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EXAFS OF TERNARY SEMICONDUCTORS

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1. Introduction

III-IV and II-VI pseudobinary solid solutions of the $A_{1-x}B_xC$ (cation alloy) and $DBA_{1-x}C_x$ (anion alloy) type can generate, in principle, a great number of semiconductors with a variety of band gap widths. Several of these alloys have important present or potential applications in heterojunction⁽¹⁾ and optoelectronic devices. A large number of X-ray diffraction studies⁽¹⁾ show that these materials have a zinc-blende structure, with one of the two fcc sublattices occupied by the C anion (D cation) and the other occupied by both B and A cations (anions). With few exceptions, the lattice parameter $a(x)$ fulfills the Vegard's law⁽²⁾, i.e. it varies almost linearly between the values of pure compounds. So far, the most common model for solid solutions was the Virtual Crystal Approximation (VCA). As in zincblende structures the bondlength is $r = a\sqrt{3}/4$, in the frame of VCA both the AC and BC distances obey the rule $Y(x) = a(x)\sqrt{3}/4 = Z(x)$ i.e. they are equal and vary as the lattice parameter does. In turn, the Pauling's tetrahedral bond conservation rule gives $Z(x) = r_{BC}$ and $Y(x) = r_{AC}$ i.e. equal to that of the pure compounds. A direct measurement of these⁽³⁾ distances has been recently obtained by means of the EXAFS technique⁽³⁾. The EXAFS measurements indicate a bimodal distribution of bondlengths, closer to the Pauling than to the VCA limit.

2. Experimental

The EXAFS measurements were performed at the PULS facility at the Frascati National Laboratories. The alloys considered are $Cd_{1-x}Zn_xTe$, $HgSeTe_{1-x}$ ($x=0, 0.25, 0.5, 0.75, 1.0$) and $Cd_{1-x}Hg_xTe$ ($x=0, 0.1, 0.3, 0.5, 0.7, 1.0$).

All these systems form solid solutions in the whole range $x=0-1$ and

were measured in transmission at room temperature. Single crystals of pure compounds and of their alloys were grown with a modified Bridgman method. Their homogeneity and composition was checked with X-ray diffraction. The structural analysis was performed in k-space by using pure AB and AC compounds as standards to determine the phase and amplitude back-scattering functions⁽³⁾. The fit in k space has been carried out both with the MINUIT routine⁽⁴⁾ and with a very recent global minimization routine⁽⁵⁾ called SIGMA, which is efficient when the variability range of the parameters is large.

3. Results and discussion

In the alloys the difference in the bondlengths between the binary compounds are generally large allowing to distinguish unambiguously between the VCA-like and the Pauling-like behaviours in the nearest-neighbour (NN) shells (Fig. 1). Thanks to the good signal-to-noise ratio and sufficient separation from the outer coordination shells of Te, the analy

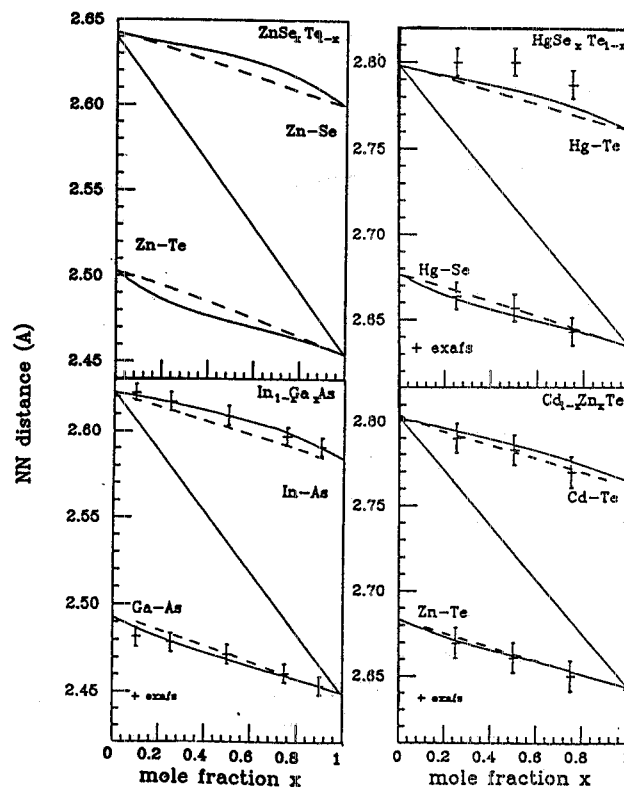


Fig. 1 - Experimental and calculated NN distances for different pseudobinary alloys. I: EXAFS; dashed line: calculated with the random probability; solid line: calculated QCA. The experimental points for $\text{In}_{1-x}\text{Ga}_x\text{As}$ are taken from Ref.(7).

sis of the NNN contribution is also possible⁽⁶⁾. For $\text{Cd}_{1-x}\text{Hg}_x\text{Te}$ the bond-lengths d_{CdTe} and d_{HgTe} are very close and difficult to resolve. In this case small uncertainties in the bondlengths of standards become critical for the EXAFS analysis.

Since NN bond-lengths clearly depart from VCA the question arises how the zincblende structure accomodates two different cation-anion distances. The experimental results on different alloys^(3,6,7) allow to state the following general conclusions on the structure of pseudobinary solid solutions:

- a) They have crystalline order.
- b) In the alloy the bond-lengths have almost the same value as in pure compounds. Thus NN distances display a bimodal distribution.
- c) On the chemically disordered sublattice the distances approach the VCA limit whereas in the ordered one the distances are bimodal. This implies that the latter sublattice is much more distorted than the former.
- d) The same behaviour characterizes both cation and anion alloys.

