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Local structure of ternary semiconducting random solid solutions: Extended x-ray-absorption fine structure of $Cd_{1-x}Mn_xTe$

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The nearest-neighbor distances around Te atoms in the random semiconducting alloy $Cd_{1-x}Mn_xTe$ have been determined by the extended x-ray-absorption fine-structure technique. The distribution of the anion-cation distances is bimodal. A model of the microscopic structure of the zinc-blende-type $A_{1-x}B_xC$ ternary alloys based on a random distribution of cations has been developed. The model describes the bimodal distribution of nearest-neighbor distances in terms of distortion of the anion sublattice, using only the lattice constant of the alloy and the bond-stretching constants of each binary component. Within the framework of this model we consider also the problem of the structural stability of $Cd_{1-x}Mn_xTe$.

The CdTe-MnTe solid solutions, which combine the semiconducting properties of CdTe with the magnetic properties of $3d^5$ states of Mn, have been recently studied with the main aim of having a consistent explanation of their magnetic and electronic properties.

CdTe and MnTe crystallize in cubic (zinc-blende) and hexagonal (NiAs) structures, respectively. Standard x-ray diffraction measurements suggest that $Cd_{1-x}Mn_xTe$ crystallizes in zinc-blende structure up to $x=0.7$ and undergoes a structural phase transition to a multiple-phase system at a higher concentration of manganese.[1] The lattice constant of this material changes linearly with x in the whole single-phase region,[2] the feature commonly referred to as Vegard's law.[3] Such a behavior does not exclude a bimodal distribution of nearest-neighbor (NN) distances in the alloy. Diffraction methods do not provide sufficient structural information on the local coordination of atoms in crystals. A new insight was recently supplied by extended x-ray-absorption fine-structure (EXAFS) analysis applied to the GaAs-InAs (Ref. 4) and ErSb-PrSb (Ref. 5) random ternary alloys. These works yield the conclusion that impurity atoms create a bimodal distribution of NN distances.

The detailed knowledge of the crystallographic structure of $Cd_{1-x}Mn_xTe$ may be of critical importance for understanding its unique properties.[2,6-9] In attempting to understand the electronic properties of the mixed ternary alloys, one usually starts with binary compounds.[10] In the case of the CdTe-MnTe system this approach cannot be followed directly because of the occurrence of the structural phase transition. Therefore, in $Cd_{1-x}Mn_xTe$ definite structural information is needed.

We report here the first EXAFS measurements of the $Cd_{1-x}Mn_x$ Te solid solutions for several alloy compositions. For data reduction we have used the pure binary compounds CdTe and MnTe as known model compounds.

The EXAFS measurements were performed at the Synchrotron Radiation Facility (PULS) in Frascati with the light emitted by the Adone storage ring (1.5 GeV, 50 mA). The experimental setup is described elsewhere.[11] Single crystals of CdTe and MnTe and their alloys were powdered and supported on Kapton or Mylar adhesive tape or deposited from a water dispersion on Millipore membranes. Pure CdTe thin films 2.6 μm thick evaporated onto a mica substrate were also used. The EXAFS spectra were measured at 300 K for Mn concentrations $x=0$, 0.1, 0.3, 0.5, 0.7, and 1, with an average resolution better than 10^{-4} in the 4–6-keV range. The edges considered were Te L_{III} and L_{I}, Cd L_{III} and L_{I}, and Mn K. The Mn K edge was measured by fluorescence. X-ray diffraction measurements were also made. They verified the excellent structure of our crystals and the linear dependence of the lattice constant upon Mn content through the entire solid-solution regime. The photoabsorption threshold has been taken to conicide with the maximum of the derivative at the absorption edge.

The extraction of the EXAFS modulation function $\chi(k)$ from the background was made with the usual procedure of data reduction.[12,13] The total phase and backscattering amplitude for any shell were obtained from the analysis in k space. Namely, the $k\chi(k)$ data were Fourier transformed (FT) to real space and the contribution of a single shell was backtransformed to extract the phase and amplitude functions. For the model compounds the phase factor was extracted, since the interatomic distance is known.

