

ASDEX and the NI group and to F. Dylla for critically reading the manuscript.

<sup>4a</sup>On leave from Academia Sinica, Peking, People's Republic of China.

<sup>1</sup>Proceedings of the International Atomic Energy Agency Workshop on Finite-Beta Limits and Transport Phenomena in Thermonuclear Plasmas, Varenna, 1982 (to be published).

<sup>2</sup>M. Keilhacker *et al.*, in *Proceedings of the Eighth International Conference on Plasma Physics and Con-*

*trolled Nuclear Fusion Research, Brussels, 1980* (International Atomic Energy Agency, Vienna, 1981), Vol. II, p. 351.

<sup>3</sup>A. Stäbler *et al.*, in *Proceedings of the Ninth International Symposium on Engineering Problems of Fusion Research, Chicago, 1981*, edited by C. K. Choi (IEEE, New York, 1981), Vol. I, p. 767.

<sup>4</sup>F. Wagner *et al.*, Max-Planck-Institut für Plasma-physik Report No. III/78, 1982 (unpublished).

<sup>5</sup>F. Wagner *et al.*, in *Proceedings of the Ninth International Conference on Plasma Physics and Controlled Nuclear Fusion Research, Baltimore, 1982* (to be published), Paper No. IAEA-CN-41/A-3.

<sup>6</sup>G. Becker *et al.*, to be published.

## Atomic-Scale Structure of Random Solid Solutions: Extended X-Ray-Absorption Fine-Structure Study of $\text{Ga}_{1-x}\text{In}_x\text{As}$

J. C. Mikkelsen, Jr., and J. B. Boyce

*Xerox Palo Alto Research Centers, Palo Alto, California 94304*

(Received 23 August 1982)

In random solid solutions of  $\text{Ga}_{1-x}\text{In}_x\text{As}$ , the Ga-As and In-As near-neighbor distances change by only 0.04 Å as  $x$  varies from 0.01 to 0.99, despite the fact that this alloy accurately follows Vegard's law, with a change in average near-neighbor spacing of 0.17 Å. This result contradicts the underlying assumption of the virtual-crystal approximation. Nonetheless, the cation sublattice approaches a virtual crystal with a broadened single distribution of second-neighbor distances, whereas the anion sublattice exhibits a bimodal anion-anion second-neighbor distribution.

PACS numbers: 61.55.Hg, 78.70.Dm

In random solid solutions the atomic-scale structure, i.e., the nature of the near-neighbor (nn) environment, is not well understood because of the fact that standard diffraction techniques average the structure over distances which are large on the scale of a lattice constant. One consequence of this lack of microscopic information is that calculations of the properties of solid solutions have often relied on simple approximations. One of the most used of these models is the virtual-crystal approximation (VCA)<sup>1</sup> which assumes that all atoms occupy the average lattice positions defined by the x-ray lattice constants. With use of the VCA, properties of the alloy, such as the electronic band structure, can be calculated whether or not the alloy lattice constant varies linearly with composition between those of the end members, i.e., follows Vegard's Law.<sup>2</sup> Similarly for dilute alloys, the assumption that the impurity-host distance is equal to the host-host distance is often used to calculate alloy properties, even those which may depend very sensitive-

ly on distance, e.g., the magnetic properties and the NMR and ESR spectra. However, the validity of this assumption, namely, an average distance or equal impurity and host distances, has never been systematically addressed with experimental measurements.

We have used extended x-ray-absorption fine structure (EXAFS) to address these issues in random solid solutions since this technique is well suited to the study of local bonding, especially the determination of nn distances relative to a well-defined standard. As a result EXAFS has been used successfully to study other issues in alloys. These include studies of dilute binary metal alloy systems<sup>3</sup> where the main issues addressed were local clustering or chemical order, such as Guinier-Preston zones, and deviations from the continuum elastic theory. Other EXAFS studies of ternary alloys<sup>4-6</sup> have indicated that the nn distances do differ from the average, but the main emphasis was on other issues and so these studies were not performed over a wide

range of composition on nearly ideal solid solutions.

We have addressed the validity of the virtual-crystal model for alloy solid solutions by performing EXAFS measurements on a representative random solid solution, the pseudobinary alloy,  $\text{Ga}_{1-x}\text{In}_x\text{As}$ . We find that the Ga-As and In-As distances in the alloy are closer to the respective distances in the pure compounds than to an average "virtual" crystal distance. However, the Ga-As distance does increase slightly ( $+0.04 \text{ \AA}$ ) when present at 2% in InAs, while the In-As distance decreases somewhat ( $-0.05 \text{ \AA}$ ) when present at 1% in GaAs. Analysis of the second-neighbor (nn) distances indicates that the cation (Ga,In) sublattice has a broadened single distribution peaked at the average lattice distance, whereas the anion (As) sublattice exhibits a bimodal distribution. This implies that the VCA drastically underestimates the difference in nn distances but is a reasonably good approximation for second- and further-neighbor distances.

