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LOCAL STRUCTURE AND THERMODYNAMICS OF II-VI AND III-V SEMICONDUCTORS
BY EXAFS

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Resume - L'ordre à courte distance des solutions solides II-VI a été étudié par EXAFS. Les énergies de distorsion des cinq tétraédres formant le réseau de ces solutions ont été évaluées par un simple modèle de VFF (Valence Force Field). Nous avons calculé, dans ce modèle, les énergies libres de mélange, les distributions de probabilité et les diagrammes de phases pour différents alliages II-VI et III-V, à partir de l'approximation quasi chimique du III ordre.

Abstract - The short-range order of II-VI substitutional solid solutions is investigated experimentally using the EXAFS technique. The distortion energies of the five tetrahedra which form the basic lattice framework of these solutions are evaluated by a simple Valence-Force-Field (VFF) model. Within the modified (III order) Quasi Chemical Approximation, we compute the free energy of mixing, the probability distribution and the coherent phase diagrams of several II-VI and III-V pseudobinary alloys.

INTRODUCTION

II-V and II-VI pseudobinary solid solutions of the A_{1-x}B_{x}C (cation alloy) and DB_{x}A_{1-x}C (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 and optoelectronic devices. A large number of X-ray diffraction measurements on pseudobinary alloys are available [1]. They 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 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 $\gamma(x)=a(x)/\sqrt{3/4}=2(x)$ i.e. they are equal and vary as the lattice parameter does. In turn, the Pauling's tetrahedral bond conservation rule gives $2(x)=r_{BC}$ and $\gamma(x)=r_{AB}$ i.e. equal to that of the pure compounds. A direct measurement of these 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 limit than to the VCA.

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EXPERIMENTAL

The EXAFS measurements were performed at the PULS facility at the Frascati Laboratory (Italy) with the light emitted by the ADONE storage ring. The alloys considered are Cd$_{1-x}$Zn$_x$Te, Hg$_{Se_x}Te_{1-x}$ (x=0,0.25,0.5,0.75,1) and Cd$_{1-x}$Hg$_x$Te (x=0,0.1,0.3,0.5,0.7,1). Both in the CdTe-ZnTe and HgTe-HgSe alloys the mixed compounds have rather different lattice parameters, and the alloys follow the Vegard's law. For Cd$_{1-x}$Hg$_x$Te the lattice parameters of the binaries (x=0,1) are very similar. 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 extraction of the EXAFS modulation function $\chi(k)$ from the experimental spectra was made with the standard procedure of data reduction [3]. The structural analysis was performed in $k$-space by using pure AB and AC compounds as standards to determine the phase and amplitude backscattering functions.

The fit in $k$ space has been carried out both with the MINUIT routine [4] and with a very recent global minimization routine called SIGMA [5], which seems to be more efficient when the range of variability for the parameters is larger.

RESULTS AND DISCUSSION

The F(r)'s are shown in Fig. 1a for Cd$_{1-x}$Zn$_x$Te around the L$_{III}$ edge of Te (4341 eV) and in Fig. 1b for Hg$_{Se_x}Te_{1-x}$ around the L$_{III}$ edge of Hg (12284 eV), in both the alloys the difference in the bondlengths between the binary compounds are large allowing us to distinguish unambiguously between the VCA-like and the Pauling-like behaviours. Thanks to the good signal-to-noise ratio and sufficient separation from the outer coordination shells of Te, the analysis of the NNN contribution to F(r) in Cd$_{1-x}$Zn$_x$Te is also possible [6]. We have measured also the Te-L$_{III}$ edge for Cd$_{1-x}$Hg$_x$Te but the two bondlengths d$_{CdTe}$ and d$_{HgTe}$ are very close and difficult to be resolved (Fig.2). 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 accommodates two different cation-anion distances. The experimental results on different alloys [3,6,7] allow us to state the following general conclusions on the structure of pseudobinary solid solutions:

![Fig. 1](image1.png)

**Fig. 1** The radial distribution function $F(r)$ extracted from the measured EXAFS around a) the L$_{III}$ edge of Te in Cd$_{1-x}$Zn$_x$Te and b) the L$_{III}$ edge of Hg in HgCd$_{x}Te_{1-x}$.

![Fig. 2](image2.png)

**Fig. 2** NN distances in Hg$_{1-x}$Cd$_x$Te from EXAFS (+) and from X-ray diffraction (solid line).
Fig. 3 The five possible tetrahedra in a pseudobinary alloy.

Fig. 4 Experimental and calculated NN distances for different pseudobinary alloys. The experiments of In$_{1-x}$Ga$_x$As were taken from ref. [7].

i) they have crystalline order.
ii) In the alloy the bond-lengths have almost the same value as in pure compounds. Thus NN distances display a bimodal distribution (Fig. 4).
iii) 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.
iv) The same behaviour characterizes both cation and anion alloys.

We have recently developed a model for the microscopic structure of zinc-blende pseudobinary alloys that incorporate all these points [3]. 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 (DB$_{A_1-x}$A$_x$ anion alloys) or an anion C (A$_{1-x}$B$_x$C 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 (Fig. 3). We suppose that all the physical properties of the alloy will be 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 $Z_n(x)$ and $Y_n(x)$ through the minimization of the tetrahedron distortion energy $\eta_n$ 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 distribution for the five possible tetrahedra. A random distribution [3] and a $T$ dependent distribution:

$$P(\Omega)(x,T) = \frac{\gamma(x)}{\sum_{n=0}^{4} \gamma_n(x)} e^{-\gamma_n(x)}$$

derived within the III order Quasi Chemical Approximation [9] were used. Here $A = a(4)\gamma_n(A)\gamma_0/A_0^4$ is the only real and positive solution of the fourth-order polynomial equation:

$$\sum_{n=0}^{4} (n-4n)^4 e^{-\gamma_n(x)} = 0$$
The distribution probability $P(Q)$ depends not only on $x$, as the Bernoulli distribution does, but also on $T$. It is peculiar to 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 $q_i$'s. The distances calculated with the latter probability distribution are in better agreement with the experiments (Fig.4), showing sensitive deviations from the randomness, especially for In$_{1-x}$Ga$_x$As and HgSe$_{1-x}$Te.

**PHASE DIAGRAMS**

Starting from the probability distribution (4) we can calculate the Gibbs free energy of mixing and hence the phase diagrams of the alloys [9,10]. We can observe that the alloys whose enthalpy is not fully dominated by the elastic energy (i.e. the lattice-matched Hg$_{1-x}$Cd$_x$Te alloy) behave qualitatively as Bragg-Williams solutions (Fig.5a). A different behaviour characterizes the alloys dominated by the elastic deformation energy (Fig.5b). Apart from the usual change from a convex to a concave function when the temperature is lowered, the $g_2(x)$'s of these materials show regions of convexity around the mole fraction $x=0.25,0.50,0.75$. Due to the shape of $g_2(x)$, 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.

**CONCLUSIONS**

Starting from the EXAFS results we have developed a thermodynamic model of zincblende pseudobinary alloys which incorporates on equal grounds both the elastic deformation and the charge rearrangement. The model does not require adjustable parameters and proves particularly valuable in describing the local structure, the clustering properties and the equilibrium phase diagrams of lattice-matched and mismatched alloys.

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