mathcal{H}'|i\rangle}{E_i + \hbar\omega - E_n} \right|^2 \quad (2.46)$$

where we have explicitly taken the case of elastic scattering, with the final electronic state being the same as the initial state $|i\rangle$, and $\hbar\omega$ is the incident photon energy. Thus terms in the perturbing Hamiltonian $\mathcal{H}'$ which are quadratic in $\mathbf{A}$ will contribute to scattering via the first order term in perturbation, whereas terms in $\mathcal{H}'$ that are linear in $\mathbf{A}$ will cause scattering in

the second order term. It is this second order term with the energy denominator which causes resonant scattering. As the photon energy $\hbar\omega \rightarrow E_i - E_n$ approaches the energy difference between the initial state and some intermediate electronic state $|n\rangle$ virtual electrons are excited to $|n\rangle$ and fall back down creating the scattered photon. Using synchrotron radiation sources, we can tune the energy of the incident x-ray photon to be the same as the energy difference between a core and valence electronic state for a particular atom and hence obtain a resonant enhancement of the elastic scattering signal.

In addition, due to the Pauli exclusion principle, the intermediate state $|n\rangle$ must be unoccupied, which restricts the allowed angular momentum of the excited electrons. This gives rise to an exchange-like interaction which means that the scattered photons are sensitive to the magnetisation of the outer shell to which the virtual electron is excited. Thus although the transitions are *electric* multipole in nature, they reveal the *magnetic* properties of the intermediate state $|n\rangle$ (Hannon et al., 1988).

The expression for the resonant scattering form factor is derived in appendix D, but we shall sketch this derivation here. Briefly, the perturbing Hamiltonian, $\mathcal{H}'$, contains a term $\frac{e}{m}\mathbf{p} \cdot \mathbf{A}$ which comes from the substitution of the momentum operator $\mathbf{p} \rightarrow (\mathbf{p} - e\mathbf{A})$ in order to include the effects of the photon's electric and magnetic field on the electrons. The vector potential is a sum of plane waves, and a multipole expansion is used to extract the dependence on the polarisation and wavevector of the photon. Because the form factor depends on the product $\langle i|\mathbf{p} \cdot \mathbf{A}'|n\rangle\langle n|\mathbf{p} \cdot \mathbf{A}|i\rangle$ of the sum of spherical harmonics which we have expanded $\mathbf{A}$ into, a recoupling is necessary to separate the terms which depend only on the properties of the photon, $\mathbf{A}$, and that of the electron, $\mathbf{p}$. This recoupling gives rises to a sum over Wigner coefficients (3- j symbols). Finally, the form factor for a particular multipole transition EL, between an initial state $|i\rangle$ and final state $|n\rangle$ whose orbital quantum numbers differ by L , is given by equation D.15,

$$f_{EL}^{\text{res}} \sim \sum_{K=0}^{2L} \left[\sum_{Q,Q'} T_Q^{(K)} \langle i|F_{Q'}^{(K)}(f)|i\rangle \begin{pmatrix} K & K & 0 \\ Q & Q' & 0 \end{pmatrix} \right]$$

where the quantity in round brackets is a 3- j symbol, whose selection rules ensure that $Q' = -Q$. The operator $F_Q^{(K)}(f)$ depends on the electronic properties of the system, whereas $T_Q^{(K)}$ (not the same as the tensor operators previously mentioned in section 2.2) depends on the properties of the photon. We shall be interested only in the dipole transition, E1, because the Uranium M_{IV}

resonance which we use in the case of UPd₃ is a dipolar transition. The quadrupolar transition, E2, is also important but will not be considered here.

We have chosen to use this multipolar expansion because each rank K term in the sum is sensitive to a particular multipole moment of the electron charge or magnetisation density. For the E1 case, $K = 0$ corresponds to the isotropic electric charge, $K = 1$ to the magnetic dipole moment, and $K = 2$ to the electric quadrupole moment. In particular if a system exhibits a particular multipolar order then the $F_{Q'}^{(K)}(f)$ term for the corresponding K will be non-zero, and vice versa. In order to calculate the energy dependence of the scattering we shall then need to know this term, which is given in equation D.17. However, the polarisation dependence of the scattering at a particular energy may be calculated with only knowledge of the $T_Q^{(K)}$ term, and treating $F_{Q'}^{(K)}(f)$ as a constant which multiplies the intensity by some factor. This operator is given by equation D.16 (Carra & Thole, 1994),

$$T_Q^{(K)} = \sqrt{\frac{2K+1}{2L+1}} \sum_{M,M'} \hat{\mathbf{e}}' \cdot \mathbf{Y}_{LM'}(\mathbf{k}') \mathbf{Y}_{LM}(\mathbf{k}) \cdot \hat{\mathbf{e}} \begin{pmatrix} L & L & K \\ M' & M & Q \end{pmatrix}$$

where $\mathbf{Y}_{LM}$ is a spherical harmonic function, $\hat{\mathbf{e}}^{(l)}$ is the polarisation vector and $\mathbf{k}^{(l)}$ is the wavevector of the incident (scattered) photon. Taking the polarisation vectors outside the sum over M and M' , then substituting analytical expressions for the 3- j symbol for particular K and finally using some vector identities, we can expand the sum above and derive the polarisation dependence as follows (Wilkins et al., 2004),

$$f_{\text{E1}}^{\text{res}} \sim \begin{cases} \hat{\mathbf{e}}' \cdot \hat{\mathbf{e}} & K = 0 \\ \hat{\mathbf{e}}' \times \hat{\mathbf{e}} \cdot \mathbf{z} & K = 1 \\ \hat{\mathbf{e}}' \cdot \mathbf{f} \cdot \hat{\mathbf{e}} & K = 2 \end{cases} \quad (2.47)$$

where $\mathbf{z}$ is the unit vector in the direction of the ordered magnetic moment, and $\mathbf{f}$ is a tensor representing the quadrupolar moments of all n atoms in the unit cell. As we only used azimuth scans, the wavevector remained constant, so this tensor is also constant for a particular symmetry, and is given in Cartesian coordinates by:

$$f_{ij} = \sum_n e^{i\mathbf{Q} \cdot \mathbf{r}_n} \left[\frac{1}{2}(r_i r_j + r_j r_i) - \frac{1}{3} \delta_{ij} \sum_k r_k r_k \right] \quad (2.48)$$

where the r_i 's are the directions x , y , or z , and $\mathbf{Q}$ is the scattering vector and $\mathbf{r}_n$ the position of

the n^{th} atom.

In order to perform calculations, we need to rotate the incident and scattered polarisation vectors by the azimuth angle, and for ease of use, we also apply an additional transformation to the conventional coordinate system of Blume & Gibbs (1988). The details of these calculations are given the appendix of Wilkins et al. (2004).

2.6 Intermediate Coupling

Until this point we have only considered the ground spin-orbit state, and further that this state is a pure state with defined quantum numbers L , S and J , and that there is no mixing of excited states which would affect the properties of the system at the temperatures of interest. This is the LS -coupling approximation, and for rare earth systems it generally holds true, however for many actinide systems this approximation breaks down.

Spectroscopic studies have shown that the spin-orbit coupling strength in actinides is approximately twice that found in lanthanides (Carnall, 1992; Carnall et al., 1989). This combined with the strength of the crystal field interactions usually found in actinide compounds, which is about an order of magnitude greater than the lanthanides, means that the Russell-Saunders (LS) coupling scheme breaks down. Instead we are forced to calculate the physical properties of actinide compounds in the intermediate coupling scheme. To this end we will calculate the energy matrix taking into account the Coulomb, spin-orbit (SO), and crystal field (CF) interactions. This matrix is then solved for its eigenvalues and eigenfunctions, which yields respectively the (relative) energy levels and corresponding wavefunctions in whichever basis we choose.

To simplify the calculations and to use the powerful group theoretical methods of Racah (1949; Judd, 1963), we take into account only the lowest energy configuration f^n . We will choose the basis $|\alpha W U S L J J_z\rangle$ where states are labeled by the spin (S), orbital (L), and total (J , J_z) angular momentum quantum numbers, and in addition three other quantum numbers: W and U which are related to a group theoretical description of the states (Racah, 1942), and α which distinguishes between those states with the same values of all the previous quantum numbers. This classification is discussed in more detail in appendix C.1. The list of allowed states for each f^n configuration and matrix elements for the Coulomb and spin-orbit interactions are tabulated by Neilson & Koster (1963).

Finally, spectroscopists have found that they also need to include the effects of the inter-

action of other configurations on the configuration of interest. In the case where a single (linear configuration interaction) or two electrons are excited from the configuration l^n to another configuration, the perturbation in the energy levels of l^n up to second order, may be included by three effective scalar operators (Rajnak & Wybourne, 1963). The parameters of these operators are usually fitted to observed spectra, although they may be calculated for each type of configuration interaction from the Coulomb interaction (Rajnak & Wybourne, 1963). Thus, the Hamiltonian that we wish to calculate is given by:

$$\mathcal{H}_C = \sum_{k=0}^l e_k E^k + \xi \sum_i \mathbf{s}_i \cdot \mathbf{l}_i + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \sum_{k,q} A_k^q \langle r^k \rangle \bar{O}_{k,q} \quad (2.49)$$

The first term on the right hand side gives the Coulomb interaction in the formulation of Racah, where the e_k are operators and E^k are parameters which are related to Condon & Shortley's (1935) F_k parameters and the Slater integrals F^k . For the f -shell, these relations are:

$$\begin{aligned} E^0 &= F_0 - 10F_2 - 33F_4 - 286F_6 & F_0 &= F^0 \\ E^1 &= \frac{1}{9}(70F_2 + 231F_4 + 2002F_6) & F_2 &= \frac{1}{225}F^2 \\ E^2 &= \frac{1}{9}(F_2 - 3F_4 + 7F_6) & F_4 &= \frac{1}{1089}F^4 \\ E^3 &= \frac{1}{3}(5F_2 + 6F_4 - 91F_6) & F_6 &= \frac{25}{184041}F^6 \end{aligned} \quad (2.50)$$

The second term in equation 2.49 gives the spin-orbit interaction, whilst the next three terms represent the configuration interaction (CI) and the last term the crystal field interactions. The scalar operators $G(G_2)$ and $G(R_7)$ are Casimir's operators for the group G_2 and R_7 ⁷ respectively and may be calculated in the $|\alpha WUSL\rangle$ basis by expressions given by Racah (1949).

The operators $\bar{O}_{k,q}$ are not strictly Stevens' operator equivalents because as we are not dealing with a single J -multiplet, their equivalence to angular momentum operators no longer holds. However, they still obey equation 2.12, and the matrix elements of $T_q^{(k)}$ may be calculated in the $|\alpha WUSLJJ_z\rangle$ basis using equation 2.11 but with a reduced matrix element which now

⁷The symbol R_7 was used in the spectroscopy literature to denote the rotation (or special orthogonal) group in seven dimensions, but it is now more usual to write it as $SO(7)$.

depends on the quantum numbers W , U , S , and L in addition to J , and is given by equation C.14.

The matrix elements were calculated using *Matlab* functions. Their values were checked primarily by comparison with the digitised values from the source code of the Spectra program of Hannah Crosswhite (Crosswhite & Crosswhite, 1984)⁸. These gave the matrix elements as a single-precision floating point number. Supplementary to this, the values were also checked from the tables of Neilson and Koster whose values are exact and expressed using powers of prime notation. The energy matrix was then diagonalised in *Matlab*, to obtain the energy levels and wavefunctions. The heat capacity may then be calculated in a straightforward manner from the energy levels, whilst the magnetisation may be calculated by first including the Zeeman interaction term: $\mathcal{H}_Z = -\mu_B H \sum_i \mathbf{l}_i + g_s \mathbf{s}_i$. The matrix elements for the magnetic moment operator $\sum_i \mathbf{l}_i + g_s \mathbf{s}_i$ is given by Chan & Lam (1970). The new Hamiltonian ($\mathcal{H}_C + \mathcal{H}_Z$) may then be diagonalised and the magnetisation calculated for a specific magnetic field H , as in section 2.5.1.

Finally, the matrix element calculation routines have been incorporated into the *McPhase* program package, and may be used for a mean field calculation. At present, however, the calculation times are too long to be practicable for use on personal computers, except for configurations with few f electrons, or corresponding holes, for example up to f^3 or from f^{11} . The equations for the matrix elements of the operators listed above is derived in appendix C.

⁸available at: <http://chemistry.anl.gov/downloads/spectra/index.html>

Chapter 3

Experimental Techniques

In this chapter, the experimental techniques employed in this work are outlined, and related to the quantities described in the previous chapter on theoretical background.

3.1 Thermodynamic Properties

The bulk thermodynamic measurement techniques employed in this work are SQUID magnetometry, heat capacity and magnetostriction. In the first two cases commercial equipment from Quantum Design¹ was used to characterise the samples. For the magnetostriction measurements a miniature capacitance dilatometer designed by Rotter et al. (1998) was used. The following section will discuss each method in turn.

3.1.1 Magnetisation

The magnetisation, as calculated in equation 2.26, may be measured by applying a magnetic field to a sample and measuring the resulting magnetic moment. In this work, a SQUID (superconducting quantum interference device (Tinkham, 2004)) magnetometer in a commercially available liquid helium cryostat, the Magnetic Property Measurement System (MPMS) by Quantum Design, was used. The SQUID² is a superconducting niobium ring which is interrupted by two Josephson junctions which are constrictions in the niobium ring.

A magnetic field perpendicular to the ring then produces a difference, $\Delta\phi$, in the superconducting phase of the current flowing either clockwise or anticlockwise around the ring between the two Josephson junctions. However, because the superconducting electrons (Cooper pairs) are in a single state, they may only have a single phase. So, the phase difference around the ring must be an integral number of 2π . In addition to magnetic fields, a supercurrent may also

¹<http://www.qdusa.com/>

²A Quantum Design Model 50, <http://www.qdusa.com/products/brochures/squid3.pdf>

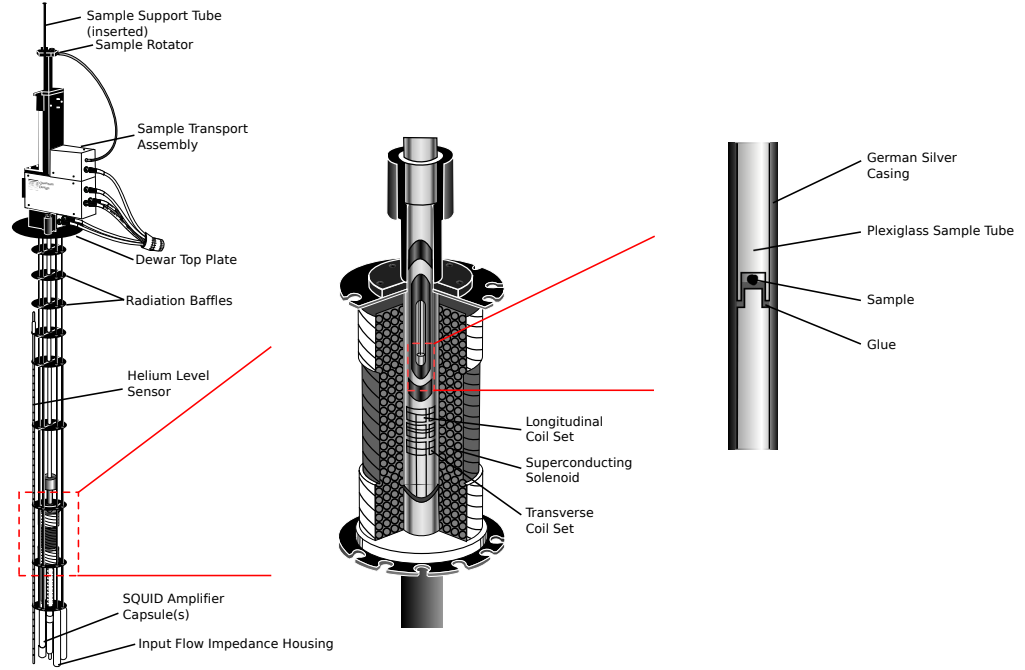


Figure 3.1: Schematic of the *Quantum Design Magnetic Properties Measurement System* showing the sample stick and sample area. Partly from the QD brochure, 2005.³

produce a phase difference in the Cooper pairs. So, in order to ensure that $\Delta\phi = 2\pi n$, a small current is also induced to balance the magnetic field created phase difference.

The change in the superconducting phase due to a magnetic field is given by $\Delta\phi = 2\pi\Phi_A/\Phi_0$ where Φ_A is the flux produced by the field and Φ_0 is the flux quantum. The current through a Josephson junction is $I = I_c \sin\Delta\phi$, but the SQUID has two Josephson junctions and the phase change due to a magnetic field is balanced between both, so the resulting current in the ring is $I = I_c \sin\pi\Phi_A/\Phi_0$. Thus as Φ_A increases from an integer number of flux quanta, a small current will increasingly flow in one direction to compensate, until Φ_A approaches a half-integer number of flux quanta where the current will begin to flow in the opposite direction, decreasing until no current is needed as Φ_A becomes an integral number of flux quanta again.

In order to measure the magnetic field, or the magnetic moment of a sample, the number of these oscillations may be counted to obtain the flux induced by the field in number of flux

³<http://www.qdusa.com/products/brochures/mpmsBro2-05.pdf>

quanta. The current induced by the field in this way is very small, however, and in normal d.c. operating mode, a constant bias measuring current, I_m , is applied to the ring. As this current opposes the current I generated by the field in one half of the SQUID ring, and reinforces it in the other half, the phase change across each Josephson junction is now no longer the same. However this only introduces another modulation on top of the signal described above. If for a particular field value the maximum value of the I_m is measured, then the original modulation may still be discerned as the field is swept over the SQUID, or similarly if a magnetic sample is moved through it.

This second method of oscillating the sample through a SQUID coil is used by the MPMS. Figure 3.1 shows a schematic drawing of the sample column and coil sets of the instrument. The model used in this work has only a single longitudinal SQUID coil, although the MPMS may have the option of a second set of transversely mounted coils.

In standard measurements samples are mounted in a polystyrene straw and then attached to the sample column, however as we deal with active samples, a more involved encapsulation process was required. After arc-melting, the sample is transferred in sealed containers to a glove box, where it is placed into a plexiglass holder. This consists of two sections with a hollow centre into which the sample is placed, which screws together, and is subsequently filled with glue in order to ensure that the sample does not move within the holder during the measurement process. Finally the plexiglass is placed inside an outer tube of non-magnetic German silver (*neusilber*, an alloy of Nickel, Copper and Zinc), which is attached to the sample column of the MPMS as shown in figure 3.1.

3.1.2 Heat Capacity

The heat capacity, equation 2.28, of a sample was measured with a Quantum Design Physical Property Measurement System (PPMS) setup⁴, using the adiabatic relaxation method. The sample is mounted on a microcalorimeter platform which is suspended by eight thin wires to a "puck", which is a removable sample insert. The eight wires provide electrical and thermal connections to the embedded heater and thermometer on the microcalorimeter platform, and also ensure a degree of thermal isolation. In addition, the puck has a thermometer and thermal shield, and is mounted in a high vacuum vessel kept at a pressure of approximately 0.01 μ Bar. Figure 3.2 shows a schematic drawing of the sample area and sample stick.

⁴<http://www.qdusa.com/pdf/brochures/heat.pdf>

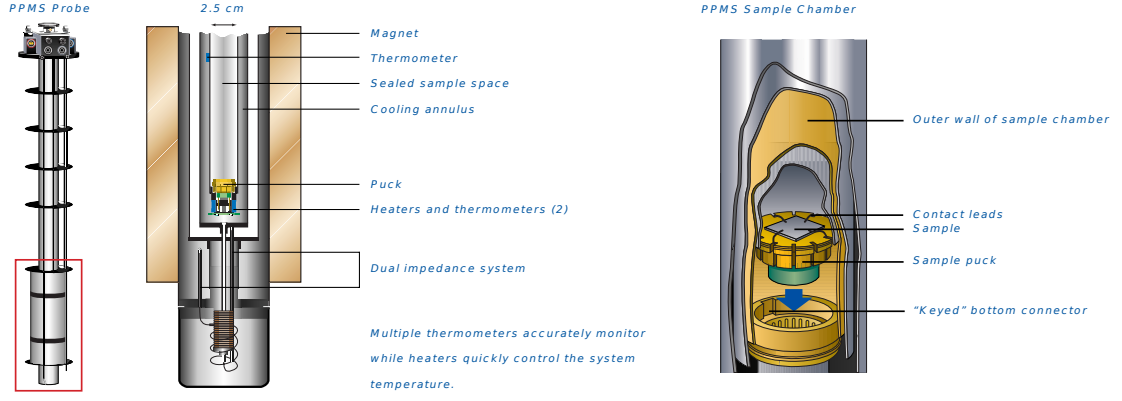


Figure 3.2: Schematic of the Quantum Design Physical Properties Measurement System showing the sample stick and sample area. Taken from the QD brochure, 2006.⁵

The measurement process consists of stabilising the sample, platform and puck to a particular temperature, then applying power to the platform heater for a specified time, and finally measuring the temperature of the combined sample and platform after the heater is switched off as the system relaxes adiabatically back to the puck temperature. This temperature data is then analysed using a *two tau model* (Hwang et al., 1997), whereby the relaxation is described by two time constants, τ_1 , which represents the relaxation time between the platform and the puck, and τ_2 which is the relaxation time between the sample and the platform. Finally a measurement is made of the addenda, that is the sample and puck and any material used to encapsulate and attach the sample, but without the sample. This is then subtracted from the measurements with the sample in order to determine the heat capacity.

3.1.3 Magnetostriction

The change in the lattice constant of a crystal may be measured in bulk using a single crystal with a well cut flat face using a capacitance dilatometer. In this method, an expansion or contraction of the single crystal in a particular direction results in movement of the plates of the dilatometer and hence in its capacitance. The measured relative change in the lattice constant is then related to the magnetoelastic strain by

$$\epsilon^\mu(T, \mathbf{H}) = \frac{\Delta l(T, \mathbf{H})}{l_0} \quad (3.1)$$

where $\Delta l = l(T, \mathbf{H}) - l_0$ and $l_0 = l(T, \mathbf{H} = \mathbf{0})$. The indices μ denote the direction of the strain and magnetic field, using Voigt's abbreviation such that $\mu = 1, 2, 3, 4, 5, 6$ denote 11, 22, 33, 12,

⁵http://www.qdusa.com/pdf/brochures/ppms_9_06.pdf

13, 23. In this work we measured only the change in lattice constant at a constant temperature.

For the miniature dilatometers used (Rotter et al., 1998), one plate is fixed, but the other plate of the capacitor is pivoted on needle bearings which allows irregularly shaped single crystals to be measured, provided one surface (attached to the lower plate) is flat. The plates are constructed of silver, and the needle bearings are brass with sapphire washers to ensure electrical insulation. The initial position of the plates may be adjusted to accommodate different sized samples via brass nuts mounted on Cu-Be disk springs, which is electrically isolated by a Kapton ring. Figure 3.3 shows a schematic drawing of the dilatometer.

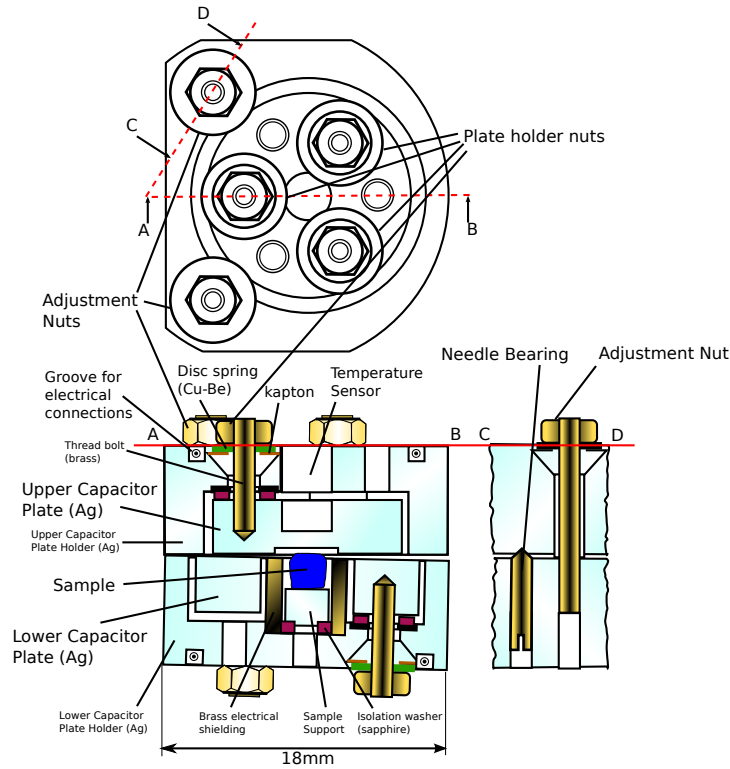


Figure 3.3: *Schematic of the miniature capacitance dilatometer used for the magnetostriction measurements.* After Rotter et al., (1998).

Because of the tilted plate design, calibration of dilatometer is less straightforward than with a flat plate capacitor, as the equations relating the capacitance to the gap size is not exactly solvable. However, solutions may be obtained iteratively with a computer, and in practice, the device is also physically calibrated by measuring the gap between the plate without a sample by using a micrometer screw to move the upper plate.

Further experimental details relating to this technique, as applied to UPd₃ may be found in Section 5.4.

3.2 Neutron Scattering

The neutron has several benefits as a probe for condensed matter, and particularly for magnetic materials. In the first place the mass of the neutron means that neutrons with wavelengths comparable to atomic spacings have energies which are around room temperature or below, and as such may also probe the dynamics of a material. Secondly the neutron has a magnetic moment, and no electric charge, which means that its interaction with atomic electrons is purely magnetic. As the magnetic interaction is relatively weak, the neutron may penetrate deeply well into the bulk of a sample. This also simplifies the sample environment because a larger number of materials are relatively neutron transparent and thus may be used around the sample.

The disadvantages which come with these properties is that the flux of thermal neutrons is much smaller than may be obtained for photons with x-ray synchrotrons, resulting in relatively long counting times. The weak magnetic interaction means that much larger samples are required for neutron experiments - of the order of cm^3 or grams, rather than mm^3 and mg as for an x-ray experiment.

In this work we deal exclusively with inelastic neutron scattering, in order to determine the low energy magnetic excitations which arise from the crystal field interaction in the paramagnetic phase or exchange interaction in the ordered phase. This requirement to probe low energy excitations trumps the disadvantages listed because there are few other techniques which are sensitive to these low energy transfers. Inelastic x-ray scattering is a relatively new technique which may in future compete with neutron scattering, however at present it is quite technically difficult to perform such experiments. This is because the incident x-ray energy is many orders of magnitude higher than the energy of the excitations, thus requiring a very high degree of accuracy in measuring the scattered x-ray energy.

The aim of an inelastic neutron scattering experiment is to measure the scattering function $S(\mathbf{Q}, \omega)$ which was discussed in section 2.5.4. In practice this means counting the number of neutrons scattered from a sample with a particular wavevector, $\mathbf{Q}$, and energy transfer, $\hbar\omega$. The scattering function in absolute units may then be obtained by comparing these counts to the number of neutrons scattered from a standard Vanadium sample. In this work we used two different techniques to determine $\mathbf{Q}$ and ω . Firstly by controlling all the necessary angles using a triple-axis spectrometer. Secondly, by measuring the neutron's velocity (and hence energy) by counting as a function of time in a time-of-flight spectrometer.

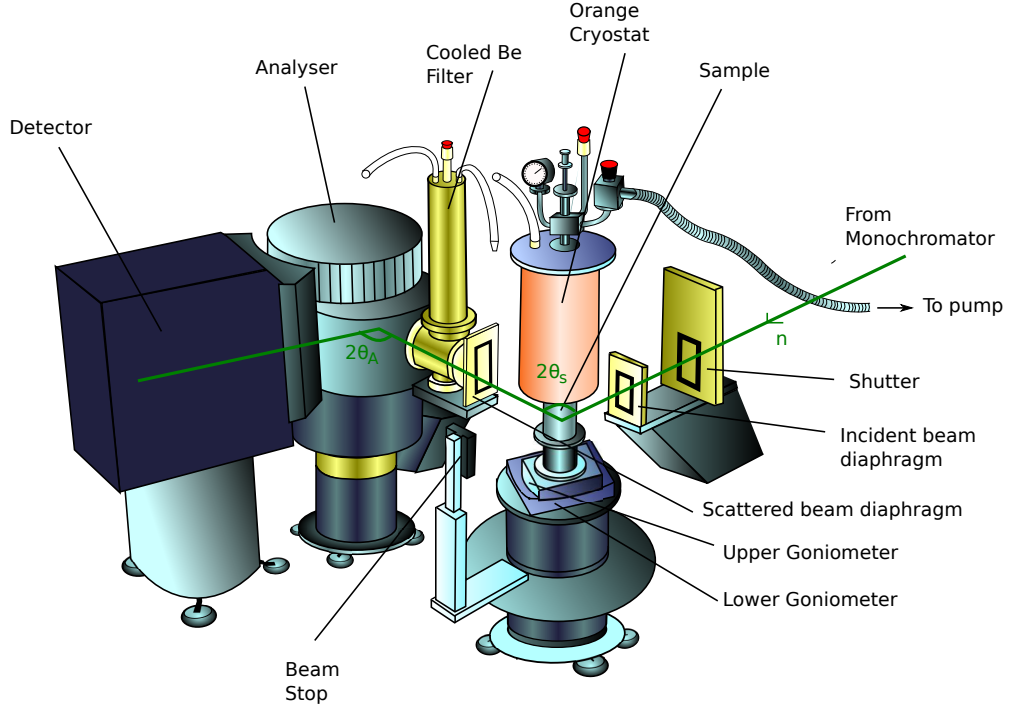


Figure 3.4: *Sketch of the FLEX triple-axis spectrometer in Z-configuration. The neutron guide and monochromator are not shown.*

For the ordered phase magnetic excitations in PrB_6 we used a triple-axis spectrometer, which allows great flexibility in exploring the dispersion of these modes. Figure 3.4 shows a sketch of the FLEX spectrometer which was used in the measurement. The three axes are the monochromator (not shown), sample and analyser. In our measurements the (002) reflection of a pyrolytic graphite crystal was used as the monochromator and analyser.

Each crystal may be rotated by an angle θ_m (monochromator), θ_s (sample), or θ_a (analyser) about the relevant axes. In addition, the alignment of other axes with respect to each of the monochromator, sample and analyser defines another three angles, $2\theta_m$, $2\theta_s$, and $2\theta_a$, as shown in the figure. By changing θ_m and $2\theta_m$, we can change the incident energy, whilst the scattered energy may be changed by varying θ_a and $2\theta_a$. This defines the energy transfer E_T , whereas the wavevector transfer is defined by the sample angles θ_s and $2\theta_s$, in combination with the monochromator and analyser angles which gives $|Q| \propto E_T^{1/2}$.

In addition to this the beam is defined by diaphragms before and after the samples, and by collimators between the monochromator and sample, sample and analyser, and analyser and detectors (not shown in the figure). In addition a Be filter cooled to liquid nitrogen temperatures was placed between the sample and analyser and used to remove higher order scattering.

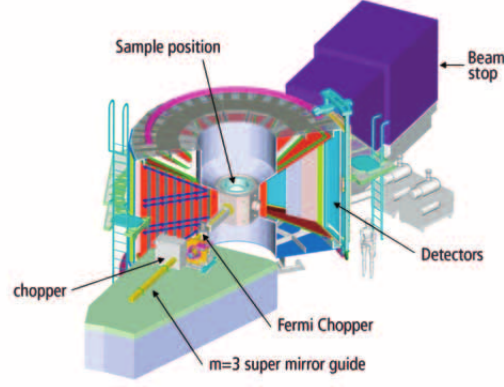


Figure 3.5: *Schematic drawing of the MERLIN chopper spectrometer.* After (Bewley et al., 2009).

The crystal field excitations in UPd_3 and NpPd_3 were measured using time-of-flight (ToF) spectrometers, rather than a triple-axis instrument because they are relative dispersionless so the flexibility of a triple-axis spectrometer to change energy and wavevector transfer at will was not needed. On the other hand the wide angle detectors of time-of-flight spectrometers allow a large volume of reciprocal space to be mapped at one time. This is useful in that it may be used to determine whether a given peak in energy is a phonon or magnetic excitation from a single scan by comparing the scattering at low angles (low wavevector transfer) and at high angles (high wavevector transfer). The magnetic form factor is small at high angles, so if the peak intensity is the same at both high and low angles, then it is likely to be a phonon.

Figure 3.5 shows a schematic drawing of the MERLIN spectrometer, on which the NpPd_3 measurements were made. MERLIN has a very large area detector bank, covering $\sim \pi$ sr of solid angle. In addition it also has a super mirror guide which greatly increases the flux at lower energies. Instead of a monochromator crystal, ToF spectrometers use a mechanical chopper to select neutrons of certain velocity. A disc chopper is used initially to remove fast neutrons, followed by a Fermi chopper to monochromate the beam. The neutrons then have nearly uniform velocity and take a constant time to hit the sample. Inelastic scattering then results in a change of velocity of the neutrons, and the subsequent time it takes for the neutron to strike a detector may be used to calculate this change in speed, and defines the energy transfer. The position of the detector defines the scattered angle and hence the wavevector transfer. Because of the large number of detectors (MERLIN has 69000 detector elements) a specialised software, *libisis* is needed to handle the data.

3.3 Resonant X-ray Scattering

Finally, this work also employs resonant x-ray scattering to probe the quadrupolar ordering of the Uranium $5f$ electrons on the quasi-cubic sites of UPd_3 . As detailed in section 2.5.5, the resonant scattering cross-section is sensitive to different terms in the multipolar expansion of the charge and magnetisation densities of the electrons, depending on the order of the virtual transition between a core and valence states induced by the photon. In particular, the dipolar transitions between electronic states differing in $l = \pm 1$, called E1, is sensitive to the isotropic charge distribution, the magnetic dipole, and electric quadrupole moment, with distinct polarisation dependence for each. The relevant equations are described in section 2.5.5, and appendix D.

We shall be interested only in the terms involving the electric quadrupole moment. In this case, depending on which of the five possible order parameters, the intensity of the diffracted beam will vary as a function of the azimuth angle. We thus conducted several experiments to measure this dependence in the various ordered phases of UPd_3 . In the following, we discuss some of the experimental considerations pertaining to these experiments.

Synchrotron radiation is produced by the acceleration of electrons moving at relativistic speeds, by magnets placed around its path. A constant magnetic field perpendicular to the direction of motion of the electrons will, via the Lorentz force, cause them to move in a circular trajectory emitting radiation tangential to this curve. In a synchrotron these magnetic fields (and additionally electric fields to accelerate the electrons) are synchronised to the position of the electrons around the accelerator. In practice it is easier to construct a synchrotron of large diameter⁶ using straight sections between the circular arcs of the bending magnets, rather than a continuous circle. These straight sections also enable the inclusion of insertion devices such as wigglers and undulators magnets which cause the electrons passing through them to execute small oscillations and hence produce radiation.

The ID20 beamline at the ESRF on which the measurements discussed in Chapter 5 were taken, may use either wigglers or undulators. In the configurations for the experiments on UPd_3 , three undulators (two with a magnet period of 35mm and one with 32mm) were used. Undulators produce more intense beams than wigglers because they induce small amplitude oscillations in the path of the electrons which then radiates X-rays whose intensity add coherently, whereas wigglers produce larger amplitude oscillations in the electrons giving rise to radiation that add

⁶The European Synchrotron Radiation Facility (ESRF) has a ring with a circumference of 844m

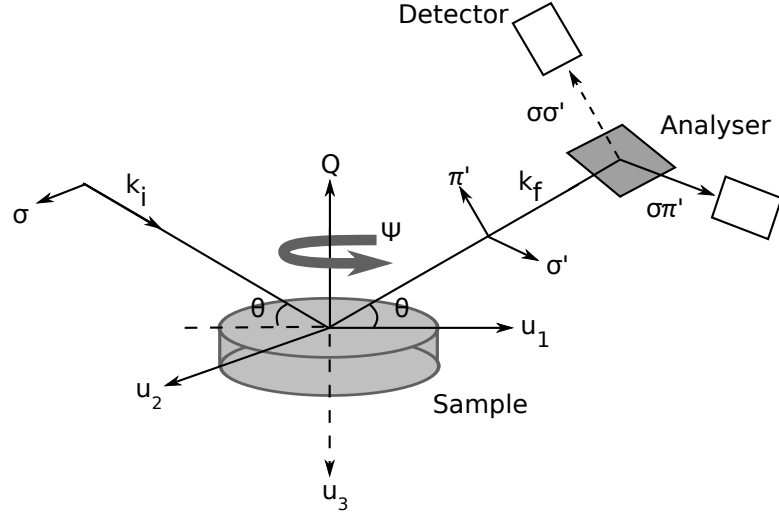


Figure 3.6: Schematic drawing of the azimuth dependent XRS setup. After Walker, (2006)

incoherently.

The key features of synchrotron radiation to our applications is the ability to tune the energy of the incident beam by using a series of crystal monochromators, and the naturally plane polarized nature of the radiation due to the Lorentz contraction of the electrons' movement. The former enables the incident photons to be tuned to a particular absorption energy, which in our case is the U M_{IV} transition between the $3d_{5/2}$ and $5f$ states, which have an energy difference of $\sim 3.72\text{keV}$. The latter allows the easy use of polarisation analysis by using a plane polarizer only on the diffracted beam. In addition, synchrotron radiation also has the advantage by being highly intense, and highly collimated with very small beam divergence, which means that shorter measurement times and smaller samples are sufficient, and giving very good spatial resolution. These factors are not crucial to us, but do allow easier measurements.

The magnetic or quadrupolar order parameter may be determined by the azimuth-dependent intensity of the super-lattice Bragg peak in the ordered phase. This intensity is proportional to $\epsilon(\Psi) \cdot \mathbf{f} \cdot \epsilon'(\Psi)$ as shown in section 2.5.5, where the tensor $\mathbf{f}$ depends on the order parameter. Figure 3.6 shows a schematic drawing of a setup for such an azimuth scan. $\epsilon^{(l)}(\Psi)$ is the incident (scattered) polarisation vector which changes with the azimuth angle Ψ , and is calculated in the coordinate system defined by the axes u_1, u_2, u_3 after the method of Blume & Gibbs (1988). The incident x-ray is horizontally polarised (σ polarisation), and is analysed into unrotated (σ') or rotated (π') channels by the (111) reflection of a Au crystal, which gives the closest match to the U M_{IV} edge.

Chapter 4

Magnetic excitations in the ordered phases of PrB_6

4.1 Background

The major experimental works comprising this thesis will explore the properties of two series of compounds. The first is the rare-earth hexaborides, and the second is the actinides-palladium-3 which is discussed in the three chapters following this. In both cases we concentrate on the light elements of the series, and in particular on how the quadrupolar and magnetic interactions, and electronic localisation changes as the number of f -electrons increases.

The rare-earth hexaboride series is relatively well known, with extensive bulk properties and neutron diffraction measurements studied on all compounds¹. CeB_6 , with a single f -electron exhibits both quadrupolar and magnetic order with a quadrupolar transition temperature $T_Q \approx 3.3$ K and a Néel temperature $T_N \approx 2.4$ K. The quadrupolar structure was determined by resonant x-ray scattering (Yakhov et al., 2001; Nakao et al., 2001) to have an ordering wavevector $\mathbf{k} = [1/2 \ 1/2 \ 1/2]$. The magnetic structure, in contrast, is double- $\mathbf{k}$ with ordering wavevectors $\mathbf{k}_1 = [1/4 \ 1/4 \ 0]$ and $\mathbf{k}_2 = [1/4 \ 1/4 \ 1/2]$ (Effantin et al., 1985). By NdB_6 with three f -electrons, however, there is only a single antiferromagnetic transition at $T_N \approx 8.5$ K to a simple A-type structure in which alternating planes of atoms have opposite moments.

In between and with two f -electrons, PrB_6 has two antiferromagnetic phase transitions, at $T_{\text{IC}} \approx 7$ K and $T_{\text{C}} \approx 4.2$ K, first to a magnetic structure incommensurate (IC) with the nuclear lattice, and second to a double- $\mathbf{k}$ structure which is commensurate (C). The ordering wavevectors $\mathbf{k} = \pm[1/4 \ 1/4 \ 1/2]$ is similar to that in the lower temperature antiferromagnetic structure

¹For CeB_6 see Lee & Bell (1972) and references therein; for PrB_6 see Kobayashi et al. (2001) and for NdB_6 see McCarthy & Thompson (1980) and references therein.

of CeB_6 . This similarity suggests that quadrupolar interactions are important in stabilising the non-collinear magnetic structure, even if there is no ordering of the electric multipole moments. However, high field magnetisation measurements suggests that there is a co-existence of quadrupolar order with the magnetic order (Kobayashi et al., 2001). Recent resonant x-ray scattering measurements by Walker et al. (2009) found a superlattice peak at $(\frac{1}{2} \frac{3}{2} \frac{3}{2})$ at the $E1$ resonance, with a polarisation dependence which is consistent with quadrupolar ordering at this wavevector. However, the $E1$ resonance does not probe the $4f$ electrons directly, and as such this observation is not a conclusive determination of whether this system exhibits quadrupolar order.

In this work, we investigate the quadrupolar interactions, by measuring the dispersion of the low energy magnetic excitations using inelastic neutron scattering. Then using a mean field model of the quadrupolar and magnetic indirect exchange interaction, we fit this measured dispersion to the exchange parameters.

4.1.1 Crystal and Magnetic Structure of PrB_6

The crystal structure of the rare-earth hexaboride compounds is relatively simple, consisting of a B_6 octahedra around the body-centred position of a simple cubic lattice of rare-earth atoms, with lattice parameter $a = 4.13 \text{ \AA}$, as shown in figure 4.1. There is only one magnetic atom in the unit cell, whose cubic site symmetry yields a simple two parameter single ion crystal field interaction. Throughout the series though, the crystal field interaction, particularly the fourth order term B_4 , is quite strong and leads to a large overall crystal field splitting of the ground spin-orbit term, and more importantly a large gap between the crystal field ground state and excited states, of the order of hundreds of Kelvin. Thus to a good approximation, at low temperatures, the physics of the system may be considered by taking into account only the ground state levels. In the case of PrB_6 , the lowest spin-orbit multiplet is $^3\text{H}_4$ by Hund's rules, and the cubic crystal field splits these 9 levels ($J = 4$) into two triplets (of symmetry Γ_5 and Γ_4), a doublet (Γ_3) and singlet (Γ_1). Earlier inelastic neutron scattering work on polycrystalline PrB_6 by Loewenhaupt & Prager (1986) revealed crystal field excitations at 27 and 32 meV, from which the authors deduced the LLW crystal field parameters as $x = 0.95$ and $W = 0.82 \text{ meV}$, which yields the levels shown in figure 4.2. In this scheme, the ground state is the Γ_5 triplet which is 314 K below the first excited state. Thus the system may be considered an effective $S=1$ triplet.

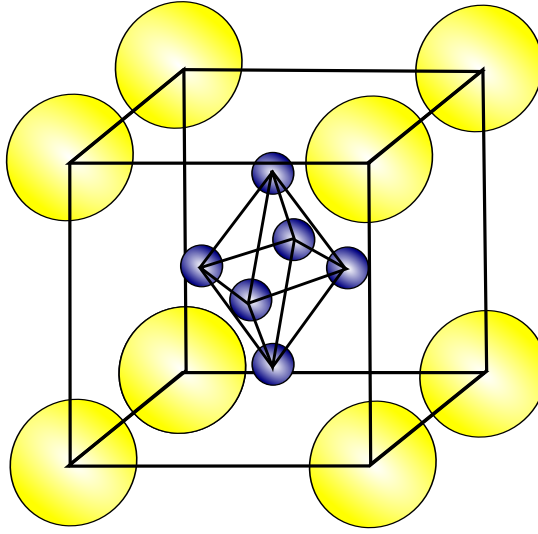


Figure 4.1: *The crystal structure of PrB_6 . The Pr atoms are at the vertex of the cube and enclose a B_6 octahedron.*

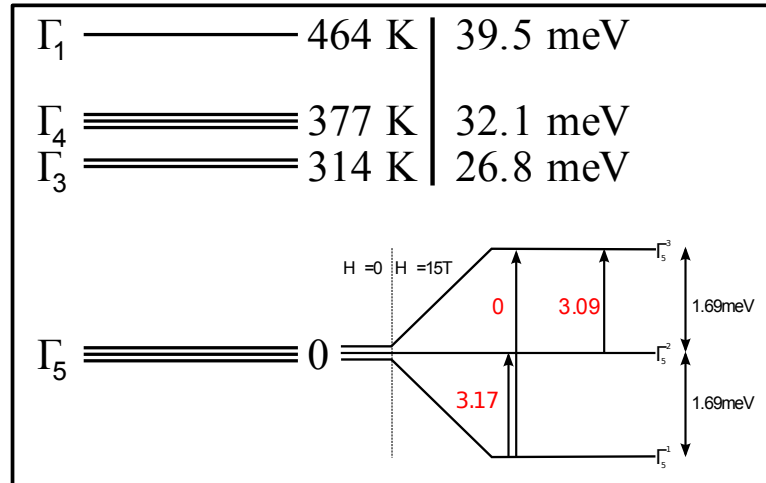


Figure 4.2: *The crystal field levels of PrB_6 . The LLW parameters deduced by (Loewenhaupt & Prager, 1986) are $x = 0.95$, $W = 9.5$ K (0.82 meV). The lower right corner shows the splitting of the ground state triplet in a molecular field of 15 T, and the red numbers denote the dipole transition matrix elements between the states shown.*

The magnetic structure in the ordered phases was deduced from neutron diffraction data by Burlet et al. (1988), who showed that below $T_N = 7$ K, the Pr moments order in an incommensurate (IC) antiferromagnetic (AFM) phase with wave vector $\mathbf{q}_{IC} = (1/4 - \delta, 1/4, 1/2)$ where $\delta \approx 0.05$. Below $T_2 = 4.2$ K, the moments lock in to an arrangement which is commensurate with the lattice, with $\mathbf{q}_C = (1/4, 1/4, 1/2)$. The magnetic structure in each phase is shown in figure 4.3a. Burlet et al. also measured the ordered moment in the commensurate (C) phase as $1.1 \mu_B$ per Pr atom, which is much less than the $2.0 \mu_B$ per Pr atom expected from the Γ_5 triplet ground state. This reduction has been attributed to the coexistence of antiferroquadrupolar (AFQ) ordering together with the AFM ordering by Kobayashi et al. (2001).

4.2 Experimental Details

The inelastic neutron scattering measurements were performed on the V2-Flex triple axis spectrometer at the BER-II reactor of the Berlin Neutron Scattering Centre, Hahn-Meitner-Institut², Berlin. A single crystal of PrB_6 was grown by Dr. Seong-Su Lee using a travelling solvent floating zone method in a mirror furnace equipped with Xe lamps at Hiroshima University under the supervision of Prof. F. Iga, as part of a collaboration also involving Prof. Je-Geun Park of Sungkyunkwan University, Seoul. In order to avoid the high neutron absorption of natural boron, the starting material used was enriched to consist 99% of the low absorption ^{11}B isotope. For the experiments a sample of dimension $5 \times 5 \times 30 \text{ mm}^3$ with faces parallel to the $(0\ 0\ 1)$ and $(1\ 1\ 0)$ planes was cut, and mounted with the $[0\ 0\ 1]$ and $[1\ 1\ 0]$ directions defining the horizontal scattering plane.

The spectrometer was generally operated with fixed final wavevector, $k_f = 1.55 \text{ \AA}^{-1}$ using PG(002) crystals for both the monochromator and analyser. 60° collimators were installed between the monochromator, sample, analyser and detector as appropriate to define the beam size and ensure an adequate resolution yet permit reasonable counting times. A Be filter cooled to liquid nitrogen temperatures was installed between the sample and analyser to reduce higher order contamination. In this configuration the experimental resolution, measured with a Vanadium sample, was 0.14 meV at zero energy transfer, and calculated to be 0.17 and 0.19 meV at $\Delta E = 1.0$ and 2.0 meV, respectively.

For some scans at low energy and high resolution, however, $k_f = 1.3 \text{ \AA}^{-1}$ was used, and in order to maintain the flux, the collimators between the sample, analyser and detector were

²Now the Helmholtz Zentrum Berlin für Materialien und Energie.

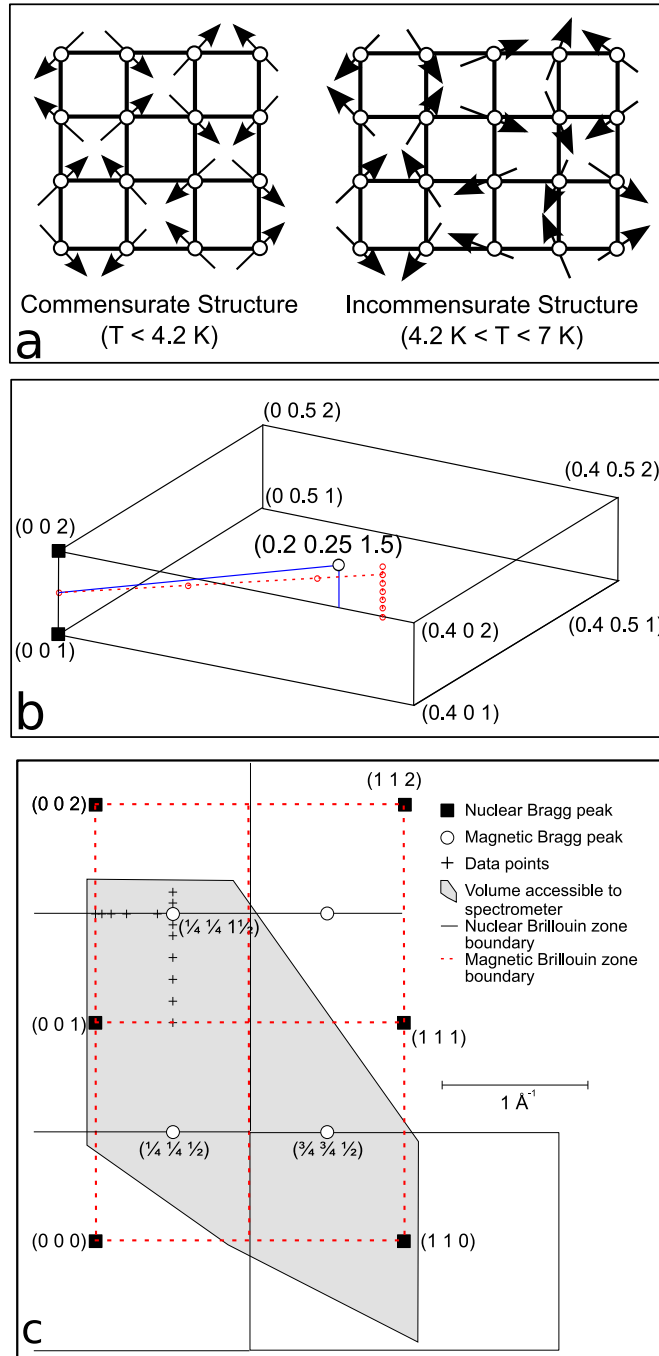


Figure 4.3: *Magnetic structure and reciprocal space diagram.* **Panel a)** shows the magnetic structure in the commensurate and incommensurate phases. **Panel b)** shows the magnetic Brillouin zone in the incommensurate phase at 5 K. The blue solid lines indicate the major symmetry directions, whilst the red dashed lines and open circles show the wavevectors at which data were taken. Note that the horizontal scales have been exaggerated to emphasize the difference between the high symmetry and data directions. **Panel c)** shows the scattering plane in the commensurate phase at 2 K, with the nuclear and magnetic Brillouin zones and wavevectors where data were taken.

removed and the analyser was automatically focused. This relaxed the wavevector resolution, but tightened the energy resolution to approximately 0.1 meV.