Figure 1 shows the FT of the EXAFS data measured above the Te L_{III} edge for x increasing from 0.1 to 0.7. The FT was calculated in the range $2.6 \leq k \leq 8.1$ Å^{-1} using a Hanning window function. The first and second peaks of the radial distribution function $F(R)$ correspond to the NN Mn and Cd atoms, respectively, in the first shell surrounding Te. By increasing the mole fraction of Mn the intensity of the Mn peak increases and, correspondingly, the intensity of the Cd peak decreases. In pure CdTe the $F(R)$ measured at the Te L_{III} edge has shown that the Cd peak is doubled[14] because of the characteristic amplitude function of

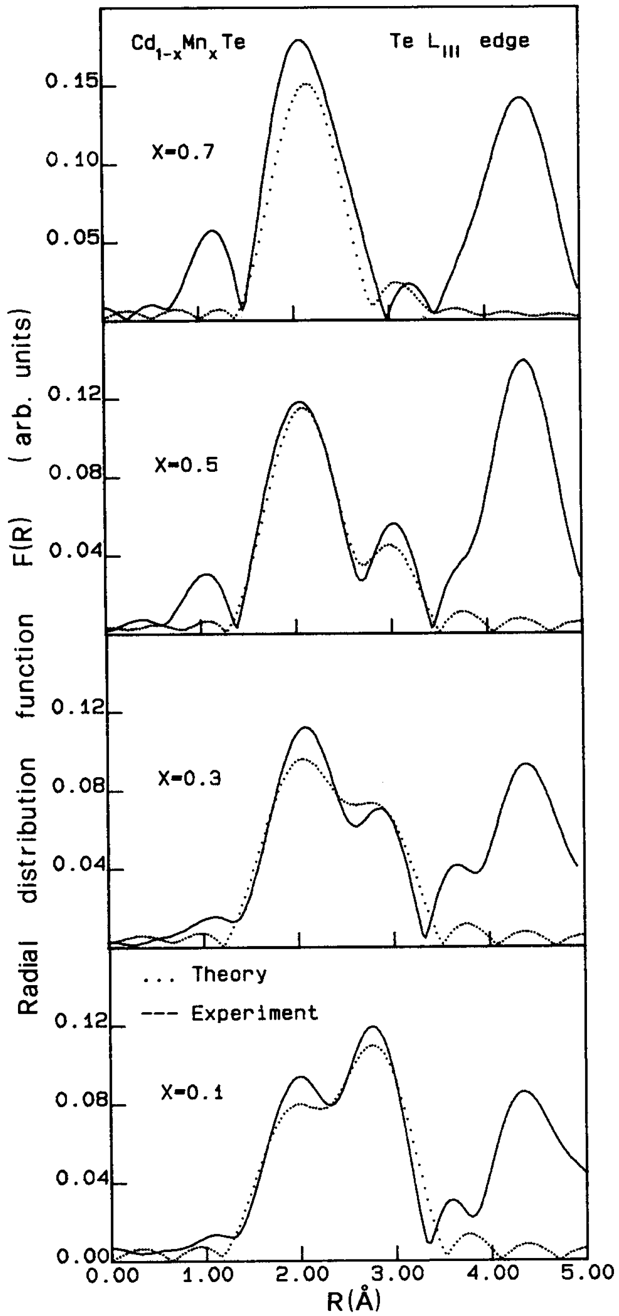

FIG. 1. Modulus $F(R)$ of the FT of $\chi(k)$ at the Te L_{III} edge for four Mn concentrations x in $Cd_{1-x}Mn_xTe$ (solid lines). The dotted lines are the best-fit curves for the nearest-neighbor Mn and Cd atoms surrounding Te.

intermediate-Z atoms due to the Ramsauer-Townsend[12,13] effect. Thus the Mn peak in the alloy is superimposed on the lateral peak of Cd.

