EXAFS DETERMINATION OF BOND LENGTHS IN $Zn_{1-x}Fe_xS$ TERNARY ALLOYS

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Studies of local atomic structure in the zinc-blende $Zn_{1-x}Fe_xS$ ($x = 0.11$–0.50) diluted magnetic semiconductors with the use of the EXAFS technique are reported for the first time. They include the K-edge EXAFS measurements for both cationic elements (Zn, Fe). The experiment was carried out at room temperature in the transmission mode using synchrotron radiation of the DCI storage ring in Orsay, France. A detailed EXAFS analysis for different crystal compositions (x) gave a convincing evidence for a bimodal distribution of the nearest-neighbour interatomic distances in $Zn_{1-x}Fe_xS$ within the iron solid-solubility limit. It has also revealed, within the accuracy of this method, constancy of both the nearest-neighbour cation–anion distances (i.e. Zn–S and Fe–S) in the composition range studied.

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1. Introduction

The interest in the $A_{1-x}^{II}M_xB^{VI}$ (where M is the transition metal) compounds, known as the diluted magnetic semiconductors (DMS), is dated since the early 70s [1] and remains highly motivated by their recent and prospective applications, especially in optoelectronics (e.g. [2]). The determination of their local atomic structure is of fundamental importance in calculating and predicting the properties of these alloys. The technique of extended X-ray absorption fine structure (EXAFS) seems adequate for this purpose, since it enables us to determine interatomic distances, a coordination number and a type of atomic species surrounding an X-ray absorbing atom [3]. Therefore, the EXAFS method has been successfully applied for investigating the local structure of the wide-gap II–VI compounds with Mn content (e.g. [4–7]) as well as with the other transition metals [8].

The objective of the paper is to report preliminary results of the EXAFS analysis performed for determination of the bond lengths in $Zn_{1-x}Fe_xS$ mixed crystals within the Fe solid-solubility range.

2. Experiment

The $Zn_{1-x}Fe_xS$ mixed crystals, with the compositions $x = 0.11$, 0.24 and 0.50, were grown at the Institute of Physics, Polish Academy of Sciences, by triple sintering of ZnS with FeS at 1200°C. Their composition has been determined by the use of the electron microprobe JEOL JSM-50A, whereas the X-ray diffraction measurements [9] confirmed their zinc-blende structure, which is characteristic of the solid-solubility range of iron in ZnS (see [10]).

The recent experiment included EXAFS measurements at the cation (Zn and Fe) K-edges of the crystals studied. The absorption spectra have been recorded at room temperature in the transmission mode using synchrotron radiation of the DCI storage ring at the Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (LURE) in Orsay, France. A Si (331) channel-cut crystal monochromator provided a spectral range of 6–30 keV with energy resolution $\Delta E/E \approx 10^{-4}$. The ring was operating at $E = 1.85$ GeV and the beam current ranged within 200–300 mA.

3. Results and analysis

The analysis of the acquired EXAFS spectra followed the standard procedure [3] and was performed analogously (including the same computer program [11]) as in the earlier papers of our group [7, 8]. The EXAFS modulation function, $\chi(k)$, was extracted from the absorption spectrum by usual subtraction of its extrapolated pre-edge part. The value of a photoabsorption threshold was taken equal to the energy of a maximum of the first derivative at an absorption slope. The absorption spectrum above the edge was fitted with splines to simulate an atomic cross section.

The normalized and k^2-weighted EXAFS oscillations for the K-edges of Zn and Fe in the representative sample $x = 0.24$ are shown in Figs. 1a and 2a,
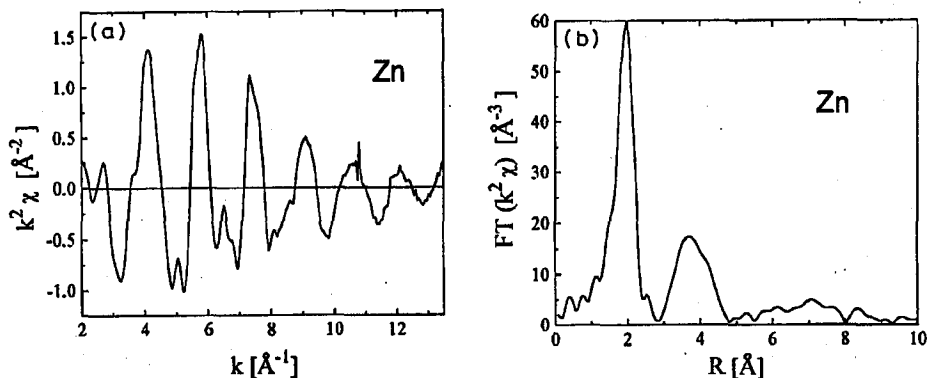

Fig. 1. (a) Normalized EXAFS oscillations for the Zn K-edge of $Zn_{1-x}Fe_xS$ crystal with $x = 0.24$. (b) Magnitude of Fourier transform (FT) for the Zn K-edge of $Zn_{1-x}Fe_xS$ with $x = 0.24$. The inverse FT for the first shell was calculated in the range of R: 0.92–2.76 Å.