In the commensurate phase below 4.2 K, we performed energy scans at points in reciprocal space around the magnetic Brillouin zone centre at $(1/4, 1/4, 3/2)$, along the $[1, 1, 0]$ and $[0, 0, 1]$ directions. The configuration of the spectrometer (scattering sense -1, -1, 1) meant that around this wavevector we could measure up to energy transfer of ~ 5 meV. However, for higher resolution scans we performed measurements at equivalent wavevectors around the magnetic zone center at $(1/4, 1/4, 1/2)$ for which the scattering cross-section is higher due to the magnetic form-factor.

The measurements in a magnetic field were performed with 60° collimation between the monochromator and sample, with the analyser curved and automatically focused to obtain a higher neutron signal at the expense of poorer wavevector resolution. Again both $k_f = 1.55 \text{ \AA}^{-1}$ and $1.3 \text{ \AA}^{-1}$ configurations were used, and energy scans were performed at similar wavevectors to those in zero field.

The magnetic Brillouin zone centre in the incommensurate phase at $(1/5, 1/4, 1/2)$ is out of the scattering plane of the spectrometer, and we were unable to tilt the sample (especially with the magnet) sufficiently to reach it. Thus the energy scans at 5 K in this phase were performed at the same wavevectors as in the commensurate phase. This meant that the mapped dispersion is not along a symmetry direction of the system, and adds complexity to the analysis.

The following sections will discuss the results in the commensurate phase, at zero fields and in fields up to 6 T, and in the incommensurate phase. We also performed measurements at 10 K in the paramagnetic phase, which will be discussed.

4.2.1 The Commensurate Phase ($T \leq 4.2$ K)

Figures 4.4 and 4.5 shows constant wavevector scans for $q = [h, h, 3/2]$ and $q = [1/4, 1/4, 1]$ respectively in the commensurate phase of PrB_6 at 2 K and zero applied field. The data is shown normalised to 2 million monitor counts, which corresponds to approximately 15 minutes per point. This was generally the counting time for most of the data. However, in some cases much longer counting times were used in order to discern low intensity peaks. The full list of scans is given in Appendix B. Figure 4.6 and 4.7 shows the dispersion as colour maps which are derived from the data by 2D linear interpolation. The crosses indicate the energy and wavevector transfer of the measured data.

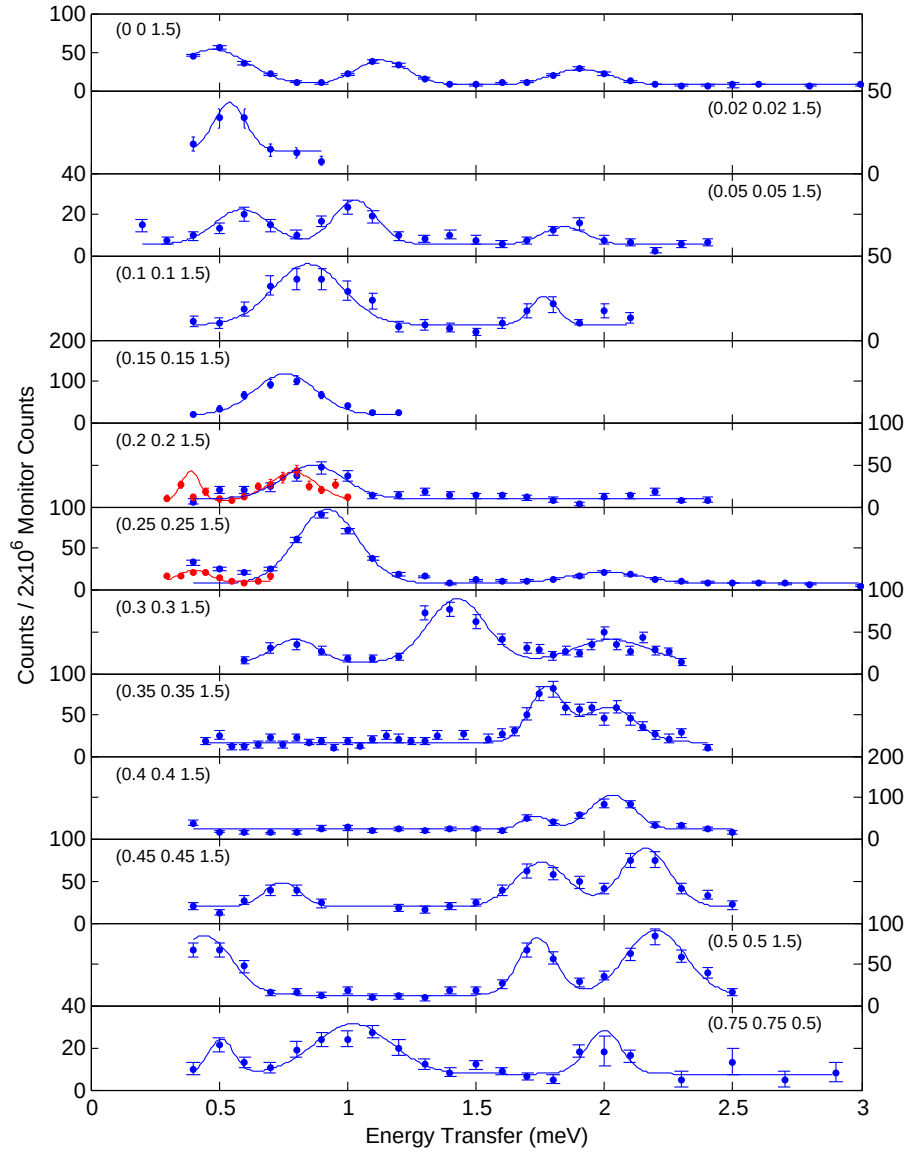


Figure 4.4: Energy scans for $[h h \frac{3}{2}]$ in the commensurate phase of PrB_6 , at zero field. Blue data points indicate data taken with fixed $k_f = 1.55 \text{ \AA}^{-1}$ at the indicated wavevector, whilst red points are data taken at $k_f = 1.3 \text{ \AA}^{-1}$, with $\mathbf{Q} = (h h \frac{1}{2})$.

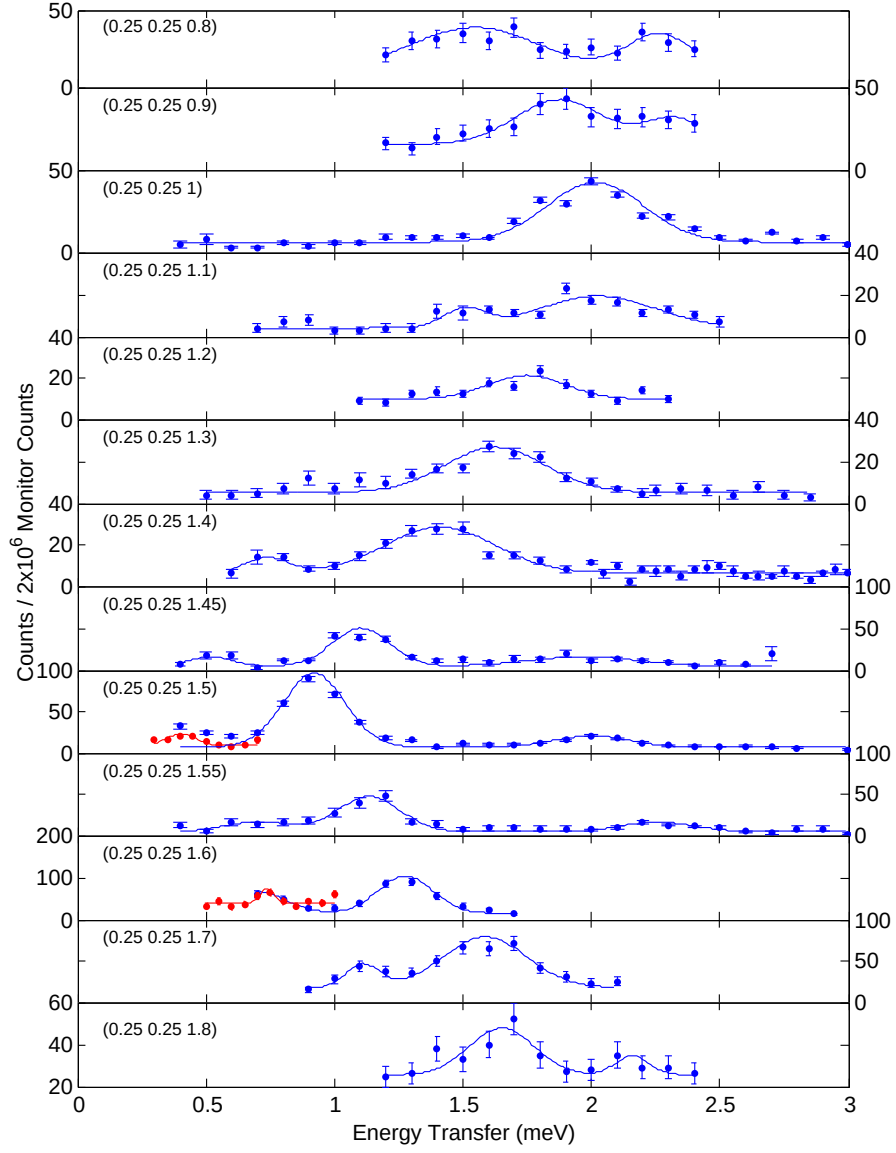


Figure 4.5: Energy scans for $[1/4 \ 1/4 \ l]$ in the commensurate phase of PrB_6 , at zero field. Blue data points indicate data taken with fixed $k_f = 1.55 \text{ \AA}^{-1}$ at the indicated wavevector, whilst red points are data taken at $k_f = 1.3 \text{ \AA}^{-1}$, with $\mathbf{Q} = (1/4 \ 1/4 \ l - 1)$. The $k_f = 1.3 \text{ \AA}^{-1}$ data at $\mathbf{Q} = (1/4 \ 1/4 \ 0.6)$ has been scaled up by a factor of 5.

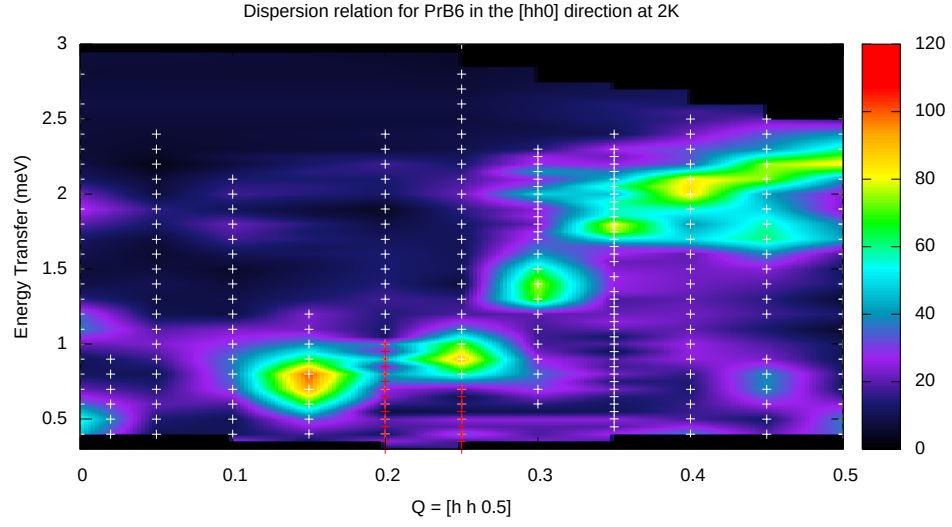


Figure 4.6: *Dispersion of magnetic excitations in the commensurate phase of PrB_6 at zero field along $[h h \frac{3}{2}]$. The white crosses show the energy and wavevector of data points taken with fixed $k_f = 1.55 \text{ \AA}^{-1}$, whilst the red crosses are data at $k_f = 1.3 \text{ \AA}^{-1}$. The data has been linearly interpolated, and the scale shows counts per 2×10^6 monitor counts.*

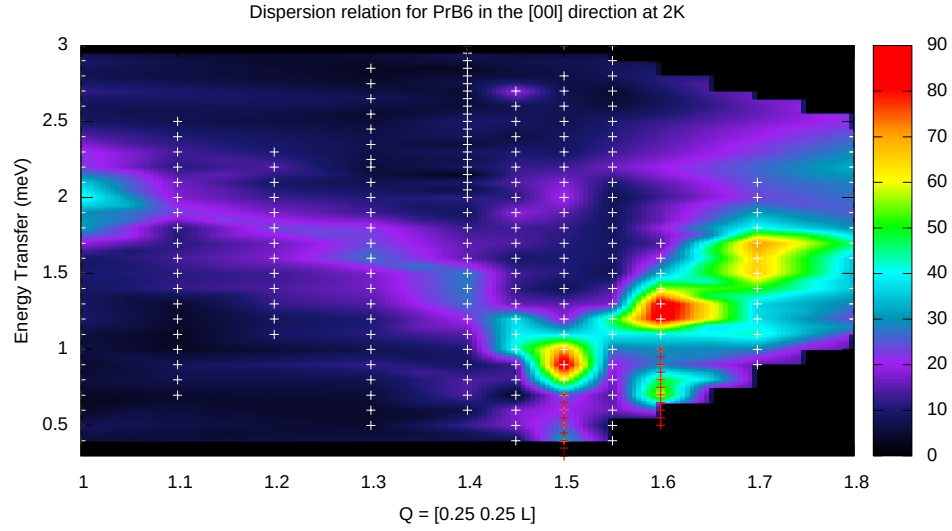


Figure 4.7: *Dispersion of magnetic excitations in the commensurate phase of PrB_6 at zero field along $[\frac{1}{4} \frac{1}{4} l]$. The white crosses show the energy and wavevector of data points taken with fixed $k_f = 1.55 \text{ \AA}^{-1}$, whilst the red crosses are data at $k_f = 1.3 \text{ \AA}^{-1}$. The data has been linearly interpolated, and the scale shows counts per 2×10^6 monitor counts.*

We were able to observe three excitations across most of the Brillouin zone, as shown in the figures. The highest energy mode, centred at ≈ 1.9 meV, is relatively dispersionless along the $[h h \frac{3}{2}]$ direction, and showed a fairly constant, and almost resolution limited width (≈ 0.2 meV) and intensity (≈ 35 counts/ 4×10^6 monitor counts in the peak).

However, along the $[\frac{1}{4} \frac{1}{4} l]$ direction, this mode appears to be asymmetric about the magnetic Brillouin zone centre. This is a surprise because the lower two modes show a more usual dispersion in this direction that is symmetric about the zone centre at $q=(\frac{1}{4} \frac{1}{4} \frac{3}{2})$, and monotonically increasing in energy going towards the zone boundaries. However, the high energy excitation was observed to be quite broad (FWHM ≈ 0.33 meV) and weak. In addition, mean-field calculations detailed below in section 4.3 suggests that there are two modes which cross at the zone centre but that one is much stronger than the other. Thus it may be that we only observed one of these modes, and that the overall dispersion is still symmetric about the zone centre.

In the $[h h \frac{3}{2}]$ direction, though, the dispersion of the two lower energy modes appears to be symmetric about $q=(\frac{1}{2} \frac{1}{2} \frac{3}{2})$ rather than $(\frac{1}{4} \frac{1}{4} \frac{3}{2})$. This and the merging of the two lower energy modes are reproduced in the mean-field calculations (see figure 4.15), which suggests that this is intrinsic to the double- k structure.

4.2.2 The Commensurate Phase in applied fields up to 6 T

Burlet et al. (1988) reported that PrB_6 undergoes a transition from the double- k structure at zero field to a single- k structure above an applied field of 2 T. In addition, the applied magnetic field favours two of the three zero-field domains where the moments are parallel to the field.

We measured the dispersion over much of the Brillouin zone with an applied field of 2 T and more extensively at 6 T. In addition, we also measured the magnetic excitations at the main symmetry positions at 4 T. The full list of scans is in appendix B. We found that the dispersion at 2 T was very similar to that at 6 T, which suggests that the transition is lower than 2 T and that we are already in the single- k structure.

Figures 4.8 and 4.9 shows constant $\mathbf{Q}$ scans along the main symmetry directions, fitted with Gaussian functions. Along the $[h h 0]$ direction, we can see that the dispersion is asymmetric about the magnetic Brillouin zone centre at $(\frac{1}{4} \frac{1}{4} \frac{3}{2})$ and there is only one strong mode at lower energies. This mode maps on well with one of the modes in the zero field dispersion, but we did not observe the other zero-field low energy mode. In addition, we also saw the higher

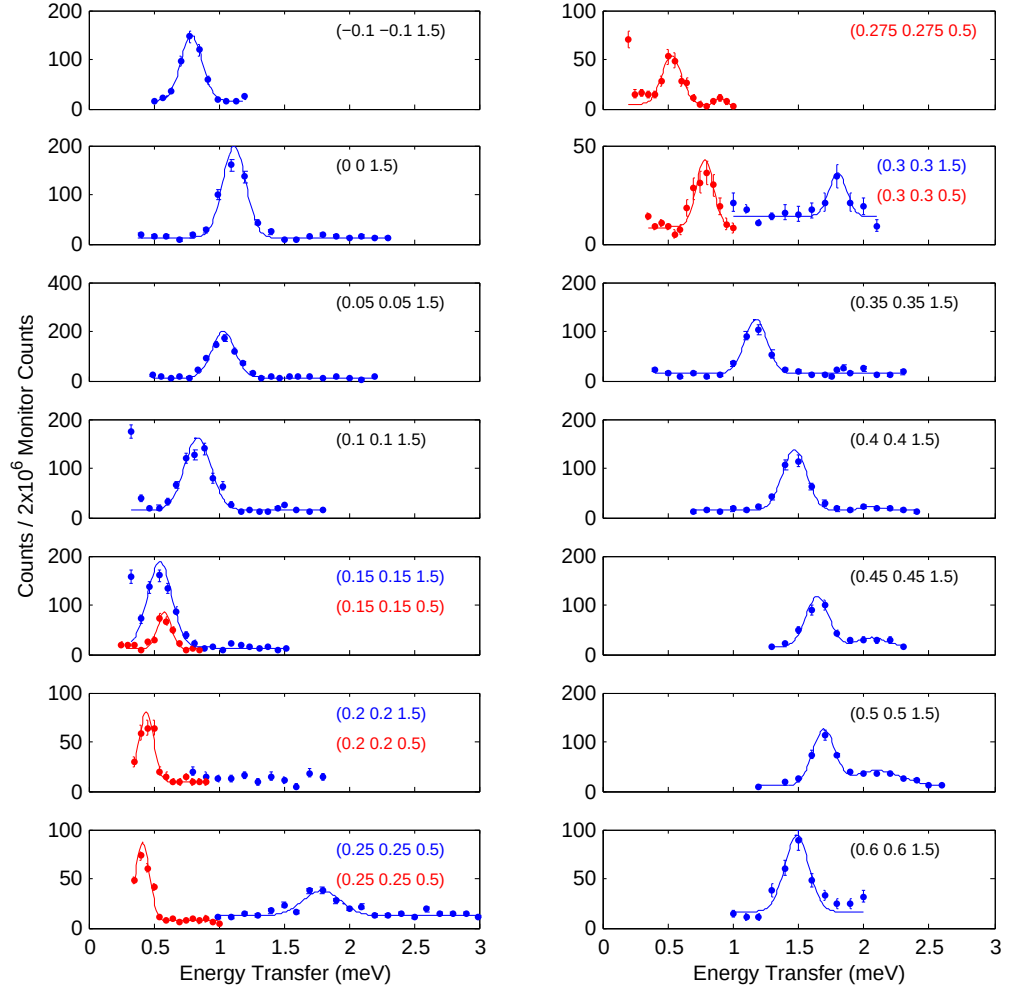


Figure 4.8: Scans along $[h h 3/2]$ in the commensurate phase of PrB_6 in an applied field of 6 T. Blue data points indicate data taken with fixed $k_f = 1.55 \text{ \AA}^{-1}$, at the wavevector indicated in blue, whilst red points are data taken at $k_f = 1.3 \text{ \AA}^{-1}$ at the wavevector indicated in red.

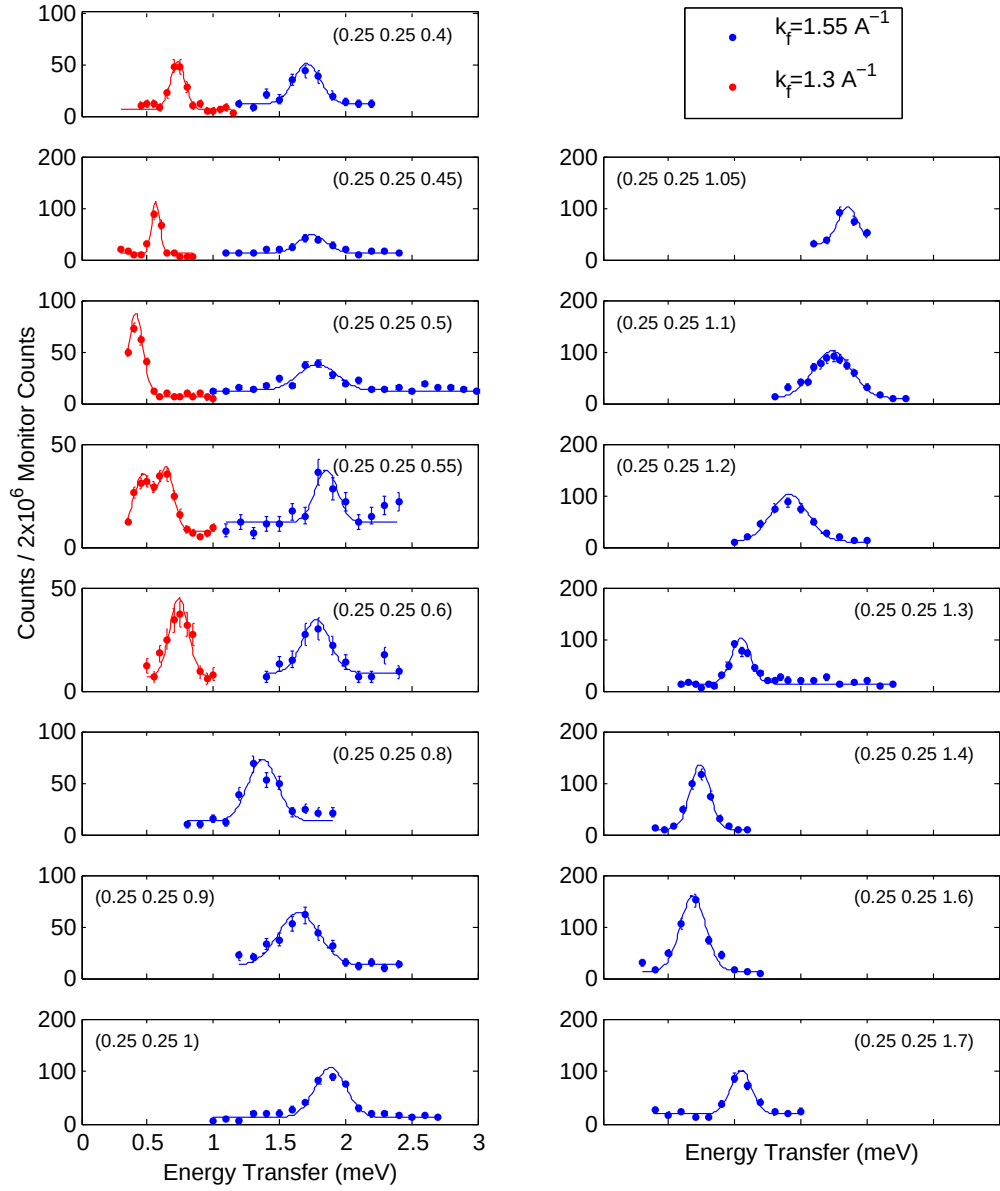


Figure 4.9: Scans along $[1/4 \ 1/4 \ l]$ in the commensurate phase of PrB_6 in an applied field of 6 T. Blue data points indicate data taken with fixed $k_f = 1.55 \text{ \AA}^{-1}$ whilst red points are data taken at $k_f = 1.3 \text{ \AA}^{-1}$.

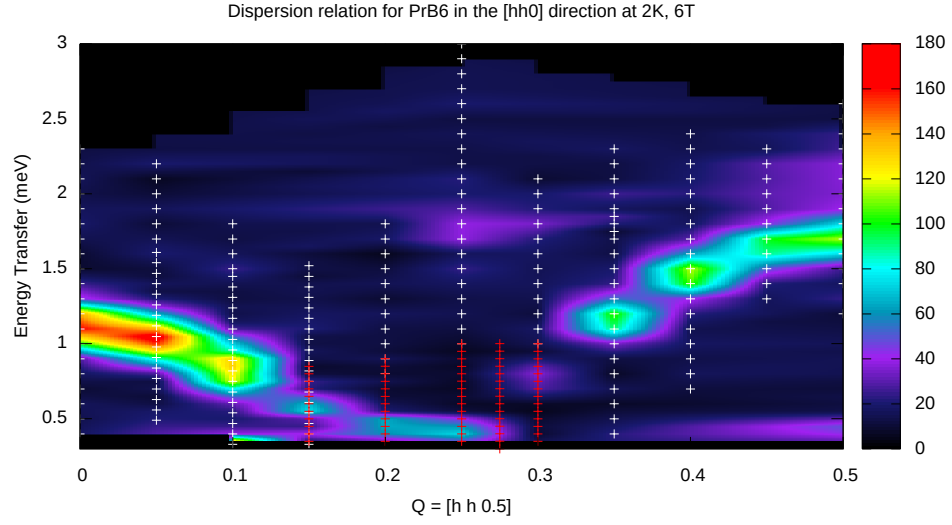


Figure 4.10: *Dispersion of magnetic excitations in the commensurate phase of PrB₆ in an applied field of 6 T along $[h h \frac{3}{2}]$.* The white crosses show the energy and wavevector of data points taken with fixed $k_f = 1.55 \text{ \AA}^{-1}$, whilst the red crosses are data at $k_f = 1.3 \text{ \AA}^{-1}$. The data has been linearly interpolated, and the scale shows counts per 2×10^6 monitor counts.

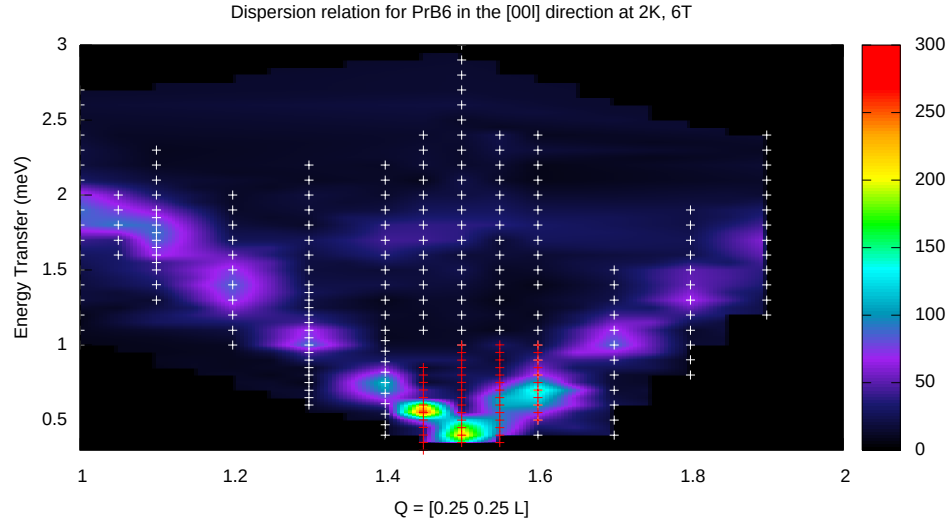


Figure 4.11: *Dispersion of magnetic excitations in the commensurate phase of PrB₆ in an applied field of 6 T along $[\frac{1}{4} \frac{1}{4} l]$.* The white crosses show the energy and wavevector of data points taken with fixed $k_f = 1.55 \text{ \AA}^{-1}$, whilst the red crosses are data at $k_f = 1.3 \text{ \AA}^{-1}$. The data has been linearly interpolated, and the scale shows counts per 2×10^6 monitor counts.

energy, mainly dispersionless mode. Figures 4.10 and 4.11 shows the dispersion as colour maps, and shows clearly this asymmetry.

In the $[0\ 0\ l]$ direction, we again pick out only one mode which showed much dispersion, in this case the lower energy mode (with a minimum energy of ≈ 0.4 meV) which is much stronger in intensity than at zero field; along with the higher energy dispersionless mode.

4.2.3 The Incommensurate Phase ($4.2\text{ K} \leq T \leq 7\text{ K}$)

Figure 4.12 show scans in the incommensurate phase at 5 K. Unfortunately because of the orientation of the sample and cryostat, we were unable to tilt far enough to access wavevectors along the high symmetry directions in the incommensurate phase, i.e. along $\mathbf{Q}=(0.2\ 0.25\ l)$ or $\mathbf{Q}=(h\ 5/4h\ 3/2)$. The wavevectors at which data were taken, and for comparison, the high symmetry directions, are marked in figure 4.3b.

In contrast to the shape of the dispersion of the excitations along $[h\ h\ 3/2]$ in the C phase, in the IC phase, as shown on the right of figure 4.12, the modes have a minimum of 0.6 meV at $\mathbf{Q}=(1/4\ 1/4\ 3/2)$, the C phase magnetic zone centre, and a maximum of 1.3 meV at the magnetic zone boundary, $\mathbf{Q}=(0\ 0\ 3/2)$. In between these two end points, we observed a broad range of scattering at $\mathbf{Q}=(0.1\ 0.1\ 3/2)$ which we have interpreted to be two modes that are just resolved. The second, higher energy, mode may also be seen at $\mathbf{Q}=(0.2\ 0.2\ 3/2)$ as a shoulder to the higher intensity low energy peak.

The dispersive modes along $[1/4\ 1/4\ l]$ observed in the C phase were again seen in the IC phase, shown on the left of figure 4.12. However, in this phase we observed two modes across most of the magnetic Brillouin zone, separated in energy by ≈ 0.5 meV. The lower energy mode is softened by ≈ 0.5 meV with respect to the mode observed in the C phase at 2 K. The peaks in this phase were much broader than in the C phase, with $\text{FWHM} \approx 0.4$ meV, so it was difficult to resolve some of them. We note that, at $\mathbf{Q}=(1/4\ 1/4\ 3/2)$, the C phase magnetic zone centre, there appears to be only a single excitation at 0.53 meV. This corresponds to the minimum energy of the lower mode, whilst the intensity of the upper mode has apparently vanished.

4.2.4 Temperature Dependence of the Excitations

Finally, figure 4.13 shows scans at the magnetic Brillouin zone edge, at $\mathbf{Q}=(0\ 0\ 3/2)$, and zone centre, at $\mathbf{Q}=(1/4\ 1/4\ 3/2)$, measured at 2 K and 3.8 K in the C phase, at 5 K in the IC phase, and at 10 K in the paramagnetic phase. The inelastic peaks and the elastic peaks in the C and IC phases were fitted with Gaussian peaks, but the quasielastic broadening in the paramagnetic phase was

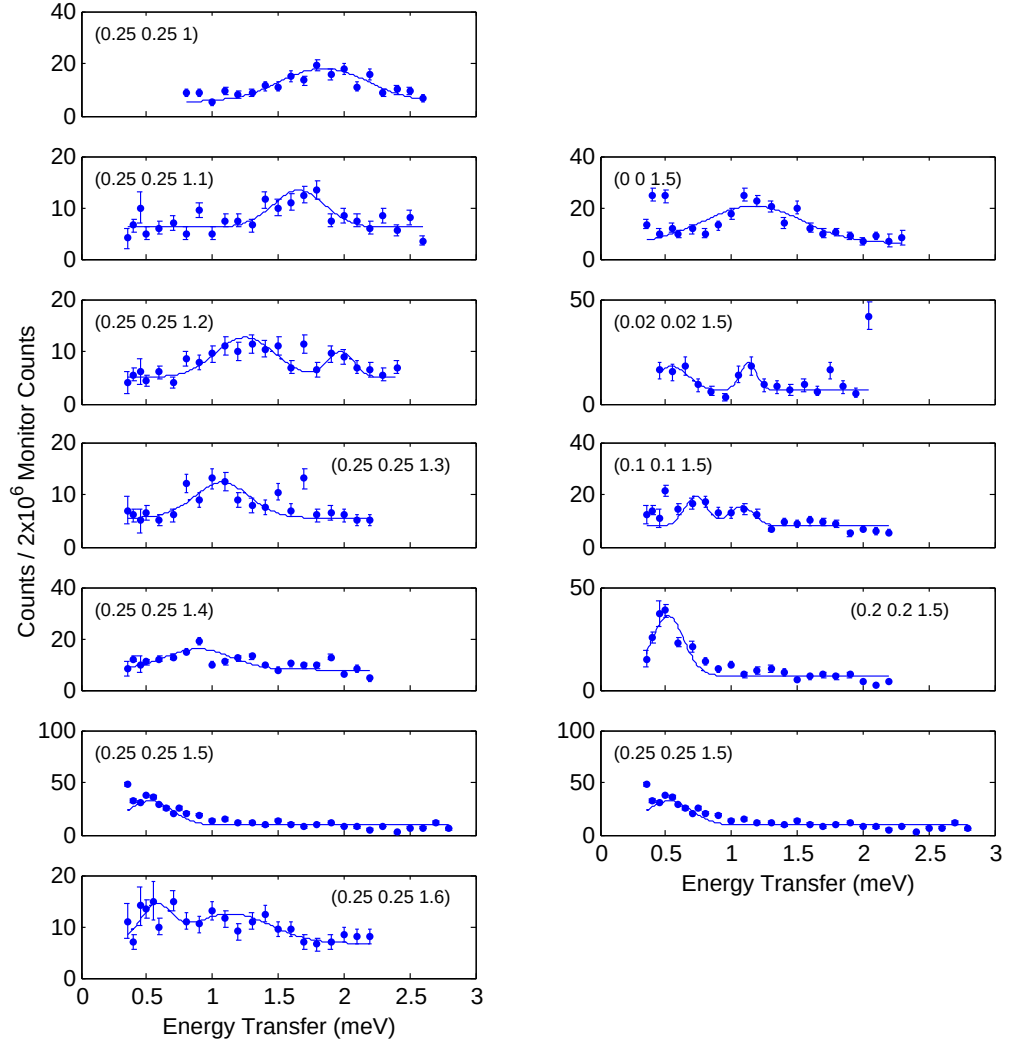


Figure 4.12: *Scans in the incommensurate phase of PrB_6 at zero field.* All data points were taken with fixed $k_f = 1.55 \text{ \AA}^{-1}$. The left panel shows scans along $[\frac{1}{4} \frac{1}{4} l]$ whilst the right panel shows scans along $[h h \frac{3}{2}]$.

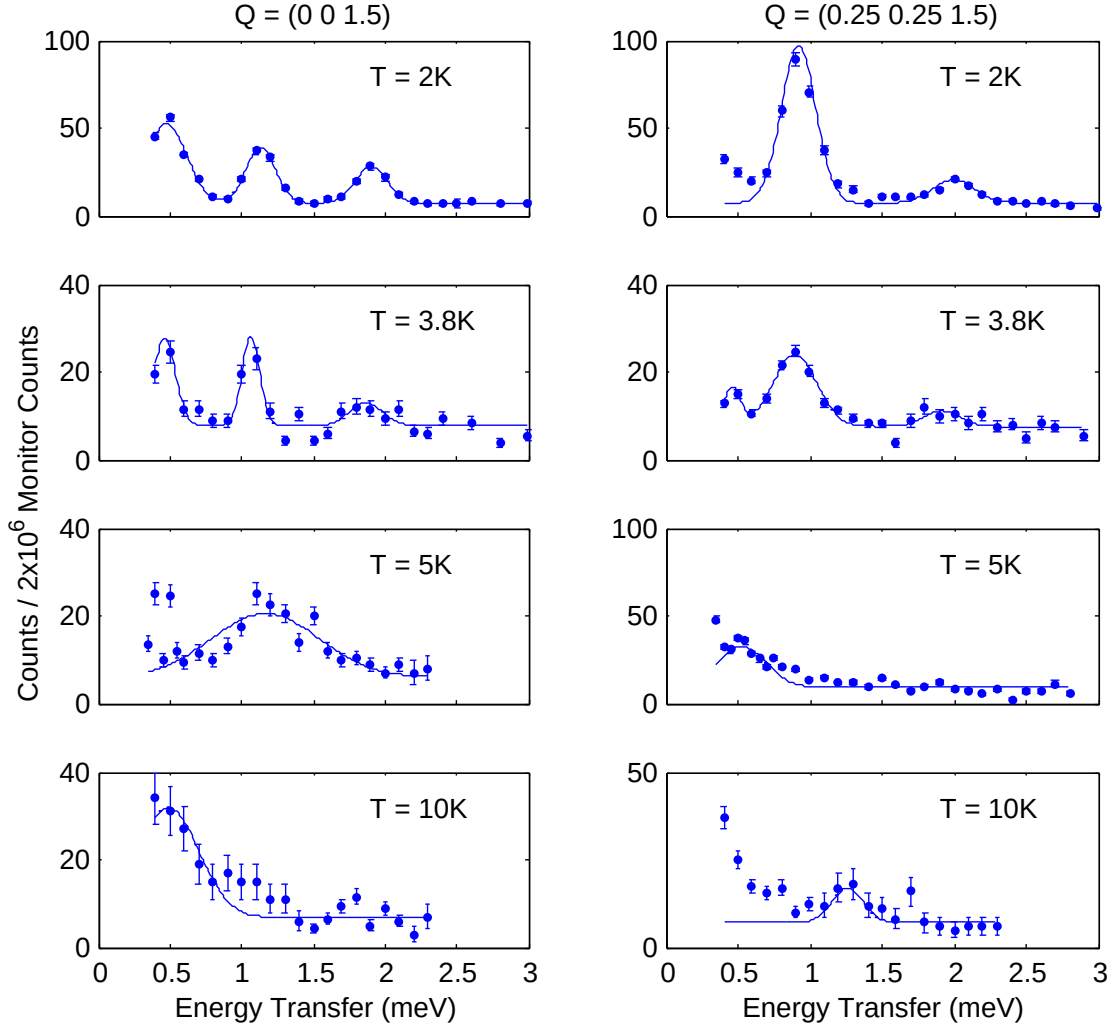


Figure 4.13: *Temperature dependence of the inelastic spectra.* The left panel shows spectra from the magnetic Brillouin zone edge and the right panel shows spectra from the zone centre. The solid lines are fits using Gaussians for the inelastic peaks.

fitted using a pseudo-Voigt function with both Gaussian and Lorentzian components having the same widths and centred on zero energy transfer. We observed that the three modes in the C phase at the magnetic zone edge appear to become one mode in the IC phase, and that there is a steady decrease of intensity with increasing temperature which is in accord with the reduction in the thermal occupation of the ground state. A similar reduction in intensity was observed at the magnetic zone centre, where we also saw that the two modes in the C phase become a single mode in the IC phase, although as noted above from the dispersion of the modes along $[0\ 0\ 1]$ we should expect two peaks at this wavevector in the IC phase also.

We also observed a small inelastic peak in the paramagnetic phase, centred at 1.25 meV at the magnetic zone centre, which appears to be softened to around 0.5 meV at the magnetic zone

edge. This peak may arise from short range AFM ordering as observed in bulk measurements and noted by Kobayashi et al. (2001).

4.3 Analysis

4.3.1 Model Hamiltonian

The effects of the quadrupolar interactions in cubic rare earth systems have been extensively reviewed by Morin & Schmitt (1990), and we shall be using the formalism which they proposed. Under this approach, the Hamiltonian is given by:

$$\mathcal{H} = \mathcal{H}_{CF} + \mathcal{H}_Z + \mathcal{H}_{EX} + \mathcal{H}_Q \quad (4.1)$$

The first term is the crystal field Hamiltonian, which for a cubic system is given by:

$$\mathcal{H}_{CF} = B_4 (\bar{O}_{40} + 5\bar{O}_{44}) + B_6 (\bar{O}_{60} - 21\bar{O}_{64}) \quad (4.2)$$

In the case of PrB_6 , the parameters are $B_4=0.013$ meV and $B_6=3.25 \times 10^{-5}$ meV, deduced by Loewenhaupt & Prager (1986) from neutron scattering data, resulting in the level scheme shown in figure 4.2. The second term in equation 4.1 is the Zeeman term, $\mathcal{H}_Z = -g_J \mu_B \mathbf{H} \cdot \mathbf{J}$, and the third term is the two ion magnetic exchange interaction:

$$\mathcal{H}_{EX} = -\frac{1}{2} \sum_{ij} J(ij) \mathbf{J}_i \cdot \mathbf{J}_j \quad (4.3)$$

The last term in equation 4.1 represents the two-ion quadrupolar exchange interaction. This is similar to the magnetic exchange term above but with second order Stevens operators $\bar{O}_{2q}(i)$ in place of the J_i . However, not all components q of these operators are allowed by symmetry. In the case of cubic symmetry the quadrupolar interaction, along with other magnetoelastic interactions, acts to deform the lattice in one of two symmetry lowering directions. These two *strain modes* are the tetragonal (γ) and trigonal (ϵ)³. The allowed quadrupolar operators $\bar{O}_{2q}$ (or linear combinations of them) are those which transform according to the same irreducible representation as that of either of the symmetry lowering modes. For the tetragonal mode, these are $\bar{O}_{20}$ and $\bar{O}_{22}$, whilst for the trigonal mode, these are $\bar{O}_{21}$, $\bar{O}_{2,-1}$ and $P_{xy} \equiv \frac{1}{2}\bar{O}_{2,-2}$. The tetragonal mode in PrB_6 was estimated to be quite small (Morin et al., 1991), though, so we

³The other strain mode, α , involves the isotropic expansion or compression of the lattice and so is not mediated by quadrupolar interactions.

shall ignore it for the present. Thus the quadrupolar interaction is given by:

$$\mathcal{H}_Q = -\frac{1}{2} \sum_{ij} G^\epsilon(ij) \left[\bar{O}_{21}(i) \bar{O}_{21}(j) + \bar{O}_{2,-1}(i) \bar{O}_{2,-1}(j) + \frac{1}{4} \bar{O}_{2,-2}(i) \bar{O}_{2,-2}(j) \right] \quad (4.4)$$

Morin et al. (1991) used measurements of the elastic constants to estimate the strength of the quadrupolar coupling, which is effectively the sum of a two-ion exchange term and a one-ion magnetoelastic term (Morin & Schmitt, 1990):

$$G^\epsilon(q=0) = \sum_{ij} G^\epsilon(ij) = \frac{(B^\epsilon)^2}{C_0^\epsilon} + K^\epsilon \quad (4.5)$$

Measurements of the $C_{44} = \frac{1}{2} C^\epsilon$ elastic constant gave estimates of the magnetoelastic term $B^\epsilon = 530$ K, and the exchange term $K^\epsilon = -0.6$ K, and background elastic constant $C_{44}^0 \approx 38 \times 10^4$ K. Thus $G^\epsilon(q=0) \approx -0.23$ K, which gives us an estimate of the magnitude of the quadrupolar interactions. We found that a nearest- and next-nearest-neighbour quadrupolar interaction was sufficient to stabilise the magnetic structure observed by Burlet et al. (1988), that is we need the quadrupolar exchange parameters $G^\epsilon(1,0,0)$ and $G^\epsilon(1,1,0)$.

4.3.2 Mean Field Structure and Calculated Dispersion

In order to stabilise the double- k ground state we found that we need to include the following bilinear exchange parameters, $\mathcal{J}(1,0,0)$, $\mathcal{J}(1,1,0)$, $\mathcal{J}(1,1,1)$, $\mathcal{J}(2,0,0)$, in the summation 4.3. Taking the ratio of the parameters to vary as the inverse square of their distance, an initial value of $\mathcal{J}(1,0,0) \approx -0.06$ meV $= 2\mathcal{J}(1,1,0) = 3\mathcal{J}(1,1,1) = 4\mathcal{J}(2,0,0)$, was found to give an ordered phase below $T \sim 8$ K with ordering wavevector $\mathbf{k} = [1/4 \ 1/4 \ 1/2]$. This structure however was single- k . A non-zero quadrupolar interaction is required to stabilise the double- k structure and is discussed below. An initial value for these parameters was estimated to be $G^\epsilon(1,0,0) \approx -0.012$ meV $= 2G^\epsilon(1,1,0)$ such that $G^\epsilon(1,0,0) + G^\epsilon(1,1,0) \approx -0.23$ K from the analysis of the elastic constants given above.

These initial parameters were then used in a non-linear least squares fit to the measured dispersion using the Nelder-Mead Simplex algorithm. This algorithm was chosen in order to lessen computing time because it is relatively efficient at finding local minima⁴ For each iteration, the magnetic structure was first calculated at $T = 2$ K, $B = 0$ T, in the mean-field

⁴Note that each iteration takes up to 30 mins to compute.

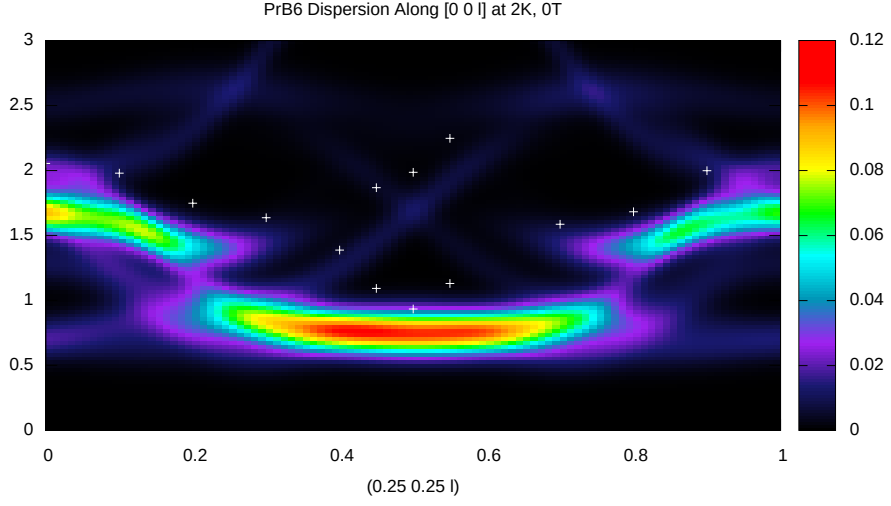


Figure 4.14: *Calculated magnetic dispersion in the commensurate phase of PrB_6 along the $[0\ 0\ l]$ direction. This is the average of the calculated dispersion along $[h\ 0\ 0]$, $[0\ k\ 0]$, and $[0\ 0\ l]$, at 2 K, 0 T. White crosses denote the positions of peaks in the measured data.*

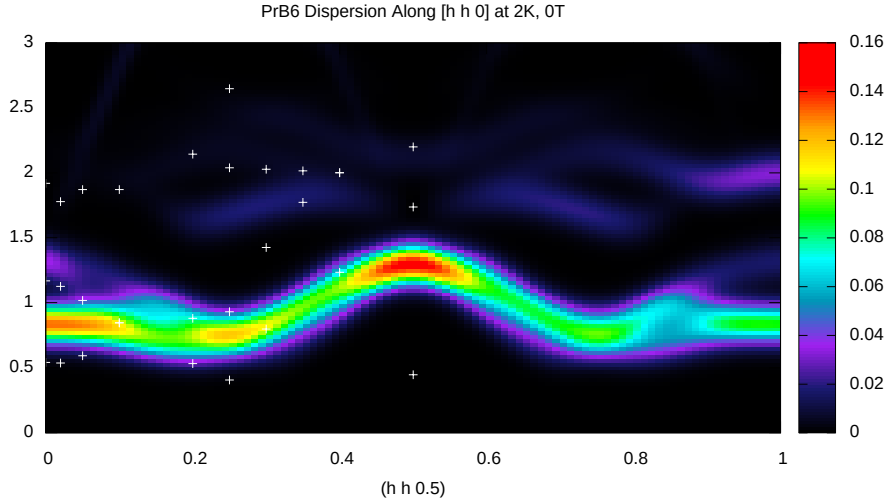


Figure 4.15: *Calculated magnetic dispersion in the commensurate phase of PrB_6 along the $[h\ h\ 0]$ direction. This is the average of the calculated dispersion along $[h\ h\ 0]$, $[0\ k\ k]$, and $[h\ 0\ h]$, at 2 K, 0 T. White crosses denote the positions of peaks in the measured data.*

$J(1,0,0)$	-0.0721	$G^e(1,0,0)$	-0.0155
$J(1,1,0)$	-0.0229	$G^e(1,1,0)$	-0.0043
$J(1,1,1)$	-0.0181	$G^e(1,1,1)$	-0.0028
$J(2,0,0)$	-0.0179		

Table 4.1: *Exchange parameters for PrB_6 in meV.*

approximation according to equations 4.1 and 2.23, with the expectation values of the magnetic moments extended to include the expectation $\langle \bar{O}_{2q}(i) \rangle$. If the stabilised mean-field structure did not have an ordering wavevector of the form $\langle 1/4 \ 1/4 \ 1/2 \rangle$, the set of parameters which produced it was discarded from the fit. Second, from this structure and exchange parameters the dispersion was calculated in the random-phase approximation according to equations 2.44 and 2.45. The calculated energies, E_n and relative intensities, I_n , were then compared to the measured data, to obtain a goodness-of-fit parameter,

$$\chi_{\text{fit}}^2 = \sum_{\text{hkl}} \sum_n [(E_n^{\text{meas}} - E_n^{\text{calc}}) + (I_n^{\text{meas}} - I_n^{\text{calc}})]^2$$

which was minimised by the Simplex method. As we have no a-priori information to which dispersion branch the measured excitations belong, the n^{th} calculated transition was assigned to the nearest measured peak in energy. This is somewhat unsatisfactory, because it ignores degenerate or nearly degenerate levels. However, the procedure did produce a satisfactory fit which is shown in figures 4.15 and 4.14, with parameters summarised in Table 4.1.

As mentioned above, we found that the double- k structure may only be stabilised with non-zero quadrupolar exchange parameters. For example using the parameters of table 4.1 with $G^e(1,0,0) = G^e(1,1,0) = 0$ gives the structure shown in figure 4.16a.⁵ This is in contrast to the double- k structure shown in figure 4.3a, and reproduced in figure 4.16b. In this case, the ordered quadrupolar moments as shown in figure 4.16d cause the free energy of the system to be lowered if the magnetic moment on alternate atoms is rotated in order to align with the antiferro-structure of the quadrupolar moments. Figure 4.16c (d) shows the signs of the expectation value of the magnetic (quadrupolar) moments, stabilised without (with) quadrupolar interactions.

Thus the magnetic exchange interaction alone is not enough to stabilise the double- k structure, whereas inclusion of a negative G^e term does. However, including the quadrupolar interaction means that this structure is stable even with a magnetic field applied along $\langle 1 \ 1 \ 1 \rangle$, so that the model cannot accommodate the findings of Burlet et al. (1988)⁶. As a demonstration of this, we show in figures 4.17 and 4.18 the calculated dispersion at 6 T, in which the double- k structure is calculated to have the lowest calculated free energy. The calculated dispersion, although different to the zero-field calculations in figures 4.14 and 4.15 does not fit the measured

⁵Note that this collinear single- k structure is not the same as that postulated by Burlet et al. (1988) for the metamagnetic phase above 2 T.

