Local structure around Mn in Mn containing ZnO nanocrystals

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Received zzz, revised zzz, accepted zzz
Published online zzz

PACS 61.72.Vv, 61.72.-y, 61.46.Hk, 61.10.Ht

Among the diluted magnetic semiconductors of current interest, especially ZnO is experiencing a renaissance with the incorporation of Mn because of the recent predictions from theory. We have obtained local structure information from X-ray Absorption Spectroscopy (XAS) complementing previous electron paramagnetic resonance (EPR) studies on Mn in ZnO nanocrystals and $Zn(OH)_2$. Mn is found to be incorporated substitutionally into the ZnO nanocrystals with a sizeable distortion as compared to the regular ZnO lattice structure. Depending on the preparation of the nanocrystals Mn is found in the ZnO core as well as in a $Zn(OH)_2$ surface shell with a fraction which decreases upon annealing as the shell disintegrates forming additional ZnO. No indications for Mn clusters were found.

1 Introduction

Diluted magnetic semiconductors, either in form of thin films or in form of nanostructures have been of great interest in the last years due to the combined magnetic properties from the magnetic elements and the transport properties from the carriers of the host. Especially ZnO is experiencing a renaissance with the incorporation of Mn because of the recent predictions of a high Curie temperature [1]. The contributions to the latest international conference on spintronics in semiconductors underline the increase of the importance of the ZnMnO system [2]. Obviously, there is an urgent need to understand the basic atomic structure of Mn in ZnO for future applications. However, we noticed that except for the very early work by Dorain [3] information about the symmetry and electronic structure of Mn in ZnO is lacking, and until now there is no work reported on ZnO:Mn nanocrystals. To probe the symmetry and electronic structure of the ground state Mn^{2+} in ZnO nanocrystals, we have conducted electron paramagnetic resonance (EPR) measurements. Three distinct EPR signals could be detected. In accordance with the preparation of the Mn doped nanocrystals we could make the following assignments [4]: One fraction revealed Mn ions in hexagonal structure with a hyperfine coupling constant close to that of Mn in bulk ZnO. We have therefore associated this fraction with substitutional Mn in the ZnO core. The second part was interpreted as Mn in $Zn(OH)_2$ as a surface shell around the ZnO core because of the larger coupling constant and the decreasing fraction upon annealing. The origin of the third component is less clear and was tentatively interpreted as originating from Mn clusters or dipole-dipole interactions.

In this contribution we complement the earlier EPR investigation with X-ray absorption experiments which were performed to obtain more direct information on the local atomic arrangement of the Mn atom

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incorporated in nanocrystalline ZnO. With extended absorption fine structure spectroscopy (EXAFS) local distances, bond length and coordination, are determined. Additional information is provided in the near-edge region of the absorption (x-ray absorption near edge spectroscopy, XANES) which is influenced by the electronic structure thereby reflecting the electronic bond situation (chemical effect). Therefore absorption spectroscopy is expected to allow to provide independent support for the assignments based on the EPR experiments and to additionally test the occurrence of clusters.

2 Experiment

The ZnO nanocrystals were prepared from of Zn nitrate (containing additional Mn nitrate for doping) in alcoholic solution and NaOH in alcoholic solution, as described in greater detail in [4]. The resultant nanocrystals of ZnO containing Mn with different concentrations gave similar results both in X-ray diffraction and in Raman spectroscopy as the undoped system studied earlier [5]. The average particle size of the doped nanocrystals varied from the as-grown 5 nm in diameter to 10 nm in the sample annealed up to 773 K. The Mn concentration was checked by electron energy dispersion spectroscopy. In the present study concentrations of 5 and 11 % were used.

We have measured the X-ray absorption at the K-edge on both cations, Zn and Mn, in the fluorescence yield mode at the E4-beamline of HASYLAB at DESY. The fluorescence was detected in line with the polarisation vector of the incoming synchrotron radiation using a 7-segments Ge detector. As samples we mixed the Mn doped or undoped nanocrystalline ZnO, resp., as well as $Zn(OH)_2$ samples with graphite and polyethylene, and pressed the powder into pellets. To follow the changes with annealing temperature samples made out of the powder as prepared (unannealed), and out of the powder annealed at 423 K, 573 K, and 773 K were measured. For the measurements, the samples were mounted on a cold finger of a liquid nitrogen cryostat, keeping the temperature at approximately 78 or 300 K.

The analysis of the observed absorption spectra was done following the standard FEFF procedure [6, 7] including the background treatment with AUTOBK [8].

