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EXAFS STUDIES OF $Zn_{1-x}Mn_xS$
TERNARY COMPOUNDS*

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We performed extended X-ray absorption fine structure (EXAFS) measurements of $Zn_{1-x}Mn_xS$ solid solution for various concentrations x in the range of $0 \leq x \leq 0.4$. Data were collected on Zn and Mn K -edges with the use of synchrotron radiation from the ADONE storage ring in Frascati utilizing the Si(111) channel-cut monochromator. Applying the usual procedure of data reduction described elsewhere, we found well-defined different nearest-neighbor Zn-S and Mn-S distances, according to the previous results, almost independent on x . For Mn-S distances in the range of $0.1 \leq x \leq 1.0$ we found, within the limit of experimental error, a constant value equal to 2.430 ± 0.008 Å. For Zn-S distances for concentration changing from $x = 0.0$ to $x = 0.4$ we observed a weak, linear increase from 2.343 ± 0.008 Å to 2.354 ± 0.008 Å, respectively.

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The ternary alloys $Zn_{1-x}Mn_xS$ belong to the wide group of materials $A_{1-x}^{II}Mn_xC^{VI}$ ($A^{II} = Zn, Cd, Hg$; $C^{VI} = S, Se, Te$), known as diluted magnetic semiconductors (DMSs). In each type of these materials the group-II cations A^{II} are, in part, randomly replaced by substitutional Mn^{2+} ions. The extensive studies have shown that DMSs exhibit unique electrical, optical and magnetic properties [1], associated with the short ranged exchange interactions between the spins of Mn^{2+} ion and between $3d$ electrons of Mn^{2+} and band electrons. The predominant type of exchange mechanism between Mn^{2+} ions in DMSs is via the intervening anion in the form of superexchange [2]. Therefore it is important to understand the nature of the microscopic distortion of the local structure of DMSs.

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Extended X-ray absorption fine structure (EXAFS) is a powerful probe for local structure in condensed matter systems. This technique determines distances, coordination number, and type of atoms nearby an X-ray excited atom. Moreover, this information can be obtained for each type of atom separately [3].

The purpose of this paper is to report on our study of the local structure of the Mn^{2+} ion in the ZnS host lattice, the variation of cation-anion distances with the concentration x of manganese.

We performed EXAFS measurements on $Zn_{1-x}Mn_xS$ samples of various Mn concentration ($x = 0.00, 0.05, 0.10, 0.20, 0.30, 0.40, 1.00$), using the synchrotron radiation from the ADONE storage ring in Frascati and utilizing the Si(111) channel-cut monochromator. The possibility of the harmonic contaminations is very small because of the low critical energy of the ADONE bending magnet

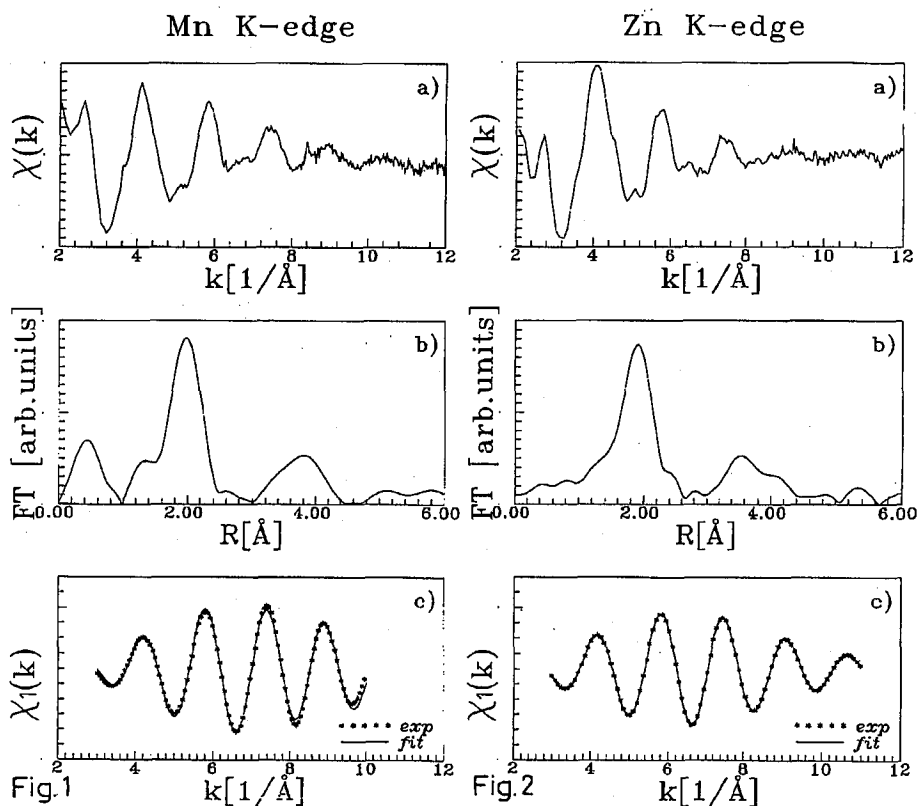


Fig. 1. Results of EXAFS data analysis for Mn K -edge of $Zn_{0.9}Mn_{0.1}S$ at room temperature. (a) $\chi(k)$ EXAFS oscillations; (b) magnitude of Fourier transform; (c) the best fit of theoretical EXAFS function to the experimental data for the first shell.