⁶J. Jensen, personal communication, Aug. 2008

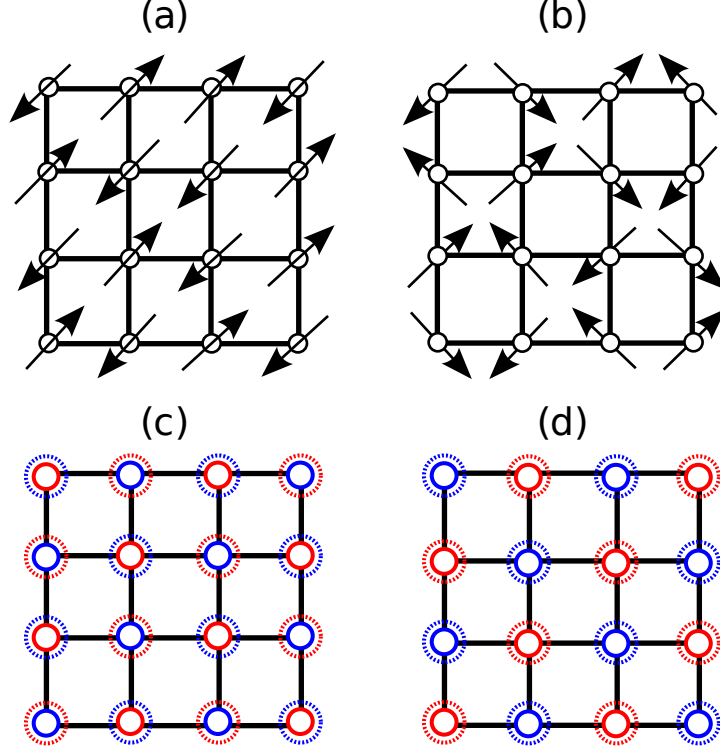


Figure 4.16: *The double- k and single- k structure and sign of the expectation values of the magnetic and quadrupolar interactions.* a) Shows the single- k phase above 2 T in the commensurate phase, and b) shows the double- k phase at zero field. c) shows the sign of the expectation value $\langle J_x \rangle$ stabilised when quadrupolar interactions are set to zero. d) shows the sign of $\langle O_2^{-2} \rangle$ in the double- k phase stabilised with non-zero quadrupolar interactions. Red circles denote values < 0 , blue circles for value > 0 . Inner circles denote atoms on the $z = 0$ plane, and outer dashed circles atoms on the $z = 1$ plane.

data. In particular in the $[h\ h\ 0]$ direction at the Brillouin zone edge the calculation gives a broad peak due to several excitations, rather than a single narrow peak which was measured.

In addition, we note that the parameters deduced above give rise to an ordered quadrupolar structure in the mean-field approximation. The ordering involves the $\bar{O}_{2,-1} \equiv Q_{yz}$ quadrupoles at a wavevector $\mathbf{k} = [1/2\ 1/2\ 1/2]$. The wavevector is consistent with the model of Kobayashi et al. (2001) and observations of Walker et al. (2009), but not the ordered quadrupolar moment, which was predicted to be $\bar{O}_{2,-2} \equiv Q_{xy}$. A resolution of this issue would require further resonant x-ray scattering measurements.

Finally, the inability to stabilise a single- k structure in the field is only one of the major failings in the model at present. The other is that the calculated ordered moment is $\sim 2\ \mu_B/\text{Pr}$ which is twice the $1.1\ \mu_B/\text{Pr}$ measured by Burlet et al. (1988). However an older neutron powder diffraction study by McCarthy et al. (1980) gives the moment as $1.77(5)\ \mu_B/\text{Pr}$. This suggests

that the single crystal study may have missed some diffraction peaks, and thus that the structure of Burlet et al. (1988) is incomplete.

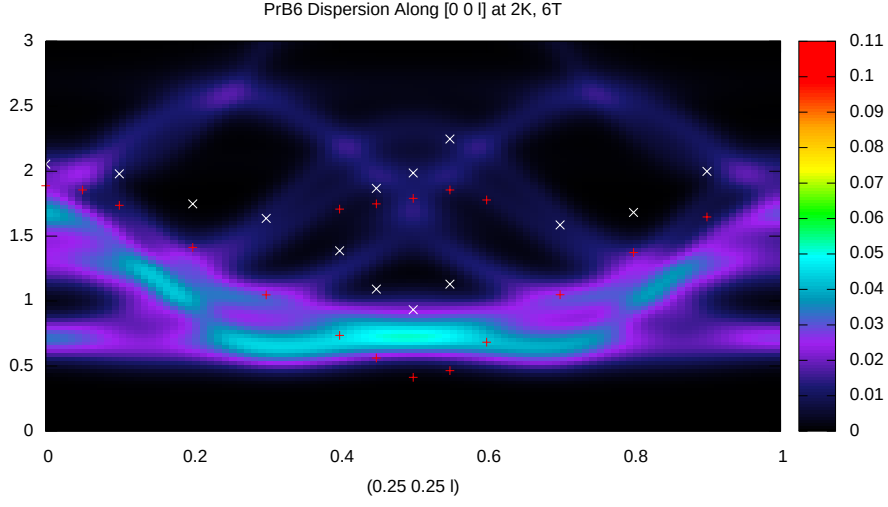


Figure 4.17: *Calculated magnetic dispersion along [0 0 l] at 6 T. White crosses denote the positions of peaks in the measured data at zero field, whilst red crosses those measured at 6 T.*

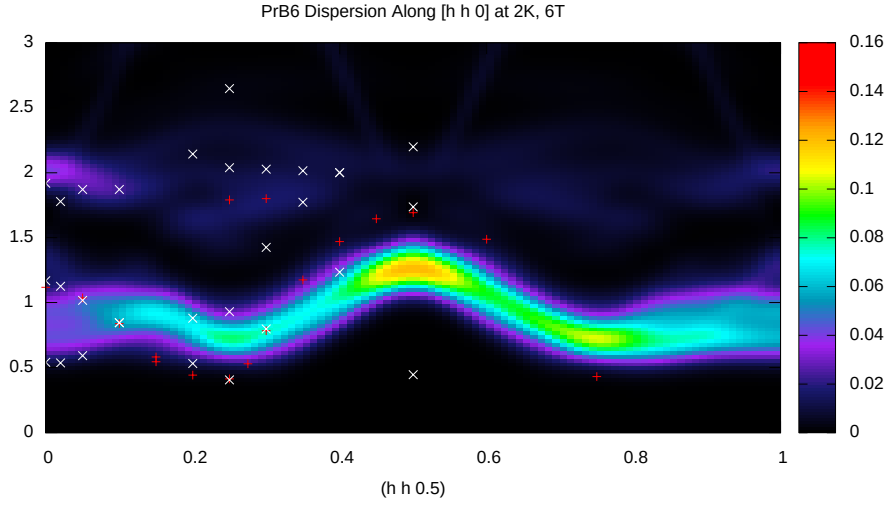


Figure 4.18: *Calculated magnetic dispersion along [h h 0] at 6 T. White crosses denote the positions of peaks in the measured data at zero field, whilst red crosses those measured at 6 T.*

4.3.3 Diffraction Experiments

As a result we began a diffraction study to determine if there are other super-lattice peaks which were previously not observed. The measurements were taken using the D10 four-circle, three-axis diffractometer at the ILL, using a single crystal of dimension $5 \times 5 \times 3 \text{ mm}^3$, which was also grown at Hiroshima University using the same procedure as for the inelastic studies.

Initially we looked for the $\{1/2 \ 1/2 \ 0\}$ and $\{1/4 \ 1/2 \ 0\}$ type peaks, to determine if these

were the ‘missing’ peaks responsible for the low estimates of the ordered moment in the study of Burlet et al. (1988). We were able to observe the second harmonic peaks $\{1/2 \ 1/2 \ 0\}$ in two-axis mode with an area detector, although they proved to be very weak. The $\{1/4 \ 1/2 \ 0\}$ type peaks however were not detected at all, even in three-axis mode in order to improve the signal to noise ratio, and measured with counting times over twenty times longer than the scans for the second harmonic peaks ($\approx 2\text{min/pt}$, counting for 10^6 monitor counts). Nonetheless we were able to measure 879 magnetic peaks with $\sin\theta/\lambda \leq 0.4 \text{ \AA}^{-1}$ in the commensurate phase and 467 peaks in the incommensurate phase, and a magnetic structure refinement is in progress.

However the experiment did show a very unusual temperature dependence of the magnetic Bragg peaks, as shown in figure 4.19. It appears that the commensurate peaks of the type $\{3/4 \ 3/4 \ 1/2\}$ persist into the incommensurate phase, as do incommensurate peaks of the type $\{3/4 - \delta \ 3/4 \ 1/2\}$ into the commensurate phase. The measurement was taken starting from 2 K, with each peak measured at the same temperature before the temperature was increased. However these measurements were completed near the end of the experiment, so there was not enough time available to make an extensive survey of the $\{3/4 - \delta \ 3/4 \ 1/2\}$ type peaks below 4.2 K, and the $\{3/4 \ 3/4 \ 1/2\}$ between 4.2 K and 7 K. Further experiments are thus required in order to explain this observation.

Finally we also observed double peaks around some wavevectors of the incommensurate type $\{1/4 - \delta \ 1/4 \ 1/2\}$, the origin of which is not satisfactorily resolved. One may consider that they arise from different crystallites in the sample which have a slight mis-alignment. However the double peaks were only observed around these wavevectors in the incommensurate phase, and not around the structural Bragg peaks nor the commensurate phase peaks, nor in the commensurate phase. This would suggest that these peaks were intrinsic to the incommensurate structure, but a full structural refinement is needed and is in progress.

4.4 Conclusions

We have measured the dispersion of the low energy magnetic excitations in PrB_6 in both ordered phases at zero field and in an applied field along the $[1 \ \bar{1} \ 0]$ direction up to 6 T. The dispersion and deduced mean-field model shows the importance of the quadrupolar interactions to stabilise the double- k structure at zero field, and also predicts ordering of the Q_{yz} quadrupoles in tandem with the magnetic ordering.

Comparing the transition temperatures of the ordered phases, it appears that the strength

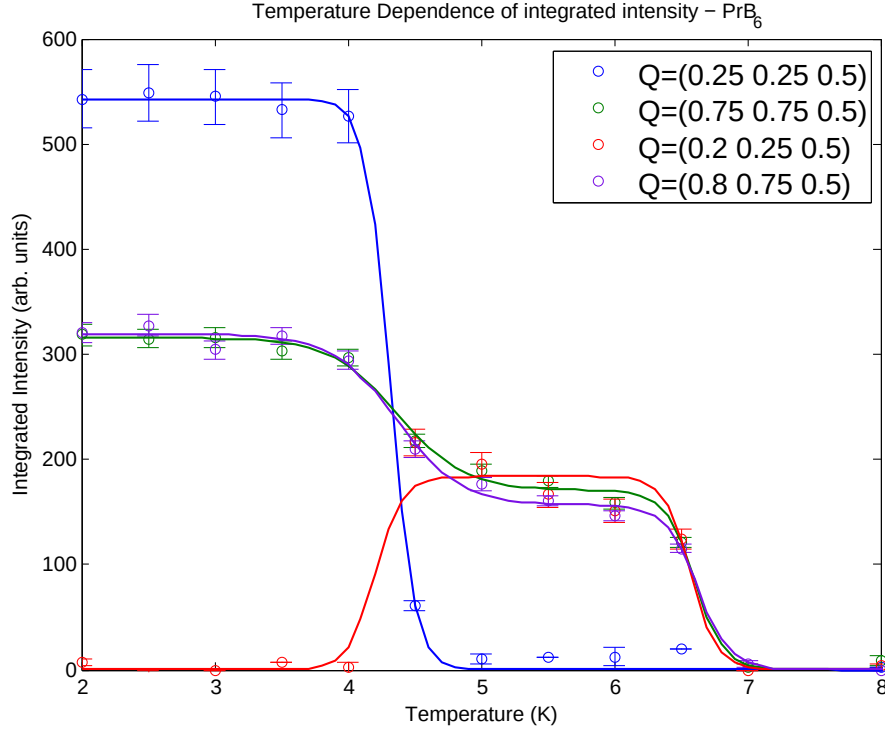


Figure 4.19: *Temperature dependence of the magnetic Bragg peaks in PrB₆.*

of the quadrupolar interactions in CeB₆ ($T_Q = 3.2$ K, $T_N = 2.3$ K) and PrB₆ ($T_C = 4.2$ K, $T_{IC} = 7$ K) is similar, but that the magnetic interactions has increased significantly. However, no quantitative model of the exchange interactions in CeB₆ is known. A model for NdB₆ deduced from the dispersion in the ordered phase (Kubo & Kuramoto, 2003) gives $G(\mathbf{k} = 0) = 107$ mK which shows that the quadrupolar interaction is less than in PrB₆ where we deduced that $G(\mathbf{k} = 0) = 230$ mK. The authors also deduced a magnetic exchange interaction $J(\mathbf{k} = [0\ 0\ 1/2]) = 0.12$ meV which is about the same as that which we deduced for PrB₆, $\sum_{ij} J(ij) = 0.13$ meV.

Thus it appears that in the rare-earth hexaborides, as one progresses to heavier elements, the quadrupolar interactions decrease whilst the magnetic interactions are of the same magnitude or greater, as surmised in the introduction. This trend may be due to the increasing magnetic moment given to these ions by the additional electrons on the one hand, and on the other by lesser crystal field interactions with surrounding ions due to the contraction of the $4f$ wavefunctions, due to poorer screening of the nuclear charge as the f -shell is filled. The crystal field splitting is observed to decrease from 540 K (46.6 meV) in CeB₆ to 459 K (39.5 meV) in PrB₆ to 272 K (24.0 meV) in NdB₆. This interactions gives rise to the aspherical, multipolar charge distribution, and thus as it decreases one would expect the multipolar interactions to

decrease also.

Finally, the mean-field model outlined in the previous section is still not completely satisfactory, and together with recent diffraction measurements suggests that the magnetic structure is not complete. There is thus much scope for further work on this system.

Chapter 5

Quadrupolar Order in UPd₃

5.1 The Actinide Palladium-3 Systems

In the following three chapters we shall be looking at the compounds UPd₃, NpPd₃, and PuPd₃. The 5*f* electrons in these compounds are localised unlike the majority of actinide intermetallic compounds in which the 5*f* electrons are itinerant. However, as we move through the series we observe a change from the double hexagonal close-packed (dhcp) structure of UPd₃ to an fcc-like structure in PuPd₃. This is the AuCu₃ structure, with actinide atoms at the corners and palladium in the face-centre position. Electronic structure calculations by Duthie & Pettifor (1977) for the rare-earth metals shows that the dhcp structure is indicative of *d*-state bonding, whereas the fcc structure results from lesser *d*-band occupancy and indicates the participation of the *f*-electrons in bonding. Thus the change in structure from UPd₃ to PuPd₃ may indicate a slightly greater *f*-hybridisation. However, photoelectron spectroscopy of PuPd₃ shows that the *f*-electrons are still quite well localised with little spectral weight at the Fermi energy (Le et al., 2008a).

In parallel with the change in structure we also observe the emergence of magnetic order at the expense of quadrupolar ordering, with the antiferromagnetic Néel temperature rising from 4.4 K in UPd₃ to 11 K in dhcp-NpPd₃, and 24 K in PuPd₃. Cubic NpPd₃ has an even higher transition temperature at 55 K. In contrast, UPd₃ has several quadrupolar ordered phases, whereas cubic NpPd₃ and PuPd₃ have no quadrupolar ordering, and the nature of the phase between 11 K and 30 K in dhcp-NpPd₃ is still uncertain. We shall begin in this chapter by looking at the quadrupolar interactions in UPd₃. The experiments detailed in the following sections cover the direct observation of quadrupolar order using resonant X-ray scattering, and the indirect observation of the magnetic-lattice coupling using magnetostriction. These results

are then discussed in the framework of a mean-field model similar to that for PrB_6 discussed in the previous chapter.

5.2 UPd_3 Background

Uranium palladium-3 is a well studied uranium intermetallic compound which exhibits four phase transitions below 8 K. These transitions arise from the ordering of the quadrupole moments of the $5f^2$ electrons on the quasi-cubic uranium sites. UPd_3 crystallises in the double hexagonal closed packed (dhcp) TiNi_3 (DO_{24}) structure (Heal & Williams, 1955). Thus, the uranium atoms occupy alternately sites of locally hexagonal and quasi-cubic symmetry, equivalent to a stacking of ABAC.

Initial magnetisation measurements showed that the compound did not order magnetically (Wernick et al., 1965), and later measurements of the specific heat (Andres et al., 1978), and inelastic neutron spectra (Buyers et al., 1980), showed that the uranium ion is well localised, with a $5f^2$ configuration, corresponding to a U^{4+} ion. The phase transitions were also first observed by Andres et al. at 7 K and 6 K.

Further bulk measurements of the thermal expansion (Ott et al., 1980; Zochowski & McEwen, 1994), magnetostriction (Zochowski & McEwen, 1994), and elastic constants (Yoshiwara et al., 1985) refined the transition temperatures to $T_1 = 6.8$ K and $T_2 = 4.5$ K, and showed that both transitions are structural, but that the second also has a magnetic component. In addition, another transition above T_1 , at $T_0 \approx 7.8$ K was revealed in further heat capacity (Zochowski et al., 1995), magnetisation (Park & McEwen, 1998; McEwen et al., 2003) and ultrasound (Lingg et al., 1999) studies. Finally, the ultrasound studies also revealed that the T_1 transition is actually two transitions, a second order transition at $T_{+1} = 6.9$ K, and a first order transition at $T_{-1} = 6.7$ K.

The structural nature of the transition at T_1 was confirmed by polarised neutron diffraction (PND) by Steigenberger et al. (1992). The authors observed superlattice reflections, at $\mathbf{Q} = (\frac{1}{2}, 0, 3)$ and $(\frac{1}{2}, 0, 4)$, below T_1 with a non-spin-flip cross-section when the neutron was polarised parallel to the scattering vector. The PND experiment also showed that the magnitude of the ordered magnetic moment was extremely small, $\approx 10^{-2} \mu_B/\text{U-ion}$. Further neutron diffraction experiments by McEwen et al. (1998) in an applied magnetic field of $\sim 4T$, along with a group theoretical analysis (Walker et al., 1994), concluded that the quadrupolar order parameter below T_0 is $Q_{x^2-y^2}$.

X-ray resonant scattering (XRS) studies by McMorrow et al. (2001) observed the quadrupolar order directly for the first time in 2001. The XRS study appeared to agree with the neutron data below T_0 , with the $Q_{x^2-y^2}$ structure giving a non-zero signal in the $(\pi - \pi)$ channel for the $(\frac{1}{2}, 0, 3)$ reflection as observed. Data below T_1 showed that the $(\sigma - \pi)$ channel dominates in the $(\frac{1}{2}, 0, 4)$ reflection which may be explained by a rotation of the charge densities. However, follow-up XRS experiments (McEwen et al., 2006; Walker et al., 2006) using azimuthal scans showed conclusively that the order parameter below T_0 is Q_{zx} .

This result may be reconciled with the earlier data if the primary order parameter, Q_{zx} , also induces a secondary order parameter $Q_{x^2-y^2}$. Thus, in the neutron experiments when a magnetic field is applied parallel to the real space a -direction, it will only induce antiferromagnetic moments aligned parallel to field for the $Q_{x^2-y^2}$ case and not for the Q_{zx} case (McEwen et al., 2007).

In addition, inelastic neutron experiments conducted below T_2 by McEwen et al. (1993) revealed four excitations below 3 meV. Two of these decrease in intensity until they disappear above T_2 , and above T_1 only one mode remained, which eventually dies off above T_0 . A mean-field model involving antiferroquadrupolar (AFQ) ordering on the uranium cubic sites was proposed to explain these modes (McEwen et al., 2003). Previous x-ray scattering measurements indicated that the low temperature crystal structure has four inequivalent quasi-cubic sites based on the orthorhombic unit cell, forming four different sublattices. In the mean-field model, the two order parameters below T_2 , $Q_{x^2-y^2}$ and Q_{zx} combine in different combinations in each of the four sublattices, giving rise to different splittings of the quasi-cubic ground state doublet. Thus each sublattice gives rise to a different transition in the inelastic neutron spectra.

Finally, there have also been angle-resolved photoemission spectroscopy studies (Ito et al., 2002) and x-ray diffraction studies under high pressure (Heathman et al., 2003). There is thus a large body of experimental work on UPd₃. However, there is still no satisfactorily comprehensive microscopic understanding of the phenomena observed. In part to rectify this we have completed some mean field calculations aimed at explaining both the bulk properties observed and the scattering data. This is described in section 5.6. First, though, a satisfactory crystal field scheme needed to be established, as the single ion crystal field interaction is much stronger than the inter-ion interactions (magnetic, quadrupolar, etc) which drives the ordering, and this is detailed in section 5.3. Finally, we also describe a magnetostriction experiment at high magnetic

Quasi-cubic				Hexagonal			
B_0^2	+	B_0^6	-	B_0^2	+	B_0^6	-
B_0^4	-	B_3^6	+	B_0^4	-	B_6^6	-
B_3^4	-	B_6^6	+				

Table 5.1: *Point charge calculations crystal parameters.* '+' and '-' indicates that the point charge calculations show that the crystal field parameters should be greater than or less than zero respectively.

fields in order to probe the high field behaviour and to verify our model, in section 5.4.

5.3 Crystal Field Interactions

The U^{4+} ion in UPd_3 is well localised with a Hund's rule $^3H_4$ spin-orbit ground state configuration. In addition, the single ion properties of uranium is found to be generally close to the *LS*-coupling limit (Moore & van der Laan, 2009), so in this chapter we treat it as such and take only the spin orbit ground state into account. The symmetry of the double hexagonal close packed (dhcp) structure means that there are two inequivalent sites, and hence two different CF splittings. The quasi-cubic site is split by a trigonal crystal field (quantised along the hexagonal c-axis, rather than along the tetragonal axis), resulting in six levels (three singlets and three doublets), whilst the hexagonal sites are split into another six levels (also three singlets and three doublets).

Figure 5.1 shows the $TiNi_3$ structure of UPd_3 , with the neighbouring Palladium ions around each hexagonal and quasi-cubic Uranium sites highlighted. Using these ionic positions, a point charge calculation was used to determine the signs of the applicable crystal field parameters given this symmetry. The results are summarised in table 5.1.

However, these point charge calculations usually give a singlet ground state for both Uranium sites, as noted by Buyers et. al. (Buyers et al., 1980), whereas we now believe that the quasi-cubic sites have a doublet ground state, as deduced from specific heat measurements at low temperatures (McEwen et al., 2003). Nevertheless, the point charge calculations can give a good indication of the sign of the crystal field parameters.

In addition, because we now know that the quadrupolar order parameter for the phase below T_0 is Q_{zx} from the XRS data, we also have a restriction on the wavefunction of this quasi-cubic doublet ground state. This follows from the mean-field Landau theory of phase transitions, because the eigenvalues of the Q_{zx} operator are not the same if we change the opera-

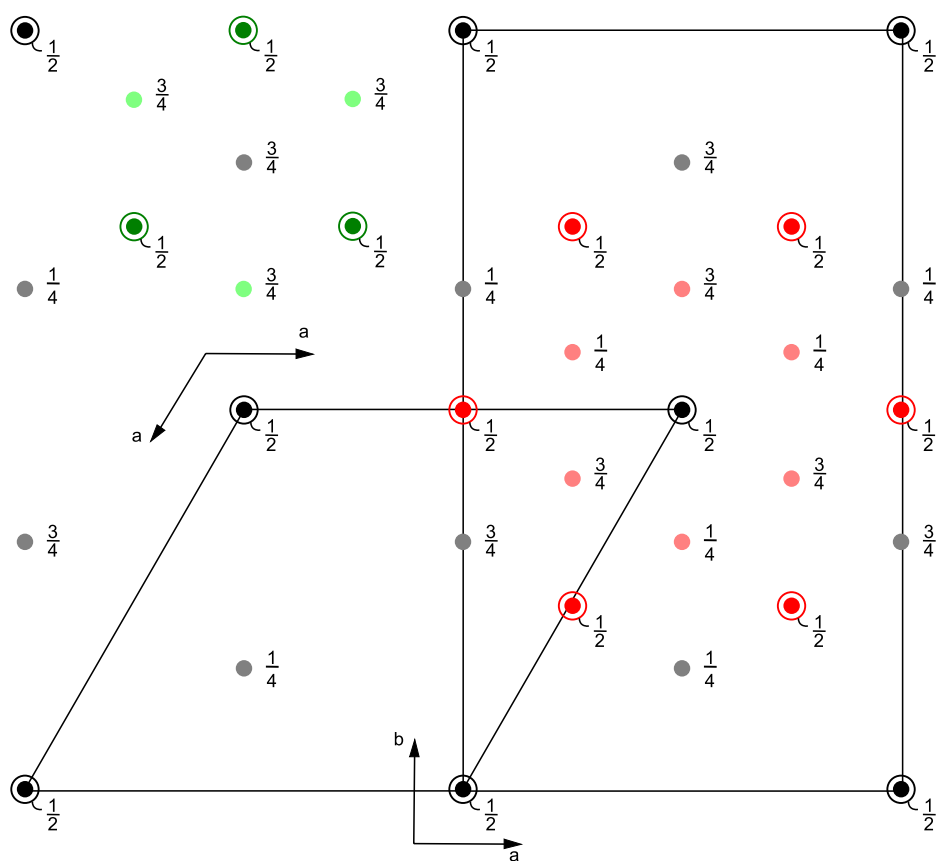


Figure 5.1: *The $TiNi_3$ structure.* The fractions beside each atom indicates the z -coordinates. Uranium quasi-cubic sites are shown in black, hexagonal sites in grey. The Palladium ions neighbouring the quasi-cubic Uranium ions are shown in red, whilst those neighbouring the hexagonal sites in green. Also shown is the hexagonal unit cell, and the orthorhombic unit cell as used by Walker et al. (1994) and subsequent papers.

tor from Q_{zx} to $-Q_{zx}$. Thus in the Landau free energy expansion in terms of the order parameter, we require terms up to third order, that is in Q^3 . Hence, there are two minima in the free energy as a function of the order parameter at constant temperature, and at the transition temperature the global minima (that is the equilibrium value of the order parameter) discontinuously change from one of the minima to the other (that is zero above the transition temperature, and finite below it), indicating a first order phase transition. However, all experimental observations so far indicate that the transition at T_0 is second order, or at best, very weakly first order. Thus we need to restrict the matrix element of Q_{zx} to ensure that its eigenvalues are the same for Q as for $-Q$, so that the free energy expansion needs to only include up to quadratic terms.

Expressing the Q_{zx} operator in matrix form with the three lowest states of the quasi-cubic sites (the doublets $|d_1\rangle$ and $|d_2\rangle$ and singlet $|s\rangle$)¹ as basis states, we get:

$$\hat{Q}_{zx} = \begin{pmatrix} 0 & A' & A' \\ A' & 0 & B' \\ A' & B' & 0 \end{pmatrix} \quad (5.1)$$

In order to ensure that the eigenvalues of $\hat{Q}_{zx}$ is the same as $-\hat{Q}_{zx}$ we need the matrix element $B' = \langle d_1|Q_{zx}|d_2\rangle = \langle d_2|Q_{zx}|d_1\rangle$ to be approximately zero. The wavefunctions of the ground state doublet expressed in terms of the eigenstates of the J, J_z operators is:

$$\begin{aligned} |d_1\rangle &= a|J=4, m_J=4\rangle + b|J=4, m_J=1\rangle + c|J=4, m_J=-2\rangle \\ |d_2\rangle &= a|J=4, m_J=-4\rangle - b|J=4, m_J=-1\rangle + c|J=4, m_J=2\rangle \end{aligned} \quad (5.2)$$

Thus the above requirement for the matrix element B' means that the product $bc \approx 0$.

5.3.1 Inelastic Neutron Data

Extensive data were taken on single crystalline UPd₃ using the IN8 triple-axis spectrometer at the ILL by Martin-Martin (2000) which revealed the dispersion of the CF modes in UPd₃. In addition, we have also recently measured the inelastic excitations at 60 K and 160 K so as to thermally occupy the 15 meV excited doublet on the hexagonal sites in order to determine the hexagonal site CF splitting. These measurements were made on a 50g powder sample on the HET spectrometer at the ISIS facility.

¹see McEwen et al. (2003) for details

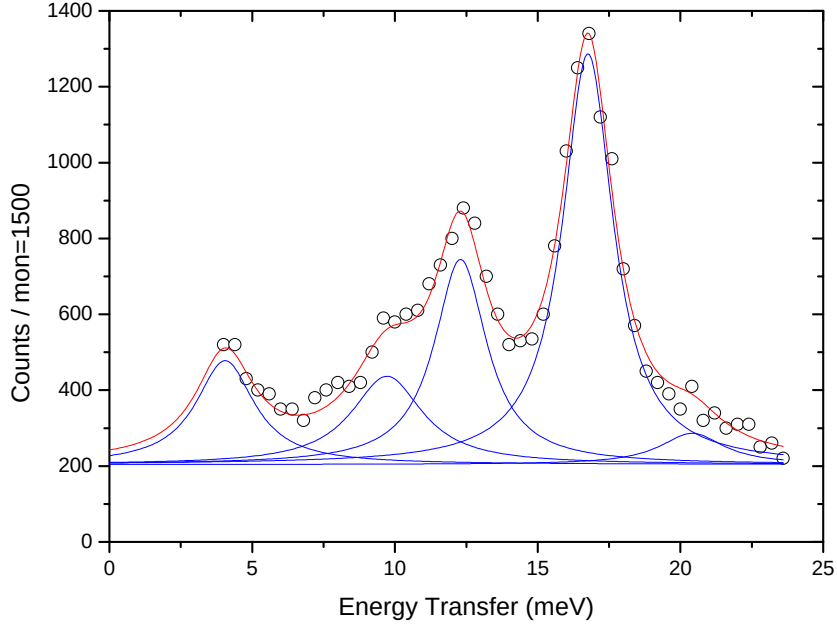


Figure 5.2: *Inelastic neutron spectra from single crystal UPd₃ (Martin-Martin, 2000).* The solid lines show the fit to the data using five Lorentzian peaks, with centres at: 4.05 meV, 9.72 meV, 12.3 meV, 16.76 meV, 20.41 meV.

Figure 5.2 shows a scan from the ILL data at $\mathbf{Q} = (2.5, 0, 0)$ at 10 K showing the crystal field excitations. The data is well fitted by five Lorentzian peaks, which apart from the large peak at 16.7 meV are attributed to transitions from the quasi-cubic doublet ground state to its excited state. These energies will be used to fix the crystal field parameters on the quasi-cubic sites.

Figure 5.3 shows the high energy spectra of UPd₃ taken on HET, at 10 K with 50 meV incident energy. There is a shoulder on the elastic line which corresponds to the mode at ~ 4 meV in the IN8 data. The 16 meV peak from the hexagonal sites shows clearly, but we may also discern a shoulder to this peak at ~ 12 meV and ~ 20 meV which is also in agreement with the IN8 data. Finally we also see a low intensity peak with a large width at ~ 30 meV which was not previously observed, and which we attribute to the quasi-cubic sites.

The large peak at 16 meV energy transfer was first observed by Buyers et al. (1980) and attributed to the transition from the ground state $|m_J = 0\rangle$ singlet to an excited doublet with wavefunctions $|m_J = 1\rangle$ and $|m_J = -1\rangle$ on the hexagonal sites. As the other states on these sites do not have wavefunctions with $|m_J = \pm 1\rangle$, there are no dipole matrix elements connecting them to the ground state, and they are thus not observed by neutron scattering, unless the temperature is sufficiently high that excited states are populated.

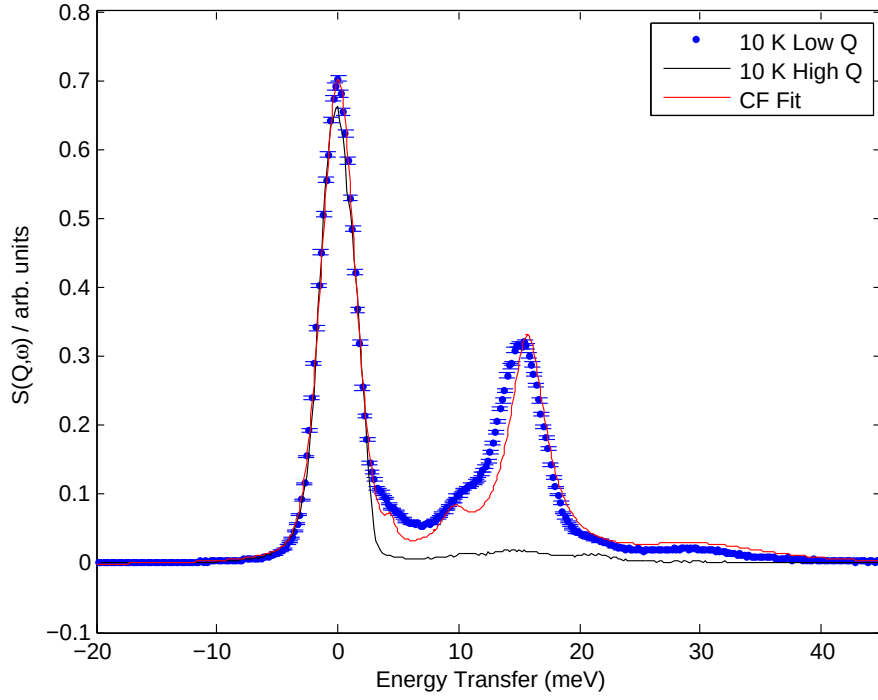


Figure 5.3: *Inelastic neutron spectra from HET at 10 K with 50 meV neutron incident energy.* The red line shows the spectra calculated from the crystal field parameters in table 5.2. The peak position and relative integrated intensity is fixed by the CF model, but their widths were varied to better fit the experimental data.

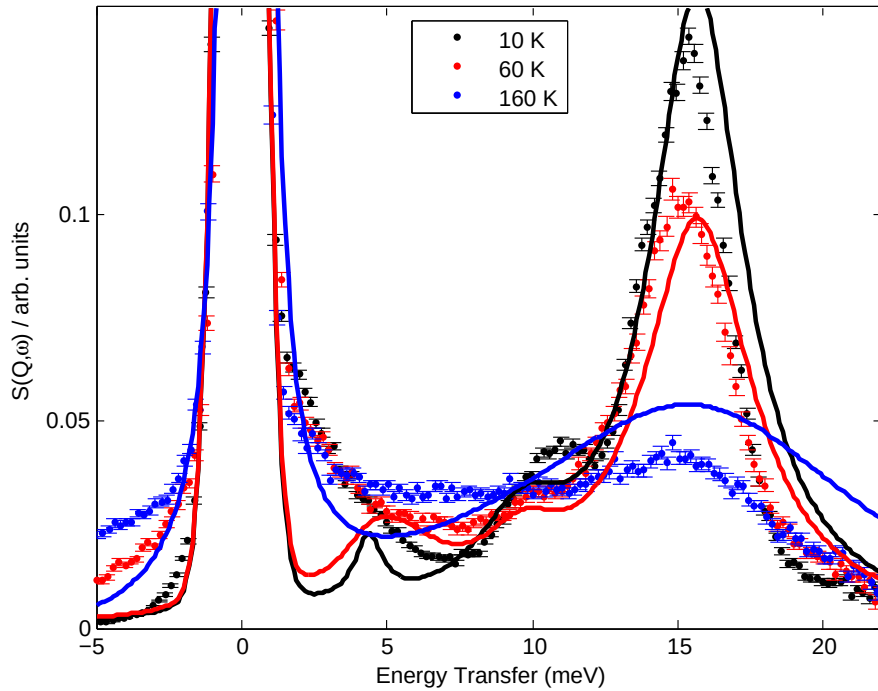


Figure 5.4: *Inelastic neutron spectra from HET at various temperatures with 23 meV neutron incident energy.* Solid lines are fit using the crystal field parameters in table 5.2 to calculate the peak position and relative intensities, whilst fitting the peak widths.

Figure 5.4 shows scans from the HET data at various temperatures. The intensity of the 16 meV peak at 10 K and 60 K scales with the factor $1 - 2 \exp(-\frac{E_2}{k_B T})$ with $E_2=16$ meV. This suggests that there are no crystal field levels close to the ground state, as these would be occupied and hence change the temperature dependence of the 16 meV level. It is unlikely that there are levels below 10 meV, and probably no doublets below the 16 meV level. However, the width of the 16 meV peak at 160 K is much broader, and its intensity does not match so well with the Boltzmann factor expectation, which may indicate that there are other crystal field levels near this energy, in addition to the $|\pm 1\rangle$ doublet. We also observe a plateau of scattering at lower energies which is probably from excitations between this doublet, which is now thermally occupied, and other hexagonal site levels, as well as from thermally occupied quasi-cubic levels.

5.3.2 Crystal Field Parameter Fitting

Using the routines in the work of Newman & Ng (2000), a Matlab program was developed to calculate the crystal field (CF) parameters which would give a certain CF splitting. The program relies on the orthogonality properties of tensor operators, $T_q^{(k)}$, within a single J -multiplet which are composed of the Wigner $3j$ symbols:

$$\sum_{M_1, M_2} \langle J, M_1 | T_q^{(k)} | J, M_2 \rangle \langle J, M_2 | T_{q'}^{(k')} | J, M_1 \rangle = 0 \text{ if } k \neq k', q \neq q' \quad (5.3)$$

Appendix A details the derivation of the relationship between the crystal field parameters and the energy and wavefunctions resulting from diagonalising a Hamiltonian with such parameters:

$$\begin{aligned} B_q^k &= \sum_n \sum_{M_1, M_2} E_n |V_n\rangle \langle V_n| \langle J, M_1 | \bar{O}_{kq} | J, M_2 \rangle \bigg/ \sum_{M_1, M_2} \langle J, M_1 | \bar{O}_{kq} | J, M_2 \rangle \langle J, M_2 | \bar{O}_{kq} | J, M_1 \rangle \\ &= \sum_n \sum_{M_1, M_2} E_n |V_n\rangle \langle V_n| \langle J, M_1 | \bar{O}_{kq} | J, M_2 \rangle \bigg/ \text{Tr} \left(\bar{O}_{kq} [\bar{O}_{kq}]^T \right) \end{aligned} \quad (5.4)$$

where the E_n and $|V_n\rangle$ denotes the eigenvalues (energies) and eigenvectors (wavefunctions) of the crystal field Hamiltonian, $|\rangle\langle|$ indicates an outer product, and $\bar{O}_{kq}$ the Stevens operator matrix.

Thus in fitting to the energy splitting, E_n , the algorithm relies on finding a set of CF pa-

rameters, B_q^k , from an initial set of wavefunctions, $|V_n\rangle$, using this new set of CF parameters to generate a new set of wavefunctions, and then iteratively feed this back until the energies (eigenvalues) generated are close to the desired values. However, this means the algorithm does not fit the wavefunctions, only the energy. Thus, it was used initially to fit to the energies observed using the neutron spectra shown above, and subsequently the parameters were altered by hand to produce the desired wavefunctions.

Following the qualitative model of McEwen et al. (2003) we concentrate mainly on the quasi-cubic sites, where the three lowest crystal field levels are shown in figure 5.5. From entropy measurements and the expectation values of the $\hat{J}_z$ and $\hat{J}_x$ operators deduced from the site-specific susceptibility measured by neutron diffraction, McEwen et al. (2003) determined that the ground state is a doublet, with a first excited state at ~ 4 meV. The observed magnetic susceptibility in the basal plane also shows an increase below each of the quadrupolar transitions. This may be explained if there is a large $\hat{J}_x$ matrix element between the excited ground state and some higher excited state which increases the x -direction susceptibility in the ordered phases as progressively more of the singlet excited state is mixed in with the doublet ground state.²

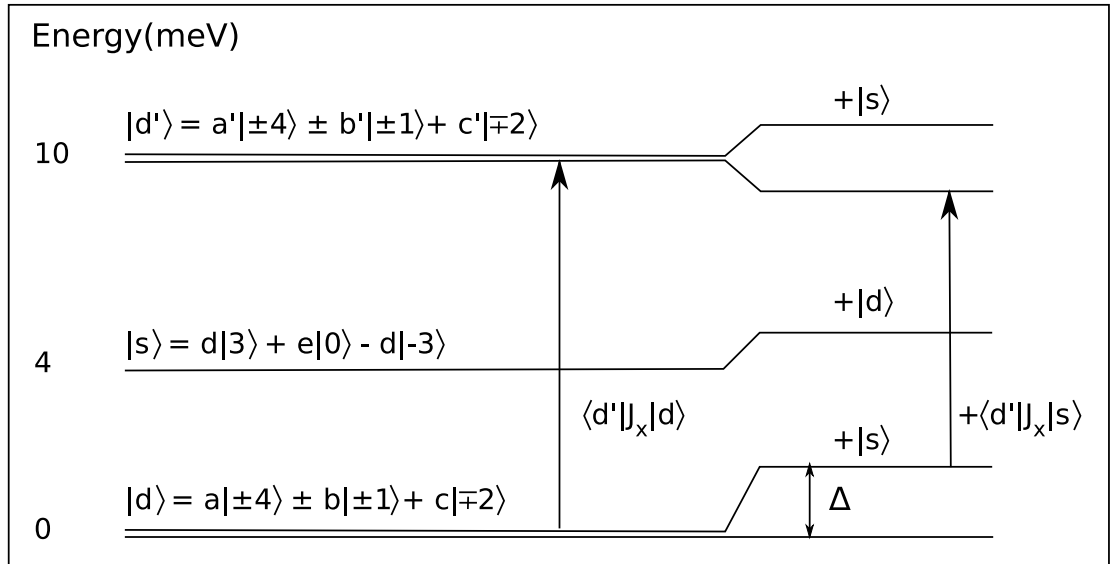


Figure 5.5: *Quasi-cubic site crystal field scheme.* The lowest three crystal field levels on the quasi-cubic sites, as expected from bulk measurements.

Because the singlet levels have wavefunctions which are of the form $d|3\rangle + e|0\rangle - d|-3\rangle$ or $\frac{1}{\sqrt{2}}(|3\rangle + |-3\rangle)$, there are zero $\hat{J}_x$ matrix elements between singlet levels, so we expect the

²G A Gehring, private communication (2008).

Quasi-cubic				Hexagonal			
B_0^2	0.035	B_0^6	-0.00012	B_0^2	0.21	B_0^6	0.00033
B_0^4	-0.012	B_3^6	0.0025	B_0^4	-0.0117	B_6^6	0.0014
B_3^4	-0.027	B_6^6	0.0068				

Table 5.2: *Crystal field parameters in Stevens normalisation in meV.* The parameters were deduced from fitting to inelastic neutron spectra and separate requirements for the wavefunctions of the lowest three energy levels of the quasi-cubic sites as described in the text.

second excited CF level to be a doublet. Now, it was noted above that the symmetry of the order parameter below T_0 required that the product of the coefficient of the doublet ground state wavefunction $bc \approx 0$. If we chose the coefficient $b \approx 0$ for the ground state doublet $|d\rangle$, and $b' \approx 1$ for the excited state doublet $|d'\rangle$, then this condition would be satisfied, and at the same time the expectation value of $\hat{J}_x$ would increase if some of the singlet levels $|s\rangle$ is mixed into the ground state $|d\rangle$ in the ordered phase, because the matrix element $\langle d'|\hat{J}_x|d\rangle \approx 0$ whilst $\langle d'|\hat{J}_x|s\rangle$ will be finite. We can maximise the increase in the susceptibility by making $e \approx 1$, so that $\langle d'|\hat{J}_x|s\rangle \approx 1$.

These requirements were met with the crystal field parameters in table 5.2, such that $b = 0.02$, $b' = 0.99$ and $e = 0.92$. It should be noted that the values for B_2^0 for the hexagonal site was chosen to match the site-selective magnetisation data taken on the D3 diffractometer at the ILL, where the crystal field anisotropy can be estimated from the susceptibility parallel to and perpendicular to the applied field. Finally, figure 5.6 shows the resulting crystal energy splitting and wavefunctions.

5.4 Magnetostriction Experiments

Whilst there are a wealth of data at zero applied magnetic fields of the various bulk and microscopic properties, the field dependence of many of these properties in single-crystalline UPd₃ has only been measured up to 12 T for the magnetisation (McEwen et al., 1995), and 7 T for magnetostriction (Zochowski & McEwen, 1994). The crystal field scheme discussed in the previous section gives a ground state doublet on the uranium quasi-cubic sites, with an excited singlet 4 meV above this. An applied magnetic field would split the ground state doublet, and lower the singlet, so that at a certain critical field, a level crossing would occur, resulting in a phase transition. From the energy of the excited singlet, this crossing was predicted to be with an applied field in the basal plane in the region of $4 \text{ meV}/g_J\mu_B J \approx 20 \text{ T}$.

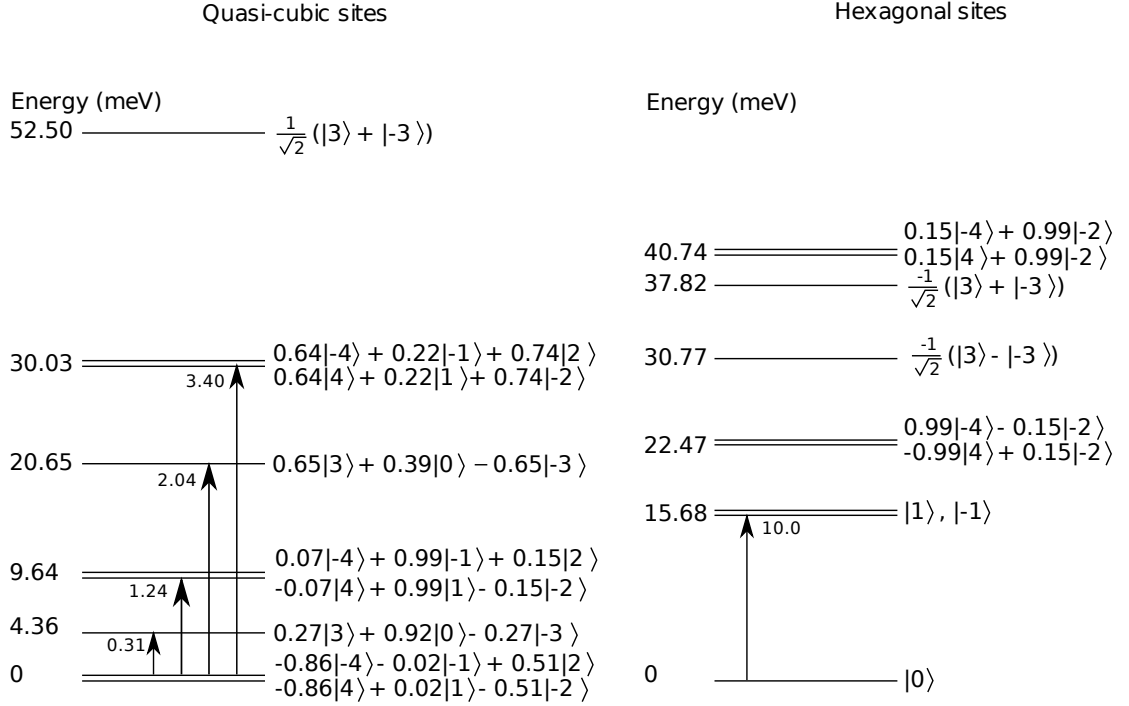


Figure 5.6: *Crystal Field Scheme*. The crystal field energy levels and corresponding wavefunction expressed in the $|J = 4, J_z\rangle$ basis. Arrows denote transitions from the ground state with non-negligible dipole matrix elements squared whose values are shown as numbers near the arrow.

There is thus a need both to explore the behaviour of UPd₃ at higher fields than had been measured, and in particular in the region around 20 T where a phase transition is expected. This is a higher field than may be obtained in a lab setting, but in November 2005, we were able to measure the magnetostriction of UPd₃ up to 33 T at the National High Magnetic Field Laboratory (NHMFL), Tallahassee, Florida.

5.4.1 Experimental Methods

The measurements were made using capacitance dilatometers constructed by Rotter et al. (1998) and mounted in a ⁴He cryostat in a 33 T Bitter resistive magnet cell. Three dilatometers were used: the D-cell, constructed in Dresden by M. Doerr, the W-cell, constructed in Vienna, and the WP-cell, also constructed in Vienna by M. Rotter. The W- and D-cells have a diameter of 22mm whilst the WP-cell has a diameter of 20mm. In addition the WP-cell has a small resistive heater which is controlled by a Conductus LTC-20 temperature controller.

Each cell has its own Cernox resistance thermometer, denoted by R_S (serial numbers X09555, X30533, X11005 respectively for the D-, W- and WP-cells), which was connected to the LTC-20. The cells were connected by dual-in-line pin and socket connection to a PCB

mounted on a sample stick. On the PCB are mounted another Cernox thermometer, denoted R_c (serial number X31765) and a capacitance thermometer, denoted C_T . These sensors were connected by gold wires to a 37-pin DT12 connector into which a coaxial cable attached to a breakout box was plugged. The dilatometer was connected separately by gold wires to two BNC connectors which plug into an Andeen Hagerling AH2500A capacitance bridge. The R_c thermometer was connected to a Lake Shore LS340 temperature controller, and the C_T thermometer to an Andeen Hagerling AH2700 capacitance bridge. Unfortunately early in the experiment the AH2700 bridge malfunctioned, and we were only able to replace it with another AH2500A, which subsequently caused interference with the bridge measuring the capacitance of the dilatometer because both bridges only operated at 1kHz. This meant that we were unable to use the C_T thermometer.

For measurements, the sample stick was placed inside a sealed can, of outer radius 30mm, which was then evacuated and filled with ^4He exchange gas. Teflon tape was wrapped around the dilatometer and sample stick to insulate them, and keep stray wires tight against the stick body. In addition, yellow cryogenic tape was wrapped around the can to electrically isolate it. Care was taken to thermally and electrically isolate the sample stick from the can which is in direct contact with the liquid ^4He . However, because of the small dimensions involved this was not always possible. This allowed thermal contact between the sample and the cryogenic liquid which caused problems when we wanted to heat the sample to temperatures above 4.2 K. The can and stick assembly was placed in the cryostat over a long period of time in order to reduce subsequent cooling time and loss of cryogenic liquid to vaporisation. Figure 5.7 shows photographs of the dilatometer, stick, can, and mounting in the cryostat. Figure 5.8 shows schematic diagrams of the magnet, cryostat and dilatometer assembly.

The bridge and temperature controllers were connected by an IEEE 488 bus to a PowerMac G5 computer running LabView with NHMFL-designed data taking software. The software automatically reads the field strength in the magnet from its controlling software with a mean error of the order of 0.1%. The AH2500A capacitance bridge is also extremely accurate with a nominal resolution of $5 \times 10^{-7} pF$ and accuracy of 1.5×10^{-7} . However, electrical noise in the cables and connectors from the dilatometer to the bridge, and mechanical vibrations due to the resistive magnet cooling water system meant that the resolution was reduced by about two orders of magnitude with a corresponding loss in accuracy.