3 Results and discussions

To illustrate the quality of the samples and the procedure in the EXAFS analysis we present the radial distribution function, i.e. the Fourier transform of the EXAFS spectrum x(k), linearly weighted with k, for Zn in ZnO with 5 % Mn, annealed at 773 K and measured at approximately 100 K in Fig.1. The coordination shell distances were fixed and taken from the standard wurtzite bulk ZnO data. A clear signature for the nanometer crystal size is the relative height of the first (around 1.5 Å) and second peak (close to 3 Å) which is reversed as compared to bulk ZnO where the second peak is much higher than the first due to the large difference in Z between O and Zn.

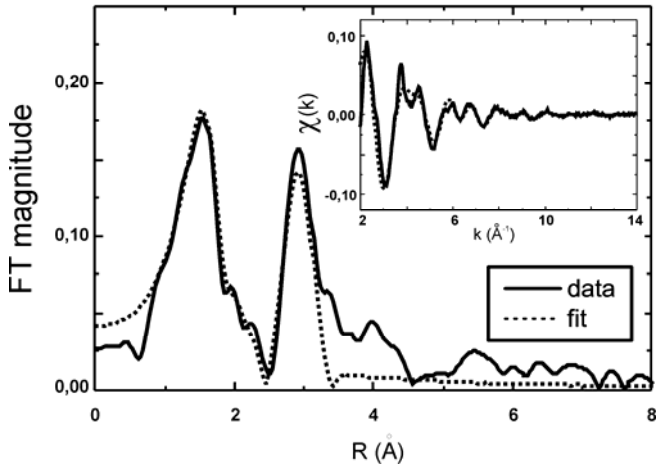

Fig. 1 Radial distribution function i.e. Fourier transform of the k-weighted EXAFS spectrum (insert) for Zn in nanocrystalline ZnO with 5 % Mn, measured at 100 K (annealing temperature in preparation 773 K). The fit was obtained leaving the distances and coordinations as taken from the ZnO lattice parameters fixed.

A comparison of such Zn EXAFS spectra for polycrystalline, high purity ZnO with nanocrystalline ZnO annealed at the different temperatures, and of $Zn(OH)_2$ showed differences too small to support the interpretation of the shell-plus-core like structure and the growth of the ZnO core on annealing at the expense of the Zn(OH)-shell studied previously for doped and undoped ZnO [4,5]. The obvious reason is the nearly equal bond length Zn-O and Zn-Zn in both compounds, ZnO and $Zn(OH)_2$.

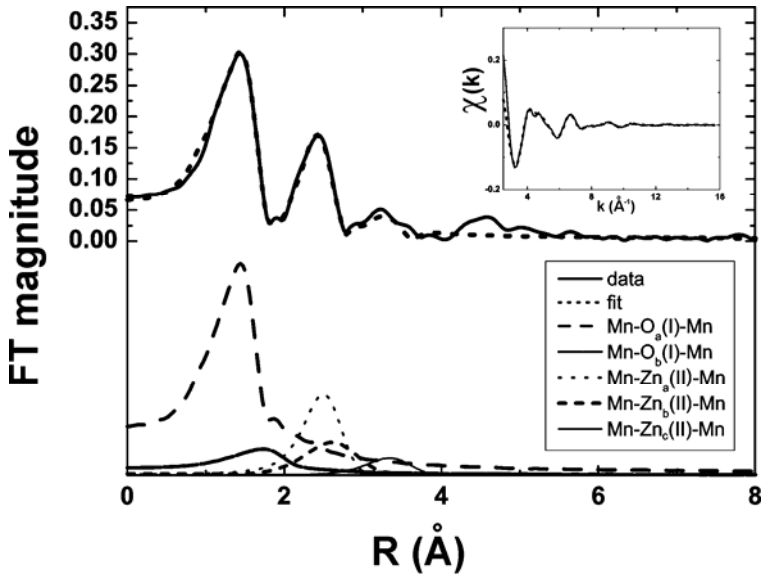

Fig. 2 Radial distribution function i.e. Fourier transform of the k-weighted EXAFS spectrum (insert) for Mn in nanocrystalline ZnO with 5 % Mn, measured at 100 K (annealing temperature in preparation 773 K). The lower part shows the contributions from different subshells.

The radial distribution function of an EXAFS spectrum taken at the Mn K-edge obtained for the same sample as in Fig.1 is given in Fig. 2. For a reasonable fit to the data one has to take the different subshells into account. The presented fit result gives a strong distortion around Mn as compared to pure ZnO. The bond length in the 3-fold coordinated first subshell is slightly reduced, while we have to include a sizeable increase in the 1-fold subshell. The positions in the second subshell occupied by Zn atoms normally differ only slightly, here, around Mn, they split further apart with sizeable differences. The actual values, however, may deviate from the ones summarized in Table 1, because these 5 subshells with their distances and weights (coordination numbers) are highly correlated. With modern computer codes using density functional theories and modelling supercells, one might be able to investigate the lattice relaxation around Mn by comparing calculated hyperfine coupling constants (A and D in EPR spectroscopy) with experimental data, both in EPR and in EXAFS, on single crystals.