We have best fitted the experimental NN $F(R)$ by using as free parameters the anion-cation NN distances (the starting values were those derived from the Cd L_{III} and Mn Kedges) and the Debye-Waller factors of Mn and Cd. Namely, from $\chi(k)$ measured on the L_{III} edge of Cd and the K edge of Mn in $Cd_{1-x}Mn_xTe$ and from the total backscattering phases measured on CdTe and MnTe, we derived the NN distances for the Cd-Te and Mn-Te pairs, respectively, in the alloys following the procedure of Martens *et al.*[15] The amplitude and phase functions were determined from the model compounds and the coordination numbers were calculated from the nominal x in the alloy. The best-fit anion-cation distances are almost independent of x and amount to 2.80 ± 0.01 Å for Cd-Te, and range between 2.76 ± 0.01 Å and 2.74 ± 0.01 Å for Mn-Te. The best-fit $F(R)$ curves are also reproduced in Fig. 1 (dotted lines) for various x and agree satisfactorily with the experimental curves. The further peaks of $F(R)$ between 3 and 5 Å were presented in a previous EXAFS work.[14] According to the analysis made there these peaks are assigned to the next-nearest-neighbor Te and Cd (Mn) atoms.

The main result of the EXAFS data is that well-defined different NN Cd-Te and Mn-Te distances (a "bimodal" distribution) exist in $Cd_{1-x}Mn_xTe$.

We present a short description of the model of the microscopic structure of the zinc-blende-type $A_{1-x}B_xC$ alloys. To start with, we consider all five possible coordinations around an anion in the alloy. Assuming a random distribution of cations, the probability of finding a tetrahedron with n B-type ($n=0,1,2,3,4$) cations for a concentration x is given by

$$P(n,x)=\binom{4}{n}x^n(1-x)^{4-n}\ . \tag{1}$$

From simple geometrical arguments it follows that the bimodal distribution of the NN distances (different distances between A-C and B-C pairs) cannot be realized if the anion sublattice stays undistorted. In the three cases of five possible configurations of a tetrahedron in which we have cations of both kinds, it is possible to move the anion in such a way that all distances from one kind of cation increase and from another decrease. Simple geometry gives the relations between these distances. In the case of the tetrahedron with four identical cations all distances are equal to $a(x)\sqrt{3}/4$, where $a(x)$ is the lattice constant of the alloy for a given concentration x. The particular A-C and B-C distances in distorted tetrahedra were calculated by minimizing the energy needed for such a distortion. The proper formula, involving the bond-stretching constants, was written on the basis of Keating's scheme of the valence-force-field approach.[16] Having all the particular NN distances, we calculated the average A-C and B-C distances with the use of the probability given by Eq. (1). The results of this calculation are presented in Fig. 2 together with the experimental data. The agreement is very good.

We would like to stress that this model only needs the lattice constant of the alloy and the bond-stretching constants of the binary components as the input data. Therefore, it can be applied directly to other zinc-blende-type $A_{1-x}B_xC$ alloys. A previous attempt to construct a model of the microscopic structure of $In_{1-x}Ga_xAs$ (for $x=0.5$) based on a chalcopyrite analogy has been done by Mikkelsen and Boyce.[4]

Our model does not consider the problem of the violation of the random distribution of cations in the alloy. All quantitative results and conclusions drawn from it when confronted with experimental data of different measurements (x-ray diffraction, EXAFS, magnetic) may or may not confirm such a violation. However, there is explicit evidence that for the diluted pseudobinary alloy $In_{1-x}Ga_xAs$ the distribution of cations is random and the deviation from randomness is estimated not to be larger than 15% for concen-

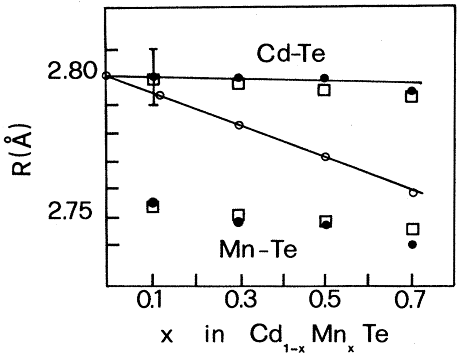

FIG. 2. The average Cd-Te and Mn-Te nearest-neighbor distances in $Cd_{1-x}Mn_xTe$ alloys vs x. ●, values from the best fit of the EXAFS data; □, values calculated from the model; ○, values of $d=\sqrt{3}a(x)/4$ as measured from x-ray diffraction.

trated alloys.[4] Investigations of the magnetic properties of $Cd_{1-x}Mn_xTe$ by Gałazka, Nagata, and Keeson[7] basically support a statistical distribution of Mn ions.[17] Further support against chemical clustering of Mn ions may be drawn from EXAFS studies of other magnetic alloys.[18] Nevertheless, we are considering the possibility, or necessity, of taking into account, in addition to the present version of the model, a correlation between different tetrahedra.