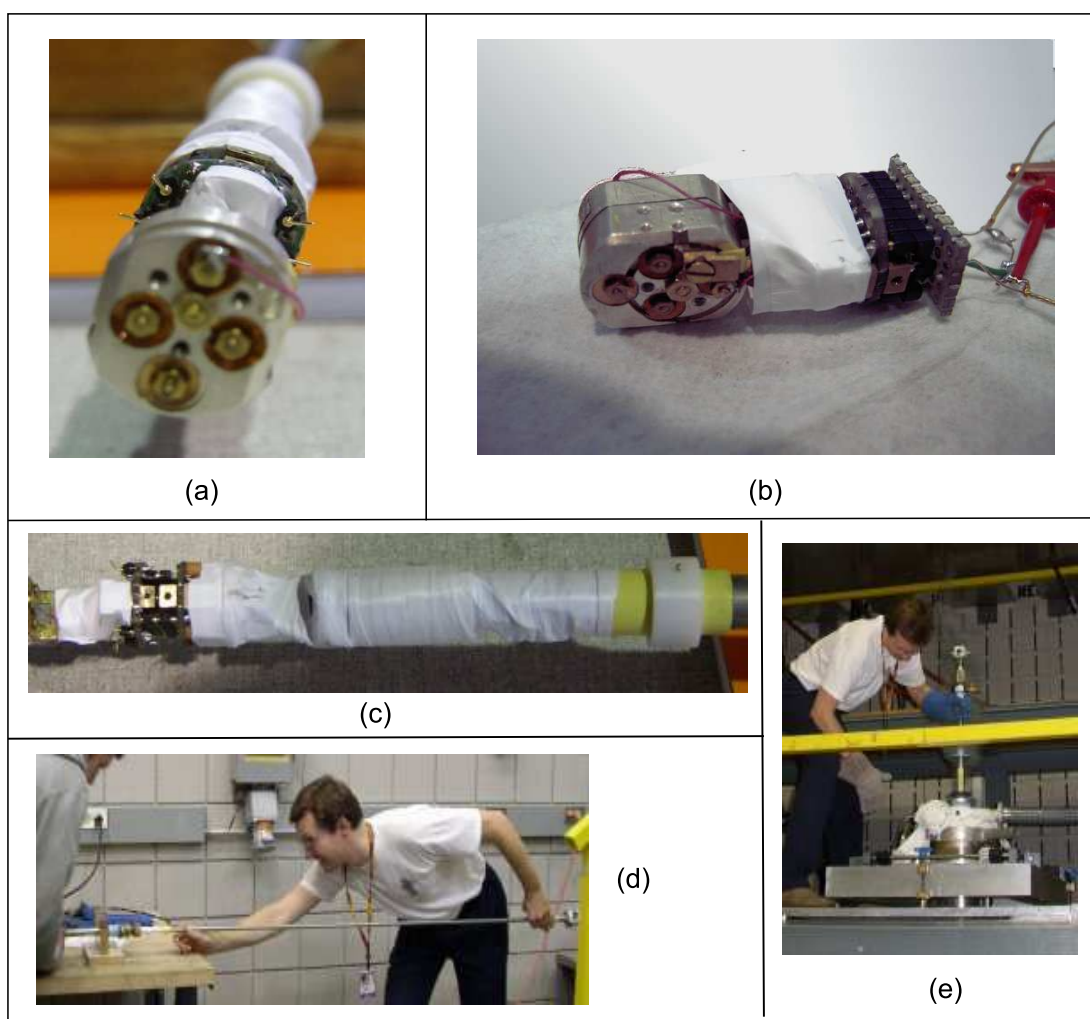


Figure 5.7: *Photographs of the experimental set up.* a) and b) the dilatometer. c) connection between the dilatometer and sample stick. d) inserting the sample stick into the can. e) mounting the can into the cryostat

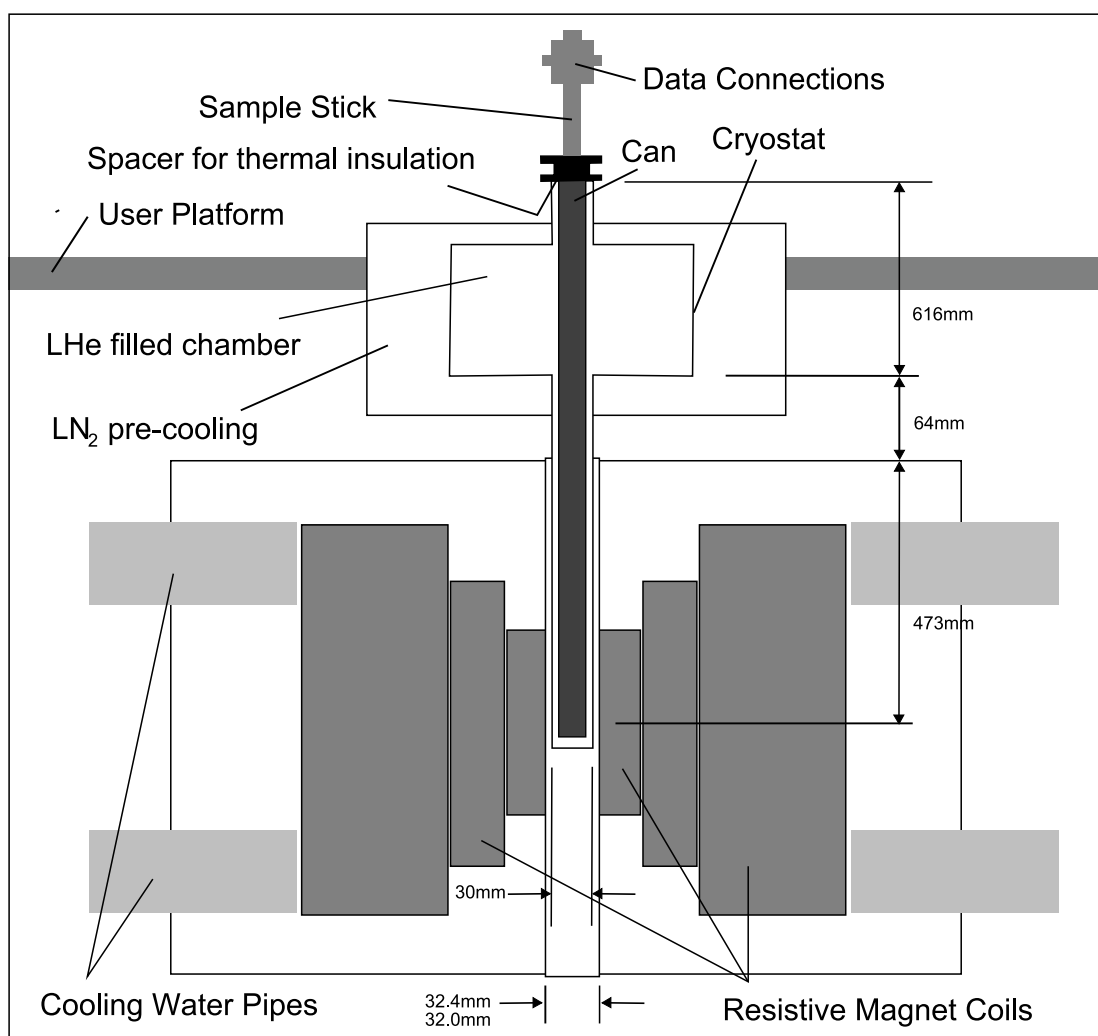


Figure 5.8: Schematic drawing of experimental set up.

During measurements, we observed the expected magneto-resistance of the Cernox temperature sensors (Brandt et al., 1999). These introduced corrections into our temperature data, which proved negligible for the 4.2 K measurements but was significant for high temperatures. In addition, we also observed a ‘bubble’ effect where at high fields, the magneto-resistance, and hence inferred temperature, on ramping up and ramping down the field were not equal, and that at around 18 T, there is a jump in the magneto-resistance on ramping down, after which the ramp up and ramp down curves were the same. This occurs because ^4He , the cryogen that we used, is diamagnetic, and hence experiences a force in the z direction proportional to $\partial B/\partial z$. It thus appears that at a critical field of around 18 T, the field gradient is high enough to force the cryogen away from the (vertical) centre of the magnet, creating a bubble around the position of the dilatometer. Since there is no cryogen to cool the exchange gas directly around the dilatometer it begins to heat up. On ramping down past 18 T, the cryogen suddenly rushes back in to fill the bubble and cools the dilatometer, accounting for the observed jump in magneto-resistance³.

5.4.2 Experimental Results

Table 5.3 summarizes the data taken. Unfortunately we did not have time to measure fully all the transverse components, but we were able to measure all three longitudinal and three of the six transverse components of the magnetostriction tensor. Each component measured was also repeated once to ensure reproducibility. The raw capacitance data showed a large hysteresis between the ramp up and ramp down curves. However, this was mostly an artefact, due to eddy currents induced in the sample. This arises because the sample is not completely regular in shape, and in particular does not have parallel sides. So, when the field is switched from ramping up to down, a large turning moment is applied to the sample, which causes it to rotate within the dilatometer cell. The rotation is usually such that the gap between the plates is less, so a higher capacitance is measured as a result. The magnitude of the moment, and hence resulting capacitance change is related to the size of the eddy currents induced and hence the ramp rate. However, time constraints meant that we could not justify a rate lower than 2 Tesla per minute. Nonetheless we were able to eliminate this artefact by treating the ramp up and ramp down curves separately and then averaging between them.

After the data measurements a calibration measurement was completed by manually adjusting the dilatometer using a micrometer screw and measuring the capacitance. This calibra-

³J Brookes, private communication (2006)

Run #	Field direction	Length change direction	Temperature (K)	Cell Name	Notes
5	c	c	4.2	RW	Field ramped at 3 T/min
6	c	c	4.2	RW	
7	a	a	4.2	RD	
8	a	a	4.2	RD	
9	b	b	4.2	RWP	
10	b	b	4.2	RWP	
11	b	b	7.5	RWP	
12	b	b	6	RWP	
13	a	c	4.2	RW	
14	a	c	4.2	RW	
17	a	b	4.2	RWP	
18	a	b	4.2	RWP	
19	b	a	4.2	RW	Interference between cap. bridges
20	b	a	4.2	RW	
22	b	a	4.2	RW	

Table 5.3: *Run list of data taken on UPd₃*. The applied magnetic field was ramped at 2 T/min except where indicated.

tion was repeated for each cell and was used in the program GCALC, written by M. Rotter, to convert the measured capacitance to a gap size in nm, using the equations outlined in Rotter et al. (1998). GCALC also took into account the thermal expansion of the dilatometer, made out of silver, using data from Touloukian et al. (1975) and assuming a temperature of 4.2 K throughout.

Before the conversion, the measured capacitance was put into bins of size 0.5 T, and the data was separated into ramp up and ramp down field components. The binning was to reduce the noise in the data due to mechanical vibrations, mostly from the cooling water for the resistive magnets. The conversion using GCALC was applied to the ramp up and down separately, and the magnetostriction, $\Delta l/l$, was calculated for the ramp up and down. These curves showed some hysteresis at low fields, with the largest effects in the longitudinal c -direction ($H||c$, $\Delta l||c$)⁴, in agreement with data in the literature (Zochowski & McEwen, 1994). There is some difference between the ramp up and ramp down curves at high fields as well, but this was generally small, and may be partly due to thermal expansion due to the 'bubble' effect described above. Thus, we combined the ramp up and ramp down data into one curve, and average the two runs for each magnetostrictive components.

The data is shown in Figures 5.9 and 5.10, showing the longitudinal and transverse components respectively. From the data, it may be seen that there is a phase transition at 27.8(5) T when the field is applied in the a -direction, whilst it is at 26.7(5) T when the field is in the b -direction. In the c -direction there is a peak at 10.3(5) T, which may be another transition.

Unfortunately the magneto-resistive dependence of our temperature resistor, R_c combined with the 'bubble' effect described above, meant that the heater control at temperatures higher than base temperature was not constant with field. We observed that the heater power was markedly higher on ramping up than ramping down at the same fields. Thus we were unable to maintain a constant temperature for the (nominal) 6 K and 7.5 K scans. Instead we observed large differences between the ramp up and ramp down curves, which is most likely to be due to thermal expansion due to the increased heater power on the ramp up. In addition, whereas the magnetostriction at 4 K in the longitudinal b -direction showed that the crystal becomes increasingly compressed at high fields, the data at 6 K and 7.5 K appear to show the crystal expanding. However this is mostly likely to be due to thermal expansion. This is supported by the data at low fields (0-10 T) which closely follow the 4 K data. It is also interesting to note

⁴ a , b , and c are the orthorhombic unit cell directions

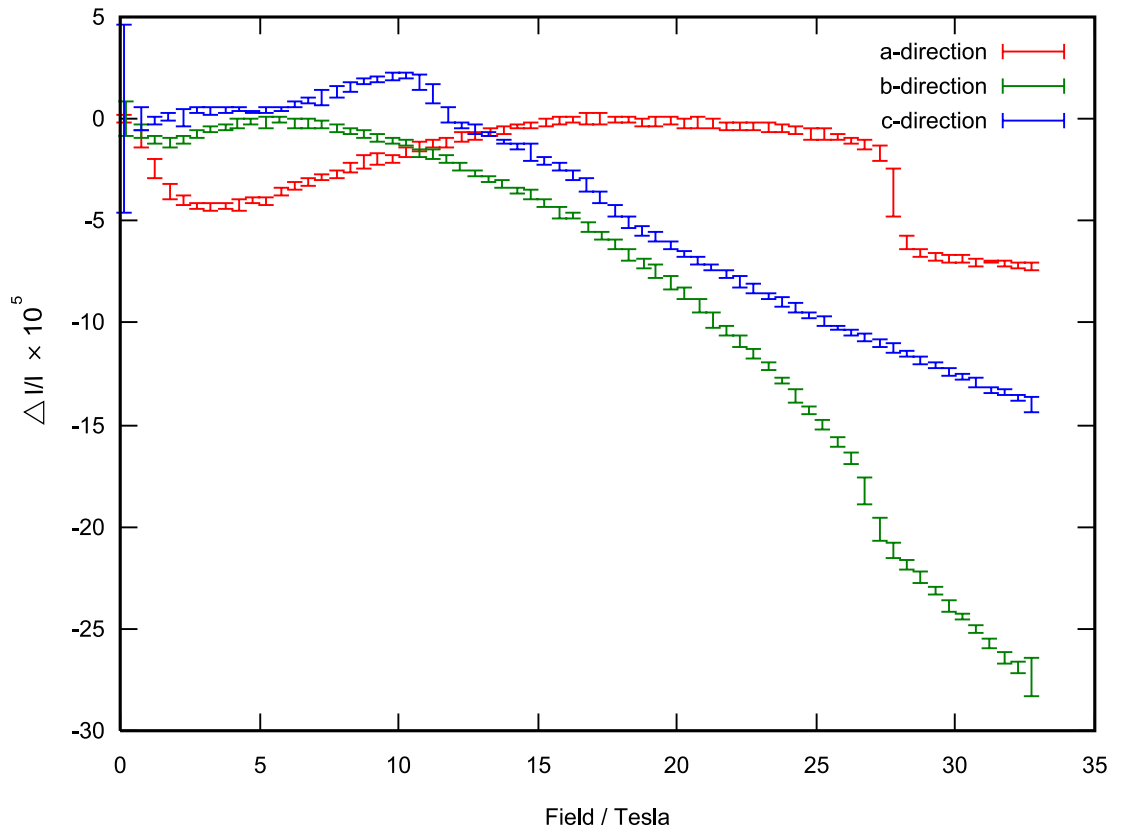


Figure 5.9: *Longitudinal Magnetostriction of UPd₃ at 4.2 K.* The data has been put into 0.5 T bins, and ramp up and down, and repeated measurements averaged. High field transitions are seen at 27.8 ± 0.5 T in the *a*-direction and 26.7 ± 0.5 T in the *b*-direction.

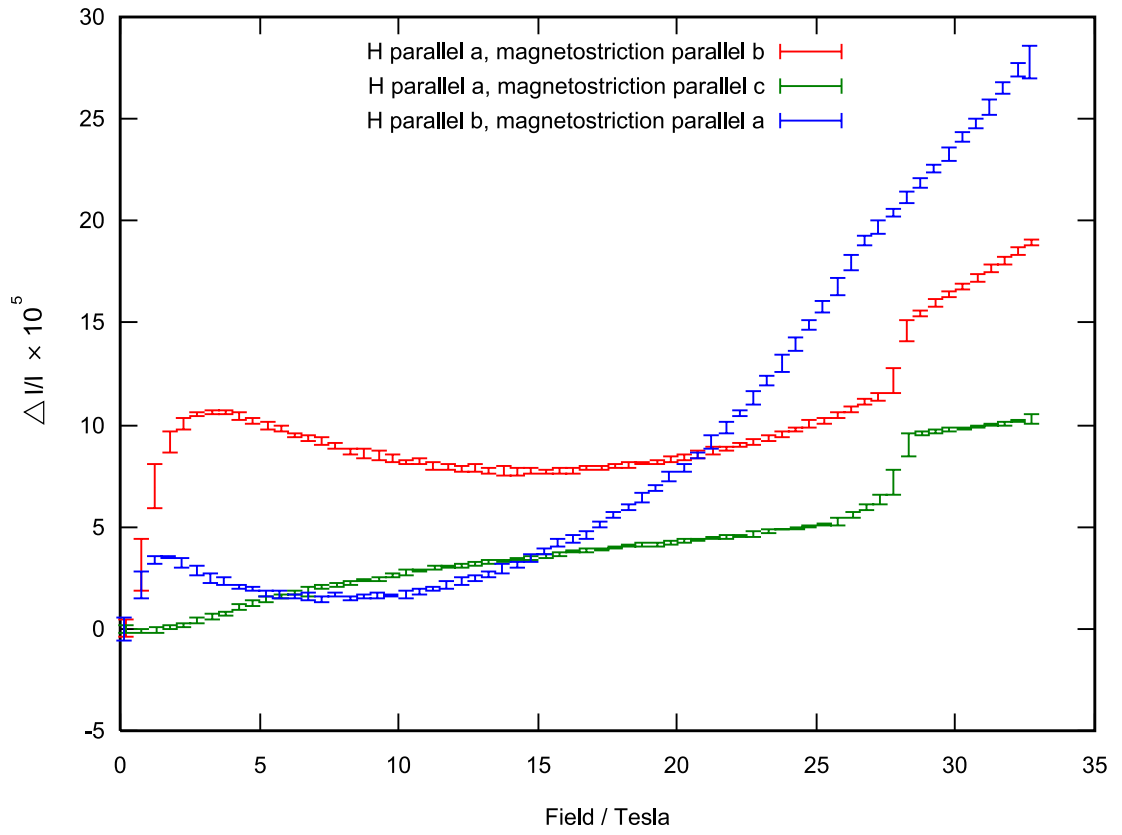


Figure 5.10: *Transverse Magnetostriction of UPd_3 at 4.2 K.* The data has been put into 0.5 T bins, and ramp up and down, and repeated measurements averaged. High field transitions are seen at 27.8 ± 0.5 T with the field in the a-direction and 26.7 ± 0.5 T in the b-direction.

that we did not observe any high field transitions in the 7.5 K data, but there is a suggestion of a transition in the 6 K data. However, this is not conclusive due to the thermometry problems noted above.

In summary, we have measured six of the nine components of the magnetostriction tensor at 4 K in the lowest temperature ordered phase of UPd₃, in an applied magnetic field up to 33 T. We found that there are transitions with the field in the *a* and *b*-directions at 27.8(5) T and 26.7(5) T respectively, whilst the transition with the field in the *c*-direction occurs at a much lower field of 10.3(5) T. The nature of the phase at higher fields is not known, but may be paramagnetic.

5.5 XRS Experiments

As discussed in section 5.2, extensive X-ray resonant scattering work had already been done on UPd₃, starting with the first study of McMorro et al. (2001). These measurements in zero field showed that the super-lattice peaks at $(1\ 0\ l)^5$ with *l* odd appear below $T_0 = 7.9$ K, and additionally $(1\ 0\ l)$ with *l* even appears below $T_1 = 6.7$ K, in agreement with earlier polarised neutron diffraction (PND) experiments in a magnetic field. The PND measurements could only detect an antiferromagnetic moment induced by the field, rather than the antiferroquadrupolar order directly at zero field. These super-lattice peaks represent inphase (*l* even) and anti-phase (*l* odd) stacking of the quadrupolar moment on the quasi-cubic sites, along the *c*-axis.

Later experiments by Walker et al. (2006) measured the azimuth dependence at 7 K, in the phase between T_0 and T_{+1} , after a new helium flow cryostat was installed on the ID20 beamline at the ESRF where the measurements were taken. The same single crystal, grown by D. Fort at Birmingham University was used in both experiments. It was cut parallel to the $(2\ 0\ 7)$ face, so that the super-lattice peaks $(1\ 0\ 3)$ and $(1\ 0\ 4)$ are both easily accessible with a minimum tilting of the stage, thus allowing a greater range of azimuth angles to be reached.

We have conducted further azimuth dependence studies of the $(1\ 0\ 3)$ and $(1\ 0\ 4)$ peaks in the other phases of UPd₃, at 5 K and 2 K (Walker et al., 2008) using the same sample as previous experiments, also using the ID20 beamline. The $(1\ 0\ 3)$ peak represents a *antiferro*-type anti-phase stacking of moments along the *c*-axis, whereas the $(1\ 0\ 4)$ peak gives the *ferro*-type component.

The azimuth dependence was fitted using equations D.15- D.18 and 2.47, giving a scatter-

⁵All peaks are indexed using the orthorhombic system.

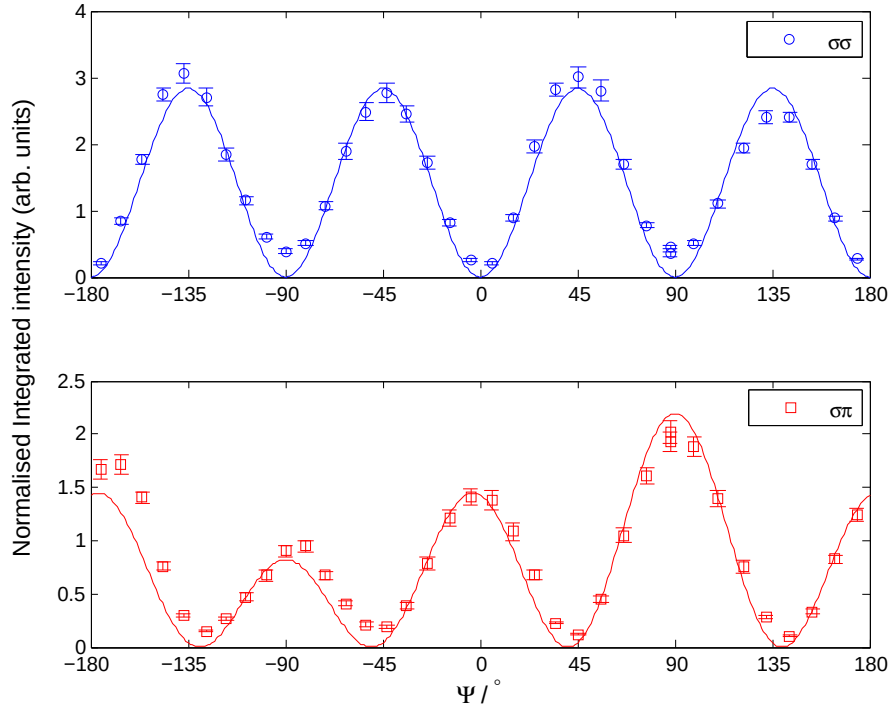


Figure 5.11: *The azimuth dependence of the (1 0 4) peak in UPd₃ at 5 K. The solid line is a simultaneous fit to both polarisation channels using equation 5.5 and the matrices T_{xy} from table 5.4 and then scaled in intensity to match the data.*

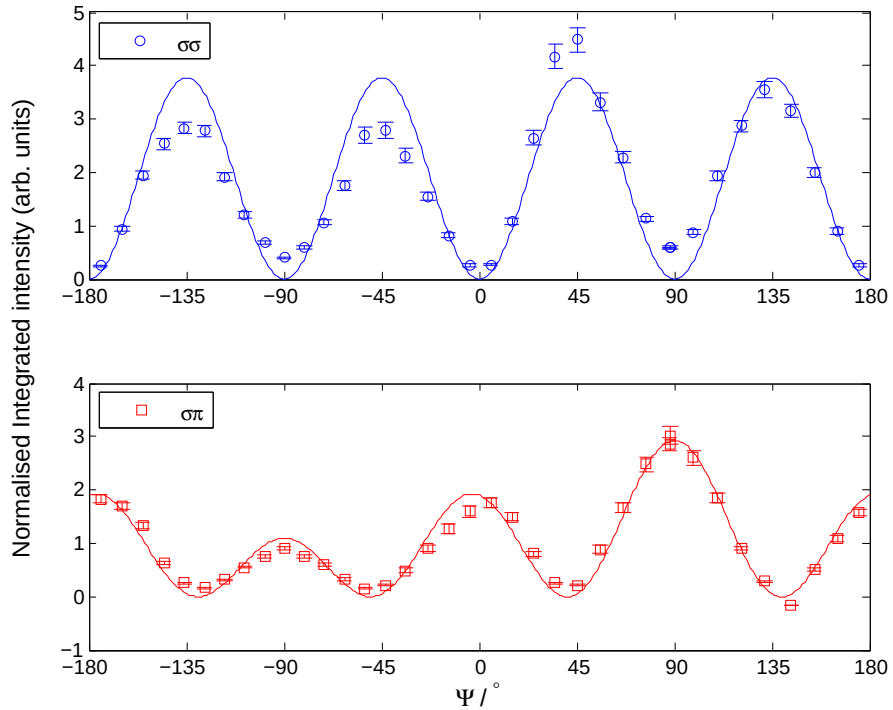


Figure 5.12: *The azimuth dependence of the (1 0 4) peak in UPd₃ at 2 K. The solid line is a simultaneous fit to both polarisation channels using equation 5.5 and the matrices T_{xy} from table 5.4 and then scaled in intensity to match the data.*

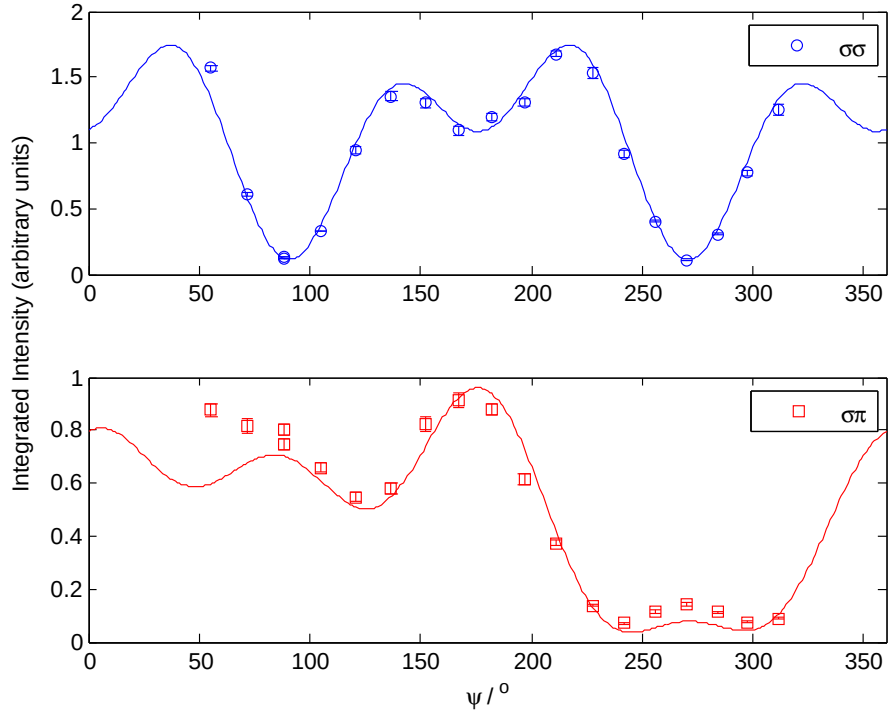


Figure 5.13: *The azimuth dependence of the (1 0 3) peak in UPd₃ at 2 K. The solid line is a simultaneous fit to both polarisation channels using equation 5.5 and the matrices $(0.44 + 4.8i)T_{xy} + 2.3T_{x^2-y^2} - 7.6T_{z^2}$ from table 5.4 and then scaled in intensity to match the data.*

Dipole	Quadrupole
$T_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{pmatrix}$	$T_{zx} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$
$T_y = \begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{pmatrix}$	$T_{xy} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$
$T_z = \begin{pmatrix} 0 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$T_{yz} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$
	$T_{x^2-y^2} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$
	$T_{z^2} = \begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$

Table 5.4: *Matrices representing the dipolar and quadrupolar tensor scattering factors.*

	(1 0 3)	(1 0 4)
7 K	$Q_{zx}^{\dagger}$	(Peak not present)
5 K	$Q_{zx}(77\%), Q_{x^2-y^2}(13\%), Q_{xy}(10\%)^{\dagger}$	$Q_{xy}(93\%), Q_{yz}(7\%)^*$
2 K	$Q_{z^2}(67\%), Q_{xy}(27\%), Q_{x^2-y^2}(6\%)$	$Q_{xy}(89\%), Q_{yz}(11\%)^*$

Table 5.5: *Quadrupolar order parameters determined from the azimuth dependence of the XRS scattering amplitude.* The (104) peaks represent in-phase stacking on the quasi-cubic sites along the c-axis, whereas the (103) peaks represent anti-phase stacking along c. † is from (Walker et al., 2006), * from (Walker et al., 2008).

ing amplitude

$$f \propto \epsilon' \cdot \mathbf{T} \cdot \epsilon \quad (5.5)$$

where $\epsilon^{(l)}$ is the incident (scattered) polarisation vector which depends on the azimuth, and there is a tensor scattering factor $\mathbf{T}$ which depends on the quadrupolar order parameter. A more extensive description of the theory is given in Appendix D, but for present purposes we summarise the 3×3 matrices which represents $T(Q)$ for each of the 5 quadrupolar order parameters and 3 dipolar order parameters in the quasi-cubic sites of a dhcp structure in table 5.4.

The experimental data for the (1 0 4) peaks are given in figures 5.11 and 5.12 at 5 K and 2 K respectively, together with a simultaneous fit to both $\sigma - \sigma$ and $\sigma - \pi$ channels using the equation 5.5. The Q_{xy} order parameter proved a good fit to both the 5 K and 2 K data. Figure 5.13 shows the azimuth dependence of the quadrupolar Bragg intensity at $Q = (1\ 0\ 3)$, at 2 K. The symmetry of this peak is more complicated than for the (1 0 4) peak previously, and may only be fitted by a complex superposition of the Q_{xy} , $Q_{x^2-y^2}$ and Q_{z^2} . In particular a complex xy tensor was required so that the trough at $\sim 120^\circ$ in the $(\sigma - \pi)$ channel does not drop to zero intensity, in addition to decreasing the intensity of the peak at $\sim 270^\circ$. This requirement for an imaginary xy component suggests that there may be ordering on the hexagonal sites. Finally we found that the zx term which had been the order parameter at 5 K, is not required to fit the azimuth dependence at 2 K.

Thus, the order parameter of the ferro-type component measured from the (1 0 4) peak is very similar in the two low temperature phases at 5 K and 2 K. However, the order parameter of the antiferro-type component from the (1 0 3) peak is markedly different between 2 K and 5 K, with a suppression of the Q_{zx} order parameter in favour of the z^2 and xy terms. Finally, combined with previously published work, the succession of order parameters measured is summarised in

table 5.5. The phase between $T_{+1} = 6.9$ K and $T_{-1} = 6.7$ K has not been measured because it is very difficult to maintain a stable temperature with this narrow range.

These order parameters provide one of the main criterion to determine the mean field model which follows. The model will seek to reproduce this sequence of order parameters, with suitable transition temperatures.

5.6 Mean Field Calculations

We used the *McPhase* program (Rotter, 2004) to calculate self consistently the mean field Hamiltonian:

$$\mathcal{H} = \sum_i \left[\mathcal{H}_{\text{cf}}^i + \mathcal{H}_Z - \frac{1}{2} \sum_j \sum_{\alpha} \mathcal{K}_{\alpha}^{ij} Q_{\alpha}^i Q_{\alpha}^j \right] \quad (5.6)$$

where i and j index the sites, and α index the quadrupolar operators Q_{zx} and $Q_{x^2-y^2}$. The crystal field Hamiltonians are:

$$\begin{aligned} \mathcal{H}_{\text{cf}}^{\text{quasi-cubic}} &= \sum_{k=2,4,6} B_0^k \bar{O}_{k0} + \sum_{k=4,6} B_3^k \bar{O}_{k3} + B_6^6 \bar{O}_{66} \\ \mathcal{H}_{\text{cf}}^{\text{hexagonal}} &= \sum_{k=2,4,6} B_0^k \bar{O}_{k0} + B_6^6 \bar{O}_{66} \end{aligned} \quad (5.7)$$

and the Zeeman Hamiltonian is:

$$\mathcal{H}_Z = -g_J \mu_B \mathbf{J}_i \mathbf{H} \quad (5.8)$$

In our mean field calculations we considered two sets of exchange parameters between nearest neighbour quadrupolar moments, $\mathcal{K}^{ab}$ for moments in the basal plane, and $\mathcal{K}^c$ for moments perpendicular to this.⁶ In terms of figure 5.14, the former set considers the interaction between ions 1 and 3, and the later between ions 1 and 2. Inspection of table 5.5 for the order parameters determined by XRS suggests that the major couplings are between the Q_{zx} and Q_{xy} quadrupoles, with couplings between either of these and the Q_{yz} and $Q_{x^2-y^2}$ quadrupoles having a lesser role.

To simplify matters we may treat the two transitions T_{+1} and T_{-1} as one, ignoring the ordering of the Q_{yz} which occurs at T_{-1} . Furthermore, we shall ignore the couplings with mo-

⁶In this section, a , b , and c shall denote the orthogonal directions in the orthorhombic unit cell.

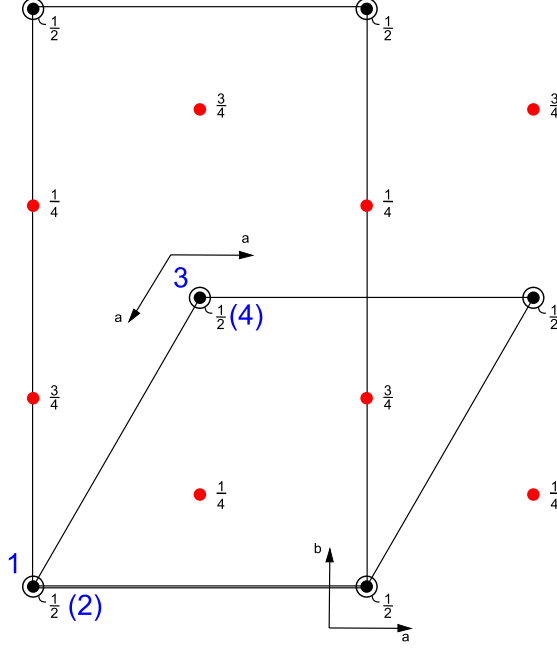


Figure 5.14: *Uranium site positions.* The hexagonal sites are in red, the quasi-cubic sites in black. The fractions indicate the z -coordinates, and whole numbers indicate the quasi-cubic site index.

ments on the hexagonal sites of the dhcp structure in this analysis as the experimental evidence suggests they do not contribute to the ordering. Thus the system we seek to model would first order with Q_{zx} moments on the quasi-cubic sites in anti-phase, followed at lower temperatures by the inphase (and then antiphase) ordering of the Q_{xy} moments.

In order to stabilise a structure with anti-phase (inphase) stacking we require $\mathcal{K}^c < 0$ ($\mathcal{K}^c > 0$), with $\mathcal{K}^{ab} < 0$. If we consider only the Q_{xy} and Q_{zx} couplings, we should expect $\mathcal{K}_{zx}^c < 0$, $\mathcal{K}_{xy}^c > 0$, with $|\mathcal{K}_{zx}^c| > |\mathcal{K}_{zx}|$, and $\mathcal{K}_{xy}^{ab} < \mathcal{K}_{zx}^{ab} < 0$, which follows from the lower transition temperature of the Q_{xy} ordered phase. However, these exchange parameters would only yield a single transition to a phase with Q_{zx} ordered in anti-phase, because the interaction between Q_{zx} quadrupoles swamps the Q_{xy} interaction. In addition, inelastic neutron scattering data from McEwen et al. (1993) showed that below $T_2 = 4.4$ K, there were four relatively dispersionless peaks at energy transfers of 1.28, 1.68, 2.20 and 2.60 meV. These peaks probably come from transitions between the ground state doublet on the quasi-cubic sites which have now been split by the quadrupolar ordering. That there are four peaks suggests that on each of the ions 1-4 of figure 5.14, the magnitude of the quadrupolar moments is different from each other. This yields different splittings of the crystal field ground state doublet. These findings may be explained by including the other quadrupolar interactions into the Hamiltonian. This is

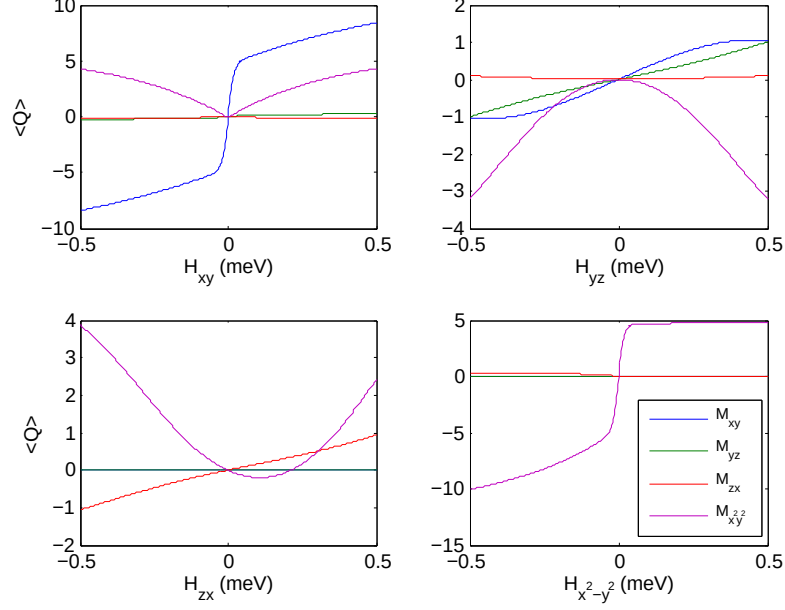


Figure 5.15: *Calculated single-ion quadrupolar moments under various applied quadrupolar field, after equation 5.9.*

because a Q_{yz} ($Q_{x^2-y^2}$) interaction would also yield some Q_{xy} (Q_{zx}) moment, which will allow the coexistence of the different order parameters, and their interference will cause the moments on each site to be different.

The relative strength of these induced moments may be calculated by just considering the single-ion interactions, without the mean field term. The quadrupolar moments $M_\beta = H_\alpha^Q \chi_{\alpha\beta}^Q$ induced by a quadrupolar 'field' H_α^Q , where α and β are any of zx , xy , yz , $x^2 - y^2$ and z^2 , is calculated using

$$\mathcal{H}_q^{(1)} = \mathcal{H}_{CF}^{\text{quasi-cubic}} - H_\alpha^Q \cdot Q_\alpha \quad (5.9)$$

$$M_\beta = \frac{1}{Z} \sum_n \langle \psi_n | Q_\beta | \psi_n \rangle \exp\left(\frac{-E_n}{k_B T}\right) \quad (5.10)$$

where Z is the partition function, E_n and $|\psi_n\rangle$ are the energies (eigenvalues) and wavefunctions (eigenvectors) of the single-ion Hamiltonian $\mathcal{H}_q^{(1)}$.

Figure 5.15 shows the calculated induced single-ion quadrupolar moments. We can see that neither the Q_{xy} nor Q_{yz} moments are induced by a Q_{zx} or $Q_{x^2-y^2}$ field. Thus we should concentrate on exchange parameters for the xy and yz terms in the lowest temperature phase in order to produce the desired different splittings of the ground state doublet on the four quasi-

J_{xy}^{ab}	0.00148	J_{xy}^c	-0.00889
J_{yz}^{ab}	-0.0819	J_{yz}^c	0.0685
J_{zx}^{ab}	0.0217	J_{zx}^c	-0.228
$J_{x^2-y^2}^{ab}$	-0.00275	$J_{x^2-y^2}^c$	0.00646

Table 5.6: *Deduced exchange parameters in meV.*

cubic sites. In addition, we note that the xy interaction is about an order of magnitude larger than the yz interaction, and similarly with $x^2 - y^2$ and zx . However, an initial investigation with just the xy and yz terms failed to find the four-ways splitting of the doublet ground state expected.

This may be explained by a closer examination of figure 5.15. This shows that the magnitude of the $|M_{xy}|$ or $|M_{yz}|$ moment is symmetric about $H_{xy}=0$ or $H_{yz}=0$, which is not the case for the $|M_{zx}|$ or $|M_{x^2-y^2}|$ moments. This asymmetry means that the interference between the zx and $x^2 - y^2$ term is much greater than for the xy and yz terms. Indeed by trial and error we found that the parameters $\mathcal{K}_{zx}^{ab} = -0.027$ meV, $\mathcal{K}_{zx}^c = -0.21$ meV, $\mathcal{K}_{x^2-y^2}^{ab} = -0.0023$ meV and $\mathcal{K}_{x^2-y^2}^c = 0.009$ meV give the desired four-way splitting of the doublet ground state and a transition temperature of ~ 8 K.

Starting from these considerations, a systematic search of all 8 exchange parameters was undertaken by calculating the mean field ordered structure at 2 K for the 8-dimensional grid defined by these parameters. In order to reduce computational time, the above parameters for the zx and $x^2 - y^2$ exchange interaction were used as a starting point. In addition, the parameters for the xy interaction was estimated by taking the basal plane and c -direction interaction to be equal, and calculating exchange parameter which most closely reproduces the observed ordering temperature. This gives $\mathcal{K}_{xy}^{ab} = -\mathcal{K}_{xy}^c = 0.0035$ meV, and a corresponding transition temperature $T_{xy} \sim 6.5$ K. The yz starting parameters were then estimated from figure 5.15 by finding the value of H_{yz} which gives the same yz moment as the corresponding value of H_{xy} , yielding $\mathcal{K}_{yz}^{ab} = -\mathcal{K}_{yz}^c = 0.1$ meV. The grid covered a parameter space of ± 0.02 meV in each direction centred on these position, with three steps per direction giving $3^8 = 6561$ points.

Analysis of this grid yielded a set of parameters which have been further fitted using the Nelder-Mead simplex algorithm to the measured transition temperatures, and also to the measured values of the four-way doublet splittings. The final parameters are shown in table 5.6, Figure 5.16 shows the calculated susceptibility and heat capacity as compared to the measured data from McEwen et al. (2003) and Walker et al. (2006).

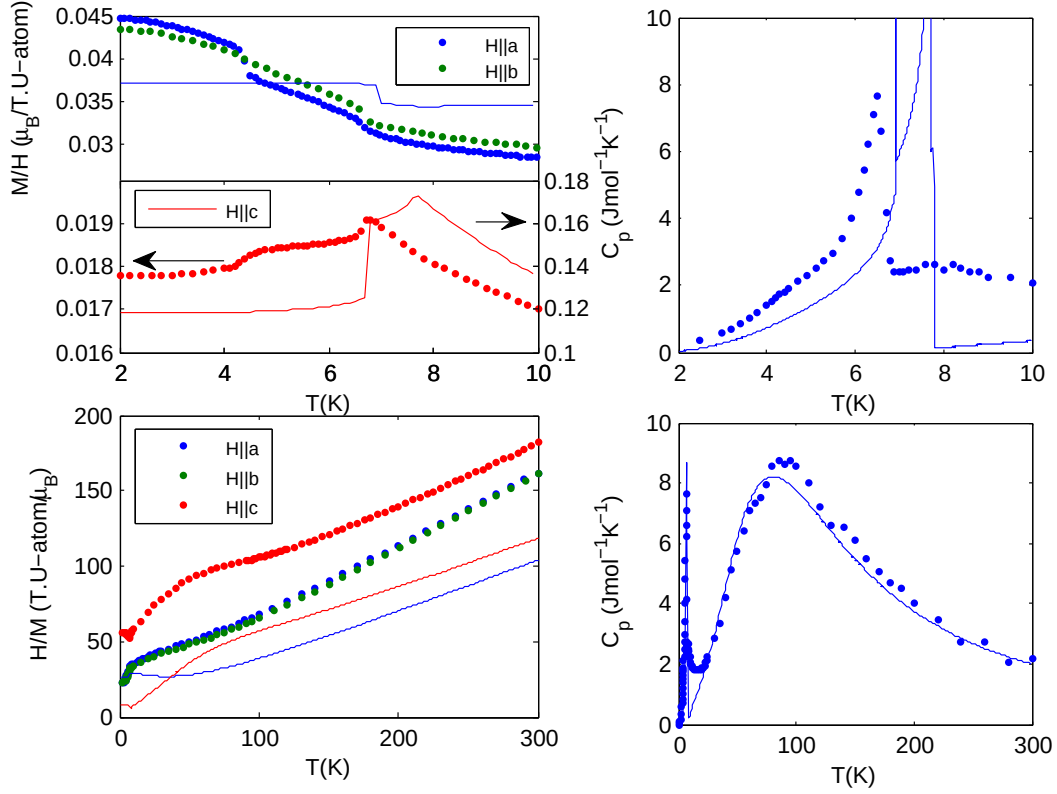


Figure 5.16: *Mean field model calculation of physical properties.* Left panels: Low temperature susceptibility and high temperature inverse susceptibility. Right panels: Specific heat.

At 2 K, the mean field model predicts that the splitting of the doublet ground state on ions 1-4 of figure 5.14 is 1.34, 1.61, 2.20, and 2.61 meV, compared to the measured values of 1.28, 1.68, 2.20 and 2.60 meV. These splittings were calculated from diagonalising the mean field Hamiltonian, and without consideration of the dispersion (i.e. without calculating the dynamical susceptibility, equation 2.45). However the neutron experiments of (McEwen et al., 1993) showed that the excitations were relatively flat in the basal plane. This is not the case along $\mathbf{Q} = [0\ 0\ l]$, with a dispersion of ~ 0.6 meV, but only two modes were observed. This suggests that the exchange in the c direction is stronger than in the basal plane, which the mean field model supports, and also that the excitations in the basal plane are close to the ‘single-ion’ energies as we have calculated.

The model also predicts that below 7.7 K, an ordered quadrupolar phase occurs with order parameters Q_{xy} and Q_{yz} in-phase, and Q_{zx} and $Q_{x^2-y^2}$ in anti-phase, with Q_{xy} and Q_{zx} as the dominant parameters. This is in agreement with the low temperature XRS azimuth measurements, at 5 K and 2 K. However, at this temperature the XRS measurements show that there should be no in-phase ordering at all, which we cannot reconcile with the mean-field model.

In addition, the model yields another phase transition at 6.7 K to a phase with the same order parameter, but with a greater magnitude of the quadrupolar moment. However in this phase, the dominant in-phase order parameter is Q_{yz} which is again in disagreement with experimental findings.

Nonetheless the model qualitatively reproduces the measured magnetisation, as the calculated susceptibility increase at each transition with the field in the a direction, whilst with the field parallel to c the susceptibility decreases at each transition from a peak at the higher temperature transition. The heat capacity is also qualitatively in agreement with the experiment with a large, sharp transition at 6.7 K and a smaller transition at 7.8 K.

As a function of field, with the field in the c direction, the mean field model predicts a transition at 5.4T to a phase without quadrupolar ordering whilst with the field in the a , there is a transition at 15.5T. The model does not give any transition below 35T with the field in the b direction. These critical fields are a factor of 2 lower than observed in the magnetostriction experiments, however.

It must be noted that we have not included the exchange interaction between magnetic dipole moments into the model. The magnetic susceptibility measurements show that there is a large antiferromagnetic exchange field, because the measured inverse susceptibility is significantly higher than the single-ion calculation above the ordering temperature, both in the basal plane and perpendicular to it. In addition, the low critical fields which we calculate compared to that measured shows that the internal field experienced by the $5f$ electrons is significantly lower than the external applied field, whichever the direction of the applied field. This would be consistent with a large antiferromagnetic exchange interaction. However, including a large enough dipole term in the mean field model to reproduce the measured susceptibility results in an antiferromagnetic ordered phase, rather than a quadrupolar ordered phase. Further modelling will be required to resolve this situation.

In order to model the magnetostriction, we return to equations 2.33 and 2.34, which for the quasi-cubic sites labeled 1-4 as in figure 5.14, is

$$\epsilon^\mu = \frac{1}{V} \sum_{i=1}^4 \left[-A_i^\mu \langle \bar{O}_{20}(i) \rangle + \frac{1}{2} \sum_{j=1}^4 \sum_{\nu} K_{ij}^{\mu\nu} \langle J_i^\nu J_j^\nu \rangle \right] \quad (5.11)$$

However, because in the model the exchange interaction is the same on each of the four quasi-cubic sites, each i term in the above sum is identical. The static correlation functions $\langle J_i^\nu J_j^\nu \rangle$ is

$\mu =$	a	b	c
A^μ	1×10^{-4}	-2×10^{-4}	4×10^{-4}
$2K_1^\mu$	-5×10^{-6}	1×10^{-5}	-7×10^{-6}
$2K_2^\mu$	5×10^{-6}	1×10^{-5}	-7×10^{-6}
$2K_3^\mu$	5×10^{-6}	-2×10^{-5}	-7×10^{-6}
$2K_4^\mu$	5×10^{-6}	-1×10^{-5}	-1×10^{-6}

Table 5.7: *Deduced magnetoelastic strain parameters.*

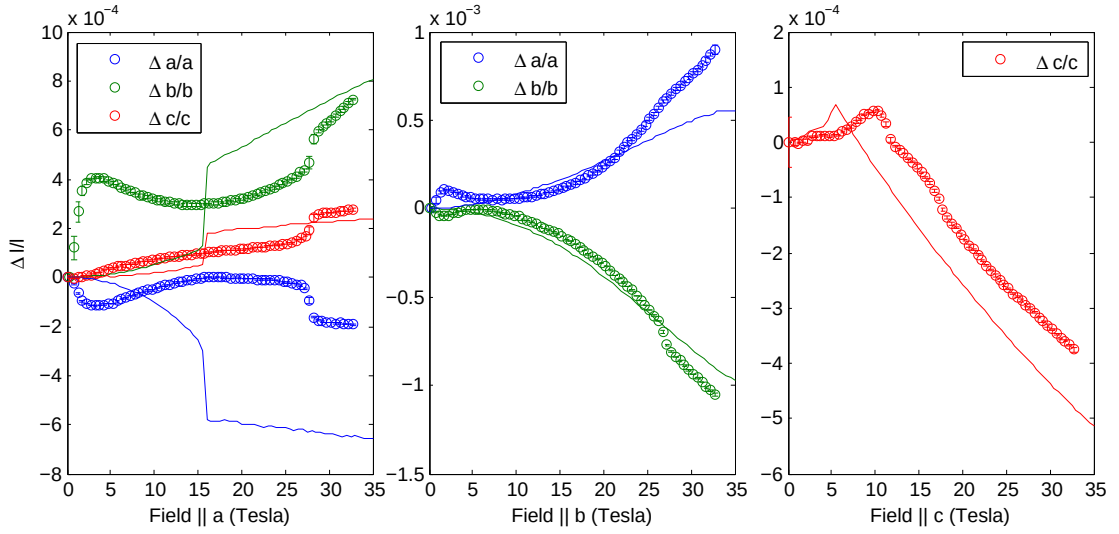


Figure 5.17: *Mean field model calculation of the magnetostriction.* Left panel: Field parallel to a . Middle panel: Field parallel to b . Right Panel: Field parallel to c .

still different for each j however, so we still require this sum, leaving,

$$\varepsilon^\mu = \frac{4}{V} \left[-A^\mu \langle \bar{O}_{20} \rangle + \frac{1}{2} \sum_{j=1}^4 \sum_{\nu} K_j^{\mu\nu} \langle J_1^\nu J_j^\nu \rangle \right]$$

The parameters A^μ and $B_j^{\mu\nu}$ are proportional to the product of the elastic compliance and the derivative of the crystal field and exchange parameters respectively. We found however that qualitative agreement with the measured longitudinal magnetostriction data may be obtained using just the first, crystal field striction term, with the parameters A^μ shown in table 5.7. The transverse magnetostriction data may also be qualitatively explained by considering in addition a $\langle J_i^{x^2-y^2} J_j^{x^2-y^2} \rangle^7$ exchange-striction term. This term was found to be the largest magnitude correlation function. Dropping the $\nu \equiv x^2 - y^2$ superscript from $K_i^{\mu\nu}$, the relevant parameters are also listed in table 5.7, and the calculated magnetostriction shown in figure 5.17.

