

Manganese local structure in $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$

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Experiment n. 08-01-742

Introduction

We proposed to study atomic ordering around Mn in the $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ ternary semiconductor alloy, a II-VI diluted magnetic semiconductor which has recently attracted considerable interest.

In fact, incorporating magnetic properties into semiconductor heterostructures allow to manipulate not only the charge of the carriers as in usual microelectronics, but also their spin. This is of interest in order to achieve semiconductor spintronics [1]. II-VI diluted magnetic semiconductors [2] (DMS) are known to be good candidates for effective spin injection into a non-magnetic semiconductor (NMS). A very promising II-VI DMS for spin injection is $(\text{Zn},\text{Mn})\text{Se}$, which has been previously used for spin injection experiments into GaAs [3] and ZnSe [4]. Successful synthesis is achieved also in Mn-containing ZnSe quantum dots [5] (QDs).

We had nine beam-time shifts to investigate the local structure around Mn atoms by Extended X-ray Absorption Fine Structure (EXAFS) experiment. Analysis of the EXAFS spectra will provide precious and unavailable information on: 1. Atomic ordering. If Mn inclusion in ZnSe doesn't follow binomial distribution, there should be an enrichment of Mn in the second coordination shell of Mn itself. Due to the difference in atomic number, Mn is well distinguishable from Zn and Se by EXAFS. 2. Local relaxation. A measurement of the bond lengths around Mn in relation to the concentration will provide information on the lattice relaxation and on the degree of strain induced in the matrix.

The aim of this report is to show experimental aspects and the preliminary analysis results of the experiment n. 08-01-742 approved for beam-time at GILDA - BM08 Italian beam-line at the European Synchrotron Radiation Facility (ESRF).

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Experimental aspects

The investigated samples were three $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ epilayers of 250 nm deposited on GaAs[100] substrates by Molecular Beam Epitaxy (MBE) at CEA-Grenoble (*Equipe de nanophysique et semiconducteurs*). Three Mn compositions were studied: $x = 0.10$ (M1579), $x = 0.074$ (M1578) and $x = 0.06$ (M1580).

EXAFS measurements have been performed at the Italian BM08 beam-line - GILDA CRG. Experimental setup consisted of a Si(111) double crystal monochromator running in dynamical focusing mode [6] and Pd coated mirrors at high incidence for harmonic rejection. Spectra were collected at Mn K edge in fluorescence mode at liquid nitrogen temperature (to minimize the thermal damping of XAFS signal) using a 13 elements high purity Ge detector. Incident and transmitted X-ray beams were monitored by two nitrogen-filled ionization chambers, collecting signal from Mn foil for precise energy calibration.

Thanks to the valuable advice and support of the beam-line staff, good quality spectra have been collected. On the other hand, due to Mn low concentration, four spectra per sample with high integration times (15 s) were mandatory to obtain a good signal-to-noise ratio.

The normalized EXAFS oscillations $k^2\chi(k)$ for the Mn K edge of M1580, M1578, M1579 and their corresponding Fourier Transforms (FT) using Hanning-type window in the range $k = [3.0, 12.5] \text{ \AA}^{-1}$ with $dk = 1.5$ and k -weight = 2 are shown in Fig. 1. The short k -range used was due to hardware problems during data acquisition (I0 normalization, harmonic rejection) and Bragg peaks raising-up from substrate reflections, that introduce distortions and glitches (manually removed when possible).

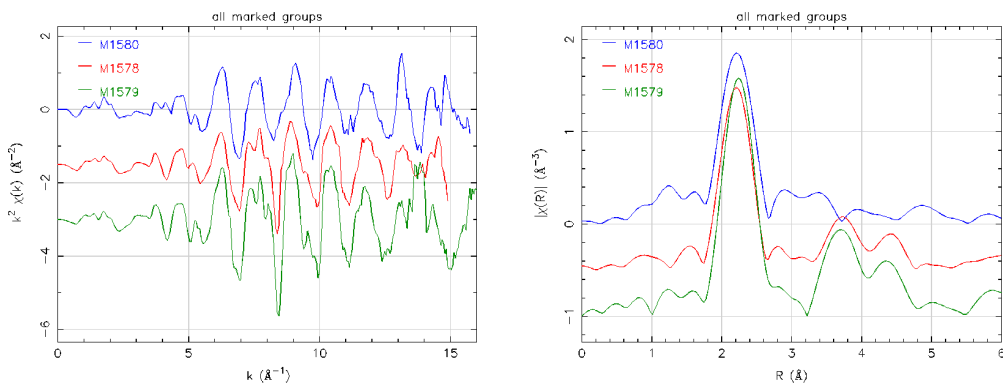


Figure 1: (left) Normalized EXAFS oscillations $k^2\chi(k)$ for the Mn K edge of $\text{Zn}_{0.94}\text{Mn}_{0.06}\text{Se}$ (M1580), $\text{Zn}_{0.926}\text{Mn}_{0.074}\text{Se}$ (M1578) and $\text{Zn}_{0.90}\text{Mn}_{0.10}\text{Se}$ (M1579). (right) Corresponding Fourier-transformed spectra.