$\text{Ga}_{1-x}\text{In}_x\text{As}$  was chosen because it has the simple zinc-blende crystal structure, it closely approximates an ideal solid solution, i.e., follows Vegard's Law from  $x=0$  to  $x=1.0$ ,<sup>7</sup> and its nn distances vary significantly from  $2.448 \text{ \AA}$  in GaAs to  $2.623 \text{ \AA}$  in InAs. In addition all three elements have readily accessible  $K$ -absorption edges for EXAFS measurements. Our x-ray results indicated that the annealed polycrystalline alloys were homogeneous and obeyed Vegard's Law. The EXAFS measurements were made in transmission through films of powdered alloys mounted in epoxy, at  $77 \text{ K}$  to reduce the Debye-Waller broadening, and at  $298 \text{ K}$  to compare with the room-temperature x-ray data. Standard techniques<sup>8</sup> were used to reduce the data.

Figure 1 shows an example of the EXAFS on the Ga  $K$  edge, transformed to real space for  $\text{Ga}_{0.1}\text{In}_{0.9}\text{As}$  as well as for pure GaAs. The first peak in each case corresponds to the four As first neighbors to the Ga, the second peak to the cation second neighbors, and so on. From this figure three conclusions concerning the environment around the Ga can be drawn. First, the change in the Ga-As distance [first peak in Figs. 1(a) and 1(b)] between the alloy and pure GaAs is small. This implies that the Ga-As nn distance in the 10% alloy is closer to that of pure GaAs than it is to that of the InAs host. Second, the widths of the nn peaks are approximately the same. This implies that there is little additional broadening of the nn distribution in the alloy com-

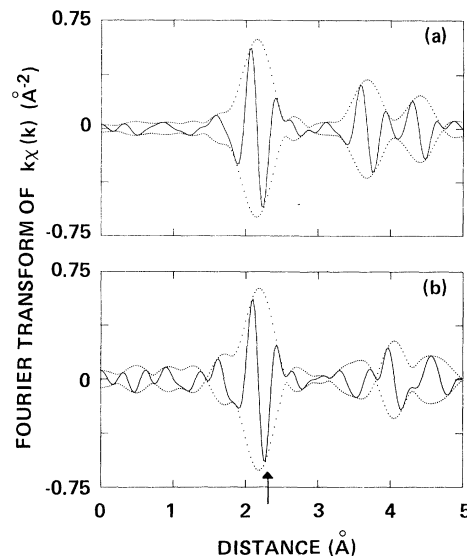


FIG. 1. The real part (solid line) and magnitude of the Fourier transform of the EXAFS,  $k\chi(k)$ , on the Ga  $K$  edge for (a) pure GaAs and (b)  $\text{Ga}_{0.1}\text{In}_{0.9}\text{As}$ . The data were transformed by using a square window from  $k=3.4$  to  $14 \text{ \AA}^{-1}$ , broadened by convolution with a Gaussian of half-width  $0.5 \text{ \AA}^{-1}$ . The arrow marks the expected peak position for the alloy if the Ga-As distance were the average cation-anion distance calculated from the lattice constant.

pared with that of pure GaAs despite the disorder in the random solid solution. Third, the further-neighbor peaks are altered in the alloy as a result of the disorder on the cation sublattice, and the nn distances in  $\text{Ga}_{0.1}\text{In}_{0.9}\text{As}$  are closer to those in the InAs host than in GaAs, in contrast to the situation for the nn peak. We now discuss each of these points using a quantitative analysis of eight alloy concentrations and the EXAFS on the  $K$  edges of all three elements. In each case the structural results were obtained in a least-squares fit to the data in real space with use of the pure binary compounds as known structural standards, and under the assumption that the nn distribution is a Gaussian with adjustable position, width, and amplitude, i.e., number of neighbors. Such a procedure gave good fits to all the data with amplitudes consistent with the known number of neighbors in the zinc-blende structure.

We first discuss the results on the nn distance. The measured Ga-As and In-As distances in the alloys are indicated by the lower and upper curves in Fig. 2, respectively. We estimate error bars of  $0.005 \text{ \AA}$  in nn spacings as the point at which the reliability-of-fit parameter increases by a factor of 2 from a minimum value (with the other

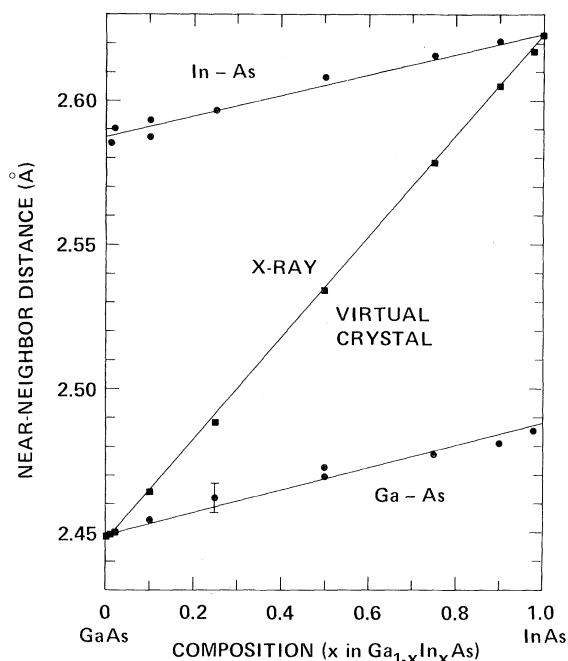


FIG. 2. Near-neighbor distances, Ga-As (lower curve) and In-As (upper curve), vs mole fraction InAs in the alloy  $\text{Ga}_{1-x}\text{In}_x\text{As}$ . The average cation-anion spacing calculated from the measured lattice constant, namely,  $3^{1/2}a_0/4$  (middle curve), is seen to accurately follow Vegard's Law.