⁷Note that $J^{x^2-y^2} \equiv Q_{x^2-y^2}$

In conclusion, although the mean-field model does not quantitatively reproduce the bulk experimental properties, its qualitative agreement is satisfactory. In addition, the model only yields two quadrupolar ordered phases, below 6.7 K, and between 6.7 K and 7.7 K, in contrast to the four phases observed. Tweaking the exchange parameters in table 5.6 may decrease the lower transition temperature from ~ 6.7 K to ~ 5 K in better agreement with measurements, however this decreases the energy splitting of the CF doublet ground state, so that they no longer match the measured neutron data. Further change of the parameters to decrease the lower transition temperature further causes a single anti-phase $Q_{zx}/Q_{x^2-y^2}$ phase to dominate and yields only a single phase transition.

It must be noted that the model only takes into account interactions between $5f$ electrons on the Uranium quasi-cubic sites, as much of the XRS measurements suggested that the hexagonal sites do not order. However, it may be necessary to include these hexagonal site interactions into the model. In addition, in order to model four transitions, it is likely that more exchange parameters taking in next-next-nearest neighbours and further need to be included. Magnetic dipole exchange terms should also be considered, although initial attempts to include them have favoured a magnetic, rather than quadrupolar, ordered phase. These considerations add much greater complexity to the model however, and it was found difficult to obtain a satisfactory model.

Finally, we have planned a further inelastic neutron experiment with a UPd₃ single crystal using the Merlin chopper spectrometer at the ISIS facility. We hope to measure in greater detail the low energy ordered-phase dispersion, and from this we should be able to better refine the mean field model.

Chapter 6

Crystal Fields in NpPd₃

6.1 Introduction

Like UPd₃, NpPd₃ also crystallises in the double-hexagonal closed packed structure in equilibrium. However, if it is quenched from the melt, it may instead form a cubic AuCu₃ structure, and unless the sample is annealed carefully, this phase will be present as an impurity. We shall be focusing on the hexagonal compound, which exhibits two phase transitions at 10 K, and 30 K. In contrast, the cubic compound has an antiferromagnetic transition at 55 K, as determined by neutron diffraction. The same diffraction study by Nellis et al. (1974) on the dhcp phase, however, failed to observe any super-lattice peaks or change in nuclear peak intensity between 4.2 K and 78 K. The authors estimate that if there *is* antiferromagnetic order which was too weak to be observed, the maximum possible ordered moment is $\sim 0.5\mu_B/\text{Np atom}$.

In addition, Nellis et al. (1974) also presented magnetisation, resistivity and Mössbauer spectroscopy data for both dhcp and cubic NpPd₃, using single crystals. The magnetisation data for dhcp NpPd₃ imply that the ordered phase below 30 K is magnetic in character. This interpretation is supported by the resistivity at low temperatures which is best fitted by expressions including contributions from phonon and spin-wave scattering.

However the Mössbauer data showed a broadening of the spectra below the transition temperature which is of similar width to the cubic phase Mössbauer spectra, and thus implies an ordered moment of similar magnitude, $\sim 1\text{--}2\mu_B/\text{Np atom}$. This would rule out the possibility discussed above that there may be long range antiferromagnetic order with a weak moment, and the authors suggest the possibility that there may be short-ranged magnetic order. Despite this, it must be noted that the Mössbauer data is not clean enough to be fitted to any hyperfine patterns, even taking into account the two inequivalent sites of the dhcp structure. Furthermore,

it may be that with the improvement in neutron flux of more modern instruments, one may be able to observe peaks undetectable thirty years ago. Thus the possibility of long range magnetic ordering should not be completely discounted. Further bulk properties investigations, involving magnetisation, resistivity and heat capacity measurements, focusing on the dhcp phase of NpPd_3 and Np diluted UPd_3 were undertaken by Walker et al. (2007) using polycrystalline samples. The magnetisation and resistivity data largely supports the earlier work, whilst the heat capacity measurements confirms the two transitions, at 10 K and 30 K which were observed as lambda anomalies. In addition, the magnetic entropy deduced from the difference between the NpPd_3 data and a ThPd_3 phonon blank is $\sim R \ln 4$ at 40 K, which suggests that there is a doublet ground state on both the hexagonal and quasi-cubic sites.

Again, the field dependence of the magnetisation and heat capacity suggests that at least the phase below 10 K possess long range antiferromagnetic order, whereas the phase between 10 and 30 K is more problematical. Walker et al. (2007) conjecture that this phase may be quadrupolar ordered like UPd_3 due to the smoothing of the lambda anomalies at high applied magnetic fields. This would yield a transition temperature similar to that of the REB_2C_2 , but would be considerably higher than for UPd_3 .

6.2 Experimental Results

Inelastic neutrons scattering measurements were carried out using the newly commissioned Merlin time-of-flight spectrometer at the ISIS facility, Rutherford Appleton Laboratory, on 4.65 g of powder in a sealed disc-shaped Aluminium sample holder with the faces perpendicular to the beam. The sample was prepared by arc-melting and then crushing the resulting polycrystalline pellets. The powder was then sealed into the holder using stycast. The preparation was completed at the Institute for Transuranium Elements, Karlsruhe, and the sealed sample sent to ISIS.

The sample holder was constructed with a thin central section, to reduce absorption of the beam by Aluminium. It was designed for use on the older HET spectrometer which possesses a much narrower bank of detectors. However, due to a delay of over a year in getting the sample to ISIS, until after HET ceased operation, it was more appropriate to conduct the experiment on Merlin. Thus, the window on the sample holder permitted an unobstructed view of $\sim 30^\circ$ in 2θ from the direct beam, appropriate to HET, whereas the detector banks on Merlin covers an arc between -45° to 135° . We were thus unable to make full use of the higher angle detectors.

Temperature (K)	E_i (meV)	Chopper Frequency (Hz)	Proton Flux (μ Ahrs)	
			Powder	Empty
8	10	100	539.02	250.08
8	10	150	1000.12	
8	16	250	1298.33	250.09
8	25	250	1300.21 [†]	300.07
8	40	200	300.09	200.10
8	60	300	800.09	200.08
8	100	250	318.09	100.09
8	800	600	1000.13	200.09
20	16	250	550.11	100.11
20	25	250	1000.08	100.10
35	16	250	800.09	200.10
35	25	250	1258.02 [†]	300.02
35	100	250	600.12	100.11
60	25	250	1000.10	134.38
100	25	250	1300.10	
100	100	250	600.12	
100	1000	600	494.68	

Table 6.1: $NpPd_3$ inelastic data runs. Lines indicated by [†] denote where runs of the same temperature and incident energy have been combined.

However, the Merlin detectors, at 3 m long, are also longer than similar detectors on other ISIS spectrometers, and so we were still able to obtain much higher flux than with HET.

Nonetheless, the less than ideal design of the sample holder introduced a significant background due to Aluminium phonons, especially at high angles, as shown in figure 6.1. Cadmium sheets were placed around the sample holder in order to reduce this background by permitting neutrons to only pass through the windows. However, this proved to be unsuccessful, so in order to subtract this background, we conducted scans with an empty sample holder, including the Cd covers, filled with Helium exchange gas. This background signal was then subtracted from the data gathered with the powder sample to obtain the NpPd_3 signal, as shown in the figure.

In addition to the background Al signal, we also detected some cubic phase impurity in the elastic data. The cubic phase diffraction peaks are much weaker than the dhcp phase, however, and many coincide with or lie very close in 2θ to the dhcp peaks. Despite this, we attempted to estimate the amount of cubic phase impurity present in the sample using data from a whitebeam run, with the Fermi chopper removed, in addition to data from the monochromatic runs around the elastic line. However, the resolution in the data was too poor to distinguish many cubic-phase peaks from dhcp-phase peak, with the exception of the (1 0 0). Nonetheless the intense (1 1 1) cubic phase peak does appear to show as a shoulder on the dhcp (0 0 4) peak.

Finally, it must be noted that the lattice parameter of cubic NpPd_3 is very similar to Aluminium, and it may be that the extra peaks are due to Aluminium rather than a cubic-phase impurity. We observed these peaks at low scattering angle, however, where the beam would have traversed the least thickness of Aluminium. Whilst these data may have a lower background signal from Aluminium, they also have the worst resolution. Thus we were unable to quantitatively determine the amount of cubic impurity present using Rietveld refinement.

Data was taken at 8, 20, 35, 60 and 100 K, and with incident energies of 10, 16, 25, 40, 60, 100, and 800 meV, as summarised in table 6.1. Figure 6.1 shows the data with and without the sample, and their subtraction at 8 K and with $E_i=40$ and 100 meV. The subtracted data shows four distinct dispersionless excitations, summarised in table 6.2.

Figure 6.2 shows cuts through the data integrated over low scattering angles below the lowest phase transition at 8 K, above the dhcp phase ordering temperature at 35 K, and above the cubic phase ordering temperature at 100 K; and at various temperatures with $E_i=25$ meV.

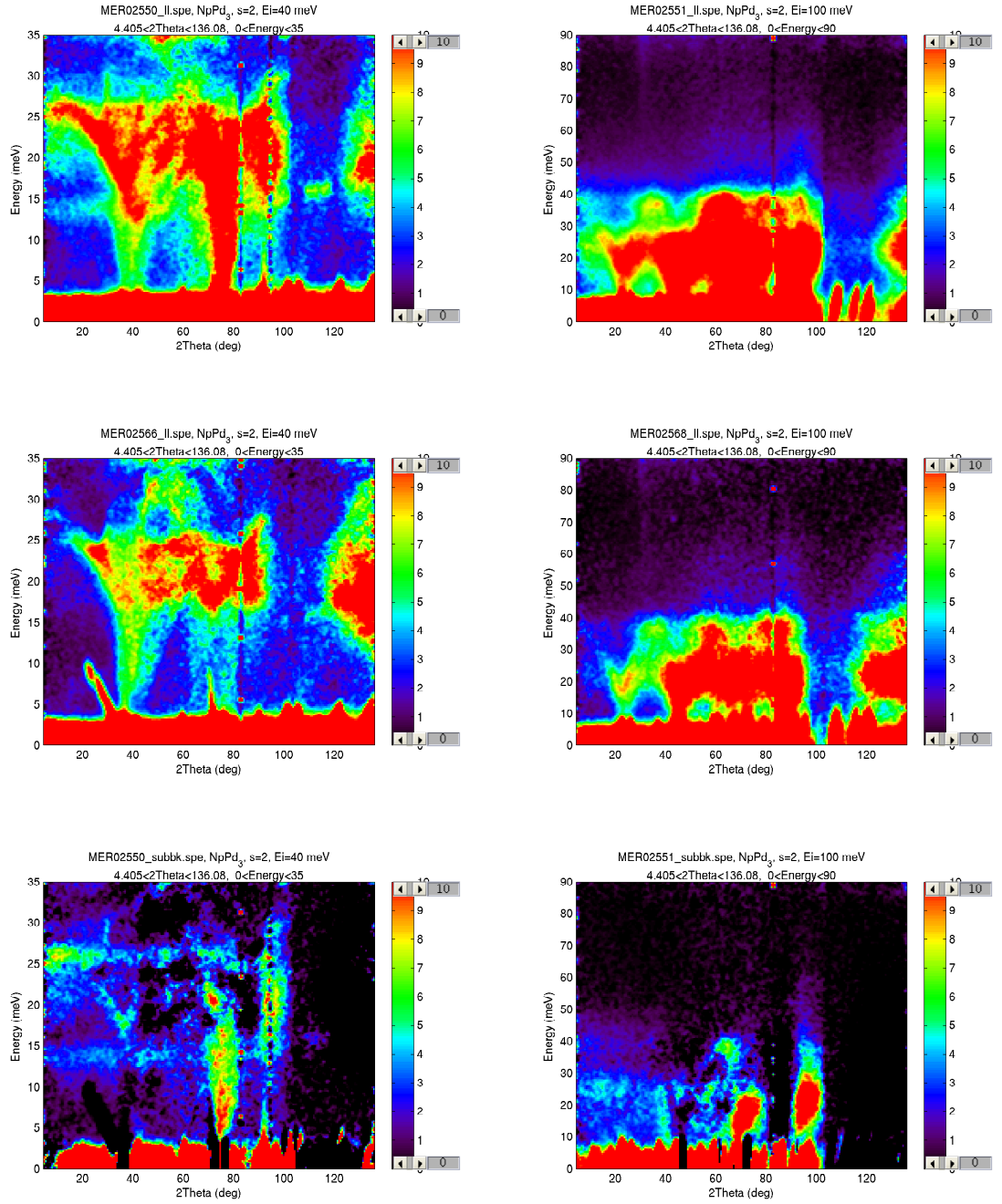


Figure 6.1: NpPd_3 inelastic spectra at 8 K. The data shows normalised counts, summed over rings in detector space at constant 2θ scattering angle, as the sample is polycrystalline. The left column shows data using $E_i=40$ meV, whilst the right column shows data with $E_i=100$ meV. The top row is the data with the powder sample, middle row is the empty sample holder data, and the bottom row is their normalised difference.

Energy (meV)	Relative Intensity
13	0.36
21	0.27
25.5	1
40	0.42

Table 6.2: *Measured inelastic excitations.* The integrated intensities are relative to the most intense level, at 25.5 meV.

The similarity of the data at 8, 20 and 35 K with each showing a peak at ~ 13 meV, shows that this is either due to a crystal field excitation, or an ordered excitation of the cubic phase. The 60 K data does not appear to show this peak, which may lend weight to the latter possibility, however it is broadened from excitations due to the thermal occupation of excited states, and these signal may block out the previous 13 meV peak. In addition, the peak is at a relatively high energy and shows very little dispersion, so we take it to be a crystal field excitation. Similar arguments pertain to the other three observed excitations.

The lack of change in the $E_i = 25$ meV spectra up to 35 K suggests that there are no levels below this energy which would otherwise be thermally populated. The 60 K spectra, in contrast, shows significant broadening of the peak which suggests that there is a level at approximately this energy (~ 7 meV), which has become populated. However, no evidence of this level was observed in the low incident energy spectra at low temperatures. Thus if this level exists, it probably has no dipole matrix element with the ground state. This would be most likely be the $|J = 4, m_J = 0\rangle$ singlet of the hexagonal site, which has a matrix element only with the $|J = 4, m_J = \pm 1\rangle$ levels. However this single transition would not explain the broad plateau of scattering observed at 60 K, whilst any other level would also have a matrix element with a doublet ground state, on either site. In addition, we were also unable to observe any peaks on the neutron energy gain side which would result from a electron falling from a thermally excited level back to the ground state.

This suggests that the lowest excited level is indeed the 13 meV observed in the data. In this case, there is no *a priori* restriction on its matrix elements with other states, and if there are several nearby levels, with which the 13 meV level has large dipole matrix elements, this may explain the several unresolved transitions seen. The thermal population of a level at 13 meV level at 60 K is approximately 10%, however, and it seems unlikely that this would be enough to cause the intensity observed, either at 60 K or at 100 K.

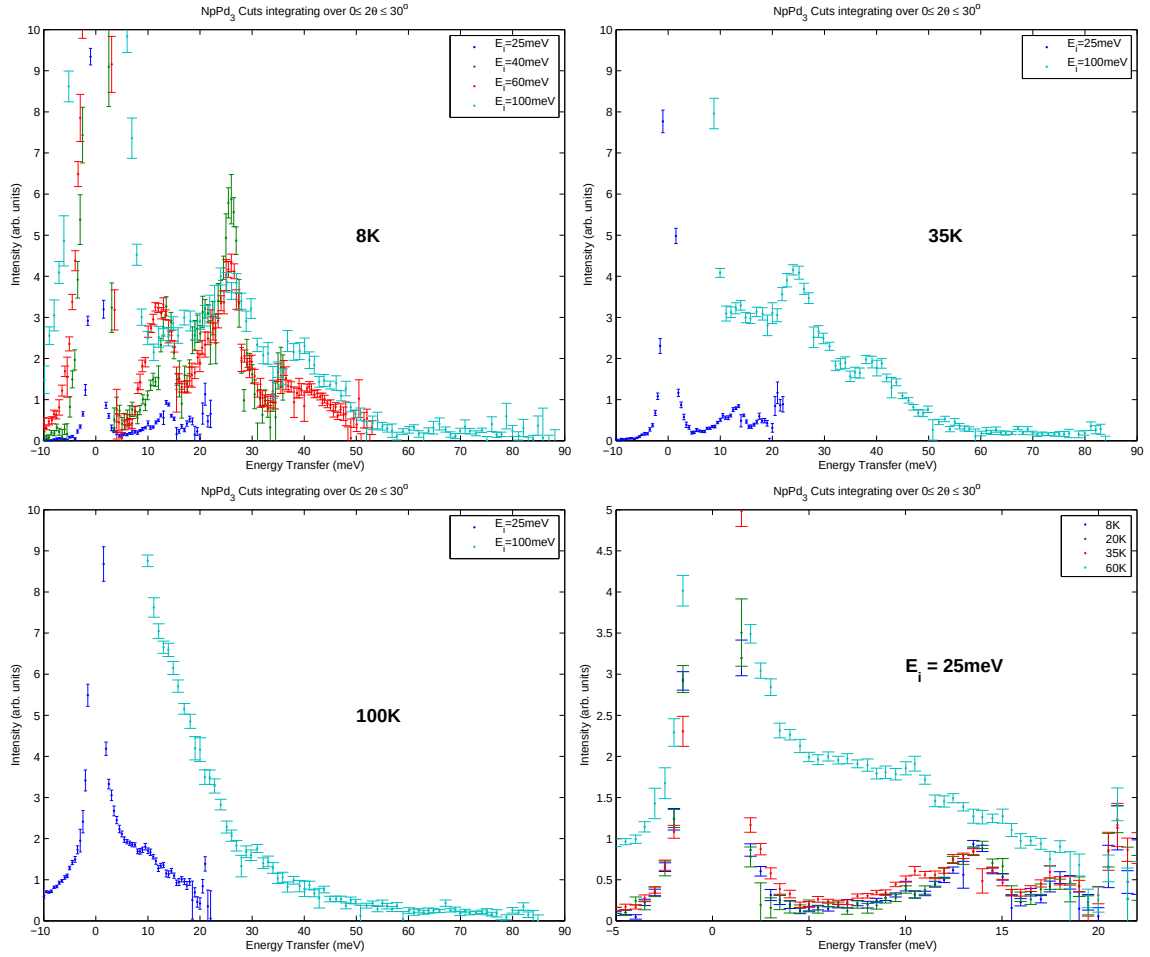


Figure 6.2: NpPd_3 energy spectra summed over scattering angles $0^\circ \leq 2\theta \leq 30^\circ$. These spectra show the intensity obtained after subtracting the Aluminium background signal measured with an empty sample holder filled with He exchange gas. The top panels and bottom left show the data at 8 K, 35 K, and 100 K respectively at incident energies of 25 meV (blue), 40 meV (green), 60 meV (red) and 100 meV (cyan). The bottom right panel shows the $E_i = 25$ meV at different temperatures.

k	q	$K_{kq}(\theta, \phi)$
2	0	$\frac{1}{2}(3\cos^2\theta - 1)$
	1	$3\sin 2\theta \cos \phi$
	2	$\frac{3}{2}\sin^2\theta \cos 2\phi$
4	0	$\frac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3)$
	1	$5(7\cos^3\theta - 3\cos\theta)\sin\theta \cos \phi$
	2	$\frac{5}{2}(7\cos^2\theta - 1)\sin^2\theta \cos 2\phi$
	3	$35\cos\theta \sin^2\theta \cos 3\phi$
	4	$\frac{35}{8}\sin^4\theta \cos 4\phi$
6	0	$\frac{1}{16}(231\cos^6\theta - 315\cos^4\theta + 105\cos^2\theta - 5)$
	1	$\frac{21}{4}(33\cos^5\theta - 30\cos^3\theta + 5\cos\theta)\sin\theta \cos \phi$
	2	$\frac{105}{32}(33\cos^4\theta - 18\cos^2\theta + 1)\sin^2\theta \cos 2\phi$
	3	$\frac{105}{8}(11\cos^3\theta - 3\cos\theta)\sin^3\theta \cos 3\phi$
	4	$\frac{63}{16}(11\cos^2\theta - 1)\sin^4\theta \cos 4\phi$
	5	$\frac{693}{8}\cos\theta \sin^5\theta \cos 5\phi$
	6	$\frac{231}{32}\sin^6\theta \cos 6\phi$

Table 6.3: *The coordination factors for the superposition model.* These factors are in Stevens normalisation. For Wybourne normalisation, multiply each K_{kq} term by $\lambda_{k0}/\lambda_{kq}$ from table 2.1. Negative q terms are obtained by replacing $\cos q\phi$ by $\sin |q|\phi$.

The cuts were fitted using a pseudo-Voigt function for the elastic line, and Lorentzian functions for the excitation peaks, and the integrated intensities relative to the most intense peak is given in table 6.2. These peak positions and relative intensities were then employed in the quantitative analysis of the 8 K spectra, using the superposition model of crystal fields.

6.3 The Superposition Model

As we were only able to experimentally determine four crystal field levels, and due to the dhcp structure with two inequivalent sites, there are too many crystal field parameters to determine reliably using conventional methods. We must therefore find a method to constrain some of the allowed crystal field parameters, and to this end we resort to the superposition model of Newman & Ng (1989).

In this model, the crystal field is represented as a sum of contributions from individual ligands. The model thus assumes that such a superposition is possible and that the strength of the crystal field depends only on the ligand type (in this case, solely Pd ligands around each Np site), and its length. The model also assumes that each ligand's crystal field contribution is

$r/\text{\AA}$	$\theta/^\circ$	$\phi/^\circ$	x/rlu	y/rlu	z/rlu	Magnetic Ion Type
1.654	90	90	0	$\sqrt{1/12}$	0	dhcp Hexagonal
1.654	90	210	$-1/4$	$-\sqrt{1/48}$	0	"
1.654	90	330	$1/4$	$-\sqrt{1/48}$	0	"
2.925	35	30	$1/4$	$\sqrt{1/48}$	$1/4$	dhcp Hexagonal
2.925	35	150	$-1/4$	$\sqrt{1/48}$	$1/4$	"
2.925	35	270	0	$-\sqrt{1/12}$	$1/4$	"
2.925	145	30	$1/4$	$\sqrt{1/48}$	$-1/4$	"
2.925	145	150	$-1/4$	$\sqrt{1/48}$	$-1/4$	"
2.925	145	270	0	$-\sqrt{1/12}$	$-1/4$	"
2.865	90	0	$1/2$	0	0	dhcp Quasi-Cubic
2.865	90	60	$1/4$	$\sqrt{3/16}$	0	"
2.865	90	120	$-1/4$	$\sqrt{3/16}$	0	"
2.865	90	180	$-1/2$	0	0	"
2.865	90	240	$-1/4$	$-\sqrt{3/16}$	0	"
2.865	90	300	$1/4$	$-\sqrt{3/16}$	0	"
2.925	35	30	$1/4$	$\sqrt{1/48}$	$1/4$	dhcp Quasi-Cubic
2.925	35	150	$-1/4$	$\sqrt{1/48}$	$1/4$	"
2.925	35	270	0	$-\sqrt{1/12}$	$1/4$	"
2.925	145	90	0	$\sqrt{1/12}$	$-1/4$	"
2.925	145	210	$-1/4$	$-\sqrt{1/48}$	$-1/4$	"
2.925	145	330	$1/4$	$-\sqrt{1/48}$	$-1/4$	"
2.896	45	0,180	$\pm 1/2$	0	$1/2$	AuCu ₃
2.896	45	± 90	0	$\pm 1/2$	$1/2$	"
2.896	90	± 45	$1/2$	$\pm 1/2$	0	"
2.896	90	± 135	$-1/2$	$\pm 1/2$	0	"
2.896	135	0,180	$\pm 1/2$	0	$-1/2$	"
2.896	135	± 90	0	$\pm 1/2$	$-1/2$	"

Table 6.4: *The coordinates of the Pd ligands for NpPd₃.* The Cartesian coordinates x , y , and z for the dhcp structure are with respect to the orthorhombic, rather than hexagonal unit cell. This cell is the same as in figure 5.1, but with lattice parameters, $a = 5.766 \text{ \AA}$ and $c = 9.544 \text{ \AA}$. The cubic phase has lattice parameter $a = 4.095 \text{ \AA}$.

axially symmetric about the line joining the centres of the magnetic ion and the ligand ion. The axial crystal field may be expressed in terms of the three zeroth order parameters B_0^2 , B_0^4 , and B_0^6 . The sums of each ligand may then be rotated into a common axes system by the coordination factors $K_{kq}(\theta, \phi)$, and the full crystal field expressed as a sum,

$$B_q^k = \sum_L \bar{B}_k(r_L) K_{kq}(\theta_L, \phi_L) \quad (6.1)$$

over the ligands L . The coordination factors are given in table 6.3, and the ligands in the case of dhcp and cubic NpPd₃ are given in table 6.4.

In addition, we have also applied an extra constraint in that we assume the dependence of the crystal field follows a power law with distance, with exponent t_k ,

$$\bar{B}_k(r) = \bar{B}_k(r_0) \left(\frac{r_0}{r} \right)^{t_k} \quad (6.2)$$

which justifies ignoring any but the near neighbours of the magnetic ions in the calculations. By these assumptions, we reduce the ten possible crystal field parameters in the dhcp structure to six. The simulated annealing algorithm of Corana et al. (1987) was then employed to fit these parameters to the four measured levels and their three relative integrated intensities.

6.4 Crystal Field parameters

Walker et al. (2007) determined that the valence state of the Np ion is Np³⁺, with a ground state ⁵I₄ spin orbit multiplet. As $J = 4$, this means that the crystal field scheme would have the same levels as UPd₃, that is three doublets and three singlets on each inequivalent site. The

Superposition Model		dhcp Hexagonal		dhcp Quasi-Cubic		AuCu ₃	
$\bar{B}_2(r_0)$	0.22	B_0^2	0.27	B_0^2	0.0096	B^4	-0.0015
$\bar{B}_4(r_0)$	0.001	B_0^4	0.00031	B_0^4	0.0011	B^6	-0.00035
$\bar{B}_6(r_0)$	0.00017	B_0^6	-0.00051	B_{-3}^4	0.027		
t_2	0.18	B_6^6	-0.0038	B_0^6	-0.00062		
t_4	0.36			B_{-3}^6	0.0076		
t_6	0.27			B_6^6	0.006		

Table 6.5: *The fitted crystal field parameters for NpPd₃. The $\bar{B}_k(r_0)$ superposition model parameters is calculated at the nearest neighbour Np-Pd distance, $r_0 = 1.65\text{\AA}$. All crystal field parameters, $\bar{B}_k$ and B_q^k are in meV, whilst the exponential parameter t_k is a pure number.*

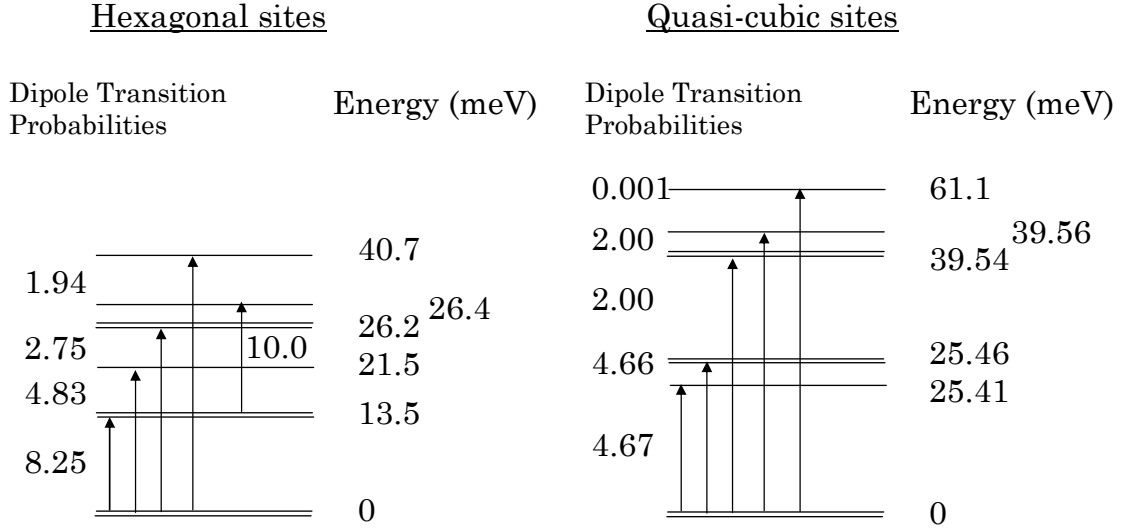


Figure 6.3: *The crystal field scheme for NpPd₃ based on the superposition model.*

fitted crystal field parameters from the procedure described above are shown in table 6.5, and the resulting crystal field scheme in figure 6.3. Finally, figure 6.4 shows the fitted excitations at 8 K, which is a sum of Lorentzian peaks whose centres and area are fixed by the energies and dipole transition matrix elements calculated by crystal field, but whose width was allowed to vary.

The constraints made by the superposition model means that the levels of the quasi-cubic sites are very close to what it would be if the point symmetry is actually cubic. That is, if the $c/a = 9.544/5.766 = 1.655$ ratio is perfect, $c/a = \sqrt[8]{3} = 1.633$. As the ratio difference is quite small, the splitting due to the lower symmetry of the two triplets at 25 meV and 39 meV into a doublet and a singlet is minute. Furthermore as the Np-Pd distance for the quasi-cubic sites in the dhcp structure, 2.87 Å, is very similar to that in the AuCu₃ structure, 2.90 Å, the level scheme for the later is almost identical to the former.

This situation may not be realistic however. Firstly, our assumption of a power-law dependence with distance of the intrinsic crystal field parameters $\bar{B}_k(r)$ may not apply. This constraint means that the intrinsic parameters for the next-nearest neighbour hexagonal site ligands, and all the cubic and quasi-cubic ligands are very similar, because the Np-Pd distances in each of these cases are very similar, ~ 2.9 Å. If this did not apply, then on the quasi-cubic sites, the nearest neighbour and next nearest neighbour ligands may have very different intrinsic parameters, and these may yield a much greater splitting of the quasi-triplet levels at 25 and 39 meV. Finally it would mean that the crystal field scheme for cubic NpPd₃ may not resemble that of

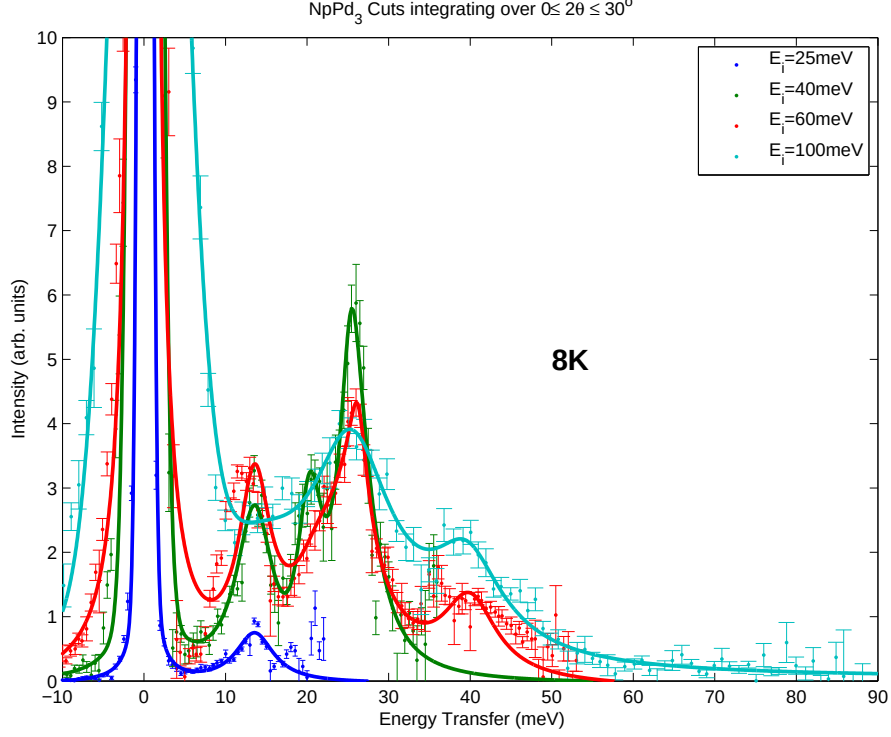


Figure 6.4: $NpPd_3$ inelastic spectra at 8 K with fitted crystal field levels. The data is a cut along energy transfer, summed over 2θ between 0° and 30° .

the quasi-cubic sites in dhcp $NpPd_3$, something which we would not *a priori* expect in any case.

Secondly, some of the postulates of the superposition model may not be valid in this case. Equation 6.1 requires that the contribution from each ligands be axially symmetric, and that the full crystal field is simply their sum in a common axes system. These postulates may break down, for example, if the contribution from the overlap of the Pd wavefunctions is large enough that the crystal field at the Np site due to each Pd ligand is no longer a sole function of that particular ligand, and hence it would not be axially symmetric. The result of such ligand-ligand overlap would be that the model underestimates the rank $k = 6$ parameters (Newman & Ng, 1989). This has the effect of increasing the crystal field levels by some overall factor.

On the other hand, the model does not take into account the long range electrostatic contribution of ligands which are far from the magnetic ions, which would underestimate the $k = 2$ parameters. This would tend to spread the levels out by depressing the energy of the low lying levels and inflating those of the high energy levels. However, the errors caused by these failings in the model may be counteracted by the uncertainty in the exact position of the ligands, which may differ at cryogenic temperatures from the room temperature data with which the structure was solved.

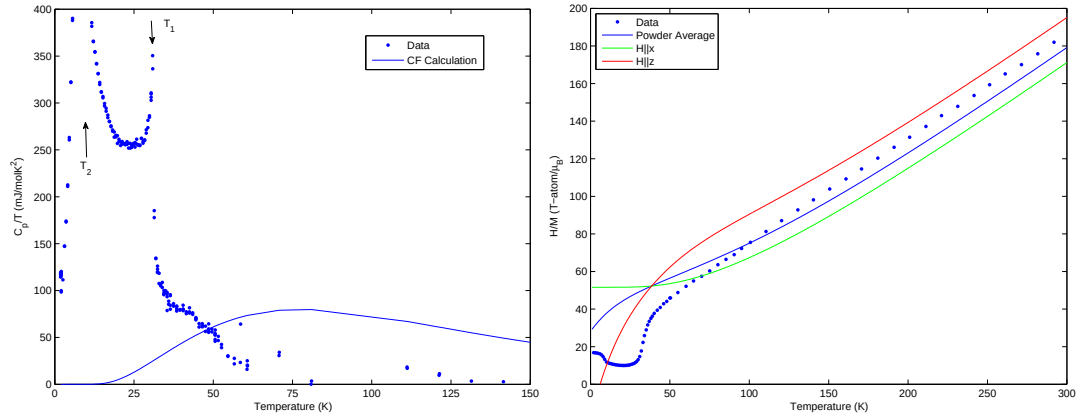


Figure 6.5: *Magnetic susceptibility and the magnetic contribution to the heat capacity of NpPd₃.* Solid lines are calculations using the crystal field parameters in table 6.5, whilst points are data from (Walker et al., 2007). The calculated magnetic susceptibility curve has been shifted down by 20 T-atom/ μ_B , and the powder average is taken by summing the contributions with magnetic fields aligned along the principal axes. The magnetic heat capacity was derived by subtracting the measured heat capacity of ThPd₃ from that of NpPd₃.

Therefore, the crystal field parameters in table 6.5 derived using the superposition model may not be accurate. In order to judge this, we have plotted the magnetisation and heat capacity calculated from these parameters in comparison with the experimental data of Walker et al. (2007), in figure 6.5. This shows that the calculated paramagnetic susceptibility agrees well with the data. However, in the heat capacity, the Schottky peak is calculated to be at ~ 85 K, whereas in the measured data, a shoulder to the lambda anomaly of the first transition is observed at ~ 42 K.

If this shoulder is due to a Schottky peak, then the overall splitting of the multiplet by the crystal field is much lower than that which we have calculated. For example, if the 26.4 meV singlet on the hexagonal site is pushed down to ~ 6 meV, as suggested in the last part of the previous section, and the 25.46 meV doublet on the quasi-cubic site is lowered to ~ 13 meV, then the Schottky peak would be at ~ 50 K. However, the calculated Schottky peak would still have a rather broad tail, and would not drop so sharply to zero with increasing temperature as in the measurements. Finally, the suggested alterations to the level scheme above would not be compatible with the observed relative intensities of the peaks in the neutron data.

6.5 Conclusions

Using inelastic neutron scattering, we were able to measure four crystal field excitations in dhcp NpPd₃. From these levels, and with the use of the superposition model, we were able to

determine the crystal field parameters. The additional constraints imposed by the superposition model means that the quasi-cubic sites level scheme strongly resembles that which would obtain for properly cubic point symmetry. This is not necessarily realistic, and we find that the deduced level scheme do not reproduce the observed magnetic heat capacity. This deviation may in part be rectified by increasing the splitting of the quasi-triplet states, that is, by moving further away from perfect cubic symmetry. However, no combination of level scheme which is compatible with the observed inelastic neutron spectra was found which reproduces the heat capacity data satisfactorily. In contrast, the deduced crystal field parameters are in fair agreement with the measured magnetic susceptibility in the paramagnetic phase.

This work may therefore serve as a basis for further investigations of the ground state of the $5f$ electrons in NpPd_3 . However, further work will need to be completed in order to resolve the discrepancy between the crystal field scheme and the heat capacity. This may either be more accurate and reliable measurements of the heat capacity in the range 50-200 K, or a better inelastic neutron spectra at higher temperatures, which would resolve the levels arising from transitions with thermally occupied excited states.

Finally, we were unable to observe any ordered phase excitations, whether spin-wave or otherwise. This may be due to the high background due to scattering from Aluminium which is in our data, however, so unfortunately, no conclusions may be drawn from this absence.

Chapter 7

Antiferromagnetic Order in PuPd_3 and the $(\text{Pu,Lu})\text{Pd}_3$ System

7.1 Introduction

Unlike the lighter actinide-palladium compounds in the previous two chapters, PuPd_3 crystallises only in the cubic AuCu_3 structure, with lattice parameter $a = 4.105 \text{ \AA}$. The compound undergoes an antiferromagnetic transition at 24 K. It was initially studied by Harvey et al. (1973) using resistivity and magnetic susceptibility measurements. The susceptibility shows a peak at the ordering temperature, whilst the resistivity drops sharply somewhat below this temperature. The paramagnetic moment was deduced to be $1.0 \mu_B/\text{Pu-atom}$, rather than the $0.85 \mu_B/\text{Pu-atom}$ expected for the $5f^5$ configuration of Pu^{3+} in the Russell-Saunders scheme. This indicates that intermediate coupling effects are important in this compound.

The neutron diffraction pattern of PuPd_3 was also measured in the same study by Nellis et al. (1974) as that of NpPd_3 discussed in the previous chapter, and revealed a G-type antiferromagnetic structure, in which nearest neighbour Pu ions have opposite moments. This structure is identical to that of cubic NpPd_3 . The ordered moment was found to be $0.8 \mu_B/\text{Pu-atom}$. Finally, more recent measurements of the photoelectron spectra shows that the $5f$ electrons are indeed well localised on the Pu sites (Le et al., 2008b), and thus that the atomic theory is applicable in this case.

We initially measured the magnetisation and heat capacity of PuPd_3 (Le et al., 2008a) as part of a program to look again at the properties of the AnPd_3 compounds discussed in these three chapters. We found that the electronic Sommerfeld coefficient deduced from the heat capacity data was relatively high, which may indicate an enhanced electronic effective mass,

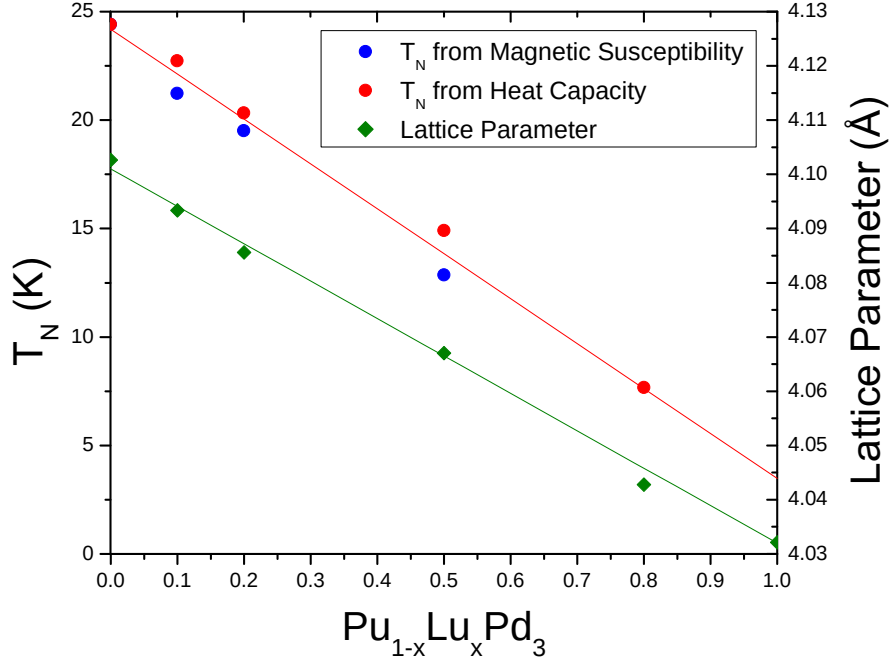


Figure 7.1: Lattice parameters and transition temperatures for $\text{Pu}_{1-x}\text{Lu}_x\text{Pd}_3$.

but that this cannot be determined with much certainty because we had used the heat capacity of ThPd_3 as a phonon blank. The difference in the crystal structure of ThPd_3 (dhcp) and PuPd_3 (cubic AuCu_3 structure), means that it is likely that the lattice contribution to the heat capacity of the two compounds will not be the same. Despite the larger mass and size difference between a Lu and Pu atom, LuPd_3 , like other lanthanide-palladium-3 compounds, has the AuCu_3 structure, and thus would prove a better phonon blank.

In addition, we were also interested in the behaviour of the compound as Pu is diluted, and the $5f$ electrons become more localised. The exchange interaction would become progressively weaker as we move towards the Lu-rich phase, and we should expect to observe greater single-ion behaviour in the magnetic properties. We thus instigated a program to measure the magnetisation and heat capacity of a series of alloys of $\text{Pu}_{1-x}\text{Lu}_x\text{Pd}_3$, with compositions, $x = 0, 0.1, 0.2, 0.5, 0.8, 1$.

Finally we analyse these measurements in intermediate coupling in the framework outlined in chapter 2, and plan further mean field calculations using *McPhase*, although at present because of the large matrix size involved, the calculation time proved too large to be practicable.

Composition	Mass (mg)	Measurement Type	Constant Temperature for Field scans (K)	Constant Fields for Temperature scans (T)
PuPd ₃	76.	Magnetisation	2, 10, 20, 50	0.1, 0.5, 2, 5, 7
PuPd ₃	1.52	Heat Capacity		0
PuPd ₃	4.72	Heat Capacity		0, 0.1, 0.5, 1, 2, 5, 7, 9
Pu _{0.9} Lu _{0.1} Pd ₃	39.04	Magnetisation	10, 40	0.1, 0.5, 2, 5, 7
Pu _{0.9} Lu _{0.1} Pd ₃	4.53	Heat Capacity		0, 7, 14
Pu _{0.8} Lu _{0.2} Pd ₃	40.68	Magnetisation	10, 40	0.1, 0.5, 2, 5, 7
Pu _{0.8} Lu _{0.2} Pd ₃	5.52	Heat Capacity		0, 7, 14
Pu _{0.5} Lu _{0.5} Pd ₃	102.66	Magnetisation	2, 10, 40	0.1, 0.5, 1, 2, 5, 7
Pu _{0.5} Lu _{0.5} Pd ₃	3.61	Heat Capacity		0, 1, 7, 10, 14
Pu _{0.2} Lu _{0.8} Pd ₃	91.30	Magnetisation	2, 4, 6, 10, 50, 300	1, 5, 7
Pu _{0.2} Lu _{0.8} Pd ₃	3.70	Heat Capacity		0, 1, 7, 9
LuPd ₃	156.78	Magnetisation	3, 10, 15, 20, 35, 50, 100	1, 7
LuPd ₃	20.85	Heat Capacity		0, 9

Table 7.1: $Pu_{1-x}Lu_xPd_3$ samples list. The temperature range for constant field scans is 2-300 K, whilst the field range for constant temperature scans is 0-7 T for magnetisation measurements, and 0-9 T for PuPd₃ and LuPd₃ samples and 0-14 T for $Pu_{1-x}Lu_xPd_3$ samples for heat capacity measurements.

7.2 Experimental Details

Polycrystalline samples of PuPd₃, LuPd₃ and $Pu_{1-x}Lu_xPd_3$, with $x = 0.1, 0.2, 0.5$, and 0.8 were produced at ITU by arc melting appropriate amounts of the constituent elements under a high purity argon atmosphere on a water-cooled copper hearth, using a Zr getter. The AuCu₃ structure was confirmed by x-ray diffraction for each sample, and the lattice parameters are shown in figure 7.1. The data show a linear dependence of the lattice parameter with increasing Lu dilution, in accordance with Vegard's Law. In addition, there also appears to be a linear dependence of the transition temperature.

Magnetisation and susceptibility measurements were taken using a SQUID magnetometer (Quantum Design MPMS-7), whilst the heat capacity was measured by the hybrid adiabatic relaxation method in a Quantum Design PPMS-9 for PuPd₃ and LuPd₃, and in a PPMS-14 for $Pu_{1-x}Lu_xPd_3$. The sample list is given in table 7.1.

Finally, the pure PuPd₃ and the 50% Lu diluted samples from the magnetisation measurements were subsequently crushed, and regularly sized pieces were extracted, polished and mounted for electrical transport measurements in the same PPMS-9 cryostat as the heat capac-

ity measurements. The zero field resistivity was measured for both PuPd_3 and $\text{Pu}_{0.5}\text{Lu}_{0.5}\text{Pd}_3$, whilst the Hall coefficient and resistivity in fields up to 9 T were measured for PuPd_3 only. Further resistivity measurements on all the doped samples have been planned.

7.2.1 Magnetisation

The magnetic susceptibility is shown in figures 7.2 and 7.3, and the inverse susceptibility in figure 7.4. The data in the paramagnetic phase above the Néel temperature are well fitted by a modified Curie-Weiss Law,

$$\frac{M}{H} = \frac{N\mu_{\text{eff}}^2\mu_B^2}{3k_B} \frac{1}{T - \theta} + \chi_0(H) \quad (7.1)$$

where N is the atomic fraction of Pu in the compound, and θ is the paramagnetic Curie temperature which under the Weiss mean field theory of ferromagnetism is the transition temperature, or in the case of antiferromagnetism the negative transition temperature. There is a field dependent residual susceptibility $\chi_0(H)$ which is due to contributions from impurities, the measurement setup, and from the Pauli susceptibility of the conduction electrons. This final quantity may be estimated from the electronic Sommerfeld coefficient of LuPd_3 , $\gamma_{\text{LuPd}_3} = 3.2(1) \text{ mJmol}^{-1}\text{K}^{-2}$, which for a free electron gas at low temperatures $T \ll T_F$ is,

$$\gamma = \frac{1}{2}\pi^2 N k_B \frac{T}{T_F}$$

where $k_B T_F = \varepsilon_F$ is the Fermi temperature. The Pauli susceptibility is,

$$\begin{aligned} \chi_{\text{Pauli}} &= \frac{N\mu_B^2}{k_B T_F} \\ &= \frac{2\gamma\mu_B^2}{\pi^2 k_B^2} \end{aligned}$$

which yields $\chi_{\text{Pauli}} \approx 5.2(2) \times 10^{-5} \mu_B/T\text{-f.u.}$ This is significantly lower than the values in table 7.2, and shows that the conduction electron susceptibility contribution is negligible. In addition the sign of many of the values for χ_0 in the table suggests that which ever impurity is contributing is weakly diamagnetic.

Finally, the effective moment in the Russell-Saunders (LS-coupling) approximation is,

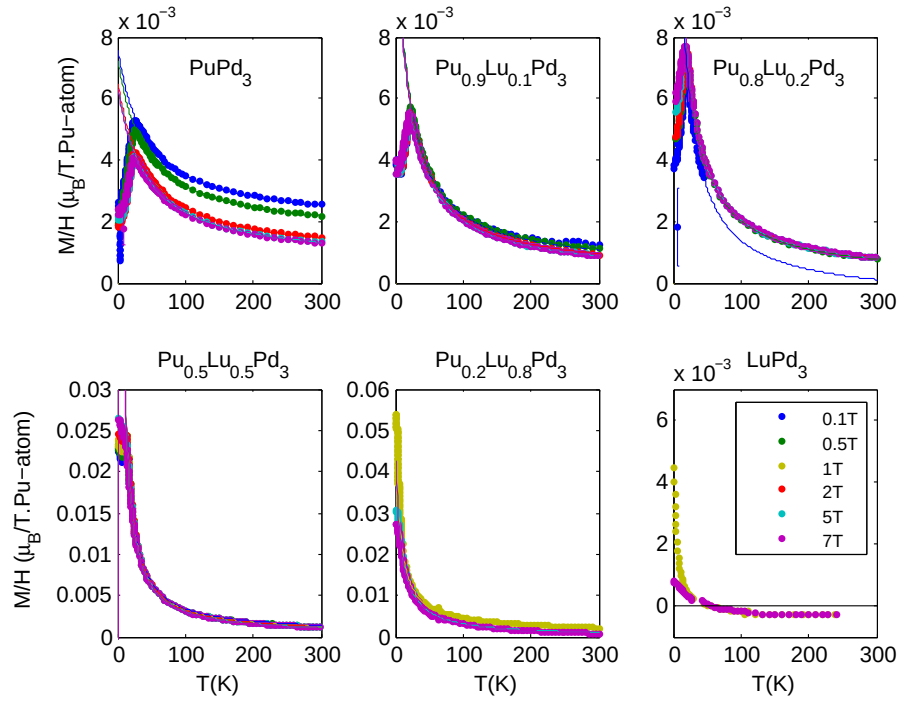


Figure 7.2: The magnetic susceptibility of $\text{Pu}_{1-x}\text{Lu}_x\text{Pd}_3$. Solid lines are fits to the modified Curie-Weiss Law.

