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EXAFS STUDY OF A QUITE RELAXED ZINC-BLENDE LATTICE : THE $\text{GaAs}_y\text{Sb}_{1-y}$ ALLOY

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Résumé : Les spectres EXAFS après les seuils K de Ga et As, et L_{III} de Sb sur $\text{GaAs}_y\text{Sb}_{1-y}$ ont été enregistrés. L'analyse des spectres, dans le cas du seuil Ga, pour des compositions situées de part et d'autre de la lacune de miscibilité ($0 \leq y \leq .11$, $.9 \leq y \leq 1$), conduit aux distances entre Ga et ses plus proches voisins (NN). La distribution des distances cation-anion est bimodale ($d(\text{Ga-As}) = 2.46 \pm .02 \text{ \AA}$, $d(\text{Ga-Sb}) = 2.63 \pm .01 \text{ \AA}$) et très proche de la limite de PAULING-HUGGINS. Cette grande relaxation de la structure blende de zinc s'explique bien à la lumière d'un modèle de champ de forces de valence (Keating), en cherchant pour quelle configuration, les forces élastiques agissant sur chaque atome s'annulent: les deux sous-réseaux apparaissent distordus, tandis qu'une distribution multimodale des distances entre seconds voisins (NNN) est prédite, en accord avec l'élargissement du pic correspondant de la fonction de distribution radiale.

Abstract : EXAFS measurements above the K-edge of Ga, As and the L_{III} -edge of Sb in $\text{GaAs}_y\text{Sb}_{1-y}$ are performed. The analysis of data above the Ga K-edge, on both sides of the miscibility gap ($0 \leq y \leq .11$, $.9 \leq y \leq 1$), leads to nearest-neighbor (NN) distances around Ga atom. The distribution of cation-anion distances is bimodal ($d(\text{Ga-As}) = 2.46 \pm .02 \text{ \AA}$, $d(\text{Ga-Sb}) = 2.63 \pm .01 \text{ \AA}$) and very close to the PAULING-HUGGINS limit. This great relaxation of the zinc-blende structure is explained by using a Valence-Force-Field model (Keating) and searching for the configuration at which the elastic forces acting upon every atom vanish: both sublattices are distorted and multimodal second-neighbor distribution of distance is predicted, in agreement with the broadening of the corresponding peak of the radial distribution (NNN distances).

1. Introduction.

Among the III V and II VI pseudobinary systems, $\text{GaAs}_y\text{Sb}_{1-y}$ is interesting because of its miscibility gap below peritectic transformation ($T = 747^\circ\text{C}$) which allows one to predict clustering tendency [1]. Further crystallographic information is needed to understand this behaviour which may influence the carrier mobility of the alloy or limit device feasibility [2-3]. On the other hand, alloy description by the virtual crystal approximation (VCA) [4] is probably inadequate, as shown in other materials [5-7]. However, a local structure study such as EXAFS analysis can provide precise information on the $\text{GaAs}_y\text{Sb}_{1-y}$ zinc blende lattice.

2. Sample preparation and analysis technics.

Bulk materials were Bridgman grown by cooling Ga-rich melt ($x_{\text{Ga}}^{\text{I}} = .50$, $t = 800 - 1150^\circ\text{C}$). Homogeneous ingots were selected by microprobe analysis of X-Ray diffraction measurements of the lattice parameter $a(y)$ [8]. Samples were then powdered (crystallite size smaller than $15\mu\text{m}$).

GaSb and GaAs were taken as structural standards for extracting the backscattering-amplitudes and phases used in the EXAFS analysis. Absorption spectra around Ga (As)K-edge and Sb L_{III} -edge were performed at LURE (ORSAY, FRANCE) using either a double Si(311) crystal or a Si(400) channel cut monochromator. The DCI storage ring energy was 1.72eV and the electron current was typically 180 mA .

The EXAFS modulation function $\chi(k)$ was extracted from the background with a Victoreen fit of the pre-edge, followed by a fit of the atomiclike smooth background (*). The $k^3 \chi(k)$ data are Fourier-transformed to real space and the contribution of the first shell (NN atoms) or the second shell (NNN atoms) is backtransformed.