We have recently developed a model for the microscopic structure of zincblende pseudobinary alloys that incorporate all these points⁽⁴⁾. We focus our attention on the tetrahedral coordination of the zincblende, i.e. we consider the tetrahedra with the four vertices on the disordered sublattice and a cation D ($\text{DB}_x\text{A}_{1-x}$ anion alloys) or an anion ($\text{A}_x\text{B}_x\text{C}_{1-x}$ cation alloys) inside as the basic units to build the crystal. These tetrahedra can be found in five different configurations according to the number $n=0,1,2,3,4$ of B-type atoms at their vertices.

We suppose that all the physical properties of the alloy are obtained by a suitable average of the corresponding properties of these tetrahedra. The EXAFS results show a tendency to maintain bonds similar to those of pure compounds, so we have derived the tetrahedral properties such as $Z(x)$ and $Y(x)$ through the minimization of the tetrahedron distortion energy η_n within the Valence Force Field (VFF) scheme of Keating⁽⁸⁾. In order to get the mean distances measured by EXAFS, i.e. $Z(x)$ and $Y(x)$, we have chosen a suitable probability⁽³⁾ distribution for the five possible tetrahedra. A random distribution⁽³⁾ and a T-dependent distribution:

$$P^{(Q)}(x,T) = \frac{\binom{4}{n} e^{-[\eta_n(x,T)+n(4-n)w]/KT} A^{n-4x}}{\sum_n \binom{4}{n} e^{-[\eta_n(x,T)+n(4-n)w]/KT} A^{n-4x}} \quad (1)$$

derived within the III order Quasi Chemical Approximation⁽⁹⁾ were used. Here $Ae^{-\lambda/KT} = A(x,T)$ is the only real and positive solution of the fourth order polynomial equation:

$$\sum_n (n-4x) \binom{4}{n} e^{-[\eta_n(x,T)+n(4-n)w]/KT} A^{n-4x} = 0. \quad (2)$$

The distribution probability $P^{(Q)}$ depends not only on x , as the Bernoulli distribution does, but also on T . It is peculiar of each alloy, as it depends on w (chemical interaction energy for a pair of neighbours) and on the elastic properties of the two compounds mixed via the η_n 's. The distances calculated with the latter probability distribution are in better agreement with the experiment (Fig. 1) showing measurable deviations from the randomness, especially for $\text{In}_{1-x}\text{Ga}_x\text{As}$ and $\text{HgSe}_{1-x}\text{Te}_x$.

4. Phase diagrams

Starting from the probability distribution (1) we can calculate the Gibbs free energy of mixing and hence the phase diagrams of the alloys^(9,10) (Fig. 2). We can observe that the alloys whose enthalpy is not fully dominated by the elastic energy (i.e. the lattice-matched

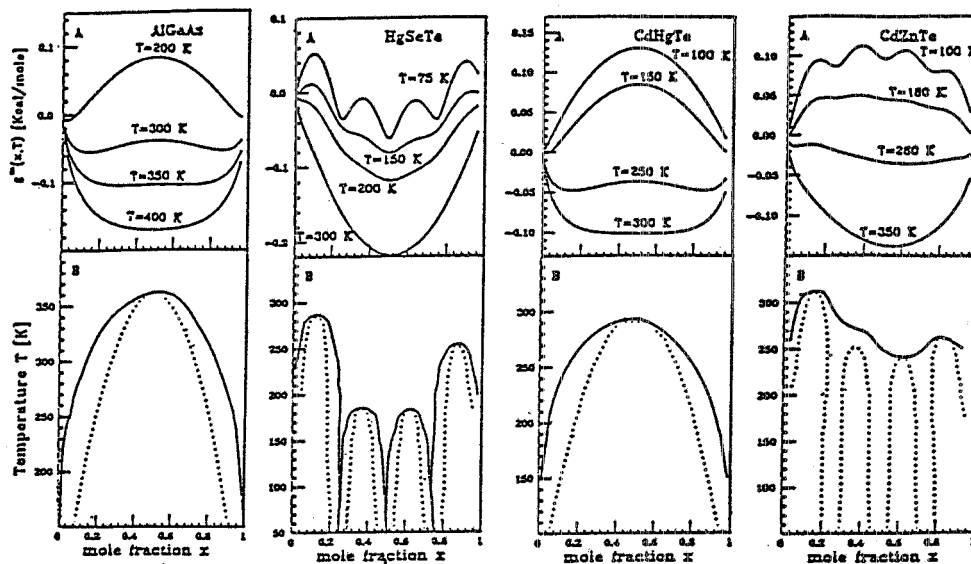


Fig. 2 - Calculated free energy of mixing (A) and phase diagrams (B) for various pseudobinary alloys.

$\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloy) behave qualitatively as Bragg-Williams solutions. A different behaviour characterizes the alloys dominated by the elastic deformation energy. Apart from the usual change from a convex to a concave function when the temperature is lowered, the $g(x)$'s of these materials show regions of convexity around the mole fraction $x=0.25, 0.50, 0.75$. Due to the shape of g^m , in this case the phase diagrams are rather complex, and three narrow metastable regions develop around the stoichiometric concentrations. Our results suggest that this could be a general feature for pseudobinary alloys whose thermodynamic properties are governed by the elastic energy.