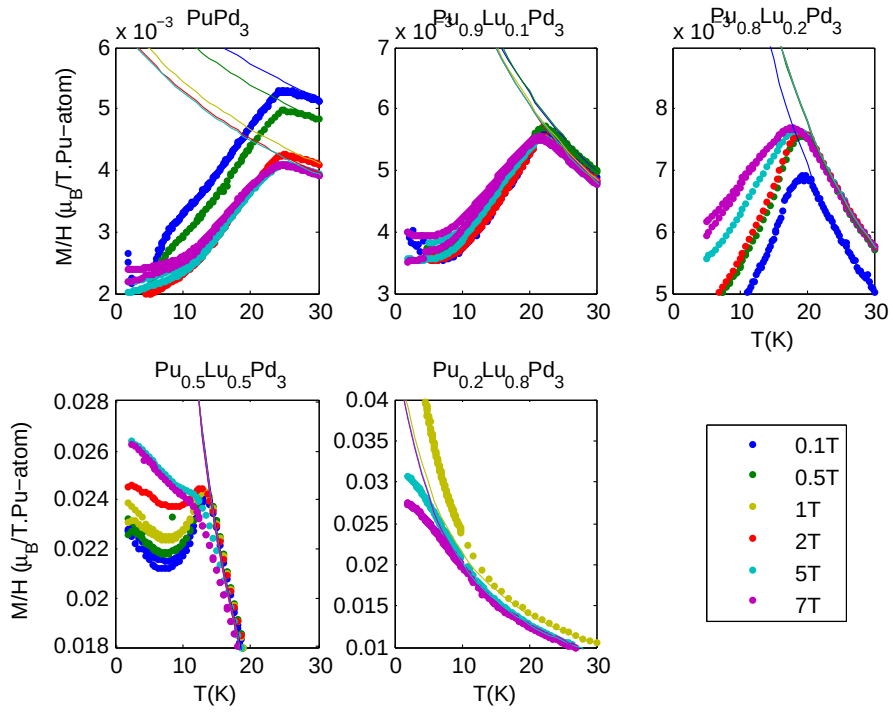


Figure 7.3: The magnetic susceptibility of $\text{Pu}_{1-x}\text{Lu}_x\text{Pd}_3$ around the transition temperature. Solid lines are fits to the modified Curie-Weiss Law.

Composition	$\mu_{\text{eff}} (\mu_B/\text{Pu})$	θ (K)	$\chi_0(H) / 10^{-3} \mu_B/\text{T-f.u.}$					
			0.1 T	0.5 T	1 T	2 T	5 T	7 T
PuPd ₃	1.020 ± 0.005	-39.90 ± 0.09	-1.8	-1.5		-0.8	-0.6	-0.6
Pu _{0.9} Lu _{0.1} Pd ₃	0.966 ± 0.004	-15.80 ± 0.05	-0.4	-0.4		-0.3	-0.2	-0.2
Pu _{0.8} Lu _{0.2} Pd ₃	0.971 ± 0.007	-7.48 ± 0.01	0.6	-0.1		-0.14	-0.13	-0.14
Pu _{0.5} Lu _{0.5} Pd ₃	1.147 ± 0.002	1.84 ± 0.03	-0.4	-0.17	-0.23	-0.21	-0.1	-0.07
Pu _{0.2} Lu _{0.8} Pd ₃	1.250 ± 0.007	-7.18 ± 0.10			-1.11		0.13	0.33

Table 7.2: Fitted parameters to the modified Curie-Weiss relation.

$$\mu_{\text{eff}} = g_J \sqrt{J(J+1)} \quad (7.2)$$

where g_J is the Landé g -factor. The fitted parameters to the Curie-Weiss relation for each sample is given in table 7.2, and figure 7.4 shows the inverse susceptibility of the different compositions with the residual susceptibility χ_0 subtracted.

The values of the effective moment all differ significantly from the LS-coupling prediction of $0.85 \mu_B$. This suggests that we should use intermediate coupling to calculate the single ion properties of the Pu ion. In addition the negative of the Curie temperature θ is higher than the

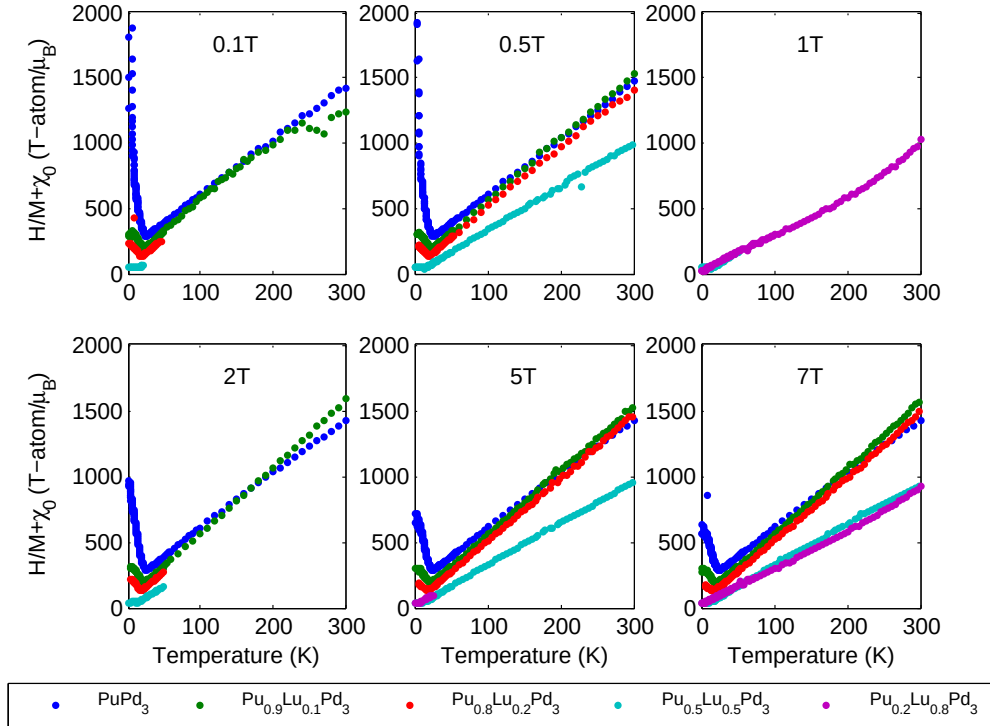


Figure 7.4: The inverse magnetic susceptibility of $\text{Pu}_{1-x}\text{Lu}_x\text{Pd}_3$ with χ_0 subtracted.

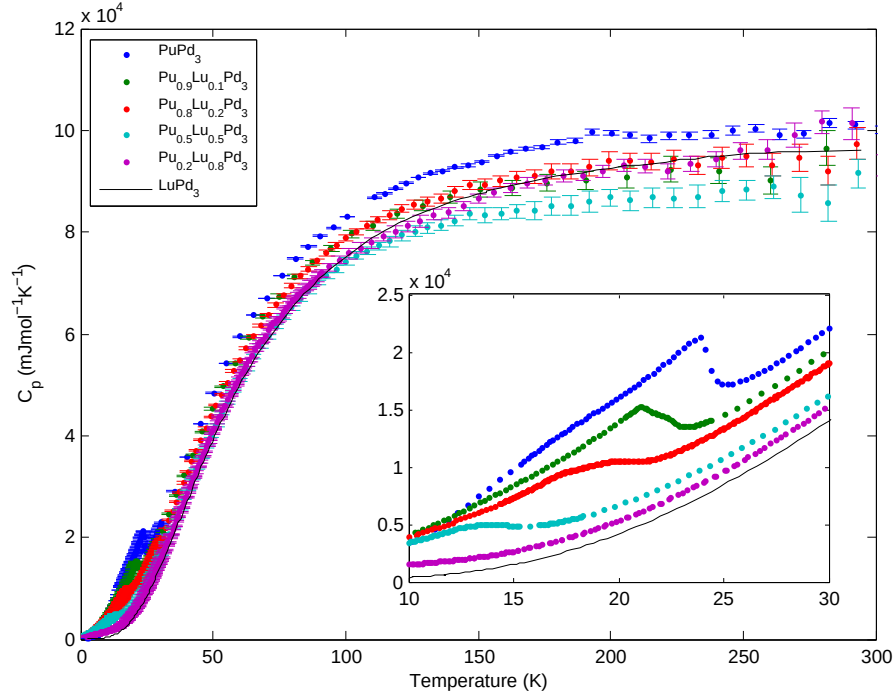


Figure 7.5: Heat capacity of $Pu_{1-x}Lu_xPd_3$ at zero applied magnetic field.

actual transition temperature, which is expected as the mean field theory usually overestimates the transition temperature.

7.2.2 Heat Capacity

The heat capacity at zero field is shown in figure 7.5. There is very little change at the highest measured fields for most compositions, with a slight decrease in the heat capacity, and a slight shift in the transition temperature, as shown in figure 7.6. The transition temperatures measured here agree well with the transition temperatures deduced from the magnetisation measurements. The former are determined by the point of inflexion of the heat capacity (and minima in $\frac{dC_p}{dT}$), or equivalently the centre of the lambda step, whilst the latter is determined by the maxima in the susceptibility, where $\frac{d\chi}{dT} = 0$. Figure 7.7 shows the numerical derivatives (differences) of the heat capacity and magnetic susceptibility with respects to temperature.

For $Pu_{0.9}Lu_{0.1}Pd_3$, the derivative in the heat capacity shows two minima, which stems from the step like nature of the transition. The higher temperature inflexion point corresponds well with the peak in the inverse susceptibility, but the lower temperature does not match any features in the magnetic susceptibility. These two inflexion points raise the possibility that there may be two transitions in this compound. However, as there is no corroborating evidence in the magnetic susceptibility, nor in the other compounds of $Pu_{1-x}Lu_xPd_3$, further investigations will

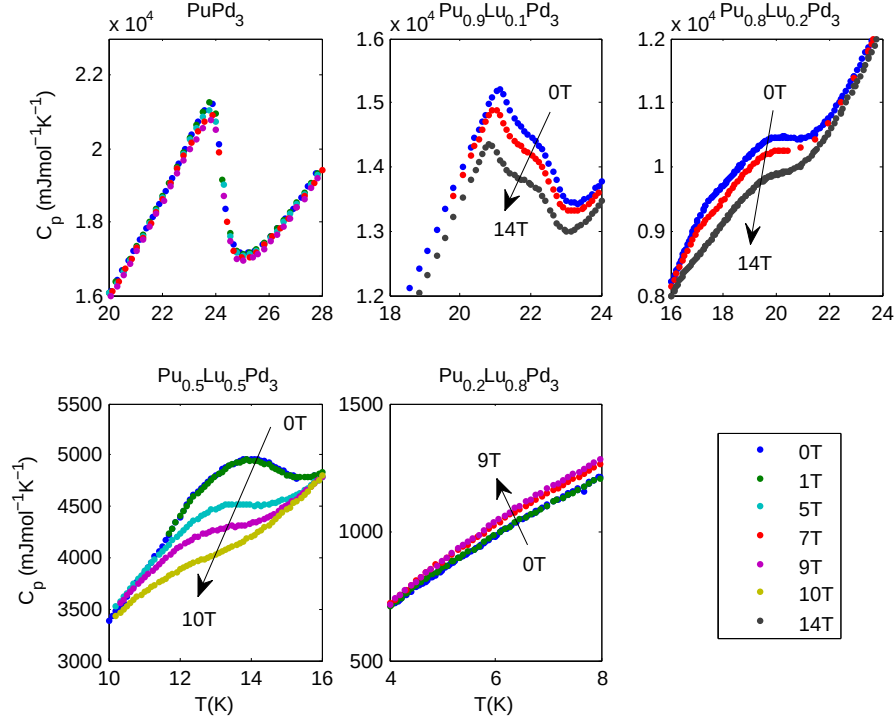


Figure 7.6: Heat capacity of $Pu_{1-x}Lu_xPd_3$ in applied magnetic field. The arrows indicate the direction of increasing field.

be needed to understand this. In particular resistivity measurements can determine if this is due to clustering or other disorder effects.

The electronic specific heat capacity $C_{el} = \gamma T$ and phonon Debye temperature θ_D is determined from the intercept of straight line sections of the C_p/T vs. T^2 curve, above (γ^+ , θ_D^+) and below (γ^- , θ_D^-) the transition, using the approximation,

$$C \sim \gamma T + \frac{12\pi^4 N_A k_B}{5} \left(\frac{T^3}{\theta_D^3} \right)$$

which is valid at low temperatures $T \ll \theta_D$. So, in principle, the line segment should be close to zero temperature to ensure this inequality holds. However, in our case the splitting of the degenerate crystal field ground state by the antiferromagnetic transition will increase the heat capacity just below the transition, and this in turn may give a false γ if the transition temperature is low, as in the case of the high Lu-doped compounds. So the values γ^+ , θ_D^+ , are probably the more reliable. Finally table 7.3 summarises the information deduced from the heat capacity.

We have used the heat capacity of $LuPd_3$ as an estimate of the phonon contribution to the heat capacity of $PuPd_3$ and the alloys, after subtracting the minimal electronic heat capacity of $LuPd_3$, estimated as $\gamma_{Lu} = 3.2(1) \text{ mJmol}^{-1} \text{ K}^{-1}$. The heat capacity $C_p(Lu) - \gamma_{Lu}T$ was then

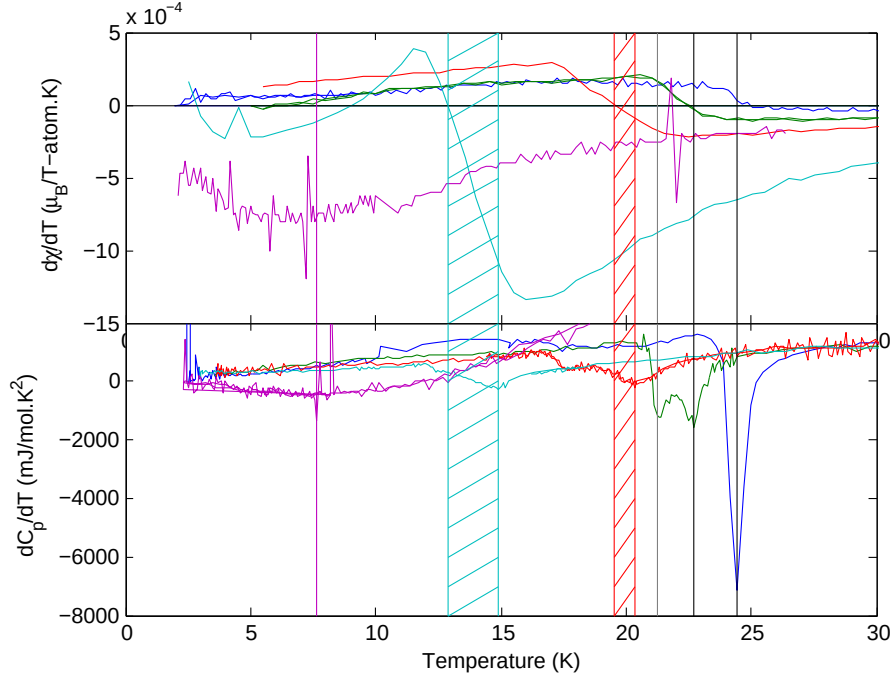


Figure 7.7: The numerical derivative to the heat capacity at zero field, and magnetic susceptibility at 2 T. The vertical lines indicate phase transitions. That is, the location of minima in the susceptibility and inflexion points in the heat capacity. The dashed cyan and red regions cover the space between the transitions as measured in the heat capacity and magnetisation. The black lines show where the two measurements agree, and the gray line indicates a possible second transition in $\text{Pu}_{0.9}\text{Lu}_{0.1}\text{Pd}_3$. Finally, the mauve line shows the inflexion point in the heat capacity of $\text{Pu}_{0.2}\text{Lu}_{0.8}\text{Pd}_3$.

Composition	T_N (K)	γ (mJ/mol.K ²)		θ_D (K)		$S_{\text{mag}}(T = T_N)$ (J/mol-Pu.K)
		γ^-	γ^+	θ_D^-	θ_D^+	
PuPd_3	24.41 ± 0.26	75.3 ± 0.4	455 ± 2	146 ± 2	292.4 ± 0.7	9.01 ± 0.09
$\text{Pu}_{0.9}\text{Lu}_{0.1}\text{Pd}_3$	22.73 ± 0.35	135.6 ± 0.9	388 ± 5	141 ± 4	292.9 ± 1.9	8.38 ± 0.10
$\text{Pu}_{0.8}\text{Lu}_{0.2}\text{Pd}_3$	20.33 ± 1.20	230.0 ± 0.9	308 ± 2	166 ± 4	278.2 ± 0.6	7.66 ± 0.08
$\text{Pu}_{0.5}\text{Lu}_{0.5}\text{Pd}_3$	14.91 ± 1.14	289.0 ± 0.3	166 ± 2	255 ± 2	264.5 ± 0.8	7.81 ± 0.06
$\text{Pu}_{0.2}\text{Lu}_{0.8}\text{Pd}_3$	7.67 ± 1.55	178.0 ± 0.4	61 ± 2	275 ± 3	247.8 ± 0.7	5.11 ± 0.05
LuPd_3		3.2 ± 0.1	3.2 ± 0.1	291 ± 1	291.2 ± 0.6	

Table 7.3: Transition temperatures and other derived quantities from the heat capacity of $\text{Pu}_{1-x}\text{Lu}_x\text{Pd}_3$. $R \ln(3) = 9.13 \text{ Jmol}^{-1} \text{ K}^{-1}$.

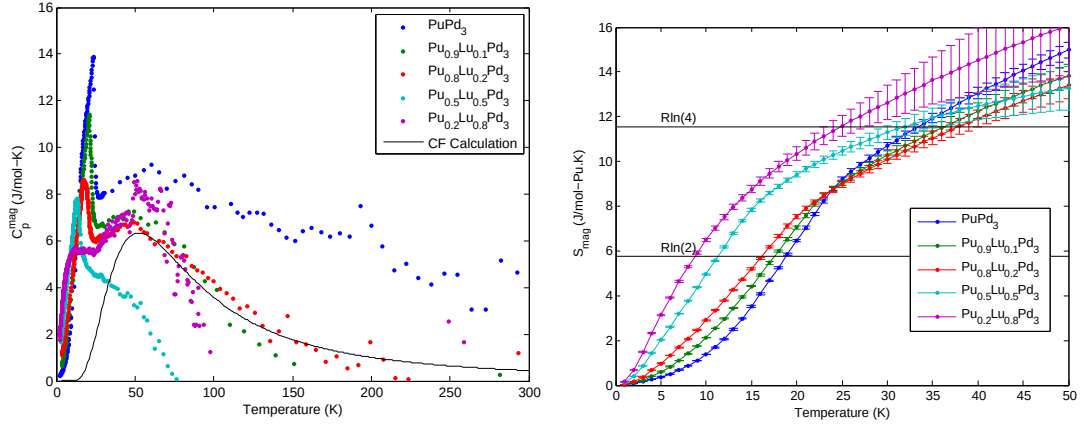


Figure 7.8: *Deduced magnetic contribution to the heat capacity and entropy.* (Left) The magnetic heat capacity C_p^{mag} of $\text{Pu}_{1-x}\text{Lu}_x\text{Pd}_3$, calculated by subtracting the heat capacity of LuPd_3 from that of the relevant compound. The solid line is a CF calculation. (Right) The magnetic entropy calculated by numerically integrating the zero field C_p^{mag}/T .

subtracted from that measured for each of the $\text{Pu}_{1-x}\text{Lu}_x\text{Pd}_3$ compounds, giving the combined magnetic and electronic contributions to the heat capacity. This is then scaled by the Pu concentration, and is shown in figure 7.8.

The magnetic heat capacity appears to show a Schottky peak at around 60 K, and that of the $\text{Pu}_{1-x}\text{Lu}_x\text{Pd}_3$ with $x=0.1, 0.2$, and 0.8 match well with the heat capacity calculated for a quartet ground state, with an excited doublet at 12 meV, as shown by the solid line on the left of figure 7.8.

The crystal field is relatively simple for these compounds because the site symmetry is cubic which means there are only two CF parameters. Furthermore, for the Pu^{3+} ion, $J = 5/2$ in the ground spin orbit state, and the rank 6 parameter has no effect on this ground multiplet, leaving a single CF parameter. There are only 6 levels, a quartet and doublet, and a negative B_4 parameter yields a quartet ground state, whereas a doublet ground state results from $B_4 > 0$. The splitting between them is proportional to the magnitude of B_4 .

This simple picture is made complex when we introduce intermediate coupling. In this case there may be mixing of higher multiplets into the ground multiplet, so that the B_6 parameter becomes important. This will change the wavefunctions of the levels, and means that the splitting will not be proportional to $|B_4|$. However, we would still be left with a quartet and doublet with some splitting Δ , so the effects would not be discernible in the heat capacity.

Figure 7.8 also shows the entropy, deduced by numerically integrating the magnetic heat

capacity,

$$S(T) = \int_0^T \frac{C_p^{\text{mag}}}{T} dT$$

The value of the entropy at the Néel temperature, summarised in table 7.3, is approximately $R \ln(3)$ for PuPd_3 , and well above $R \ln(2)$ for compositions with $x < 0.2$, which further suggests that the ground state is the quartet. $S(T_N) \approx R \ln(1.9)$ for $\text{Pu}_{0.2}\text{Lu}_{0.8}\text{Pd}_3$ however, although this may be due to the lack of data below 2 K, and hence some ‘missing’ entropy.

7.2.3 Electrical Transport

Electrical transport measurements were carried out using thin flat samples extracted by crushing the polycrystalline buttons produced by arc-melting. The resistivity in zero field and in fields up to 9 T were measured for PuPd_3 and $\text{Pu}_{0.5}\text{Lu}_{0.5}\text{Pd}_3$. In addition, the Hall coefficient and longitudinal resistivity at 9 T was also measured for PuPd_3 . In both cases the polycrystalline samples were obtained from the samples previously used to measure the magnetisation and magnetic susceptibility. However, the electrical transport measurements were completed several months after the magnetic measurements and production of the samples, so there was significant aging effects. The PuPd_3 sample was re-annealed at 800°C for 12h and its resistivity was subsequently remeasured showing a large decrease in the residual resistivity $\rho(T = 2 \text{ K})$ from 225 $\mu\Omega\text{cm}$ to 11 $\mu\Omega\text{cm}$. There was not enough time however to re-anneal the 50% sample, although further resistivity measurements on this composition and the other doped compositions are planned.

Figures 7.9 and 7.10 show photographs of the samples, with the positions of the spot welded electrical contacts and distances for the form factor calculations. The excitation current $I = 5 \mu\text{A}$ was used for all measurements. For the resistivity, the longitudinal voltage V_{xx} was measured along the direction of the current as shown, and the resistivity calculated from

$$\rho = \frac{A}{l} \frac{V_{xx}}{I} \quad (7.3)$$

whilst the magnetoresistivity, ρ_{xx} and Hall coefficient R_H , were determined from a transverse voltage V_{diag} diagonally across the sample measured at both a forward and reverse applied field of $\pm B$, with $B = 9 \text{ T}$, as follows

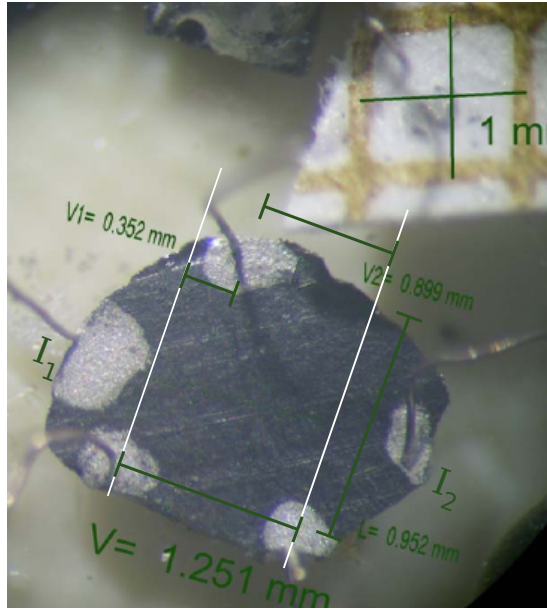


Figure 7.9: *Photograph of PuPd₃ electrical transport sample.* The excitation current is passed between the contacts labeled I_1 and I_2 . The zero-field resistivity is deduced from measuring the longitudinal voltage across the two bottom contacts, separated by the distance $l=1.251 \text{ mm}$, whilst in an applied magnetic field, the transverse voltage between the top and bottom right contacts, separated by the longitudinal distance $l'=0.899 \text{ mm}$ was measured. For calculating the cross section, the width of the sample is denoted by $L=0.952 \text{ mm}$, and the thickness (not shown) is 0.121 mm , giving a cross-section area of 0.115 mm^2 .

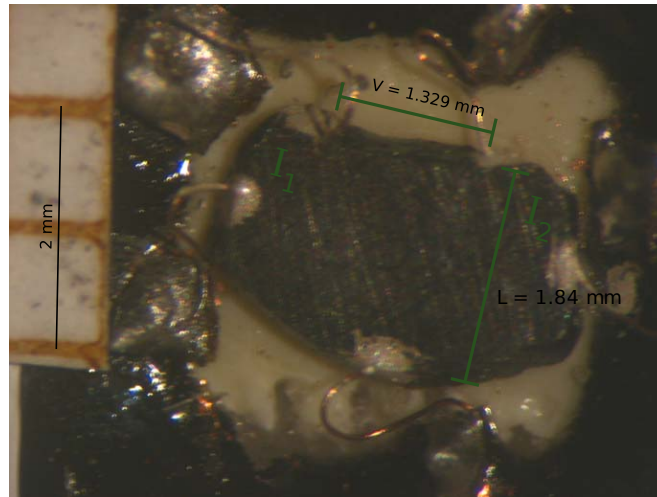


Figure 7.10: *Photograph of Pu_{0.5}Lu_{0.5}Pd₃ electrical transport sample.* The excitation current is passed between the contacts labeled I_1 and I_2 . The zero-field resistivity is deduced from measuring the longitudinal voltage across the two bottom contacts, separated by the distance $V=1.329 \text{ mm}$. For calculating the cross section, the width of the sample is denoted by $L=1.840 \text{ mm}$, and the thickness (not shown) is 0.329 mm , giving a cross-section area of 0.605 mm^2 .

	PuPd ₃	Pu _{0.5} Lu _{0.5} Pd ₃
A (mm ²)	0.115	0.605
l (mm)	1.251	1.329
l' (mm)	0.899	

Table 7.4: *Form factor parameters for (Pu,Lu)Pd₃*. A is the cross-section area of the samples, l and l' are the longitudinal distance between voltage contacts for the resistivity and magnetoresistivity respectively.

$$\begin{aligned}
\rho_{xx} &= \frac{A}{l'} \frac{V_{\text{diag}}(B) + V_{\text{diag}}(-B)}{2I} \\
R_H &= \frac{A}{l'} \frac{V_{\text{diag}}(B) - V_{\text{diag}}(-B)}{2IB}
\end{aligned} \tag{7.4}$$

Where the cross section area A , and distances l and l' are shown in figures 7.9 and 7.10, and summarised in table 7.4.

In principle, ρ_{xx} should be the same as the resistivity of equation 7.3 in an applied field, however we observed some slight differences near the Néel temperature for PuPd₃, as mentioned later. Finally, although both samples had the required contacts for a Hall coefficient measurement, in the case of the 50% sample, the quality of the aged sample and time considerations meant that the magnetoresistivity was not measured.

Figure 7.11 shows the zero field resistivity of PuPd₃ and Pu_{0.5}Lu_{0.5}Pd₃. The in field measurements of the 50% sample showed little change from the zero field data shown. The data for PuPd₃ agree well with previous measurements of Harvey et al. (1973), albeit with a slightly lower residual resistivity. We have also measured the resistivity of LuPd₃ which exhibits a very low resistivity, increasing linearly from $\sim 4 \mu\Omega\text{.cm}$ at 2 K to $\sim 31 \mu\Omega\text{.cm}$ at 300 K. This was taken as the phonon contribution to the resistivity and subtracted from the resistivity of PuPd₃ and the 50% sample to obtain the magnetic contribution to the resistivity shown in the figure.

Qualitatively, the behaviour of the resistivity may be divided into a high temperature Kondo regime, where the resistivity increases with decreasing temperature until ~ 50 K, followed by the onset of coherence, where it falls sharply with temperature. Above ~ 70 K, the resistivity is well fitted by a $\rho_0 + \rho_1 \log(T)$ term (Kondo, 1964), where ρ_0 is the residual resistivity, and ρ_1 is proportional to the interaction between the conduction electrons and Kondo impurities. The fit is shown in figure 7.11, with parameters $\rho_0 = 235.8(3) \mu\Omega\text{.cm}$ and

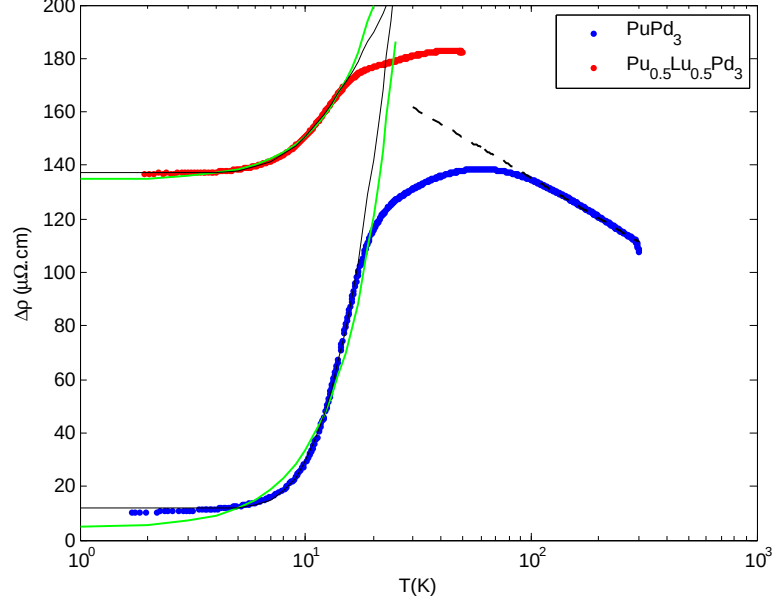


Figure 7.11: *Zero-field resistivity of PuPd_3 and $\text{Pu}_{0.5}\text{Lu}_{0.5}\text{Pd}_3$ on a logarithmic scale.* The green lines are T^2 fits to the low temperature regime, whilst the black solid lines are fit to an exponential temperature dependence. The black dashed line is a fit to a $-\ln(T)$ relation in the high temperature region.

$$\rho_1 = -21.8(1)\mu\Omega.\text{cm}.$$

The low temperature regime in contrast shows an exponential temperature dependence rather than the T^2 dependence expected of a Fermi liquid, after the onset of coherence. Figure 7.11 shows a fit to the data using both the expressions $\rho'_0 + AT^2$ (green) and $\rho'_0 + \rho'_1 \exp(-\Delta/T)$ (black), and it may be seen that the exponential relation gives the better fit. The fitted values of $\Delta = 40.1(4)$ K for PuPd_3 , and $\Delta = 26.9(2)$ K for $\text{Pu}_{0.5}\text{Lu}_{0.5}\text{Pd}_3$ is perhaps a little large to be from a splitting of the crystal field ground state due to the antiferromagnetic order, but this is not out of the question.

Furthermore, the low temperature behaviour, from the sharp increase of the resistivity to an apparent saturation up to the start of the Kondo-like behaviour may be reproduced qualitatively by a relatively simple crystal field model of the resistivity, which we shall now explore. It must be stressed though that the resistivity in $(\text{Pu},\text{Lu})\text{Pd}_3$ is probably much more complicated than may be explained by this model, and in particular it cannot reproduce an increasing resistivity with decreasing temperature. However, it does give an exponentially decreasing resistivity at low temperature as T falls.

The model, by Rao & Wallace (1970), is based on the older spin-disorder model of de Gennes & Friedel (1958) and Dekker (1965). It treats the conduction electrons as a single

simple s -band, which interacts with the localised $5f$ moment via the Hamiltonian,

$$\mathcal{H}_{s-f} = -2G\delta(\mathbf{r} - \mathbf{R})\mathbf{s} \cdot \mathbf{J} \quad (7.5)$$

where the conduction electron spin $\mathbf{s}$ at position $\mathbf{r}$ interacts with a localised moment $\mathbf{J}$ at position $\mathbf{R}$ via the exchange interaction of strength G . The operator $\mathbf{s} \cdot \mathbf{J}$ may be expressed in terms of angular momentum ladder operators as

$$\mathbf{s} \cdot \mathbf{J} = s_z J_z + \frac{1}{2}(s_+ J_- + s_- J_+) \quad (7.6)$$

with matrix elements

$$\begin{aligned} \langle m_s, m_J | s_z J_z | m_s, m_J \rangle &= m_s m_J \\ \langle m_s \pm 1, m_J \mp 1 | s_{\pm} J_{\mp} | m_s, m_J \rangle &= [J(J+1) - m_J(m_J \mp 1)]^{1/2} \end{aligned} \quad (7.7)$$

Using the first Born approximation, the scattering probability of the conduction electron by the localised moment is proportional to the square of the matrix element $\langle m'_s, \psi'_i, \mathbf{k}' | \mathcal{H}_{s-f} | m_s, \psi_i, \mathbf{k} \rangle$ where $\mathbf{k}^{(')}$ is the wavevector of the conduction electron before (after) scattering by the localised moment, and ψ_i is the i^{th} wavefunction of the localised moment system, which we take to be due to the crystal field. The relaxation time, and hence the resistivity is proportional to this squared matrix element, and following Rao & Wallace (1970) is given by,

$$\rho_{s-f} = \frac{3\pi N m^*}{\hbar e^2 E_F} G^2 (g-1)^2 \frac{1}{Z} \sum_{m_s, m'_s, i, i'} \langle m'_s, \psi'_i | \mathbf{s} \cdot \mathbf{J} | m_s, \psi_i \rangle p_i f_{ii'} \quad (7.8)$$

where the occupation factor for the crystal field level at E_i is $p_i = \exp(-E_i/k_B T)$ and the conduction electron population factor is,

$$f_{ii'} = \frac{2}{1 + \exp\left(-\frac{E_i - E_{i'}}{k_B T}\right)}$$

Finally, the wavefunctions ψ_i and energies E_i are determined by diagonalising the crystal field Hamiltonian $\mathcal{H}_{cf}$ as shown in chapter 2, or by diagonalising the sum of this and the Zeeman Hamiltonian $\mathcal{H}_{cf} + \mathcal{H}_Z$.

In the absence of a crystal field, the $2J + 1$ degenerate spin orbit ground state levels yields a temperature independent resistivity given by

$$\rho_{s-f}^{(0)} = \frac{3\pi N m^*}{\hbar e^2 E_F} G^2 (g-1)^2 J(J+1) \quad (7.9)$$

which in the presence of the crystal field is approached in the high temperature limit. In our case, with $J = 5/2$, in a cubic crystal field, and in the absence of a magnetic field, the expression 7.8 reduces to a sum of exponential functions, because the wavefunctions ψ_i are fixed, and the single crystal field parameter B_4 only changes the splitting Δ between a quartet and doublet. There is thus a universal behaviour, with the resistivity tending to $\rho_{s-f}^{(0)}$ at $T \gg \Delta$, and then falling exponentially as the temperature falls below some level such that the excited crystal field state is no longer populated.

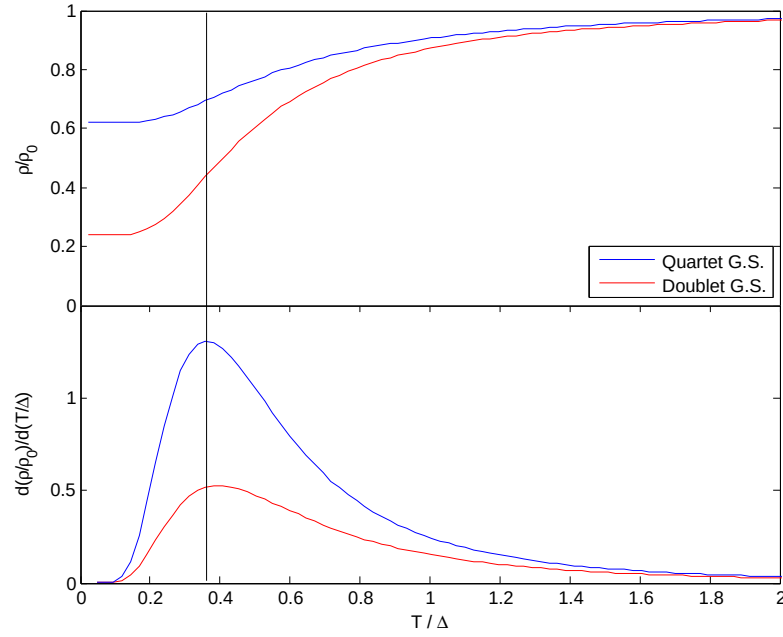


Figure 7.12: *The reduced resistivity as calculated by the localised moment crystal field model described in the text.*

We can see that the drop in resistivity occurs at $T \approx 0.4\Delta$. In both PuPd_3 and $\text{Pu}_{0.5}\text{Lu}_{0.5}\text{Pd}_3$, the observed drop in resistivity occurs at ~ 30 K, which implies a crystal field splitting of ~ 2 meV, which is much lower than that which we expected from the Schottky peak in the heat capacity.

Another problem with the model is that the resistivity is proportional to the occupation of the crystal field levels. Thus the greater degeneracy of the quartet gives a larger residual

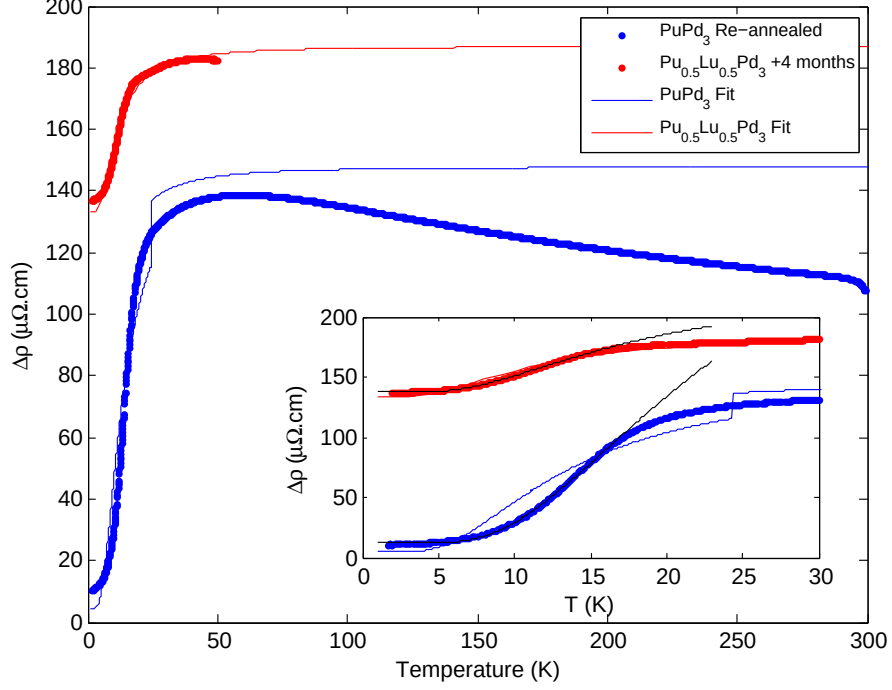


Figure 7.13: Zero-field resistivity of PuPd_3 and $\text{Pu}_{0.5}\text{Lu}_{0.5}\text{Pd}_3$. The solid lines are fit to a crystal field model described in the text. Blue and red lines are fits over the full temperature range, whilst the black lines are fits for $T < 15$ K.

resistivity, $\rho_{s-f}(T = 2\text{K})$, whilst the data has a very small residual resistivity, and thus favours a doublet ground state. This would again disagree with the heat capacity measurements which suggests a quartet ground state.

This difficulty may be overcome if we include a molecular field term $-g_J\mu_B\mathbf{J} \cdot \mathbf{H}_{\text{mf}}$ in addition to the crystal field term below T_N . Such a fit is shown in figure 7.13, and the fit parameters are in table 7.5, where we have treated the prefactor $\rho_{s-f}^{(0)}$ as a variable parameter.

The fitted resistivity yielded a quartet ground state with a splitting of 1.87 meV for PuPd_3 and 1.65 meV for $\text{Pu}_{0.5}\text{Lu}_{0.5}\text{Pd}_3$, which as noted above is much smaller than we expected from the heat capacity measurements. In addition, including the effects of the molecular field means that the simple model gives a jump in the resistivity at T_N which is not observed. However, with the molecular field, the fit at low temperature below T_N is better with a quartet ground state, whilst a doublet ground state gives a broader upturn with a flatter slope than was observed.

However, if the fit is restricted to $T < 15$ K, and we thus do not limit $\rho_{s-f}^{(0)}$ to be near the maximum measured resistivity value, a very good fit to the low temperature exponential temperature dependence is obtained as shown by the black solid lines in figure 7.13. Also in this case, we get crystal field parameters which are in better agreement with the heat capacity

	PuPd ₃	Pu _{0.5} Lu _{0.5} Pd ₃	
$\rho_{s-f}^{(0)}(\mu\Omega\cdot\text{cm})$	143 ± 1	141 ± 0.3	} $T < 300 \text{ K}$
$\rho(T = 2 \text{ K})(\mu\Omega\cdot\text{cm})$	4.5 ± 0.5	45.5 ± 0.3	
$B_4 \text{ (meV)}$	$(-5.21 \pm 0.08) \times 10^{-3}$	$(-4.59 \pm 0.01) \times 10^{-3}$	
$H_{mf} \text{ (Tesla)}$	59.5 ± 0.7		
$\rho_{s-f}^{(0)}(\mu\Omega\cdot\text{cm})$	487 ± 9	133 ± 0.5	} $T < 15 \text{ K}$
$\rho(T = 2 \text{ K})(\mu\Omega\cdot\text{cm})$	12.0 ± 0.1	137.5 ± 0.1	
$B_4 \text{ (meV)}$	$(-31.9 \pm 0.7) \times 10^{-3}$	$(-33.7 \pm 0.2) \times 10^{-3}$	
$H_{mf} \text{ (Tesla)}$	91.5 ± 0.8	67.9 ± 0.2	

Table 7.5: *Fitted parameters for (Pu,Lu)Pd₃ crystal field resistivity model.* $\rho_{s-f}^{(0)}$ proportional to the effective mass and conduction- f electron exchange interaction strength. $\rho(T = 2 \text{ K})$ is the residual resistivity. B_4 is the crystal field parameter, and H_{mf} is the molecular field strength. The top panel shows parameters fitted to the full temperature range, whilst the lower panel parameters from the fit restricted to $T < 15 \text{ K}$.

data, giving a splitting of 11.5(5) meV for PuPd₃ and 12.1(5) meV for Pu_{0.5}Lu_{0.5}Pd₃.

Finally, with this fit, we find the ratio $\rho_{s-f}^{(0)}(\text{PuPd}_3) / \rho_{s-f}^{(0)}(\text{Pu}_{0.5}\text{Lu}_{0.5}\text{Pd}_3) \approx 3.6$, which may be compared to the ratio $\gamma^+(\text{PuPd}_3) / \gamma^+(\text{Pu}_{0.5}\text{Lu}_{0.5}\text{Pd}_3) \approx 2.8$ of the Sommerfeld coefficient, and hence of the effective mass. The difference in the two ratios may be due to a decrease in the coupling G between the conduction and f electrons with Lu doping.

We now turn to the electrical transport properties in an applied magnetic field. The temperature dependence of the Hall coefficient R_H and the magnetoresistivity ρ_{xx} are shown in figure 7.14. $\rho_{xx}(T)$ follows the same behaviour as the zero field resistivity shown above, with the exception that there is a small peak just below the Néel temperature as shown in the inset to the figure. This has not previously been observed.

The temperature dependence of the Hall effect may be described phenomenologically by a scaling of the magnetisation, as in

$$\rho_{xy}(T) = R_0 B + R_1 \mu_0 M(T)$$

where R_0 is called the *ordinary* and R_1 the *extraordinary* Hall constant. In figure 7.14, the solid line shows a fit of the Hall resistance of PuPd₃ to this relation using the measured magnetisation data with the parameters $R_0 = 3.29(4) \times 10^{-8} \text{ m}^3/\text{C}$, and $R_1 = -6.97(8) \times 10^{-9} \text{ m}^3/\text{C}$. The magnetisation data was measured at 7 T, however we have scaled it to 9 T for the fitting. That is, the susceptibility shown in figure 7.2 in $\mu_B/\text{atom}/T$ was multiplied by 9 T to get the magnetisation in μ_B/atom , which was subsequently multiplied by a conversion factor ($\mu_B N_A / V_{\text{mol}}$)

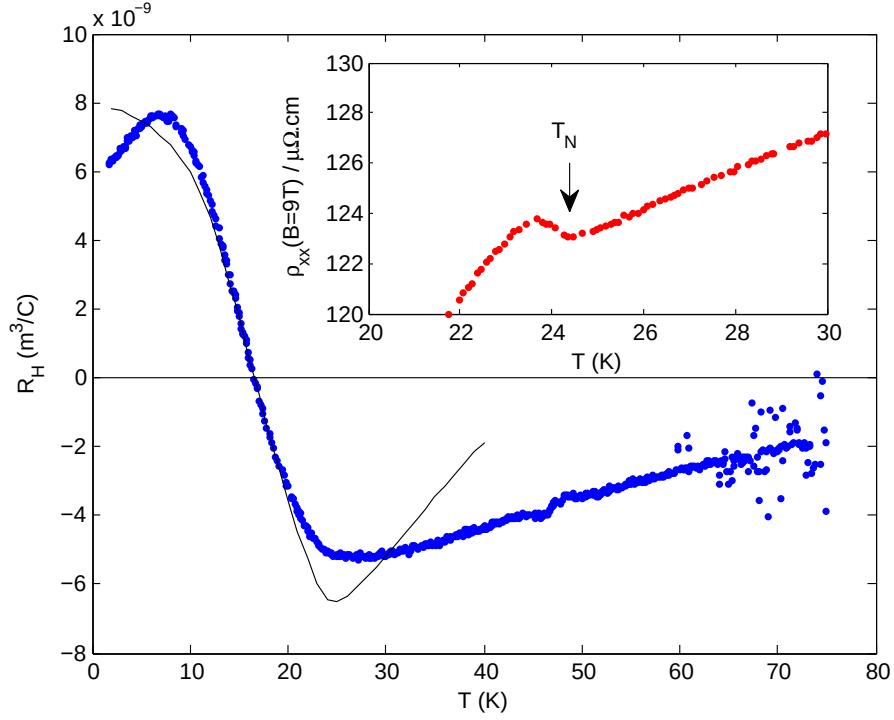


Figure 7.14: *Temperature dependence of the Hall coefficient $R_H = \rho_{xy}/B$ and magnetoresistance at 9 T (inset). The solid black line is a fit using the measured magnetic susceptibility as described in the text*

$= 1.208 \text{ emu/cm}^3$ which is finally multiplied by 10^3 to convert to SI standard units $(\text{A/m})^1$. The molar volume $V_{\text{mol}} = 41.59 \text{ cm}^3/\text{mol}$ is derived from the lattice parameter $4.103 \text{ \AA}$.

In order to obtain a Hall current, there must be an asymmetry in the scattering of electrons moving in one direction versus those moving in the opposite direction, which is called *skew scattering*. In terms of the theory described above, for this skew scattering to occur we require

$$\langle m'_s, \psi'_i, \mathbf{k}' | \mathcal{H} | m_s, \psi_i, \mathbf{k} \rangle \neq \langle m_s, \psi_i, \mathbf{k} | \mathcal{H} | m'_s, \psi'_i, \mathbf{k}' \rangle$$

Following Maranzana (1967), we consider the magnetic field induced by localised $5f$ moments on the conduction electron, which yields an interaction,

$$\mathcal{H}_{\text{f-e}} = -\frac{e}{2m} \mathbf{A} \cdot \mathbf{p} = -\frac{e}{2mr^3} \mathbf{l} \cdot \mathbf{M} \quad (7.10)$$

between the vector potential $\mathbf{A}$ or moment $\mathbf{M}$ of the $5f$ electrons and the momentum $\mathbf{p}$ or angular momentum $\mathbf{l}$ of the conduction electrons. The matrix elements of this operator have a term

¹There is also a factor 10^{-8} in converting from our use of $\mu\Omega\cdot\text{cm}$ for ρ_{xy} to the SI standard $\Omega\cdot\text{m}$ to get quantities in m^3/C for R_H

proportional to $\mathbf{k} \times \mathbf{k}'$, which gives us the necessary asymmetry due to the anti-commutation properties of the cross product. However this only holds if the transition probability includes terms which are odd powers of this matrix element, for which we must go to the second Born approximation.

Including both the spin-spin term $\mathcal{H}_{s-f}$ of equation 7.5, and the spin-orbit term $\mathcal{H}_{l-f}$ written above, Maranzana (1967) showed that this interaction leads to an anomalous Hall resistivity proportional to the magnetisation as follows²,

$$\rho'_{xy}(T) = \frac{3N \sin k_F a}{4} \frac{1}{a} \frac{1}{hE_F} G^2 g \mu_0 M(T) \quad (7.11)$$

where a is the lattice constant. Comparing equations 7.11 and 7.9, we see that the ratio of the anomalous Hall constant to the resistivity factor is

$$\frac{\rho_{s-f}^{(0)}}{R_1} = \frac{8\pi^2 a}{\sin k_F a} \frac{(g-1)^2}{g} J(J+1) \frac{m^*}{e^2} \quad (7.12)$$

If we take $\sin k_F a \approx 1$, then from the fitted parameters $\rho_{s-f}^{(0)} = 1.43(1) \times 10^{-6} \Omega \cdot \text{m}$ and $|R_1| = 6.97(8) \times 10^{-9} \text{ m}^3/\text{C}$, we get an effective mass of $m^* = 11.4(2)m_e$. In comparison, from the Sommerfeld coefficient deduced from the heat capacity measurements, $\gamma = 0.455(2) \text{ J/mol.K}^2$, and assuming a quadratic dispersion such that,

$$\gamma = \frac{k_B^2}{3\hbar^2} \left(\frac{3\pi^2 N}{V} \right)^{1/3} m^*$$

we obtain an effective mass of $m^* = 163(1)m_e$ assuming $N = 5$ f -electrons per unit cell. It must be noted that the uncertainties in both these derived quantities is probably much greater than that quoted, which was obtained from a least squares fit, because the assumptions of the underlying theories used to derive the effective mass is probably not fulfilled in PuPd₃. For example the particle-in-a-box model used to derive m^* from γ is not very realistic, and it is likely that the band structure of PuPd₃ is very much more complicated. In addition, the resistivity model discussed above still perhaps treats the conduction electrons too simplistically, again without considering the band structure for these electrons. However, both estimates show that there is a significant enhancement of the effective mass in PuPd₃.

²The equation is quoted in SI units, in the original paper equation 28 is in CGS units.

7.3 Intermediate Coupling Analysis for PuPd₃

As noted in section 7.2.1, the measured effective moment for both PuPd₃ and the doped compounds is approximately $1 \mu_B$, in contrast to the expected LS -coupling value of $g_J \sqrt{J(J+1)} = 0.85 \mu_B$, with,

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

where for Pu³⁺, the Hund's rule ground state gives $S = 5/2$, $L = 5$, $J = 5/2$, so that $g_J(LS) = \frac{2}{7}$.

LS -coupling is a good approximation in the limit that the Coulomb interaction dominates over the spin-orbit interaction. The Coulomb interaction is diagonal in L and S , whereas the spin-orbit interaction mixes states with the same L and S but is diagonal in J . Thus in the case where the spin-orbit interaction dominates, L and S are no longer good quantum numbers but J still is. We must thus couple the individual orbital and spin angular momenta l and s on each electron individually into a total angular momentum j , and couple over all electrons to get J .