We would like to emphasize that the NN distances obtained from Cd $L_{\rm III}$ and Mn K edges are in agreement with those obtained from the Te $L_{\rm III}$ edge. These results are direct experimental evidence, which confirms the bimodal distribution of the NN distances in $Cd_{1-x}Mn_xTe$ alloy, i.e., ascertains the existence of two different well-defined average distances between Te-Cd and Te-Mn.

The model of the microscopic structure of the zinc-blende-type $A_{1-x}B_xC$ alloys gives all the particular NN distances as well as the average NN distances in very good quantitative agreement with our experimental data. We believe that the local distortion in zinc-blende-like $A_{1-x}B_xC$ alloys described by our model is a *universal* feature of such alloys. One of the important consequences is that it makes "classical" definition of the virtual-crystal approximation (VCA) questionable. One either must accept that the VCA is less accurate than previously thought and that in this approximation all distortions of the sublattices of the alloys are ignored or one must consider the generalization of the VCA which includes also the proper averaging of the potential of C atoms over all possible positions in their distorted sublattice. The same can be applied to more sophisticated one-electron alloy theories such as the coherent potential approximation (CPA) or the average T-matrix approximation (ATA). Besides taking into account the scattering on the different cations, one should incorporate into these theories in some way also the effects of averaging the anion potential over different geometrical sites.

Finally, we would like to discuss the problem of the stability of the tetrahedral coordination in $Cd_{1-x}Mn_xTe$ alloy. According to the Phillips and Van Vechten approach,[19] the ionicity of CdTe is equal to 0.717, which is near the critical ionicity value (0.785) at which the transition from a covalent to ionic structure occurs, or, in other words, at the transition from the fourfold (zinc-blende, wurtzite) to the sixfold (rocksalt, NiAs) coordination. Since Mn in MnTe has sixfold coordination, MnTe is reported to be more ionic than CdTe.[20] This indication is supported by core-level shifts from x-ray photoemission spectra[21] and effective charge calculations.[22] The addition of Mn in CdTe should increase the ionicity of bonds in the alloy. The question arises how the crystal structure of $Cd_{1-x}Mn_xTe$ is still cubic up to $x=0.7$, taking into account that CdTe is quite close to the structural phase transition. The answer is that the local distortions of the lattice (distortions of the tetrahedra), as described by our model, stabilize the zinc-blende-type structure up to $x=0.7$. To understand this one should note the following:

(i) In nearly covalent compounds the center of gravity of the bonding charge is placed almost at the middle of the bond, and it shifts towards an anion when the bond ionicity increases.

(ii) The distortion of the tetrahedra containing 1, 2, or 3 Mn ions, i.e., shift of Te ions towards Mn, compensate for the displacement of the center of gravity of the bonding charge and decreases the effective bond ionicity. Such a shift is also favored by the smaller ionic radius of Mn^{2+} ions as compared with that of Cd^{2+}.

(iii) The probability of finding a tetrahedron with four Mn ions increases rapidly for $x>0.7$ [see formula (1)]. According to our model, such tetrahedra cannot distort and the displacement of the bonding charge cannot be compensated. Therefore, the fourfold coordination of $Cd_{1-x}Mn_xTe$ becomes unstable and the transition to the phase typical for ionic compounds occurs.

Summarizing the discussion about the stability of the $Cd_{1-x}Mn_xTe$ alloy, we would like to say that phenomenological considerations about the ionicity, supported by conclusions drawn from our theoretical model of the microscopic structure of the alloy, give a satisfactory, qualitative explanation of this problem.

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