Results

Is visible from Fig. 1 a difference between samples at different Mn concentrations. In fact, reducing the Mn content, the upper-shells signal goes down and disappears in sample M1580. This signal reduction is clearly visible in oscillations around $k \approx 7.5 \text{ \AA}^{-1}$, that correspond to $R \approx 3.7 \text{ \AA}$ and $R \approx 4.5 \text{ \AA}$ peaks¹ in the Fourier-transformed space.

Quantitative analysis is based on FEFF6L calculations and the IFEFFIT package [7] for fits. The starting point for fitting these data is represented by lattice parameters deduced by Yoder-Short *et al.* [8] using x-ray diffraction. Theoretical model is based on zinc blend ZnSe structure considering Mn as central atom at substitutional Zn site. For M1580 only first shell analysis is possible, using one single scattering theoretical path (Mn \leftrightarrow Se1). For M1578 and M1579 the analysis is extended up to third coordination shell, using four theoretical paths: 3 single-scattering (Mn \leftrightarrow Se1, Mn \leftrightarrow Zn1, Mn \leftrightarrow Se2), 1 multiple-scattering (triangular, Mn \rightleftharpoons Zn1 \rightleftharpoons Se1). Results are reported in Tab. 1 and Tab. 2 and plotted in Fig. 2.

| Sample | \mathcal{R} -factor | amp | E_0 (eV) | R_{Mn-Se} (\AA) | σ_{Mn-Se}^2 (10^{-3}\AA^2) |
|--------|-----------------------|---------|---------------|---------------------------------|--|
| M1580 | 0.0143 | 0.7(2) | 3(2) | 2.53(1) | 3(1) |
| M1578 | 0.0291 | 0.71(9) | 2(1) | 2.524(6) | 2.9(9) |
| M1579 | 0.0092 | 0.86(6) | 5(1) | 2.527(3) | 2.7(5) |

Table 1: Results from the I coordination shell analysis.

| Sample | R_{Mn-Zn} (\AA) | σ_{Mn-Zn}^2 (10^{-3}\AA^2) | R_{Mn-Se2} (\AA) | σ_{Mn-Se2}^2 (10^{-3}\AA^2) |
|--------|---------------------------------|--|----------------------------------|---|
| M1580 | - | - | - | - |
| M1578 | 4.07(1) | 10(2) | 4.75(2) | 10(2) |
| M1579 | 4.55(7) | 8.0(8) | 4.71(1) | 10(1) |

Table 2: Extension to II and III coordination shells analysis for samples M1578 and M1579.

In conclusion, EXAFS preliminary analysis relative to the experiment n. 08-01-742 conducted on three $Zn_{1-x}Mn_xSe$ samples at different concentrations, $x = 10\%$, $x = 7.4\%$ and $x = 6\%$, has permitted to identify the right inclusion of Mn atoms at substitutional site of the host ZnSe zinc-blend structure. Comparing

¹These values are relative to Fig. 1; real distances are obtained from the analysis and showed in Tab. 1 and 2.

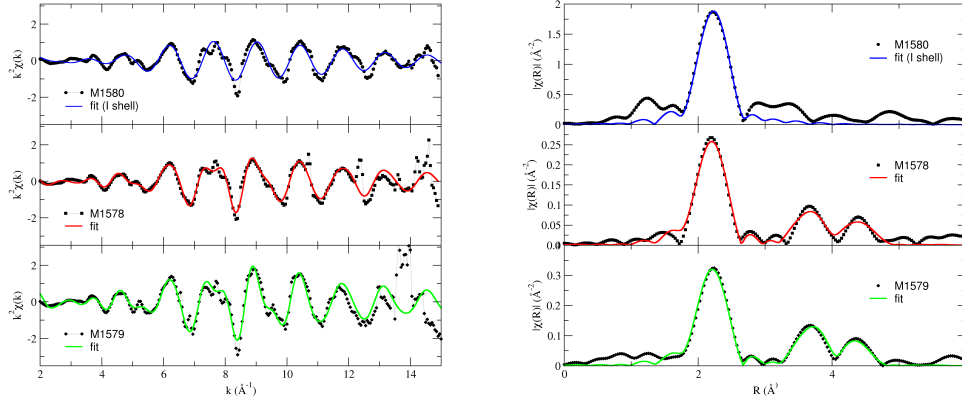


Figure 2: Fit results plotted in k -space (*left*) and the Fourier-transformed R -space (*right*).

these results with previous work in literature [9], there is an agreement, in the error limit, for the Mn–Se bond distances. On the other hand, errors are still too big and it is not possible to distinguish bond distance contraction at concentration variation. In addition, Next Nearest Neighbours bond distances are difficult to establish at Mn K edge because no *a priori* information is present for Mn coordination at the second shell. To better understand Mn local structure, a detailed EXAFS analysis is still in progress, in order to compare experimental results with theoretical calculations done on strained and relaxed alloy models at different Mn concentrations.

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