For f -electrons, $l = 3$ and $s = 1/2$, so $j = l \pm s$, with the $j = 5/2$ level being lower in energy than the $j = 7/2$ level. Thus in jj -coupling one fills up the $j = l - s$ level first, and then fill up the $j = l + s$ level. For Pu³⁺ with 5 electrons, the configuration is $(\frac{5}{2})^5$, and the combined total angular momentum $J = 5/2$ as in LS -coupling. However, the effective moment is different because the Landé g -factor above now couples the individual orbital (l) and spin (s) momenta (Rose, 1957), giving $g_j(jj) = \frac{6}{7}$, and hence an effective moment $g_J \sqrt{J(J+1)} = 2.54 \mu_B$.

Our measured effective moment is thus relatively close to the LS coupling limit, but still shows that the spin-orbit interaction is not negligible. We now use the techniques described in section 2.6 and Appendix C to calculate the magnetisation in intermediate coupling where we consider the effects of both the Coulomb and spin-orbit interaction on an equal footing. We ignore the crystal field for the moment because the splitting shown by the specific heat data is relatively small and will not significantly alter the effective moment.

We begin by using parameters for the Coulomb and spin-orbit interactions obtained using Hartree-Fock atomic calculations with relativistic corrections (Ogasawara et al., 1991), and from fitting the optical spectra of PuCl₃ and Pu³⁺ doped into LaCl₃ (Carnall, 1992), as summarised in table 7.6

Figure 7.15 shows the measured inverse susceptibility of PuPd₃ and the results of the two

	F^2	F^4	F^6	ξ	B_4	B_6
Hartree-Fock	9.70	6.31	4.63	0.307		
Optical Spectra	6.04	4.88	3.43	0.278		
Magnetisation Fit	25.13	21.09	14.42	0.677	-0.147	0.207

Table 7.6: *Coulomb and spin-orbit parameters for intermediate coupling calculations.* The parameters are derived from atomic Hartree-Fock calculations with relativistic corrections (Ogasawara et al., 1991), and from fitting the optical spectra of PuCl_3 and Pu^{3+} doped in LaCl_3 (Carnall, 1992). All values in eV. The crystal field parameters are in Wybourne normalisation.

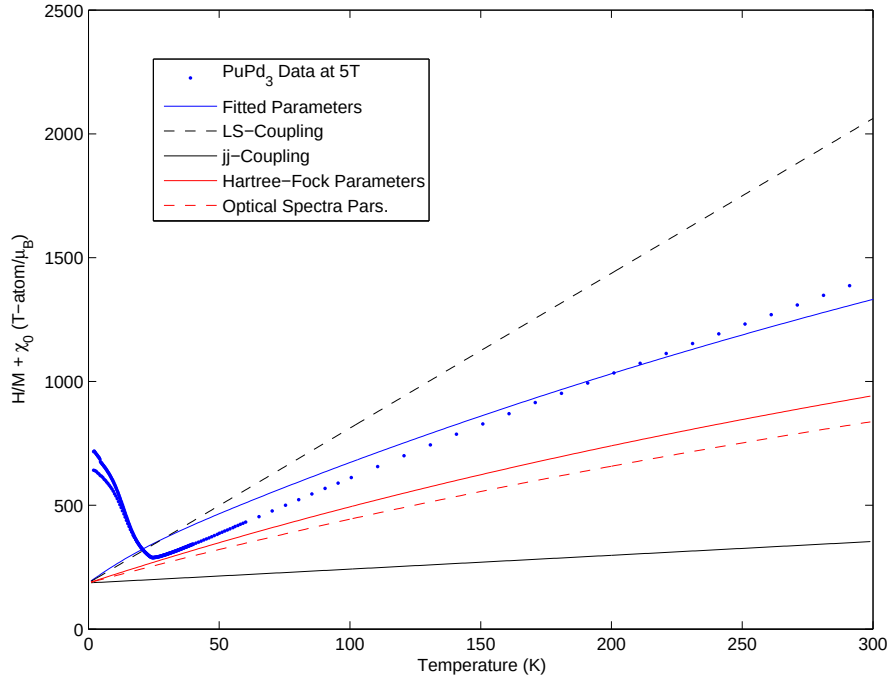


Figure 7.15: *Calculated and measured magnetisation of PuPd_3 .* The black curves are from LS and jj -coupling calculations, whereas the red curve was calculated taking into account the full Hamiltonian with Coulomb and spin-orbit terms, using the parameters given in table 7.6. The calculated curves have been shifted up by $186.4 \text{ T-atom}/\mu_B$.

intermediate coupling calculations, in addition to the LS and jj limits. Neither intermediate coupling calculation match the data, however. The calculated effective moment of $1.34 \mu_B$ for the Hartree-Fock parameters and $1.44 \mu_B$ for those deduced from optical spectra shows that system is more LS -like in our case.

It should be noted that the optical spectra were taken on transparent insulators, rather than the metallic systems we are concerned with, and that the electrons in these insulators are probably more localised than in PuPd_3 . Hartree-Fock calculated parameters also depend on the degree of localisation or delocalisation of the system as well, and are most accurate with completely localised systems. Thus there is some scope to vary the Coulomb or spin-orbit

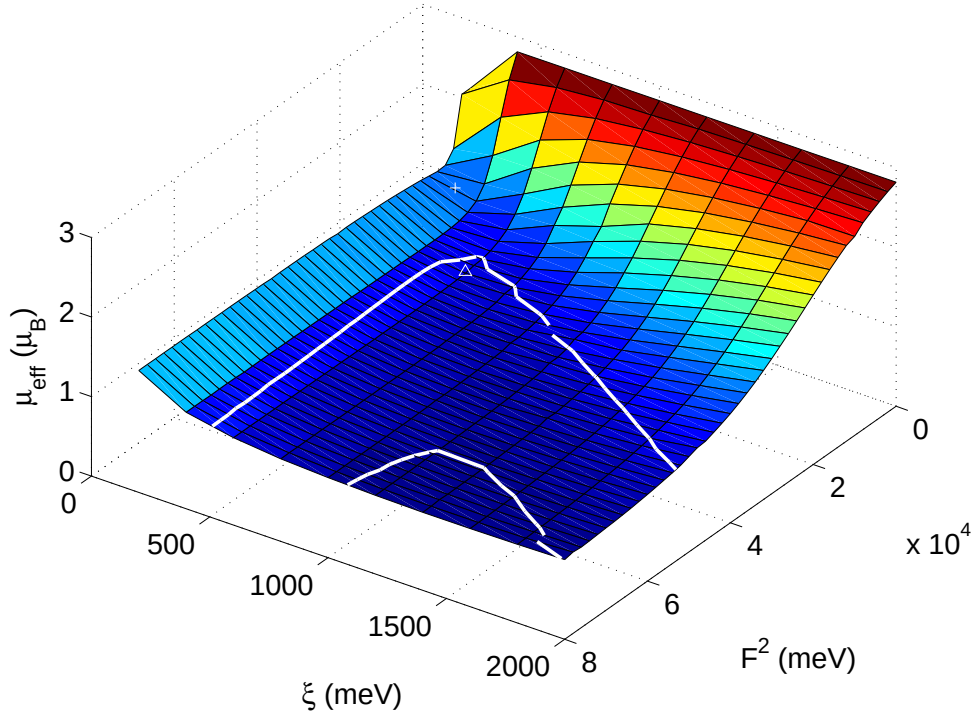


Figure 7.16: *Calculated effective moment as a function of the Coulomb and spin-orbit interaction strength.* The white lines denote contours of constant $\mu_{\text{eff}} = 1 \mu_B$ and $1.15 \mu_B$. The white cross indicates the Hartree-Fock calculated parameters, and the white triangle is the start point of the Levenberg-Marquardt Fit.

interactions to better fit the effective moment.

The LS -coupling limit assumes that the lowest spin-orbit ground state, in our case the ${}^6H_{5/2}$ multiplet is well separated from the next spin orbit multiplet, ${}^6H_{7/2}$, and that there is very little mixing of higher lying states with different L and S . This thus requires a sizeable spin-orbit interaction, and a correspondingly larger Coulomb interaction. Thus we must increase both the Slater parameter F^2 and the spin-orbit integral ξ in order to decrease the calculated effective moment from $\sim 1.3 \mu_B$ to $\sim 1 \mu_B$.

Figure 7.16 shows the calculated effective moment as a function of F^2 and ξ . We have used the ratio $F^4/F^2 = \frac{39333}{48679}$ and $F^6/F^2 = \frac{27647}{48679}$, which apply if the radial $5f$ wavefunction is hydrogen-like, to constrain the number of parameters. The assumption of hydrogenic wavefunction does not hold in practice but serves as a starting point. The region with $1.0 \leq \mu_{\text{eff}} \leq 1.15 \mu_B$ is shown between the white contour lines in the figure. We then chose the lowest value of F^2 and ξ from this to use in a Levenberg-Marquardt generalised non-linear least squares fit of the magnetisation data of PuPd_3 , varying F^2 , F^4 , F^6 , ξ , B_4 and B_6 , to finally obtain the parameters in table 7.6.

These parameters are however a factor of ~ 3 larger than the Hartree-Fock or optical spectra data. This makes it questionable whether they are physical. In addition to the Coulomb and spin-orbit interactions, there are several other magnetic and electrostatic interactions which we have not considered. In particular the configuration interaction between f^5 and higher energy configurations will act in a similar way to the Coulomb interaction, splitting terms with different L and S , whilst the spin-spin and spin-other-orbit interactions will act in a similar way to the spin-orbit interaction, splitting terms with different J . However, these effects are expected to be small.

Another explanation is that the $5f$ electrons in PuPd_3 are in fact more *delocalised* than expected, and this causes mixing of the $j = 5/2$ and $j = 7/2$ states, corresponding to a more LS -like behaviour (Moore & van der Laan, 2009). It is thus not appropriate to model with an atomic theory as we have done. However this view is in contrast to photoelectron spectroscopy measurements which shows that the $5f$ electrons are highly localised (Le et al., 2008b).

Lacking any further data on the lower energy spectra, however, it is difficult to determine the Coulomb and spin-orbit strengths.

7.4 Conclusions

We have completed extensive bulk properties measurements on antiferromagnetic PuPd_3 and the alloys $\text{Pu}_{1-x}\text{Lu}_x\text{Pd}_3$. The transition temperature was found to decrease linearly from $T_N = 24.4(3)$ K in PuPd_3 to $7(2)$ K in $\text{Pu}_{0.2}\text{Lu}_{0.8}\text{Pd}_3$. LuPd_3 was found to be very weakly diamagnetic or paramagnetic in agreement with the literature. Furthermore, the lattice parameter was found to vary linearly in accordance with Vegard's Law.

Magnetic susceptibility and magnetisation measurements show that the paramagnetic effective moment is approximately constant at $\sim 1 \mu_B/\text{atom}$ for all Lu concentrations, whilst the paramagnetic Curie-Weiss temperature becomes less negative and tending to 0 K with increasing Lu doping. An intermediate coupling model was used to fit the magnetic susceptibility, but it was found that the Coulomb and spin-orbit interactions had to be significantly enhanced leading to a greater LS -coupling like behaviour.

Heat capacity measurements showed a Schottky anomaly at ~ 60 K, which was taken to arise from a crystal field splitting between quartet ground state and an excited state doublet at ~ 12 meV. The numerically integrated entropy at T_N for PuPd_3 of $\sim R \ln(3)$ further supports the quartet ground state. Finally the deduced Sommerfeld coefficient was found to be significantly

higher than the free electron expectation, $\gamma \sim 455 \text{ mJ/mol.K}^2$ for PuPd_3 suggesting that this is a heavy fermion compound. As γ decreases with increasing Lu doping, this suggests that it is an effect of the f electrons.

Finally measurements of the resistivity, fitted to a localised moment model supports the crystal quartet ground state, however yields a much lower splitting of $\sim 2 \text{ meV}$. The transport measurements also supports an enhancement of the effective mass as indicated by the high γ values.

Chapter 8

Conclusions and Further Work

In this work, we have sought to measure the physical properties of quadrupolar ordered systems, or those in which the interactions between the electric quadrupole moment is important, and to quantitatively understand these properties in a localised moment model. We have completed extensive inelastic neutron scattering measurements on single crystal PrB_6 , mapping out the dispersion of the low energy ordered phase excitations. The mean field model deduced from fitting to these measurements is not completely satisfactory, however it does show the importance of the quadrupolar interaction in stabilising the double- k structure. However the puzzling temperature dependence of certain of the magnetic Bragg peaks as measured in a brief neutron diffraction experiment remains unexplained, and further measurements and calculations will be required to resolve this issue.

The greater portion of this work concerned the AnPd_3 series of compounds. In chapter 5 we summarised some of the extensive body of experimental and theoretical work on quadrupolar ordered UPd_3 . In addition we also detailed new measurements of the magnetostriction in high magnetic fields, and recent XRS azimuth dependence in the low temperature phases. We proposed a mean-field model for the quadrupolar ordering based on the order parameters measured in the XRS studies, which qualitatively reproduces features of the magnetisation, heat capacity and magnetostriction. The model however produces only two quadrupolar ordered phases, instead of the four observed, and predicts critical fields which are a factor of two lower than measured. A greater understanding of the exchange interactions would be required to improve the model. This information may be derived from more detailed measurements of the dispersion of the order phase excitations, and such an experiment has been planned. In addition, it would be helpful, although not critical, for the remaining three components of the magnetostriction tensor to be measured at 4 K in the lowest quadrupolar ordered phase.

Concerning NpPd_3 , discussed in chapter 6, we have begun inelastic neutron measurements which will provide the necessary information to construct a quantitative microscopic model. We measured four crystal field excitations, and from this deduced crystal field parameters which give qualitative agreement with the measured bulk magnetic susceptibility, although are in disagreement with the heat capacity data. NpPd_3 is a difficult material to handle, however, and due to various factors we were unable to observe any ordered phase excitations at the present time. There remains much scope for further scattering experiments in this compound, however. In particular the nature of the higher ordered phase, between ~ 10 K and ~ 30 K is undetermined. A numerical model in the theoretical framework of chapter 2 will have to await measurements of the dispersion of the ordered phase excitations, or the determination of the order parameter in each phase.

Finally we reported extensive bulk measurements on PuPd_3 , and its solid solution with LuPd_3 in chapter 7. These measurements are generally complete, and although it is possible to calculate a mean field model with this information, this has not been done because using intermediate coupling to calculate the single-ion properties results in calculation times that are too long to be practicable using a personal computer. The program used in the calculation is in continuous development however, and it may be that some computational method will be implemented which may reduce the computing time so as to make the mean field calculations practical.

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Appendix A

Fitting Crystal Field Energy Levels

As noted in section 2.2, the crystal field (CF) Hamiltonian (in *LS*-coupling) may be expressed as (eqn. 2.13),

$$\mathcal{H}_{\text{cf}} = \sum_k \sum_{q=-k}^k B_q^k \bar{O}_{kq}$$

where B_q^k are the CF parameters, and the operators $\bar{O}_{kq}$, given in equation 2.12, are proportional to the tensor operators $T_q^{(k)}$ 2.10 such that

$$\begin{aligned} \bar{O}_{k,0} &= \lambda_{k0} \left(T_0^{(k)} \right) \\ \bar{O}_{k,\pm q} &= \lambda_{kq} \sqrt{\pm 1} \left(T_{|q|}^{(k)} \pm (-1)^q T_{-|q|}^{(k)} \right) \\ \langle Jm_J | T_q^{(k)} | Jm_J' \rangle &= (-1)^{J-m_J} \begin{pmatrix} J & k & J \\ -M & q & M' \end{pmatrix} \langle J || T^{(k)} || J \rangle \end{aligned}$$

Now, the orthogonality relation for the $3j$ symbols are given by:

$$\sum_{M,M'} \begin{pmatrix} J & k & J \\ -M & q & M' \end{pmatrix} \begin{pmatrix} J & k' & J \\ M' & q' & -M \end{pmatrix} = \frac{1}{2k+1} \delta_{kk'} \delta_{qq'} \quad (\text{A.1})$$

and the matrix elements of the crystal field Hamiltonian can be expressed as:

$$\langle J, M_1 | \mathcal{H}_{\text{cf}} | J, M_2 \rangle = \sum_{k,q} B_q^k \langle J, M_1 | \bar{O}_{kq} | J, M_2 \rangle \quad (\text{A.2})$$

so it follows that if we right multiply by $\langle J, M_2 | \bar{O}_{k'q'} | J, M_1 \rangle$ and sum equation A.2 over all M_1, M_2 we get:

$$\sum_{M_1, M_2} \left(\sum_{k, q} B_q^k \langle J, M_1 | \bar{O}_{kq} | J, M_2 \rangle \right) \langle J, M_2 | \bar{O}_{k'q'} | J, M_1 \rangle = B_{q'}^{k'} \sum_{M_1, M_2} \langle J, M_1 | \bar{O}_{k'q'} | J, M_2 \rangle \langle J, M_2 | \bar{O}_{k'q'} | J, M_1 \rangle \quad (\text{A.3})$$

from the orthogonality relation A.1. Substituting the expression for the CF Hamiltonian (equation 2.13) in place of the first brackets and dropping the primes gives

$$B_q^k = \sum_{M_1, M_2} \langle J, M_1 | \mathcal{H}_{\text{cf}} | J, M_2 \rangle \langle J, M_2 | \bar{O}_{kq} | J, M_1 \rangle \bigg/ \sum_{M_1, M_2} \langle J, M_1 | \bar{O}_{kq} | J, M_2 \rangle \langle J, M_2 | \bar{O}_{kq} | J, M_1 \rangle \quad (\text{A.4})$$

If we express the eigenvalues (energies) and eigenvectors (wavefunctions) of $\mathcal{H}_{\text{cf}}$ as E_n and $|V_n\rangle$ respectively, then in terms of the eigenstates of the J, J_z operators, $|J, M\rangle$, we get:

$$|V_n\rangle = \sum_M c_{n,M} |J, M\rangle \quad (\text{A.5})$$

$$E_n = \langle V_n | \mathcal{H}_{\text{cf}} | V_n \rangle = \sum_{M_1, M_2} c_{n, M_1} \langle J, M_1 | \mathcal{H}_{\text{cf}} | J, M_2 \rangle c_{n, M_2} \quad (\text{A.6})$$

Now, if we form a matrix V with its column being the eigenvectors V_n , and another matrix E composed of the eigenvalues E_n along its diagonal, we can re-express the crystal field Hamiltonian matrix in terms of E and V as $\mathcal{H}_{\text{cf}} = V E V^{-1}$. However, because $\mathcal{H}_{\text{cf}}$ is hermitian, $V^{-1} = V^\top$. Explicitly this eigenvalue decomposition equation is:

$$\mathcal{H}_{\text{cf}} = \sum_n |V_n\rangle \langle V_n| E_n \quad (\text{A.7})$$

We can thus substitute the expression for $\mathcal{H}_{\text{cf}}$ in equation A.4 to get an expression for the parameters B_q^k in terms of the energy and wavefunctions. Finally, we note that the operator $\mathcal{H}_{\text{cf}}$ must be Hermitian as it corresponds to a physical observable, so that its matrix element obey:

$$\langle J, M_1 | \mathcal{H}_{\text{cf}} | J, M_2 \rangle = \langle J, M_2 | \mathcal{H}_{\text{cf}} | J, M_1 \rangle \quad (\text{A.8})$$

So that the steps leading from equation A.2 to equation A.4 may be repeated using the right hand side term in equation A.8 instead yielding equation 5.4 quoted in section 5.3.2.

Appendix B

List of Inelastic Neutron Scattering Energy Scans on PrB₆

T(K)	B(T)	(h k l)	Energy Range	k_F	Maximum Monitor	Run Numbers
2	0	(0 0 1)	-0.1600 to 3	1.55	2000000	012208, 023912
2	0	(0 0 1.4)	0.2 to 0.8	1.55	2000000	012225
2	0	(0 0 1.45)	0.2 to 0.8	1.55	2000000	012280
2	0	(0 0 1.5)	-0.2 to 3.8	1.55	4000000	012201, 012214, 012215, 012218, 012239, 012240, 012278, 017030, 017035, 019689
2	0	(0 0 1.6)	0.2 to 0.8	1.55	2000000	012226
2	0	(0.02 0.02 1.5)	0.2 to 0.9	1.55	2000000	012279, 017034
2	0	(0.05 0.05 1.5)	0.2 to 2.4	1.55	4000000	017031
2	0	(0.1 0.1 1.5)	0.3 to 2.1	1.55	2000000	012222, 012224
2	0	(0.15 0.15 1.5)	0.4 to 1.2	1.55	2000000	023954
2	0	(0.2 0.2 0.5)	0.3 to 1	1.30	2000000	023950
2	0	(0.2 0.2 1.5)	0.4 to 2.4	1.55	2000000	012238
2	0	(0.25 0.25 0.5)	0.15 to 0.7	1.30	2000000	023947, 023957
2	0	(0.25 0.25 0.6)	0.5 to 1	1.30	2000000	023948, 023949
2	0	(0.25 0.25 0.8)	1.2 to 2.4	1.55	2000000	023876
2	0	(0.25 0.25 0.9)	1.2 to 2.4	1.55	2000000	023875
2	0	(0.25 0.25 1)	0.3 to 3.2	1.55	4000000	012200, 012213, 012217, 012230, 012232, 017033, 019690
2	0	(0.25 0.25 1.1)	0.7 to 2.5	1.55	2000000	012228, 012244
2	0	(0.25 0.25 1.2)	1.1 to 2.3	1.55	2000000	012220, 012233
2	0	(0.25 0.25 1.3)	-0.3 to 3.15	1.55	2000000	012199, 012209, 012212, 012216, 012219, 016981
2	0	(0.25 0.25 1.4)	0.6 to 3	1.55	4000000	012221, 012234, 012235, 016980, 017032
2	0	(0.25 0.25 1.45)	0.4 to 4.25	1.55	2000000	012227, 012243, 012281, 016979, 019692
2	0	(0.25 0.25 1.5)	-2 to 5.1	1.55	6000000	012197, 012198, 012202, 012205, 012206, 012207, 012210, 012236, 012237, 012241, 012242, 012275, 012276, 016975, 016976, 016977, 019691
2	0	(0.25 0.25 1.55)	0.4 to 5	1.55	2000000	012229, 012277, 016978
2	0	(0.25 0.25 1.6)	0.7 to 1.7	1.55	2000000	023951
2	0	(0.25 0.25 1.7)	0.9 to 2.1	1.55	2000000	023873
2	0	(0.25 0.25 1.8)	1.2 to 2.4	1.55	2000000	023874
2	0	(0.3 0.3 1.5)	0.6 to 2.3	1.55	2000000	023862, 023863, 023868, 023869
2	0	(0.35 0.35 1.5)	0.45 to 2.4	1.55	2000000	023864, 023865, 023870
2	0	(0.4 0.4 1.5)	0.2 to 2.5	1.55	2000000	023866, 023871
2	0	(0.45 0.45 1.5)	0.3 to 2.5	1.55	2000000	023952, 023953
2	0	(0.5 0.5 0.5)	0.1 to 2.1	1.55	1200000	012190
2	0	(0.5 0.5 1.5)	0.2 to 2.5	1.55	2000000	023867, 023872
2	0	(0.75 0.75 0)	0.1 to 2.1	1.55	1200000	012188
2	0	(0.75 0.75 0.5)	0.1 to 2.9	1.55	1200000	012185, 012187, 012192, 012195, 012196
2	0	(0.75 0.75 1)	0.1 to 2.3	1.55	1200000	012189, 012191
4	0	(0 0 1.5)	-0.4 to 3.6	1.55	4000000	017026, 017027, 017028
4	0	(0.25 0.25 1)	0.7 to 2.7	1.55	4000000	017024, 017025
4	0	(0.25 0.25 1.5)	0.3 to 3.7	1.55	4000000	017022, 017023, 017029
5	0	(0 0 1.5)	-0.45 to 2.3	1.55	4000000	012257, 012261, 012262, 017036
5	0	(0.02 0.02 1.5)	0.45 to 2.05	1.55	2000000	017037
5	0	(0.1 0.1 1.5)	-0.35 to 2.2	1.55	2000000	017005, 017007, 017009, 017011
5	0	(0.2 0.2 1.5)	-0.35 to 2.2	1.55	2000000	017006, 017008, 017010, 017012
5	0	(0.25 0.25 1)	0.8 to 2.6	1.55	2000000	012258, 012263
5	0	(0.25 0.25 1.1)	-0.35 to 2.6	1.55	2000000	016988, 016990, 016997, 016998
5	0	(0.25 0.25 1.2)	-0.35 to 2.4	1.55	2000000	016987, 016989, 016995, 016996
5	0	(0.25 0.25 1.3)	-0.35 to 2.2	1.55	2000000	012256, 016983, 016985, 016986, 016993, 016994
5	0	(0.25 0.25 1.4)	-0.35 to 2.2	1.55	2000000	016982, 016984, 016991, 016992, 017018
5	0	(0.25 0.25 1.5)	-0.7 to 2.8	1.55	4000000	012252, 012253, 012254, 012255, 012259, 012260, 017003, 017004, 017013, 017014, 017015, 017016, 017017, 017019
5	0	(0.25 0.25 1.6)	-0.05 to 2.2	1.55	2000000	016999, 017000, 017001, 017002
10	0	(0 0 1.5)	-0.7 to 2.3	1.55	2000000	012268, 012269, 012270, 012271
10	0	(0.25 0.25 1.5)	-0.7 to 2.3	1.55	2000000	012265, 012266, 012267, 017020, 017021

T(K)	B(T)	(<i>h k l</i>)	Energy Range	k_F	Maximum Monitor	Run Numbers
2	2	(0 0 1)	-0.175 to 0.175	1.30	10000	019735
2	2	(0 0 1.5)	0.2 to 2.6	1.55	2000000	019708
2	2	(0.025 0.025 1.5)	0.7 to 1.54	1.55	2000000	019714
2	2	(0.05 0.05 1.5)	0.49 to 1.61	1.55	2000000	019713
2	2	(0.1 0.1 1.5)	0.33 to 1.31	1.55	2000000	019715
2	2	(0.15 0.15 1.5)	0.3 to 1.3	1.55	2000000	019718, 019729
2	2	(0.2 0.2 1.5)	0.25 to 1.4	1.55	2000000	019716, 019719, 019720
2	2	(0.25 0.25 0.5)	0.05 to 0.65	1.30	2000000	019736, 019737
2	2	(0.25 0.25 1.0)	0.5 to 2.9	1.55	2000000	019709, 019727
2	2	(0.25 0.25 1.1)	1.2 to 2.2	1.55	2000000	019726
2	2	(0.25 0.25 1.2)	0.9 to 1.9	1.55	2000000	019725
2	2	(0.25 0.25 1.3)	0.6 to 2.1	1.55	2000000	019722, 019723
2	2	(0.25 0.25 1.4)	0.3 to 1.3	1.55	2000000	019724
2	2	(0.25 0.25 1.5)	-0.3 to 2.6	1.55	2000000	019710, 019711, 019717, 019728
2	2	(0.35 0.35 1.5)	0.3 to 1	1.55	2000000	019730
2	4	(0 0 1.5)	0.5 to 2.1	1.55	2000000	019744
2	4	(0.15 0.15 1.5)	0.33 to 1.24	1.55	2000000	019747
2	4	(0.25 0.25 0.5)	0.3 to 0.6	1.30	2000000	019738
2	4	(0.25 0.25 1)	0.9 to 2.7	1.55	2000000	019746
2	4	(0.25 0.25 1.3)	0.6 to 2.2	1.55	2000000	019745
2	5	(0.25 0.25 0.4)	0.45 to 1.15	1.30	2000000	023895

T(K)	B(T)	(<i>h k l</i>)	Energy Range	<i>k_F</i>	Maximum Monitor	Run Numbers
2	6	(-0.1 -0.1 1.5)	0.5 to 1.2	1.55	2000000	023933
2	6	(0 0 1)	0.5 to 2.3	1.55	2000000	023906
2	6	(0 0 1.5)	0.2 to 2.3	1.55	2000000	019763, 019773, 019778, 023915, 023916
2	6	(0.05 0.05 1.5)	0.49 to 2.2	1.55	2000000	019774, 023914
2	6	(0.1 0.1 1.5)	0.33 to 1.8	1.55	2000000	019777, 019779, 023910, 023913
2	6	(0.15 0.15 0.5)	0.25 to 0.85	1.30	2000000	019760
2	6	(0.15 0.15 1.5)	0.33 to 1.52	1.55	2000000	019775, 019776, 023921
2	6	(0.2 0.2 0.5)	0.25 to 0.9	1.30	2000000	019758, 019764
2	6	(0.2 0.2 1.5)	0.8 to 1.8	1.55	2000000	023922
2	6	(0.25 0.25 0.4)	1.2 to 2.2	1.55	2000000	023934
2	6	(0.25 0.25 0.45)	-0.2 to 0.85	1.30	2000000	019769, 023919, 023920
2	6	(0.25 0.25 0.45)	1.1 to 2.4	1.55	2000000	023917
2	6	(0.25 0.25 0.5)	-0.2 to 1	1.30	2000000	019754, 019755, 019768, 023896, 023911
2	6	(0.25 0.25 0.5)	1 to 5	1.55	2000000	023901, 023904, 023905
2	6	(0.25 0.25 0.55)	0.25 to 1	1.30	4000000	019761, 019770, 019771
2	6	(0.25 0.25 0.55)	1.1 to 2.4	1.55	2000000	023918
2	6	(0.25 0.25 0.6)	0.5 to 1	1.30	2000000	019762
2	6	(0.25 0.25 0.6)	1.4 to 2.4	1.55	2000000	023935
2	6	(0.25 0.25 0.8)	0.8 to 1.9	1.55	2000000	023899
2	6	(0.25 0.25 0.9)	1.2 to 2.4	1.55	2000000	023900
2	6	(0.25 0.25 1)	1 to 2.7	1.55	2000000	019780, 019792
2	6	(0.25 0.25 1.05)	1.6 to 2	1.55	2000000	019794
2	6	(0.25 0.25 1.1)	1.3 to 2.3	1.55	2000000	019782, 019793
2	6	(0.25 0.25 1.2)	1 to 2	1.55	2000000	019783
2	6	(0.25 0.25 1.3)	0.6 to 2.2	1.55	2000000	019781, 023907
2	6	(0.25 0.25 1.4)	0.4 to 1.1	1.55	2000000	019784, 023908, 023909
2	6	(0.25 0.25 1.6)	0.3 to 1.2	1.55	2000000	023897
2	6	(0.25 0.25 1.7)	0.4 to 1.5	1.55	2000000	023898
2	6	(0.275 0.275 0.5)	0.2 to 1	1.30	2000000	019772
2	6	(0.3 0.3 0.5)	-0.15 to 1	1.30	2000000	019757, 019759, 019765, 019766, 019767
2	6	(0.3 0.3 1.5)	1 to 2.1	1.55	2000000	019790, 023923, 023930
2	6	(0.35 0.35 1.5)	0.4 to 2.3	1.55	2000000	019787, 019791, 023924, 023925, 023931
2	6	(0.4 0.4 1.5)	0.7 to 2.4	1.55	2000000	019788, 023926, 023927
2	6	(0.45 0.45 1.5)	1.3 to 2.3	1.55	2000000	019789, 023928
2	6	(0.5 0.5 1.5)	1.2 to 2.6	1.55	2000000	019785, 019786, 023929
2	6	(0.6 0.6 1.5)	1 to 2	1.55	2000000	023932
2	6	(0.75 0.75 0.5)	0.2 to 0.8	1.30	2000000	023902, 023903
4	6	(0.25 0.25 0.5)	0.05 to 1.15	1.30	3000000	023941
5	6	(0.00 0.00 0.5)	-0.3 to 1.5	1.30	2000000	023885, 023887, 023889
5	6	(0.0 0.0 0.5)	0.2 to 2.5	1.55	2000000	023877, 023878
5	6	(0.1 0.1 0.5)	0.3 to 1.5	1.30	2000000	023890
5	6	(0.25 0.25 0.5)	-0.3 to 1.5	1.30	2000000	019803, 023884, 023886, 023888
5	6	(0.25 0.25 0.5)	0.3 to 2.5	1.55	2000000	023879, 023882
5	6	(0.25 0.25 1.0)	0.3 to 2.5	1.55	2000000	023880, 023883
5	6	(0.25 0.25 1.3)	0.5 to 2.2	1.55	2000000	019804, 019805
5	6	(0.5 0.5 1.0)	0.5 to 2.5	1.55	2000000	023881
6	6	(0.25 0.25 0.5)	0.05 to 1.15	1.30	3000000	023942
10	6	(0.25 0.25 0.5)	-0.25 to 1.1	1.30	2000000	023943, 023944, 023945

Appendix C

Intermediate Coupling Matrix Elements

Equations for the matrix elements of the Coulomb, spin-orbit, and crystal field operators in intermediate coupling are presented in this appendix. The basis functions used will be the states of the f^n lowest energy configuration for ions with unfilled outer f -shells. These states are labeled according to which irreducible representations of the continuous groups SU_7 , R_7 , G_2 and R_3 they belong to, which is discussed in section C.1. This labelling scheme, described in section C.1, enables us to write down the states without having to compute the linear combinations of determinantal product states they correspond to.

In addition, the use of irreducible representations of continuous groups to label the states also permit a more straightforward calculation of the matrix elements of operators corresponding to the interactions that we are interested in. This is because these labels enables us to easily factorise the *coefficients of fractional parentage* (cfp), detailed in section C.2, into terms which depend only on some of these labels. The cfp allows us to express the states of a particular configuration l^n as a linear combination of the product of the states of a parent configuration l^{n-1} and the single electron n^{th} state. Because the matrix element of an n -electron operator is just n times the single-electron operator matrix element, the linear combination above means that once the cfp is known, we simply need to multiply it by the single-electron matrix element between one-electron states.

Finally, the matrix elements for the Coulomb interaction, after the method of Racah is given in section C.6; for the spin-orbit interaction in section C.5; the crystal field interaction in section C.3 and the magnetic moment operator $\mathbf{L} + g\mathbf{S}$ for the Zeeman interaction in section C.4.

C.1 The Group Theoretical Classification of the States of f^n

In systems of more than two equivalent electrons, there will be some states with the same values of the quantum numbers S and L . Thus we need some other quantum numbers to distinguish between the states. As the angular momentum labels are essentially group theoretical in nature, being the representations of the rotation group in three dimensions, R_3 , we may look for other groups whose irreducible representations may be used to label the states. Thus if two states with the same S and L belonged to two different irreducible representations of some group G , then these irreducible representations can be used as additional labels of those states. In addition, for a complete description of the states, G must also include the operations of R_3 as subgroups.

For a set of transformations to form a continuous group, (1) the result of performing any two transformations successively may be reproduced by another single transformation also belonging to the set; and (2) any transformation has a unique inverse that also belongs to the set. Condition (1) implies that any transformation can be constructed from a succession of infinitesimal transformations. Representing the action of such an infinitesimal transformation by an operator X_σ , Lie showed that these operators must satisfy the commutation relation

$$[X_\sigma, X_\rho] = c_{\sigma\rho}^\tau X_\tau \quad (\text{C.1})$$

and that the operators $1 + \delta a^\sigma X_\sigma$ form the elements of a group. The a^σ are parameters that uniquely describe the transformations of the group, whilst $c_{\sigma\rho}^\tau$ is the structure constant of the group¹.

Racah noticed that for R_3 , the infinitesimal operators X_σ ($\sigma = 1, 2, 3$), are proportional to the orbital angular momentum operators. Hence, the commutation relation C.1 are related to commutation relations for components of an angular momentum vector, which are tensors of rank 1. He then sought to investigate the commutation relations for tensors of higher rank in order to find infinitesimal operators of groups other than R_3 .

For the lowest energy configurations of equivalent electrons, where the principal, n , and orbital, l , quantum numbers must be identical, we can restrict ourselves to one-electron tensor operators $\mathbf{v}^{(k)}$ whose matrix elements satisfy

$$\langle nl || \mathbf{v}^{(k)} || n'l' \rangle = \sqrt{2k+1} \delta_{nn'} \delta_{ll'} \quad (\text{C.2})$$

¹For a full derivation see Racah (1951), or Judd (1963)

Using the Wigner-Eckart theorem, Racah (1942) showed that the components $v_q^{(k)}$ of these operators do satisfy the commutation relation C.1. Thus, these components (for a particular l) can be regarded as the infinitesimal operators of the *full linear* group GL_{2l+1} . The equivalent many-electron operators $\mathbf{V}^{(k)} = \sum_i (\mathbf{v}^{(k)})_i$ also satisfy the commutation relation C.1 and we shall now use these operators in what follows.

The group GL_{2l+1} , however, is too general for our purposes, and we may restrict it by requiring that the parameters δa^σ satisfy $\delta a_{kq}^* + (-1)^q \delta a_{k,-q} = 0$, resulting in the *unitary* group in $2l + 1$ dimensions, U_{2l+1} . Excluding the $q = 0, k = 0$ component $V_0^{(0)}$ we form the special unitary group SU_{2l+1} which is simple (it has no subgroups that contains all the conjugate of their elements, except for the identity).

Further restricting ourselves to tensor operators of odd rank, we can find two subgroups of SU_{2l+1} , depending on whether l is integral or half-integral. In the former case, the operators of the group leave invariant the distance between two points in a $(2l + 1)$ dimensional space, and hence form the infinitesimal operators of the rotation group, R_{2l+1} . In the later case, we get the *symplectic* group in $2l + 1$ dimensions Sp_{2l+1} .

In addition, Racah found that in the special case of $l = 3$ for f -electrons, the commutators involving $\mathbf{V}^{(3)}$ vanishes, and consequently the 14 components of $\mathbf{V}^{(1)}$ and $\mathbf{V}^{(5)}$ form the infinitesimal operators for a subgroup of R_7 called G_2 (Racah, 1949; Racah, 1951)². To indicate the succession of subgroups, for f -electrons, we write:

$$R_3 \subset G_2 \subset R_7 \subset SU_7 \subset U_7 \subset GL_7 \quad (\text{C.3})$$

We are now in a position to find additional labels for the states of f^n , by going through the subgroups of GL_7 from R_3 , finding the irreducible representations that differentiates between different states. Just as the orbital quantum numbers L label the different irreducible representation of R_3 , we shall then find analogous numbers for G_2 and R_7 , which we denote U and W respectively. Finally we shall find that the intrinsic angular momentum quantum number S for a certain configuration l^n corresponds to a particular irreducible representations of U_7 . Thus the labels L, S, U , and W may serve to label most states of f^n . For the few states of f^6 (or the equivalent configuration f^8) and f^7 which are still not distinguished by this scheme we add

²We have retained the notation for the groups as used by Racah, but the reader should note that the R_{2l+1} groups are now denoted the *special orthogonal* group $SO(2l + 1)$, and the unitary and special unitary groups are now more usually written $U(2l + 1)$ and $SU(2l + 1)$.

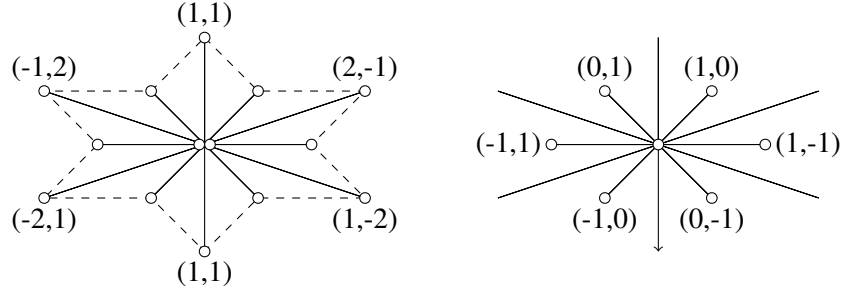


Figure C.1: *Root figure for the group G_2 .* The weights for the representation (11) [left] and (10) [right] are shown along with their values (m_1, m_2) . The maximum weights are to the upper right side, $(m_1 = 2, m_2 = -1) \equiv (u_1 = 1, u_2 = 1)$, and $(m_1 = 1, m_2 = 0) \equiv (u_1 = 1, u_2 = 0)$.

another label τ which arbitrarily separates these states.

C.1.1 The U and W Symbols

In the case of R_3 , we can identify the infinitesimal operators $\mathbf{V}^{(1)}$ discussed above³ with the angular momentum operators $\hat{L}_z$ as the $q = 0$ component $V_0^{(1)}$, and $\hat{L}_+$ and $\hat{L}_-$ as linear combinations of the $q = \pm 1$ components. We see then that the labels L are the maximum values of the eigenvalues of $\hat{L}_z$. Using the terminology of Judd, we call the $2L + 1$ eigenvalues of $\hat{L}_z$ *weights*. Now, if we define operators H_i , as a generalisation of $\hat{L}_z$, and E_α , generalisations of the shift operators, by:

$$[H_i, E_\alpha] = \alpha_i E_\alpha \quad (\text{C.4})$$

Then the eigenvalues (weights) α_i form the components of a vector α , called a *root*, in *weight space*. For R_3 , equation C.4 is just $[J_z, J_\pm] = \pm \hbar J_\pm$, so the weight space is one-dimensional, and the roots are $\pm \hbar$. A plot of the roots is called a *root figure*, which in this case is simply a line, however for larger groups may be a higher dimensional plot. The weights may be visualised as points along the vectors defined by the roots, with each representation of a group having a unique arrangement of weights.

As L_z is related to $V_0^{(1)}$, and we have used this operator for H_i of R_3 , the natural generalisation is to assign linear combinations of the $q = 0$ components $V_0^{(k)}$ of the tensor operators as H_i . The operators E_α is then formed by linear combinations of the $q \neq 0$ components of the remaining infinitesimal operators of the group.

³ k is restricted to odd values between zero and $2l$ for a particular group R_{2l+1} , and q is restricted to integers between $-k$ and k .

For the group G_2 , the infinitesimal operators are $\mathbf{V}^{(1)}$ and $\mathbf{V}^{(5)}$, so we need two operators H_1 and H_2 that are linear combinations of $V_0^{(1)}$ and $V_0^{(5)}$, and 12 operators E_α which are simply the 8 components $V_q^{(5)}$ with $q = \pm 5, \pm 4, \pm 3, \pm 2$ and the 4 linear combinations of $V_{\pm 1}^{(1)}$ and $V_{\pm 1}^{(5)}$. In order to make the symmetry of the root figure obvious we choose an oblique coordinate system defined by (Judd, 1963):

$$\begin{aligned} H_1 &= 4 \sqrt{\frac{1}{7}} V_0^{(1)} + 6 \sqrt{\frac{1}{21}} V_0^{(5)} \\ H_2 &= \sqrt{\frac{1}{7}} V_0^{(1)} - 9 \sqrt{\frac{1}{21}} V_0^{(5)} \end{aligned}$$

and choose the linear combinations of the $q = \pm 1$ components as $E_{\pm 1} = c_{\pm} V_{\pm 1}^{(1)} \pm c_{\mp} V_{\pm 1}^{(5)}$, where the coefficients $c_+ = \sqrt{9/14}$ and $c_- = \sqrt{5/14}$. We find that the eigenvalues pairs (α_1, α_2) for H_1 and H_2 form twelve points, as depicted in figure C.1. The weights may then be found by operating H_1 and H_2 on states $|f^n 2S+1 L, m_L\rangle$ and finding the pairs of eigenvalues due to H_1 and H_2 for each m_L .

We take, for example, the triplet states of the f^2 configuration, ${}^3P, {}^3F, {}^3H$. Each of these states forms a basis for a representation of R_3 , because the sole infinitesimal operator for this group, $\mathbf{V}^{(1)}$, requires that $L' = L$. However, for G_2 , we must also include the operator $\mathbf{V}^{(5)}$, which has nonzero matrix elements between ${}^3P$ and ${}^3H$. There is no coupling between ${}^3F$ and either of these states though, so we conclude that the 3 states $|{}^3P, m_L\rangle$ and 11 states $|{}^3H, m_L\rangle$ form a basis for a representation of G_2 between them, and the 7 states $|{}^3F, m_L\rangle$ forms a basis for another representation of G_2 . The 14 weights of the former are plotted superposed onto the root figure of G_2 in figure C.1. We could now use the maximum weight of these to label the representation of G_2 which ${}^3P$ and ${}^3H$ share, which is (2,-1). However, as in this case, the second weight (eigenvalue of H_2) is often negative, so we use the definition $(u_1, u_2) \equiv (m_1 + m_2, -m_2)$ instead, which labels this representation $U = (11)$. The representation to which ${}^3F$ belongs is $U = (10)$, and its weights are also shown in figure C.1.

For the group R_7 , the infinitesimal operators are $\mathbf{V}^{(1)}$, $\mathbf{V}^{(3)}$, and $\mathbf{V}^{(5)}$, and we chose the following operators to define the axes in weight-space:

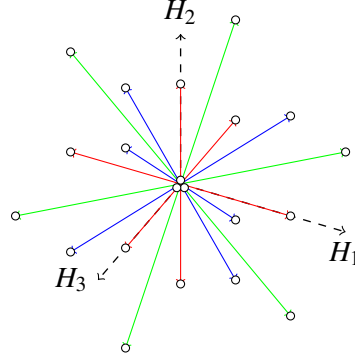


Figure C.2: Root figure for the group R_7 . Red lines denote roots $\pm \mathbf{e}_i$, blue $\pm(\mathbf{e}_i + \mathbf{e}_j)$ and green $\pm(\mathbf{e}_i - \mathbf{e}_j)$. Also shown are the weights of the irreducible representation (110).

$$\begin{aligned}
 H_1 &= 3 \sqrt{\frac{1}{7}} V_0^{(1)} + \sqrt{\frac{2}{3}} V_0^{(3)} + \sqrt{\frac{1}{21}} V_0^{(5)} \\
 H_2 &= 2 \sqrt{\frac{1}{7}} V_0^{(1)} - \sqrt{\frac{2}{3}} V_0^{(3)} - 4 \sqrt{\frac{1}{21}} V_0^{(5)} \\
 H_3 &= \sqrt{\frac{1}{7}} V_0^{(1)} - \sqrt{\frac{2}{3}} V_0^{(3)} + 5 \sqrt{\frac{1}{21}} V_0^{(5)}
 \end{aligned} \tag{C.5}$$

There are now 54 equations of the form C.4 defining 18 vectors in the three dimensional weight space which together form the root figure shown in Fig. C.2. Using the coordinate system defined by equation C.5, the roots are of the form $\pm(\mathbf{e}_i - \mathbf{e}_j)$ for linear combinations of components with $q = i + j$, $\pm(\mathbf{e}_i + \mathbf{e}_j)$ for $q = j - i$, and $\pm \mathbf{e}_i$ for $q = i$ with i and $j = 1, 2, 3$.

The $W = (w_1, w_2, w_3)$ symbol for the irreducible representations of R_7 are analogous to the U symbols above and label the highest weight of each IR. The extra infinitesimal operator $\mathbf{V}^{(3)}$ means that now all three triplet states of f^2 are connected and these 21 states form a basis for the IR $W = (110)$ of R_7 , which is also shown in figure C.2.

C.1.2 Branching Rules

Although the above prescription serves to introduce the labels of the irreducible representation, it would be very tedious to have to calculate all the weights of each representation in order to assign the highest weight as a label for every state of a particular l^n configuration. Fortunately, because each of the groups we have chosen are in turn subgroups of a larger group and the combined spin and orbital wavefunctions of the allowed states are required to be antisymmetric, there are simple rules for how the irreducible representations of a group decomposes into IRs of the subgroup below it, in the chain C.3.

S	U_7	R_7 ($w_1 w_2 w_3$)	G_2 ($u_1 u_2$)	R_3 L	Term Symbol
	$[\lambda_1 \lambda_2 \dots]$				
1	[11]	(110)	(10)	F	^3F
			(11)	P, H	$^3P, ^3H$
0	[2]	(000)	(00)	S	^1S
		(200)	(20)	D, G, I	$^1D, ^1G, ^1I$

Table C.1: *Branching rules for the f^2 configuration.*

These *branching rules* may be calculated using the standard methods of group theory, first by calculating the *characters* of the IRs of both the parent group and its subgroup. The sum of the characters of the IRs of the subgroup to which a particular IR of the parent group decomposes is then required to be equal to the character of that IR. That is if an IR A of group G decomposes into many different IRs B_H of group $\mathcal{H}$, then $\chi(A) = \sum_H c_H \chi(B_H)$ where $\chi(A)$ is the character of the IR A and c_H is the number of times the IR B_H occurs in the decomposition. The formulae for the characters of the groups in the sequence C.3 is given by Judd (1963). Finally, there are other methods which takes advantage of the simplicity of the group R_3 and the decomposition of IR of higher groups with respect to R_3 in order to calculate the decomposition of the same IR with respect to R_7 or G_2 , but we shall not delve into these calculations.

The only remaining task to determine to which IR of the highest group in the sequence C.3 the states of an l^n configuration fall into. This group is U_7 , and its infinitesimal operators are all tensors $\mathbf{V}^{(k)}$ with $0 \leq k \leq 2l$. These tensor operators all commute with $\mathbf{S}$ so we expect the $|S, m_S\rangle$ states of a given S to form a basis for a single IR of U_7 . In addition, if we re-express the infinitesimal operators as a particular linear combination of $\mathbf{V}^{(k)}$, then the determinantal product states $\Pi_i |l_i, m_i\rangle$ are eigenfunctions of these linear combinations.⁴ This means that the weights of an IR of U_7 may be calculated in a straightforward manner from the determinantal product states. These weights are a series of $2l + 1$ integers which are either 0, 1 or 2. The number of electrons n is the sum of these integers and S is half the number of 1's which occur. Finally, tables of the branching rules for $U_7 \rightarrow R_7$, $R_7 \rightarrow G_2$ and $G_2 \rightarrow R_3$ are given by Judd (1963).

We can now label all the allowed states of an f^n configuration by first determining the allowed values of S , and thus the IR of U_7 , and from the branching rules determine the allowed IR of the subgroups R_7 , G_2 and R_3 . The states of f^2 is given in table C.1 as an example.

⁴See Judd (1963), section 5-6, equation 5-30.

C.2 The Coefficients of Fractional Parentage

We may construct a state of the configuration l^n from a known state of l^{n-1} by adding a single electron state for the n^{th} electron. Denoting $|\Omega\rangle = |WU\tau SLm_Sm_L\rangle$ for the state so constructed, $|\bar{\Omega}\rangle$ for the parent state of l^{n-1} , $|\omega\rangle$ for a one-electron state and $|\omega_n\rangle$ for the n^{th} single-electron state,

$$|\Omega\rangle = \sum_{\bar{\Omega}, \omega} \langle \bar{\Omega}; \omega | \Omega \rangle |\bar{\Omega}\rangle |\omega_n\rangle \quad (\text{C.6})$$

Furthermore, because the matrix element for a single particle operator $V = \sum_i v_i$ for n electrons is just n times the matrix element of the one-electron operator,

$$\langle \Omega | V | \Omega' \rangle = n \langle \Omega | v_n | \Omega' \rangle$$

substituting in the expansion C.6,

$$\langle \Omega | V | \Omega' \rangle = n \sum_{\bar{\Omega}, \omega, \omega'} \langle \Omega | \bar{\Omega}; \omega \rangle \langle \omega | v_n | \omega' \rangle \langle \bar{\Omega}; \omega' | \Omega' \rangle \quad (\text{C.7})$$

The matrix elements $\langle \omega | v_n | \omega' \rangle$ of a one-electron operator between single-electron states is easily determined and all that is left is to work out the real coefficients $\langle \bar{\Omega}; \omega | \Omega \rangle = \langle \Omega | \bar{\Omega}; \omega \rangle$.