Table 1 Nearest neighbour and next-nearest neighbour distances, R_{nn} and R_{nnn}, around Zn and Mn in Mn doped nanocrystalline ZnO. The adopted Zn values were taken from the standard ZnO lattice parameters used in the fit to the data given in Fig.1. The Mn values were determined as one possible parameter set from a fit to our experimental EXAFS data (see Fig.2). (All values are given in units of 0.1nm (=1Å)).

Absorbing atom	First shell		Second shell	
	R_{nn} (Å)	coordination	R_{nnn} (Å)	coordination
Zn	1.974	3	3.208	6
	1.988	1	3.250	6
			3.217	1 (to O)
Mn	1.894(6)	3	2.856(9)	3
	2.27(2)	1	3.02(2)	6
			3.77(2)	3

Comparing the Mn spectra in the different ZnO samples with different annealing temperatures and in $Zn(OH)_2$, we observe a clear trend towards a decreasing $Zn(OH)_2$ fraction in the samples. The second major peak in the FT spectrum shifts towards smaller distances (Fig. 3). Although the bond length between Mn and O in ZnO and in $Zn(OH)_2$ seems to be very similar, like the Zn-O bond length, a significant difference shows up in the second major shell due to the distortion (splitting and different distances) around Mn. It also shows up in the near edge part of the absorption, the XANES spectra given in Fig. 4. Thus the interpretation of a shell-plus-core structure derived from the EPR study is supported by our absorption spectroscopy result.

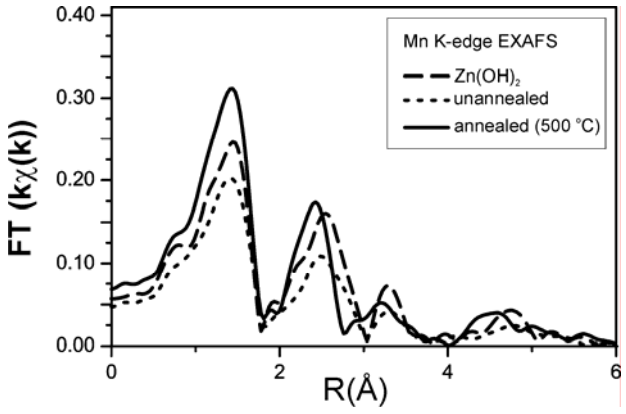

Fig. 3 Radial distribution function i.e. Fourier transform of the k-weighted EXAFS spectrum for Mn in nanocrystalline ZnO: (----) with 11 % Mn unannealed, (—) with 5% Mn annealed at 773 K, (— — —) with 5 % Mn in Zn(OH)2 (all measured at 100 K).

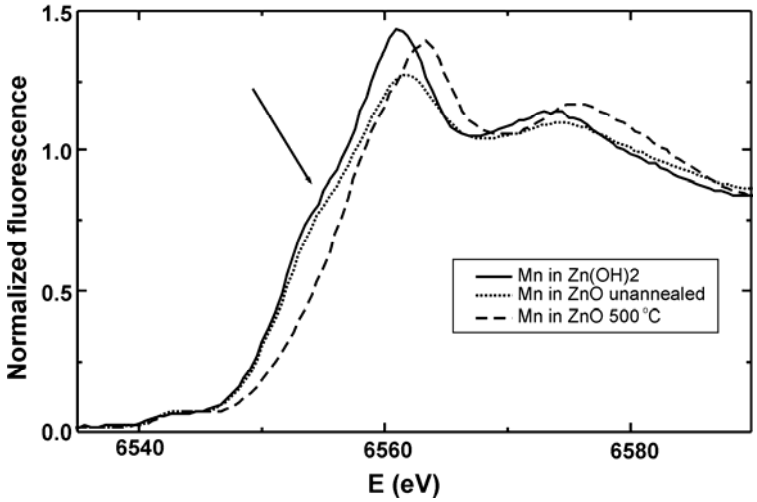

Fig. 4 XANES spectra of the Mn absorption in ZnO:Mn, annealed at 773 K, unannealed, and for comparison of Mn in $Zn(OH)_2$ illustrating the gain of ZnO at the expense of $Zn(OH)_2$ upon annealing.

From the known bond distances of Mn-Mn in Mn metal and Mn-O in MnO we can exclude contributions from such clusters in our absorption spectra with a fraction comparable to the broad background contribution in the EPR spectra which were attributed to possible clusters. The origin of this EPR background therefore must originate from dipole-dipole interactions of Mn atoms further apart than the radial sensitivity for EXAFS (which we consider to be around 1 nm).

Acknowledgements The authors are grateful to the HASYLAB staff at DESY, in particular to N. Haack and E. Welter.

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