3. Results.

The radial distribution functions $F(R)$ around the Ga or the As K-edge are suitable for analysis, but not the ones around the Sb L_{III} -edge because of the poor resolution due to the small energy range accessible between L_{III} and L_{II} -edge : $\Delta E = 250\text{ eV}$. Fig. 1 shows $F(R)$ spectra around the Ga K-edge for $y = .11$ and $y = .90$. The first peak corresponding to Ga-V distances ($V = \text{As, Sb}$) was filtered in the range $1.80 - 2.75\text{ \AA}$ and Fourier-backtransformed before fitting. From the adjustment of the resulting $k^3 \chi(k)$ up to a maximum of $16\text{ \AA}^{-1}$ and using GaAs and GaSb as reference compounds, the NN distances have been derived. As shown by Fig. 2 and Fig. 3, the fit requires two anion subshells around Ga atoms: thus, the distribution of d_{NN} is bimodal ($d_{\text{Ga-As}} \neq d_{\text{Ga-Sb}}$) with a relaxation parameter of the lattice

$$\epsilon = [d_{\text{Ga-Sb}} - d_{\text{Ga-As}}] / [(a_{\text{GaSb}}^0 - a_{\text{GaAs}}^0) \sqrt{3}/4] \text{ which does not vary with } y (\epsilon_{\text{exp}} \simeq 0.90).$$

Fig.1-Radial distribution function of Ga K-edge spectra of $\text{GaAs}_y\text{Sb}_{1-y}$.

Fig.2-Experimental $k^3 \chi(k)$ (...) fitted with 1 anion subshell (—) for the composition $y = 0.90$.

* All computer calculations (Analysis & Model) have been made at CIRCE (ORSAY, FRANCE).

Fig.3-Experimental $k^3\chi(k)$ (...) fitted with 2 anion subshells (—) for the composition $y = 0.90$.

Fitting results with fixed As and Sb atom numbers are listed in Table I.

Table I - Parameters used in the fit (σ^2 are Debye-Waller factors, ΔE_o is the edge shift, $\mathcal{R}$ is the reliability factor).

y	N_{As}	$d_{Ga-As}(\text{\AA})$	N_{Sb}	$d_{Ga-Sb}(\text{\AA})$	σ_{Ga-As}^2 ($10^{-2} \text{\AA}^2$)	σ_{Ga-Sb}^2 ($10^{-2} \text{\AA}^2$)	ΔE_o (eV)	$\mathcal{R}(\%)$
.006	0.03	2.45	3.97	2.637	0.00	0.00	-0.92	0.87
.027	0.09	2.49	3.91	2.640	0.00	0.00	1.62	0.13
.050	0.20	2.47	3.82	2.640	0.04	0.00	1.93	0.68
.065	0.26	2.47	3.79	2.640	0.00	0.00	3.05	0.48
.095	0.33	2.47	3.65	2.638	0.03	0.00	0.31	0.19
.11	0.44	2.47	3.56	2.631	0.04	0.00	0.39	0.38
.90	3.1	2.45	0.9	2.620	0.00	0.00	-0.41	0.29
.95	3.8	2.45	0.2	2.631	0.00	0.00	-2.33	0.25

Similar analysis of the As K-edge for As-rich composition alloys ($y \geq 0.90$) leads to NN distances $d_{As-Ga} = 2.447 \text{\AA}$ in excellent agreement with the above results.