We shall now factorise these coefficients using a theorem of Racah's⁵. Let A be an IR of $\mathcal{G}$ which occurs not more than once in the decomposition of the outer product $A_1 \times A_2$, and B be an IR of $\mathcal{H}$ which is a subgroup of $\mathcal{G}$. B similarly also only occurs once in the decomposition of $B_1 \times B_2$. Finally, denoting a basis function of B by b , the theorem is,

$$\langle A_1 B_1 b_1; A_2 B_2 b_2 | A B b \rangle = \langle B_1 b_1 B_2 b_2 | B b \rangle \langle A_1 B_1 + A_2 B_2 | A B \rangle \quad (\text{C.8})$$

The coefficients $\langle A_1 B_1 b_1; A_2 B_2 b_2 | A B b \rangle$ that decompose the representations of $A_1 \times A_2$ into the IR A of $\mathcal{G}$ is the product of the coefficients $\langle B_1 b_1 B_2 b_2 | B b \rangle$ that decompose the representations of $B_1 \times B_2$ into B of $\mathcal{H}$ and another factor $\langle A_1 B_1 + A_2 B_2 | A B \rangle$ independent of b , b_1 , or b_2 . This reduction means that we can separate the coefficients $\langle \bar{\Omega}; \omega | \Omega \rangle$ which depends at present on the configuration l^n and all the quantum numbers W , U , τ , S , L , m_S , and m_L into a product of terms that each depending only pairs of these quantum numbers. Coefficients which depends only on S , L , m_S or m_L are just vector-coupling coefficients (3- j symbols), and for f -electrons the factorisation gives,

⁵See section 3, equation 11 of Racah (1949).

$$\begin{aligned}
\langle \bar{\Omega}; \omega | \Omega \rangle &= \langle \bar{W} \bar{U} \bar{\tau} \bar{L} \bar{S} \bar{m}_L \bar{m}_S; l s m_l m_s | W U \tau L S m_L m_S \rangle \\
&= \langle \bar{S} \bar{m}_S s m_s | \bar{S} s S m_S \rangle \langle \bar{L} \bar{m}_L l m_l | \bar{L} l L m_L \rangle \\
&\quad \times (\bar{U} \bar{\tau} \bar{L} + l | U \tau L) (\bar{W} \bar{U} + l | W U) (l^{n-1} \bar{v} \bar{S} + l | l^n v S) \quad (C.9)
\end{aligned}$$

The last three terms may be combined into a *coefficient of fractional parentage* $(l^{n-1} \bar{\theta} | l^n \theta)$, where $|\theta\rangle = |W U \tau L S\rangle$. $s = \frac{1}{2}$ and $l = 3 = f$ in all cases considered. Racah (1949) and Wybourne (1962) have tabulated the values of the coefficients $(\bar{U} \bar{\tau} \bar{L} + l | U \tau L)$ and $(\bar{W} \bar{U} + l | W U)$ for most of the lower lying levels of all f^n configuration, and a complete tabulation is available in the program of Allison & McNulty (1974)⁶. The final term $(l^{n-1} \bar{v} \bar{S} + l | l^n v S)$ may be calculated by an algebraic expression given by Racah (1949).

C.3 The Crystal Field Interaction

We begin discussion of the matrix elements with the crystal field interaction because the operators in this case, $T_q^{(k)}$, are proportional to the operators $V_q^{(k)}$ discussed above. From equation C.6, we get for the matrix element of $V_q^{(k)}$,

$$\begin{aligned}
\langle l^n \theta m_S m_L | V_q^{(k)} | l^n \theta' m'_S m'_L \rangle &= n \sum_{\bar{\theta}} (\theta | \bar{\theta}) (\theta' | \bar{\theta}) \langle l m_l | v_q^{(k)} | l m'_l \rangle \\
&\quad \times \sum_{m_l, \bar{m}_L, m'_l} \langle \bar{L} \bar{m}_L l m_l | \bar{L} l L m_L \rangle \langle \bar{L} \bar{m}_L l m'_l | \bar{L} l L m'_L \rangle \quad (C.10) \\
&\quad \times \sum_{m_s, \bar{m}_S, m'_s} \langle \bar{S} \bar{m}_S s m_s | \bar{S} s S m_S \rangle \langle \bar{S} \bar{m}_S s m'_s | \bar{S} s S m'_S \rangle \delta_{m_s, m'_s}
\end{aligned}$$

The sum over m_s , $\bar{m}_S$ and m'_s yields $\delta_{S, S'} \delta_{m_S, m'_S}$ due the orthogonality properties of the Wigner coefficients. This is expected because the operators $\mathbf{V}^{(k)}$ are independent of spin. We now transform to the basis with $|W U \tau S L J m_J\rangle$, by using $|\theta J m_J\rangle = \sum \langle L m_L S m_S | L S J m_J \rangle |\theta m_S m_L\rangle$, and converting all the Wigner coefficients into 3- j symbols,

⁶The program is downloadable from <http://www.cpc.cs.qub.ac.uk/cpc/> with catalogue id ACRY.

$$\begin{aligned}
\langle l^n \theta J m_J | V_q^{(k)} | l^n \theta' J' m_J' \rangle &= n \sum_{\bar{\theta}} (\theta \{ |\bar{\theta} \rangle (\theta' \{ |\bar{\theta} \rangle \langle l m_l | v_q^{(k)} | l m_l' \rangle \delta_{S,S'} \delta_{m_S, m_S'} \\
&\times \sum_{m_l, \bar{m}_L, m_l'} (-1)^{m_l + m_l'} \sqrt{(2L+1)(2L'+1)} \begin{pmatrix} \bar{L} & l & L \\ \bar{m}_L & m_l & -m_L \end{pmatrix} \begin{pmatrix} \bar{L} & l & L' \\ \bar{m}_L & m_l' & -m_L' \end{pmatrix} \\
&\times \sum_{m_S, m_L, m_S', m_L'} (-1)^{L-S+m_J+L'-S'+m_J'} \sqrt{(2J+1)(2J'+1)} \\
&\times \begin{pmatrix} L & S & J \\ m_L & m_S & -m_J \end{pmatrix} \begin{pmatrix} L' & S' & J' \\ m_L' & m_S' & -m_J' \end{pmatrix}
\end{aligned} \tag{C.11}$$

Using the Wigner-Eckart theorem, we separate the (q, m_l) -dependent part of single electron matrix element as,

$$\langle l m_l | v_q^{(k)} | l m_l' \rangle = (-1)^{l-m_l} \begin{pmatrix} l & k & l \\ -m_l & q & m_l' \end{pmatrix} \langle l || v^{(k)} || l \rangle \tag{C.12}$$

where from equation C.2 we obtain $\langle l || v^{(k)} || l \rangle = \sqrt{2k+1} \delta_{m m'} \delta_{l l'}$. We now introduce the 6- j symbol which is related to a sum of 3- j symbols by,

$$\begin{aligned}
\left\{ \begin{matrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{matrix} \right\} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} &= \sum_{\mu_1, \mu_2, \mu_3} (-1)^{l_1+l_2+l_3+\mu_1+\mu_2+\mu_3} \\
&\times \begin{pmatrix} j_1 & l_2 & l_3 \\ m_1 & \mu_2 & -\mu_3 \end{pmatrix} \begin{pmatrix} l_1 & j_2 & l_3 \\ -\mu_1 & m_2 & \mu_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & j_3 \\ \mu_1 & -\mu_2 & m_3 \end{pmatrix}
\end{aligned} \tag{C.13}$$

where the curly brackets indicates the 6- j symbol. The 3- j symbol of equation C.12 is substituted into the orbital sum in equation C.11 and yields a 6- j symbol and another 3- j symbol, $\begin{pmatrix} L & k & L' \\ -m_L & q & m_L \end{pmatrix}$, which satisfies the Wigner-Eckart theorem for the matrix element $\langle \Omega | V_q^{(k)} | \Omega' \rangle$. This is then included in the second sum and another application is made of equation C.13 to give, after some rearrangement of the columns of the 3- j symbols,

$$\begin{aligned}
\langle WU\tau SLJm_J | V_q^{(k)} | W'U'\tau' SL'J'm'_J \rangle &= (-1)^{J-m_J-q} \begin{pmatrix} J' & k & J \\ -m_J & q & m'_J \end{pmatrix} \langle \theta || V^{(k)} || \theta' \rangle \\
\langle \theta J || V^{(k)} || \theta' J \rangle &= n \sum_{\bar{\theta}} (\theta \{ | \bar{\theta} \}) (\theta' \{ | \bar{\theta} \}) \langle l || v^{(k)} || l \rangle \\
&\quad \times (-1)^{\bar{L}+L+k+l} \sqrt{(2L+1)(2L'+1)} \begin{Bmatrix} L' & k & L \\ l & \bar{L} & l \end{Bmatrix} \\
&\quad \times (-1)^{k+S+L+J} \sqrt{(2J+1)(2J'+1)} \begin{Bmatrix} J' & k & J \\ L & S & L' \end{Bmatrix}
\end{aligned} \tag{C.14}$$

The sum over $\bar{\theta}$ only includes the first 6- j symbol, and these terms may be taken out and grouped together as the reduced matrix element $\langle \theta || V^{(k)} || \theta \rangle$.

In order to obtain the matrix elements $\langle \theta J m_J | T_q^{(q)} | \theta' J' m'_J \rangle$ required in section 2.6 we replace the reduced matrix element $\langle l || v^{(k)} || l \rangle$ with (Wybourne, 1965),

$$\langle l || t^{(k)} || l \rangle = (-1)^l (2l+1) \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} \tag{C.15}$$

and in order to obtain the matrix elements $\langle \theta J m_J | U_q^{(q)} | \theta' J' m'_J \rangle$ as tabulated by Neilson & Koster (1963) or given by Elliot et al. (1957), we replace $\langle l || v^{(k)} || l \rangle$ by $\langle l || u^{(k)} || l \rangle = \delta_{nn'} \delta_{ll'}$. This procedure may be followed for any other single-particle operator.

C.4 The Zeeman Interaction

The Zeeman interaction is given by equation 2.14, so the matrix element we need to calculate is for the one electron operator $\mathbf{L} + g\mathbf{S}$. Using the techniques of the previous section, we can calculate the matrix element for $\mathbf{L}$ and $\mathbf{S}$ separately, with the reduced matrix elements (Wybourne, 1965),

$$\begin{aligned}
\langle l || l || l \rangle &= \sqrt{l(l+1)(2l+1)} \\
\langle s || s || s \rangle &= \sqrt{s(s+1)(2s+1)}
\end{aligned} \tag{C.16}$$

However the expressions C.14 may be greatly simplified in this case because both operators are diagonal in $\theta = W, U, \tau, S, L$. In addition, the rank k of the operator is 1, so we may use an algebraic expression for this special case of the 6- j symbol to evaluate the sum over $\bar{\theta}$ explicitly,

yielding (Judd, 1963),

$$\sum_{\bar{\theta}} (\theta \{|\bar{\theta}\rangle)(\theta' \{|\bar{\theta}\rangle)(-1)^{\bar{L}} \left\{ \begin{matrix} L & 1 & L \\ l & \bar{L} & l \end{matrix} \right\} = \delta_{\theta\theta'} \frac{1}{n} \frac{1}{(-1)^L (2L+1)} \frac{\langle L||L||L \rangle}{\langle l||l||l \rangle}$$

where the $\delta_{\theta\theta'}$ follows from the orthonormality relation of the cfp. A similar reduction also occurs for the operator $\mathbf{S}$.

Thus, we may remove the sum over the fractional parentage coefficients in equation C.14, yielding,

$$\begin{aligned} \langle \theta J || L + gS || \theta' J' \rangle &= (-1)^{k+S+L+J} \sqrt{(2J+1)(2J'+1)} \\ &\times \left[\sqrt{L(L+1)(2L+1)} \left\{ \begin{matrix} J' & 1 & J \\ L & S & L' \end{matrix} \right\} + g_s \sqrt{S(S+1)(2S+1)} \left\{ \begin{matrix} J' & 1 & J \\ S & L & S' \end{matrix} \right\} \right] \end{aligned} \quad (\text{C.17})$$

The dependence on m_J is given by the Wigner-Eckart theorem as previously, and denoting $\mu = L + gS$, the x , y , and z components are calculated from,

$$\begin{aligned} \langle \theta J m_J | \mu_{x,y} | \theta' J' m_J' \rangle &= \frac{(-1)^{J-m_J}}{\sqrt{\pm 2}} \left[\left(\begin{matrix} J' & 1 & J \\ -m_J & -1 & m_J' \end{matrix} \right) \mp \left(\begin{matrix} J' & 1 & J \\ -m_J & 1 & m_J' \end{matrix} \right) \right] \\ &\quad \times \langle \theta J || \mu || \theta' J' \rangle \\ \langle \theta J m_J | \mu_z | \theta' J' m_J' \rangle &= (-1)^{J-m_J} \left(\begin{matrix} J' & 1 & J \\ -m_J & 0 & m_J' \end{matrix} \right) \langle \theta J || \mu || \theta' J' \rangle \end{aligned} \quad (\text{C.18})$$

C.5 The Spin-Orbit Interaction

The spin-orbit operator is $\mathbf{S} \cdot \mathbf{L}$ and acts on both the spin and orbit part of the wavefunctions $|\theta\rangle$.

In order to accommodate this we introduce the double tensor operators with components,

$$W_{\pi q}^{(\kappa k)} = S_{\pi}^{(\kappa)} V_q^{(k)} \quad , \quad \begin{aligned} \langle s || s^{(\kappa)} || s' \rangle &= \sqrt{2\kappa+1} \delta_{ss'} \\ \langle sl || w^{(\kappa k)} || s'l' \rangle &= \sqrt{(2\kappa+1)(2k+1)} \delta_{ss'} \delta_{ll'} \end{aligned}$$

which acts like a tensor of rank κ with respects to the spin coordinates and like a tensor of rank k on the orbital coordinates. The spin orbit operator corresponds to $W^{(11)}$. In an analogous way to the derivation of the matrix elements of $V^{(k)}$, we can derive the matrix elements of $W^{(\kappa k)}$, which is (Elliot et al., 1957),

$$\begin{aligned}
\langle \theta | W^{(\kappa k)} | \theta' \rangle &= n \sqrt{(2L+1)(2L'+1)(2S+1)(2S'+1)(2\kappa+1)(2k+1)} \\
&\times \sum_{\bar{\theta}} (\theta \{ | \bar{\theta} \}) (\theta' \{ | \bar{\theta} (-1)^{\bar{S}+S+s+\bar{L}+L+l+\kappa+k} \\
&\times \begin{Bmatrix} S & \kappa & S' \\ s & \bar{S} & s \end{Bmatrix} \begin{Bmatrix} L & k & L' \\ l & \bar{L} & l \end{Bmatrix} \quad (C.19)
\end{aligned}$$

with the spin orbit matrix elements being,

$$\begin{aligned}
\langle \theta J m_J | \sum \mathbf{s} \cdot \mathbf{l} | \theta J' m_J' \rangle &= \delta_{JJ'} \delta_{m_J m_J'} (-1)^{S'+L+J} \sqrt{\frac{1}{6} l(l+1)(2l+1)} \\
&\times \begin{Bmatrix} S & 1 & S' \\ L' & J & L \end{Bmatrix} \langle \theta | W^{(11)} | \theta' \rangle \quad (C.20)
\end{aligned}$$

C.6 The Coulomb Interaction

Returning to the expression for the Coulomb interaction from Chapter 2,

$$\mathcal{H}_C = \sum_{i>j} \frac{e^2}{r_{ij}}$$

we express the denominator r_{ij} as a multipole expansion in terms of Legendre polynomials,

$$\frac{1}{r_{ij}} = \frac{1}{(r_i^2 + r_j^2 + 2r_i r_j \cos \omega)^{1/2}} = \sum_k \frac{r_{<}^k}{r_{>}^{k+1}} P_k(\cos \omega)$$

where $r_{<}$ is the lesser, and $r_{>}$ the greater of r_i and r_j respectively. Using the spherical harmonics addition theorem, the Legendre polynomial may be expressed as,

$$P_k(\cos \omega) = \frac{4\pi}{2k+1} \sum_q Y_{kq}^\dagger(\theta_i, \phi_i) Y_{kq}(\theta_i, \phi_i)$$

Thus the Coulomb interaction may be expressed as,

$$\mathcal{H}_C = e^2 \sum_{ij} \sum_k \frac{r_{<}^k}{r_{>}^{k+1}} \mathbf{T}_i^{(k)} \cdot \mathbf{T}_j^{(k)} \quad (C.21)$$

where the tensor operators $\mathbf{T}^{(k)}$ are defined in equation 2.10 in section 2.2. We can subsume the

term in r_i and r_j into the *Slater integrals* which may be calculated by ab-initio methods, or in our case will be treated as parameters fitted from experimentally measured atomic spectra,

$$F^k = e^2 \int_0^\infty \int_0^\infty \frac{r_i^k}{r_{ij}^{k+1}} (R_{nl}(r_i)R_{nl}(r_j))^2 dr_i dr_j \quad (\text{C.22})$$

So, in terms of the Slater integrals, the Coulomb Hamiltonian is,

$$\mathcal{H}_C = \sum_k F^k \sum_{ij} \mathbf{T}_i^{(k)} \cdot \mathbf{T}_j^{(k)} = \sum_k F^k f^k \quad (\text{C.23})$$

with,

$$f^k = \sum_{ij} \mathbf{T}_i^{(k)} \cdot \mathbf{T}_j^{(k)} \quad (\text{C.24})$$

where i and j denote the electron number rather than the operator order.

Whilst we can use tensor operator techniques to calculate the matrix elements of $\mathbf{T}_i^{(k)} \cdot \mathbf{T}_j^{(k)}$, this becomes tedious as the shell becomes closer to half filling and the number of terms in the summation of i and j increases. Instead, we shall simplify the operators f^k using their transformation properties under the continuous groups G_2 , R_7 , and Sp_{4l+2} .

Now, we note that in order for the operators $T_q^{(k)}$ to transform in the same way as the spherical harmonics functions under the action of the operators of R_3 , they must have commutators that satisfy,

$$[J_z, T_q^{(k)}] = q T_q^{(k)} \quad , \quad [J_\pm, T_q^{(k)}] = \sqrt{k(k+1) - q(q \pm 1)} T_{q \pm 1}^{(k)}$$

whilst the actions of infinitesimal operators of R_3 on the wavefunctions $|J = k, m_J = q\rangle$ is very similar,

$$J_z |k, q\rangle = q |k, q\rangle \quad , \quad J_\pm |k, q\rangle = \sqrt{k(k+1) - q(q \pm 1)} |k, q \pm 1\rangle$$

and conclude from this that the operators $T_q^{(k)}$ transform according to the same representation of R_3 for which the wavefunctions $|k, q\rangle$ serve as a basis. Thus we can classify the operators $T_q^{(k)}$ by the representations of R_3 to which the basis states belong, namely $\mathcal{D}_L$, or the quantum number L .

In order to apply this more generally, we return to the double tensor operators defined in the previous section. These operators have commutation relation of same the form as equation C.1

and so their components must be infinitesimal operators of some continuous group, which turns out to be U_{4l+2} . By a process analogous to that in section C.1, restricting the rank $\kappa + k$ to be odd gives the infinitesimal operator of a subgroup, Sp_{4l+2} .

Working out the commutation relations of these infinitesimal operators $W_{\pi q}^{(\kappa k)}$, and their actions on the state $|S = \kappa, L = k, m_S = \pi, m_L = q\rangle$ of l^2 , we find that it is similar to the set of equations above for $T_q^{(k)}$ and $|k, q\rangle$ (Judd, 1963). Thus we can use the representations of the group Sp_{4l+2} or its subgroups for restricted values of κ and k for which the wavefunctions of l^2 serve as basis to classify the operators $W_{\pi q}^{(\kappa k)}$.

We now return to equation C.24, where for f -electrons the sum is over even $k \leq 2l = 6$. The operators $\mathbf{T}^{(k)}$ are special cases of $\mathbf{W}^{(0k)}$. With these restrictions, the operators $\mathbf{W}^{(0k)}$ form infinitesimal operators of R_7 and G_2 , and in fact the three operators with $k = 2, 4, 6$ form the components of the generalised tensor operator which transform according to the IR (200) of R_7 and (20) of G_2 , denoted (200)(20).

The representation according to which the two particle operators $\mathbf{T}_i^{(k)} \cdot \mathbf{T}_j^{(k)}$ transform is given by the decomposition of outer product (200) $\times$ (200) and (20) $\times$ (20), which is the set (000)(00), (400)(40), (220)(22) (Judd, 1963). Racah (1949) determined which linear combinations of the operators f^k would give operators which transform according to a single representation in this set, which are as follows,

$$\begin{aligned} e_0 &= f^0 = n(n-1)/2 \\ e_1 &= \frac{9}{7}f^0 + \frac{1}{42}f^2 + \frac{1}{77}f^4 + \frac{1}{462}f^6 \\ e_2 &= \frac{143}{42}f^2 - \frac{130}{77}f^4 + \frac{35}{462}f^6 \\ e_3 &= \frac{11}{42}f^2 + \frac{4}{77}f^4 - \frac{7}{462}f^6 \end{aligned} \tag{C.25}$$

where e_0 and e_1 transform according to (000)(00), and hence are diagonal in all quantum numbers; e_2 transforms according to (400)(40) and e_3 according to (220)(22). Racah showed that the matrix elements of e_0 and e_1 are,

$$\begin{aligned}
e_0 &= \frac{1}{2}n(n-1) \\
e_1 &= \frac{9}{2}(n-\nu) + \frac{1}{4}\nu(\nu+2) - S(S+1)
\end{aligned} \tag{C.26}$$

where ν is the seniority number and is related to the W quantum number.

For e_2 , the representation (400) means that it is diagonal in W , whilst there are no such simple restrictions for e_3 . For their matrix elements, we appeal to the Wigner-Eckart theorem, but in a modified form. Starting from the expression 2.8,

$$\int \phi_i^\dagger h_j \theta_k d\tau = \sum_{\beta} A_{\beta}(\Gamma_I i \beta | \Gamma_J j; \Gamma_K k)$$

we note that there maybe other sets of basis functions than ϕ_i for the IR Γ_I , or ψ_j for Γ_J , and rewrite equation 2.8 with superscripts to distinguish quantities which may have identical transformation properties,

$$\int \phi_i^{\dagger a} h_j^b \theta_k^c d\tau = \sum_{\beta} A_{\beta}(a, b, c)(\Gamma_I i \beta | \Gamma_J j; \Gamma_K k)$$

The sum over β now comprises c_I terms, where c_I is the number of times the IR Γ_I occurs in the decomposition of $\Gamma_J \times \Gamma_K$. Thus, every set of matrix elements $\int \phi_i^{\dagger a} h_j^b \theta_k^c d\tau$ for a particular a, b , or c may be expressed as a sum over c_I other independent set of integrals,

$$\int \phi_i^{\dagger a} h_j^b \theta_k^c d\tau = \sum f_{uvw}^{abc} \int \phi_i^{\dagger u} h_j^v \theta_k^w d\tau \tag{C.27}$$

Using this equation for the operator e_2 , we obtain,

$$\langle WU\tau SL | e_2 | WU'\tau' SL \rangle = f(S) \sum_{\gamma} x_{\gamma}(W, UU') \langle U\tau | \chi_{\gamma}(L) | U'\tau' \rangle \tag{C.28}$$

where $f(S) = \pm 1$ depending on whether $\nu + 2S$ is greater or less than 7. Except for $U = U' = (21)$, the sum over γ has just a single term. The coefficients $x_{\gamma}(W, UU')$ and matrix elements $\langle U\tau | \chi_{\gamma}(L) | U'\tau' \rangle$ are tabulated by Racah (1949).

For e_3 , Racah (1949) showed it is simpler to compute the matrix element of the operator $e_3 + \Omega$, where $\Omega = 11(\mathbf{T}^{(1)})^2 - 3(\mathbf{T}^{(5)})^2$ which transform according to (220)(22) as well. It turns out that the sum in C.27 reduces to a single term, giving

$$\langle f^n \nu U \tau SL | e_3 | f^n \nu' U' \tau' SL \rangle = y(f^n, \nu SU, \nu' SU') \langle U | \phi(L) | U' \rangle \quad (\text{C.29})$$

and again, the coefficients $y(f^n, \nu SU, \nu' SU')$ and matrix elements $\langle U | \phi(L) | U' \rangle$ are tabulated.

Appendix D

Resonant X-ray Scattering

The expressions for the scattering factor for resonant magnetic x-ray scattering is derived in this appendix. The main results have been quote already in section 3.3 but their derivation is reproduced here for the interested reader. These expressions were first derived mainly by Blume and co-workers in a series of papers (Blume, 1985; Hannon et al., 1988; Blume, 1994) with the polarisation dependence worked out by Blume & Gibbs (1988) and Hill & McMorow (1996). The azimuth calculations follow the framework of Wilkins et al. (2004) and Walker (2006).

D.1 The Electron-Photon Interaction

In order to incorporate the interaction of the electrons around an atom in the sample with the electric and magnetic fields of the incident photon, we modify the free electron Hamiltonian by replacing the momentum of the electron $\mathbf{p}$ by $\mathbf{p} - q\mathbf{A}$ ¹. This incorporates the vector potential $\mathbf{A}$, from which the electric field is derived as $\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t}$ and the magnetic field as $\mathbf{B} = \nabla \times \mathbf{A}$, into the expression for the kinetic energy of the electron $\frac{(\mathbf{p} - e\mathbf{A})^2}{2m}$. In addition, we also include by hand the Zeeman interaction between the electronic spin and first, the magnetic field of the photon, and second, the magnetic field induced by motion of the electrons themselves due to the photon's *electric* field, which is called the spin-orbit term in analogy with atomic physics (Lovesey & Collins, 1995). The Hamiltonian for the j^{th} atom is thus,

$$\mathcal{H}_j = \frac{(\mathbf{p} - e\mathbf{A})^2}{2m} - g_s \mu_B \mathbf{S} \cdot \left[\nabla \times \mathbf{A} + \frac{1}{2mc^2} (\mathbf{p} - e\mathbf{A}) \times \mathbf{E} \right]$$

where the last term in the square brackets comes from the expression of the magnetic field in the rest frame of the moving electron due to its motion, $\mathbf{B} = \mathbf{v} \times \mathbf{E}/c^2$. On multiplying out the square

¹We shall be using SI units for all equations in this work. The reader is advised that many of the references use cgs units, however.

in the first term on the right hand side, we get the original free electron kinetic energy $\frac{\mathbf{p}^2}{2m}$ and also the interaction Hamiltonian between the electron and photon. In addition we also multiply out the second term in the bracket and substitute $-\dot{\mathbf{A}}$ for $\mathbf{E}$, ignoring the actual spin orbit term (i.e. the term involving only the momentum of the electron). We substitute the expression $e\hbar/2m$ for the Bohr magneton, and set $g_s = 2$, to get the perturbation Hamiltonian (Blume, 1985):

$$\mathcal{H}_I = \sum_j \left[\underbrace{\frac{e\mathbf{A}(\mathbf{r}_j) \cdot \mathbf{p}_j}{m}}_{\mathcal{H}_1} + \underbrace{\frac{e^2 A^2(\mathbf{r}_j)}{2m}}_{\mathcal{H}_2} - \underbrace{\frac{e\hbar}{m} \mathbf{S}_j \cdot \nabla \times \mathbf{A}(\mathbf{r}_j)}_{\mathcal{H}_3} - \underbrace{\frac{e\hbar}{m} \frac{e}{2mc^2} \mathbf{S}_j \cdot (\dot{\mathbf{A}}(\mathbf{r}_j) \times \mathbf{A}(\mathbf{r}_j))}_{\mathcal{H}_4} \right] \quad (\text{D.1})$$

Using Fermi's Golden Rule, and second order perturbation theory with $\mathcal{H}_I$ as the perturbing Hamiltonian, we find that the transition probability is:

$$W = \frac{2\pi}{\hbar} \left| \langle f | \mathcal{H}_I | i \rangle + \sum_n \frac{\langle f | \mathcal{H}_I | n \rangle \langle n | \mathcal{H}_I | i \rangle}{E_a - E_n} \right|^2 \quad (\text{D.2})$$

The double differential cross section is obtained by multiplying the transition probability W by the density of final states, $\rho(E_f)$ and dividing by the incident flux.

$$\frac{d^2\sigma}{d\Omega dE} = \frac{W\rho(E_f)}{I_0} \quad \text{where} \quad \rho(E_f) = \frac{V}{(2\pi)^3} \frac{\omega_{\mathbf{k}'}^2}{\hbar c^3} \quad \text{and} \quad I_0 = \frac{c}{V}$$

so,

$$\frac{d^2\sigma}{d\Omega dE} = \left(\frac{V\omega}{2\pi\hbar c^2} \right)^2 \left| \langle f | \mathcal{H}_I | i \rangle + \sum_n \frac{\langle f | \mathcal{H}_I | n \rangle \langle n | \mathcal{H}_I | i \rangle}{E_a - E_n} \right|^2 \quad (\text{D.3})$$

whilst the differential cross section, $\frac{d\sigma}{d\Omega}$ is obtained from this equation in the case where $|i\rangle = |f\rangle$. The scattering amplitude is defined by $\left(\frac{d\sigma}{d\Omega}\right)^{1/2} = r_0 \sum_j e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_j} f_j(\mathbf{k}, \mathbf{k}', \hbar\omega)$, and is the Fourier transform of the form factor for the j^{th} electron, f_j .

D.2 The Non-resonant Magnetic Scattering Amplitude

Now, in order to proceed further we have to quantise the vector potential. This may be done first by writing $\mathbf{A}$ as a Fourier series of plane waves (Als-Nielsen & McMorrow, 2001),

$$\mathbf{A}(\mathbf{r}_j, t) = \sum_u \sum_{\mathbf{k}} \sqrt{\frac{\hbar}{\epsilon_0 V \omega_{\mathbf{k}}}} \left[\hat{\mathbf{e}}_{u\mathbf{k}} a_{u\mathbf{k}} e^{i(\mathbf{k} \cdot \mathbf{r}_j - \omega_{\mathbf{k}} t)} + \hat{\mathbf{e}}_{u\mathbf{k}}^* a_{u\mathbf{k}}^* e^{-i(\mathbf{k} \cdot \mathbf{r}_j - \omega_{\mathbf{k}} t)} \right] \quad (\text{D.4})$$

where $\hat{\mathbf{e}}_{u\mathbf{k}}$ is the unit polarisation vector corresponding to the $\mathbf{k}^{\text{th}}$ Fourier component and u labels two orthogonal polarisations (such as parallel or perpendicular to the scattering plane or left and right circular). Differentiating this expression twice with respects to time we find that $\ddot{\mathbf{A}}_k = -\omega_k^2 \mathbf{A}_k$ which is identical to the equation of motion of a harmonic oscillator, $\ddot{x} + \omega_0^2 x = 0$. We can thus identify the vector potential with a sum of harmonic oscillators. Furthermore we may calculate the energy of the photon from the modulus squared of the electric field, $\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t}$, which turns out to be $\hbar\omega a_{\mathbf{k}}^* a_{\mathbf{k}}$. This is equivalent to the energy of a harmonic oscillator, $\mathcal{H} = \hbar\omega(a^\dagger a + \frac{1}{2})$, and so we also identify the coefficients $a_{\mathbf{k}}^*$ and $a_{\mathbf{k}}$ with the creation and annihilation operators $a^\dagger$ and a .

The vector potential is thus linear in the creation and annihilation operators. Returning to equation D.2 we see that to first order, the first term in equation D.1, $\mathcal{H}_1$, is linear in $\mathbf{A}$ and thus may only result in the creation or destruction of a photon. Physically this usually corresponds to photoelectric absorption. The $\mathcal{H}_2$ term, however, is quadratic in $\mathbf{A}$ and hence in the creation and annihilation operators. This means that interactions involving this term will allow the simultaneous destruction of one photon in a particular state with polarisation $\hat{\mathbf{e}}_{u\mathbf{k}}$ and wavevector $\mathbf{k}$, and creation of another photon in a different state $\hat{\mathbf{e}}'_{u'\mathbf{k}'}$ and $\mathbf{k}'$. For the elastic case this corresponds to classical Thomson scattering. In general for scattering we need terms in the Hamiltonian which are quadratic in $\mathbf{A}$, and this can be achieved by taking $\mathcal{H}_2$ and $\mathcal{H}_4$ to first order and $\mathcal{H}_1$ and $\mathcal{H}_3$ to second order in perturbation, so the transition probability is now,

$$W = \frac{2\pi}{\hbar} \left| \langle f, \hat{\mathbf{e}}'_{u'\mathbf{k}'} | \mathcal{H}_2 + \mathcal{H}_4 | i, \hat{\mathbf{e}}_{u\mathbf{k}} \rangle + \sum_n \frac{\langle f, \hat{\mathbf{e}}'_{u'\mathbf{k}'} | \mathcal{H}_1 + \mathcal{H}_3 | n \rangle \langle n | \mathcal{H}_1 + \mathcal{H}_3 | i, \hat{\mathbf{e}}_{u\mathbf{k}} \rangle}{E_a + \hbar\omega_k - E_n} \right|^2 \quad (\text{D.5})$$

$$\times \delta(E_a - E_f + \hbar\omega_{\mathbf{k}} - \hbar\omega_{\mathbf{k}'})$$

where $|i(f), \hat{\mathbf{e}}_{u\mathbf{k}}^{(\prime)} \rangle$ indicates the initial (final) electronic state with an initial (final) photon polarisation and wavevector. The second order term will dominate as $\hbar\omega_k \rightarrow (E_n - E_a)$; that is, there will be a resonant enhancement in the scattering if the photon energy is the same as the energy difference between some two electronic levels in the system being probed.

We expand the first order term,

$$\langle i, \hat{\mathbf{e}}'_{\mathbf{uk}} \mathbf{k}' | \mathcal{H}_2 + \mathcal{H}_4 | i, \hat{\mathbf{e}}_{\mathbf{uk}} \mathbf{k} \rangle = \frac{e^2}{2m} \frac{\hbar}{\epsilon_0 V \omega} \left\{ \langle i | \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_j} | f \rangle \hat{\mathbf{e}}' \cdot \hat{\mathbf{e}} - \frac{\hbar}{mc^2} i \omega \langle i | \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_j} \mathbf{S}_j | f \rangle \hat{\mathbf{e}}' \times \hat{\mathbf{e}} \right\} \quad (\text{D.6})$$

where we have dropped the subscripts on the frequency and polarisation vectors, $\mathbf{K} = \mathbf{k} - \mathbf{k}'$, and $\hat{\mathbf{e}}^{(l)}$ is the incident (scattered) polarisation. The first term on the right represent Thomson charge scattering whilst the second term contributes to the non-resonant magnetic scattering cross section, and depends on the Fourier transform of the spin density $\sum_j e^{i\mathbf{K} \cdot \mathbf{r}_j} \mathbf{S}_j$. In addition we shall see that there is also another term proportional to the Fourier transform of the orbital magnetization density which comes from the second order $\mathcal{H}_3$ term in equation D.1. Turning to these second order terms, we divide them into those where (i) the intermediate state $|n\rangle$ was initially populated by first annihilating an incident photon, in which case there will be a lifetime width Γ associated with the transition; and (ii) where the intermediate state is already populated and the "scattered" photon is created first by a de-excitation of an electron from this state (Blume, 1985),

$$\begin{aligned} & \frac{\langle f, \hat{\mathbf{e}}'_{\mathbf{uk}} \mathbf{k}' | \mathcal{H}_1 + \mathcal{H}_3 | n \rangle \langle n | \mathcal{H}_1 + \mathcal{H}_3 | i, \hat{\mathbf{e}}_{\mathbf{uk}} \mathbf{k} \rangle}{E_a + \hbar \omega_k - E_n} = \\ & \frac{e^2}{m^2} \frac{\hbar}{\epsilon_0 V \omega} \sum_n \sum_{ij} \left\{ \frac{\langle a | (\hat{\mathbf{e}}' \cdot \mathbf{p}_i - i \hbar \mathbf{S}_i \cdot (\mathbf{k}' \times \hat{\mathbf{e}}')) e^{-i\mathbf{k}' \cdot \mathbf{r}_i} | n \rangle \langle n | (\hat{\mathbf{e}} \cdot \mathbf{p}_j + i \hbar \mathbf{S}_j \cdot (\mathbf{k} \times \hat{\mathbf{e}})) e^{i\mathbf{k} \cdot \mathbf{r}_j} | b \rangle}{E_a - E_n + \hbar \omega - i \frac{\Gamma}{2}} \right. \\ & \quad \left. + \frac{\langle a | (\hat{\mathbf{e}} \cdot \mathbf{p}_j + i \hbar \mathbf{S}_j \cdot (\mathbf{k} \times \hat{\mathbf{e}})) e^{i\mathbf{k} \cdot \mathbf{r}_j} | n \rangle \langle n | (\hat{\mathbf{e}}' \cdot \mathbf{p}_i - i \hbar \mathbf{S}_i \cdot (\mathbf{k}' \times \hat{\mathbf{e}}')) e^{-i\mathbf{k}' \cdot \mathbf{r}_i} | b \rangle}{E_a - E_n - \hbar \omega} \right\} \quad (\text{D.7}) \end{aligned}$$

where we have used the result $\nabla \times \mathbf{A} = i e^{i\mathbf{k} \cdot \mathbf{r}_j} \mathbf{k} \times \hat{\mathbf{e}}$ to simplify the $\mathcal{H}_3$ term. We have also relabeled the states $|i\rangle = |a\rangle$ and $|f\rangle = |b\rangle$ on the right hand side to avoid confusion with the labels i, j for the electrons. We define an operator,

$$\hat{\mathbf{O}}(\mathbf{k}) = \sum_j e^{i\mathbf{k} \cdot \mathbf{r}_j} (\hat{\mathbf{e}} \cdot \mathbf{p}_j + i \hbar \mathbf{S}_j \cdot (\mathbf{k} \times \hat{\mathbf{e}})) \quad (\text{D.8})$$

to make the following results clearer. We now wish to obtain the orbital part of the non-resonant magnetic cross-section, and proceed by employing the approximations (Blume, 1994),

$$\begin{aligned}\frac{1}{E_a - E_n + \hbar\omega - i\frac{\Gamma}{2}} &= \left(\frac{1}{E_a - E_n + \hbar\omega - i\frac{\Gamma}{2}} - \frac{1}{\hbar\omega} \right) + \frac{1}{\hbar\omega} \\ &\approx -\frac{E_a - E_n}{\hbar\omega} \cdot \frac{1}{E_a - E_n + \hbar\omega - i\frac{\Gamma}{2}} + \frac{1}{\hbar\omega}\end{aligned}$$

where $i\frac{\Gamma}{2}$ has been neglected in the numerator because it is negligible compared to $E_a - E_n - \hbar\omega$, and

$$\begin{aligned}\frac{1}{E_a - E_n - \hbar\omega} &= \left(\frac{1}{E_a - E_n - \hbar\omega} + \frac{1}{\hbar\omega} \right) - \frac{1}{\hbar\omega} \\ &= +\frac{E_a - E_n}{\hbar\omega} \frac{1}{E_a - E_n - \hbar\omega} - \frac{1}{\hbar\omega}\end{aligned}$$

Substituting these terms back into equation D.7 we get for the terms in curly brackets

$$\begin{aligned}\sum_n \left\{ -\left(\frac{E_a - E_n}{\hbar\omega} \right) \frac{\langle a | \hat{\mathbf{O}}^\dagger(\mathbf{k}') | n \rangle \langle n | \hat{\mathbf{O}}(\mathbf{k}) | b \rangle}{E_a - E_n + \hbar\omega - i\frac{\Gamma}{2}} + \left(\frac{E_a - E_n}{\hbar\omega} \right) \frac{\langle a | \hat{\mathbf{O}}(\mathbf{k}) | n \rangle \langle n | \hat{\mathbf{O}}^\dagger(\mathbf{k}') | b \rangle}{E_a - E_n - \hbar\omega} \right. \\ \left. + \frac{1}{\hbar\omega} (\langle a | \hat{\mathbf{O}}^*(\mathbf{k}') | n \rangle \langle n | \hat{\mathbf{O}}(\mathbf{k}) | b \rangle - \langle a | \hat{\mathbf{O}}(\mathbf{k}) | n \rangle \langle n | \hat{\mathbf{O}}^*(\mathbf{k}') | b \rangle) \right\} \quad (\text{D.9})\end{aligned}$$

The final term in brackets is what we are looking for, and carrying out the sum over n by closure yields the commutator (Blume, 1985)

$$\begin{aligned}\frac{1}{\hbar\omega} \langle a | [\hat{\mathbf{O}}^\dagger(\mathbf{k}'), \hat{\mathbf{O}}(\mathbf{k})] | b \rangle &= \frac{1}{\hbar\omega} \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_j} \left\{ -\hbar(\mathbf{K} \times \mathbf{p}_j) \cdot (\hat{\mathbf{e}}' \times \hat{\mathbf{e}}) \right. \\ &\quad \left. + i\hbar^2 k^2 \mathbf{S}_j \cdot [(\hat{\mathbf{k}}' \times \hat{\mathbf{e}}')(\hat{\mathbf{k}}' \cdot \hat{\mathbf{e}}) - (\hat{\mathbf{k}} \times \hat{\mathbf{e}})(\hat{\mathbf{k}} \cdot \hat{\mathbf{e}}')] - i\hbar^2 k^2 \mathbf{S}_j \cdot (\hat{\mathbf{k}}' \times \hat{\mathbf{e}}') \times (\hat{\mathbf{k}} \times \hat{\mathbf{e}}) \right\} \quad (\text{D.10})\end{aligned}$$

where we have used Lagrange's identity $(\mathbf{a} \times \mathbf{b}) \cdot (\mathbf{c} \times \mathbf{d}) \equiv (\mathbf{a} \cdot \mathbf{c})(\mathbf{b} \cdot \mathbf{d}) - (\mathbf{a} \cdot \mathbf{d})(\mathbf{b} \cdot \mathbf{c})$ to simplify the first term, and the vector quadruple product $(\mathbf{a} \times \mathbf{b}) \times (\mathbf{c} \times \mathbf{d}) \equiv (\mathbf{a} \cdot \mathbf{b} \times \mathbf{d})\mathbf{c} - (\mathbf{a} \cdot \mathbf{b} \times \mathbf{c})\mathbf{d}$ with cyclic permutations of the scalar triple product to simplify the last term on the right hand side. $\hat{\mathbf{k}}$ is the unit vector in the direction of the wavevector and k is the wavenumber $|\mathbf{k}|$.

Comparing equation D.6 and D.10, with equation D.3 shows that the non-resonant magnetic scattering amplitude is,

$$A^{\text{mag}} = r_0 \sum_j e^{i\mathbf{k} \cdot \mathbf{r}_j} \langle a | -i \frac{\hbar \omega}{mc^2} \left(\frac{-i\mathbf{K} \times \mathbf{p}_j}{\hbar k^2} \cdot \mathbf{A} + \mathbf{S}_j \cdot \mathbf{B} \right) | b \rangle$$

where $\mathbf{A} = (\hat{\mathbf{e}}' \times \hat{\mathbf{e}})$, $\mathbf{B} = (\hat{\mathbf{e}}' \times \hat{\mathbf{e}}) + (\hat{\mathbf{k}}' \times \hat{\mathbf{e}}')(\hat{\mathbf{k}}' \cdot \hat{\mathbf{e}}) - (\hat{\mathbf{k}} \times \hat{\mathbf{e}})(\hat{\mathbf{k}} \cdot \hat{\mathbf{e}}') - (\hat{\mathbf{k}}' \times \hat{\mathbf{e}}') \times (\hat{\mathbf{k}} \times \hat{\mathbf{e}})$, $r_0 = e^2/4\pi\epsilon_0 mc^2$ is the classical electron radius², and $\omega = kc$ was used to simplify the prefactor. The matrix element is usually denoted f_j^{mag} and is the non-resonant form factor. The above expression is the starting point for the analysis of the polarization dependence of the non-resonant magnetic scattering amplitude of Blume & Gibbs (1988).

D.3 The Resonant Magnetic Scattering Amplitude

However we shall instead dwell on the terms in equation D.9 with an energy denominator³, and as we are only interested in the behaviour near resonance, where $E_n - E_a \approx \hbar\omega$, we can ignore the second term. Thus the resonant scattering amplitude is,

$$A^{\text{res}} = -\frac{r_0}{m} \sum_n \left(\frac{E_a - E_n}{\hbar\omega} \right) \frac{\langle a | \hat{\mathbf{O}}^\dagger(\mathbf{k}') | n \rangle \langle n | \hat{\mathbf{O}}(\mathbf{k}) | b \rangle}{E_a - E_n + \hbar\omega - i\frac{\Gamma}{2}} \quad (\text{D.11})$$

In order to establish a link between the preceding derivation and the well established notation of Hannon et al. (1988), we shall expand the operator D.8 in a multipole series for the electric field of the photon. That is, using a cyclic permutation of the scalar triple product we re-express the operator as,

$$\hat{\mathbf{O}}(\mathbf{k}) = \sum_j e^{i\mathbf{k} \cdot \mathbf{r}_j} \hat{\mathbf{e}} \cdot (\mathbf{p}_j + i\hbar \mathbf{S}_j \times \mathbf{k})$$

Now, we expand the exponential in terms of spherical harmonics,

$$\hat{\mathbf{O}}(\mathbf{k}) = \sum_j \left[\sum_L \sum_{M=-L}^L j_L(k_j r) Y_{LM}(\mathbf{k}) Y_{LM}(\mathbf{r}_j) \right] \hat{\mathbf{e}} \cdot (\mathbf{p}_j + i\hbar \mathbf{S}_j \times \mathbf{k}) \quad (\text{D.12})$$

where j_L is a spherical Bessel function, and Y_{LM} is a rank- L , M -component spherical harmonic function. The terms with $L = 1$ is the electric dipole, or E1, transition; whilst that with $L = 2$ is the electric quadrupole transition, E2. Further terms are small and may be neglected.

We note that in the above expression, terms which relate to the properties of the radiation, the polarisation $\hat{\mathbf{e}}$ and wavevector $\mathbf{k}$, are mixed with those which relate to the electronic system,

²Note that in cgs units, $r_0 = e^2/mc^2$

³Because of the energy dependence, these effects were first called *anomalous* scattering, in analogy to the anomalous dispersion of light in certain materials.

the position $\mathbf{r}_j$, momentum $\mathbf{p}_j$, and spin $\mathbf{S}_j$. The spin term is relatively small and may be neglected, and in order to separate the operator into a product of two quantities which each depend only on the properties of the photon or electron, we perform a recoupling (Carra & Thole, 1994),

$$\hat{\mathbf{O}}(\mathbf{k}) = \sum_j \sum_L \sum_K j_L(k_j r) \left\{ \{\hat{\mathbf{e}}, Y_L(\mathbf{k})\}^K \{\mathbf{p}, Y_L(\mathbf{r}_j)\}^K \right\}_0^0 \quad (\text{D.13})$$

where the mixed tensor operator is given by,

$$\left\{ A^{(k')}, B^{(k'')} \right\}_q^k = \sum_{q', q''} A_{q'}^{(k')} B_{q''}^{(k'')} \begin{pmatrix} k' & k'' & k \\ q' & q'' & q \end{pmatrix} \quad (\text{D.14})$$

and $\hat{\mathbf{e}}$ and $\mathbf{p}$ are rank 1 tensors (vectors), and the spherical harmonics Y_L is a rank L tensor. Thus the form factor for a particular multipole L is,

$$f_{\text{EL}}^{\text{res}} = -\frac{1}{m} \frac{E_a - E_c}{\hbar \omega} \sum_{K=0}^{2L} \left\{ T^{(K)} \langle a | F^{(K)} | a \rangle \right\}_0^0 \quad (\text{D.15})$$

with (Luo et al., 1993),

$$T_Q^{(K)} = \sqrt{\frac{2K+1}{2L+1}} \sum_{M, M'} \hat{\mathbf{e}}' \cdot \mathbf{Y}_{LM'}(\mathbf{k}') \mathbf{Y}_{LM}(\mathbf{k}) \cdot \hat{\mathbf{e}} \begin{pmatrix} L & L & K \\ M' & M & Q \end{pmatrix} \quad (\text{D.16})$$

$$F_Q^{(K)} = \sum_n \frac{E_a - E_c}{E_a - E_c + \hbar \omega - i\frac{\Gamma}{2}} \left\{ \left(J^{L'} \right)^\dagger |n\rangle \langle n| J^L \right\}_Q^K \quad (\text{D.17})$$

where J^L is the current operator which is proportional to $r^k Y_{LM}$. We have expanded out the $\{\hat{\mathbf{e}}, Y_L(\mathbf{k})\}^K$ in equation D.13 in order to derive the operator $T^{(K)}$ which Hannon et al. (1988) gives explicitly. However, our expression for $T^{(K)}$ is not the same as that of Hannon et al. (1988) because they chose not to recouple the terms in $\hat{\mathbf{e}}$ and $Y_{LM}(\mathbf{k})$, but rather simply to sum over the allowed M components of the spherical harmonics which is equivalent. There is a similar difference in basis with respects to our operator $F_Q^{(K)}$ and their $F_{LM}(\omega)$. We have chosen to express the form factor in this fashion in order to show how the terms may be used to probe different electric or magnetic multipole moments of the electron system.

Each rank K term in the sum D.15 may be related to a particular multipole of the charge or magnetisation density of the electron system. Due to the triangular condition,

$|k' - k''| \leq k \leq k' + k''$, on the 3- j symbol in equation D.14, for the electric dipole transition, where $L = 1$, we are restricted to $K = 0, 1, 2$. Following the analysis of the parity and time-reversal symmetry properties of $F^{(K)}$ by Di Mateo et al. (2005), we can identify the case of $K = 0$ with the electric charge, $K = 1$ with the magnetic dipole moment and $K = 2$ with the electric quadrupole moment. Higher order multipoles may only be probed with higher order transitions. In addition, although we have neglected it here, the sum over L in equation D.13 gives rises to cross terms, such as E1-E2, in the form factor. These terms allow different K multipole to be probed (such as an electric dipole rather than a magnetic dipole moment) due to the different symmetry properties involved. Finally, the E1-E2 terms also give rise to optical activity and non-magnetic circular dichroism (Blume, 1994).

Thus in order to observe the electric quadrupole moment of the electrons on the Uranium sites in UPd₃ we must somehow separate out the $K = 2$ term. Fortunately, the polarisation dependence of each of these terms are distinct and may be calculated by considering the $T^{(K)}$ term. Furthermore, as we are not measuring the energy dependence of the form factor, the term $F^{(K)}$ is constant, and as an azimuth scan does not change $\mathbf{k}'$ or $\mathbf{k}$, we can absorb the terms involving the spherical harmonics tensors $\mathbf{Y}_{LM}(\mathbf{k})$ into a single (constant) tensor, $\mathbf{f}$, which is (Wilkins et al., 2004)

$$\mathbf{f} = \sum_Q \left[\sum_{M, M'} \mathbf{Y}_{1'M'}(\mathbf{k}') \mathbf{Y}_{1M}(\mathbf{k}) \begin{pmatrix} 1 & 1 & 2 \\ M' & M & Q \end{pmatrix} \right] F_Q^{(2)} \begin{pmatrix} 2 & 2 & 0 \\ Q & Q & 0 \end{pmatrix} = \sum_j \mathbf{e}^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}_j} \mathbf{T}_j \quad (\text{D.18})$$

where in Cartesian coordinates,

$$T_{ij} = \frac{1}{2}(q_i q_j + q_j q_i) - \frac{1}{3} \delta_{ij} \sum_k (q_k q_k)$$