Fig. 2. Results of EXAFS data analysis for Zn K -edge of $Zn_{0.9}Mn_{0.1}S$ at room temperature. (a) $\chi(k)$ EXAFS oscillations; (b) magnitude of Fourier transform; (c) the best fit of theoretical EXAFS function to the experimental data for the first shell.

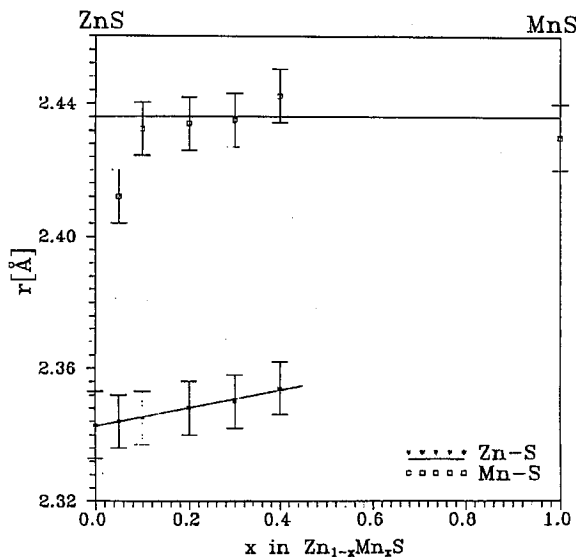


Fig. 3. Nearest-neighbor (NN) distances in $Zn_{1-x}Mn_xS$ versus Mn concentration.

TABLE
The Zn-S and Mn-S NN distances
in $Zn_{1-x}Mn_xS$ ternary alloys.

x	Zn-S [Å]	Mn-S [Å]
0.00	2.343 ± 0.010	-
0.05	2.344 ± 0.008	2.412 ± 0.008
0.10	2.345 ± 0.008	2.432 ± 0.008
0.20	2.348 ± 0.008	2.434 ± 0.008
0.30	2.350 ± 0.008	2.435 ± 0.008
0.40	2.354 ± 0.008	2.442 ± 0.008
1.00	-	2.430 ± 0.010

source $E_c = 1500$ eV. It means, also because with a Si(111) monochromator the even reflections are not allowed, that for the Mn and Zn edges the ratio of harmonic components to the fundamental one is negligible.

Powdered samples (few micron thick) were obtained from high quality monocrystals which were grown using the chemical transport with I_2 as a carrier medium. The absorption measurements were performed at K -edges of Zn and Mn at room temperature. EXAFS data analysis was done applying the procedure of data reduction described elsewhere [4]. In Figs. 1 and 2 we present the results of the successive steps of data analysis for $Zn_{0.9}Mn_{0.1}S$ sample for K -edges of Mn and Zn, respectively. Figures 1c and 2c show the best fit of the theoretical EXAFS

function to the experimental data for the first shell. For the binary compounds (MnS and ZnS), we used the amplitude and phase functions calculated previously by McKale [5]. For the ternary compounds the amplitude and phase functions were determined from the model binary compounds. Figure 3 shows the Mn-S and Zn-S nearest-neighbor (NN) distances in $Zn_{1-x}Mn_xS$ as a function of Mn concentration. Cation-anion Mn-S distances within experimental error are almost independent of x over the entire concentration range. This result is in good agreement with the previous one obtained by Mayanovic et al. [6]. For Zn-S NN distances we found a slightly different result. For the concentration changing from $x = 0.0$ to $x = 0.40$, one can observe a weak, linear increase from $2.343 \pm 0.008 \text{ \AA}$ to $2.354 \pm 0.008 \text{ \AA}$, respectively. The Mn-S distances in $Zn_{1-x}Mn_xS$ are almost the same as for pure MnS crystallizing in zinc blende structure. All the numeric results are collected in Table. The total experimental error ($\pm 0.008 \text{ \AA}$) presented in Table is the sum of the estimated error arising from noise in the data ($\pm 0.005 \text{ \AA}$), calculated according to the method described in Ref. [7], and the fitting error ($\pm 0.003 \text{ \AA}$). The fitting errors were calculated by the appropriate parameter change from its converged value until sum of squares of the residuals reached twice its minimum value.

In conclusion, the EXAFS results show that the Mn-S NN distances remain constant as a function of Mn concentration and the change of Zn-S distances is observed. This implies a distortion of the crystal structure, although the lattice parameter of $Zn_{1-x}Mn_xS$ varies linearly with Mn concentration and obeys Vegard's law [8].

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