The 12 NNN atoms around Ga atoms are Ga and contribute to the peaks of $F(R)$ between 3.20 and 4.70 $\text{\AA}$. The shape of these peaks shows the presence of two main groups of d_{Ga-Ga} . Due to the different Ga-As and Ga-Sb bondlengths, it can be predicted that the Ga-Ga distances with an As atom between Ga atoms ($d_{Ga-(As)-Ga}$) will be shorter than the Ga-Ga distances with a Sb atom ($d_{Ga-(Sb)-Ga}$). In the simulation, amplitude and backscattering phase are extracted from the second shell of GaAs for Ga-As-Ga and from the second shell of GaSb for Ga-Sb-Ga. A bimodal behaviour of the d_{Ga-Ga} distribution is still found as follows for $y = 0.90$:

$$\begin{array}{lll}
 N_{Ga} = 11.08 & d_{Ga-(As)-Ga} = 3.998 \text{\AA} & \sigma_{Ga-(As)-Ga}^2 = 0.00 (10^{-2} \text{\AA}^2) \\
 N_{Ga} = 1.40 & d_{Ga-(Sb)-Ga} = 4.319 \text{\AA} & \sigma_{Ga-(Sb)-Ga}^2 = 0.03 (10^{-2} \text{\AA}^2) \\
 \Delta E_o = 0.18 \text{ eV} & \mathcal{R} = 0.22\% &
 \end{array}$$

These cation-cation distances are rather close to that in constituent binaries GaAs and GaSb. All these results indicate a quite relaxation of the blende structure.

4. Structural model of the $\text{GaAs}_y\text{Sb}_{1-y}$ lattice.

Because of the existence of the NN and NNN distances bimodal distribution, the lattice distortion occurs in both fcc sublattices. In order to understand how zinc blende structure accommodates such distortions, the Valence-Force-Field model (VFF) in the Keating's scheme [9] is used. In this approach, the deformation energy U of each unit cell is expressed in terms of the variations of the scalar quantities

$$U = \sum_{i=1}^4 \left\{ \frac{3}{8r_0^2} \alpha_i [\Delta(\bar{r}_i, \bar{r}_i')]^2 + \sum_{\substack{s=1 \\ i>j}}^2 \sum_{\substack{i,j \\ i>j}} \beta_{ij} [\Delta(\bar{r}_i^s, \bar{r}_j^{s'})]^2 \right\}$$

Here s and s' refer to the two atoms of the unit cell while i, j refer to the 4 bonds connecting these two atoms with those at the vertices of each tetrahedron. U contains only two elastic constants: α_i (α_{GaAs} or α_{GaSb} [10]) which describes the central-part of the potential (bond-stretching) and β_{ij} (β_{GaAs} [10], β_{GaSb} [10] and $\bar{\beta} = \sqrt{\beta_{\text{GaAs}} \cdot \beta_{\text{GaSb}}}$) corresponding to the non-central forces (bond-bending); r_0 is the bond distance in the undistorted crystal ($r_0 = a\sqrt{3}/4$). The computer simulation of the alloy lattice with an anion random distribution is carried out by searching for the configuration at which the elastic forces acting upon each atom vanish. In order to minimize the influence of the surface atoms, the cluster contains 1000 atoms. Atomic radial distributions $P(d)$ around Ga, As or Sb are then obtained. In the case of $P(d)$ around Ga, the bimodal distribution of d_{NN} and d_{NNN} is obtained as a result of a great relaxation in both sublattices (Fig. 4). Good agreement between experimental and

Fig.4- Calculated atomic radial distribution around Ga for $\text{GaAs}_{0.90}\text{Sb}_{0.10}$

Fig.5-Calculated cation-anion distances (—) in $\text{GaAs}_y\text{Sb}_{1-y}$ (■ measured values, X Vegard's law).

calculated d_{NN} is shown on Fig.5, but with a calculated relaxation parameter ($\epsilon_{\text{calc}} = 0.85$) smaller than the experimental one ($\epsilon_{\text{exp}} = 0.90$) and a slight variation versus y of $d_{\text{Ga-As}}$ and $d_{\text{Ga-Sb}}$. The bimodal NNN distribution corresponds to the broadening of

the corresponding peaks in $F(R)$. The root mean square deviation of the tetrahedron angle is less than 1.40° around the 109.41° mean value.

If a non-random distribution of anions is taken into account, calculations yield similar results. Thus, clear evidence of clustering tendency could be made by using other technics, such as X-Ray diffuse scattering.

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