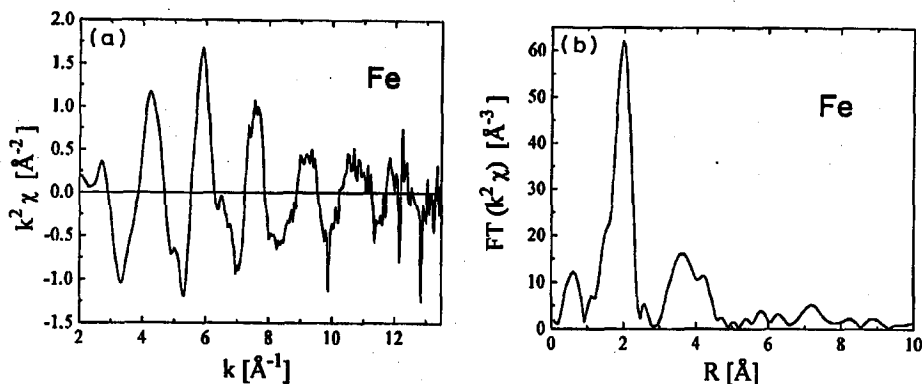Fig. 2. (a) Normalized EXAFS oscillations for the Fe K-edge of $Zn_{1-x}Fe_xS$ crystal with $x = 0.24$. (b) Magnitude of Fourier transform for the Fe K-edge of $Zn_{1-x}Fe_xS$ with $x = 0.24$. The inverse FT for the first shell was calculated in the range of R: 0.92–2.45 Å.

respectively. Their respective Fourier transforms, calculated in the range from $k_{min} = 2.8$ Å^{-1} to $k_{max} = 11.8$ Å^{-1} with use of the Kaiser window function, are plotted in Figs. 1b and 2b. The choice of k_{max} enabled us also to eliminate a group of "glitches" in the high-energy region of Fe K-edge EXAFS spectrum (Fig. 2a). On the other hand, our recent and earlier estimates [8, 7] have shown (especially for the K–Zn case) that single "glitches" and spikes in the k_{min}–k_{max} range do not influence the structural parameters derived from the EXAFS analysis.

The results of the numerical analysis of the first shell EXAFS oscillations for the cation K-edges in the alloys studied are collected in Table. This gives the structural parameters obtained from the best fits, i.e. the cation–anion nearest-neighbour (NN) distance R, mean relative displacement of each atom σ (which corresponds to the EXAFS Debye–Waller factor σ^2), the coordination number N, as well as the parameter L, which is related to the mean free path of the scattered photoelectron by the expression $\exp(-2R/L)$. Here, ΔE denotes a shift of the K-edge position. The coordination number in this case was fixed $N = 4$ (zinc-blende structure).

The standard EXAFS formula [3] was used to fit the first shell oscillations. For this purpose, we applied the theoretical phase shifts and amplitudes from Ref. [12]. Additionally, we have performed a fit of the Zn K-edge EXAFS with the use of the identical experimental phase shifts and amplitudes as in the previous papers [7, 8]. The fit parameter, listed in the last column of Table, is a sum of differences at each point between the least-square fit of the first shell EXAFS formula and the experimental first shell oscillation.

The review of the structural parameters gathered in Table leads to the conclusion of a bimodal distribution of cation–anion NN distances in the $Zn_{1-x}Fe_xS$ system within the Fe solid-solubility range. It can be noticed that both bond lengths, i.e. R_{Zn-S} and R_{Fe-S}, do not change with alloy composition, within the estimated accuracy of the method ($\Delta R = \pm 0.005$ Å). Also the other structural parameters in Table, σ and L, seem to be practically independent of x.

Set of the structure parameters obtained from the best fits of the first shell EXAFS signal for Zn and Fe cations in the $Zn_{1-x}Fe_xS$ lattice. The fits obtained with the use of the experimental phases and amplitudes are denoted by (E).

K-edge Zn	R_{Zn-S} [Å]	σ [Å]	L [Å]	N	ΔE [eV]	Fit
ZnS (from [8])	2.344	0.072	5.83	4.0	−7.86	0.083
ZnFeS, $x = 0.11$	2.343	0.070	5.01	4.0	−8.82	0.097
(E)	2.340	0.075	5.35	4.0	−0.56	0.048
ZnFeS, $x = 0.24$	2.346	0.069	5.93	4.0	−7.23	0.067
(E)	2.341	0.074	6.38	4.0	1.24	0.034
ZnFeS, $x = 0.50$	2.345	0.074	6.13	4.0	−6.65	0.033
(E)	2.342	0.076	6.52	4.0	1.57	0.051
K-edge Fe	R_{Fe-S} [Å]	σ [Å]	L [Å]	N	ΔE [eV]	Fit
ZnFeS, $x = 0.11$	2.360	0.050	5.15	4.0	−6.49	0.189
ZnFeS, $x = 0.24$	2.358	0.058	5.63	4.0	−5.93	0.079
ZnFeS, $x = 0.50$	2.356	0.059	4.93	4.0	−5.58	0.042

The estimated interatomic NN distances in $Zn_{1-x}Fe_xS$ ($x \leq 0.5$) equal here: $R_{Zn-S} = 2.344$ Å, $R_{Fe-S} = 2.358$ Å. Their reliability seem to be supported by the relatively low value of the fitting parameter (Table). One should remind that identical values of the R_{Zn-S} (and its constancy with x) have been found in $Zn_{1-x}Co_xS$ [8] and in $Zn_{1-x}Mn_xS$ [7] alloy systems, where the fits were also performed with the use of the experimental- and theoretical (from Ref. [12]) phase shifts and amplitudes.

4. Conclusions

The analysis of the K-absorption edge EXAFS of cations in $Zn_{1-x}Fe_xS$ ($x = 0.11$–0.50) revealed the bimodal distribution of cation–anion bond lengths and their constancy in the x range studied. The Fe–S bond length was found higher than that of Zn–S by 0.014 Å, thus introducing a slight deformation of a unit cell and, in consequence, the observed increase in lattice constant with alloy composition [9].

Acknowledgments

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