parameters held fixed), except for the dilute alloys (1–2 mole%) where the error is  $\sim 0.01 \text{ \AA}$ . Since our impurity distances are compared directly with well-known standards, and a large range of alloy compositions was studied, we are able to see a significant increase of  $0.04 \text{ \AA}$  in the Ga-As distances from pure GaAs to the dilute alloys. This differs from the observation that in  $\text{Pr}_{0.1}\text{-Er}_{0.9}\text{Sb}$  the Pr-Sb distance equals that in  $\text{PrSb}$ , although with a large uncertainty of  $\pm 0.1 \text{ \AA}$ .<sup>6</sup> For comparison, we have also plotted the average zinc-blende nn spacings obtained from our measured x-ray lattice constants of the alloys. Although the lattice constant exhibits truly linear behavior from GaAs to InAs, there are *two* nn distances much closer to those of the pure binary compounds than to an average "virtual crystal" distance. We refer to this situation as a bimodal nn distribution.

The second observation from the nn peak is that the widths of the distribution of Ga-As and In-As distances in the alloys are the same, to within our uncertainty of  $0.02 \text{ \AA}$ , as those in GaAs or InAs. The narrow nn distributions in the alloys are not surprising in view of the results in Fig. 2. For example, in an alloy of  $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$  there

will be fluctuations in the chemical environment which appear like  $\text{Ga}_{0.25}\text{In}_{0.75}\text{As}$  and  $\text{Ga}_{0.75}\text{In}_{0.25}\text{As}$ . For a random distribution, these will occur 4.2 times less frequently than a 50:50 local composition. In any event they will only contribute an additional  $0.02 \text{ \AA}$  to the cation nn width, consistent with our experimental observations.

We examined the nnn distances to ascertain, first, how the zinc-blende lattice accommodates different Ga-As and In-As nn distances, and second, to what extent the substitution on the cation sublattice occurs randomly. In the nnn analysis the appropriately weighted sum of two shifted and Gaussian-broadened nnn signatures were compared with the alloy. It was found that cation-cation distributions peak at a single distance, in good agreement with the VCA calculated value, whereas the anion-anion distribution is bimodal, which indicates that the anions do not occupy virtual-crystal positions. In addition we also found that all of these nnn distributions have an additional  $0.06\text{--}0.10 \text{ \AA}$  broadening compared with the pure-compound standards, in contrast to the similarity in widths for the nn distributions. This indicates that there is some local deviation from the virtual-crystal cation sublattice positions due to the random distribution of Ga and In atoms. Since the additional broadening in the alloy is less than the  $0.11 \text{ \AA}$  difference between the Ga-Ga distance in GaAs and that in the 50:50 alloy, only a small fraction of Ga-Ga distances characteristic of pure GaAs exists in the alloy. The In-In analysis leads to the same conclusion. Furthermore, we observe that both elements have nearly the expected mixture of Ga and In second neighbors corresponding to the alloy composition, consistent with random alloy formation.

We next draw an analogy between the  $\text{Ga}_{0.5}\text{In}_{0.5}\text{-As}$  alloy and the tetrahedrally coordinated chalcopyrite ( $\text{ABX}_2$ ) structure,<sup>9</sup> in which the A and B cations occupy a regular face-centered tetragonal sublattice, but all the X anions are displaced in  $\langle 100 \rangle$  directions toward 2 B cations and away from 2 A cations in each of the *identical* tetrahedra. (The displacement is zero if the parameter  $u$  is  $\frac{1}{4}$ .) If there were no tetragonal distortion ( $c_0/a_0 = 2$ ), the cations would be on a face-centered-cubic lattice, but the anions would still be displaced from an fcc array. If the cation sublattice were to disorder, we would expect that the two nn cation-anion distances would remain nearly unchanged, only long-range order would be destroyed, and the cation-cation distribution might be broadened by random fluctuations in the cation

site occupation. In the  $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$  alloy the predominant cation tetrahedral arrangement around each As is 2 Ga and 2 In. Assuming that the 2 Ga and 2 In are on the virtual-crystal sublattice, we calculated a 0.10-Å displacement of the As from a virtual-crystal (fcc) anion sublattice, which would correspond to an effective  $u$  parameter of 0.267 in a chalcopyrite lattice with  $a_0$  equal to the average lattice constant of  $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$  (5.83 Å) and  $c_0 = 11.66$  Å ( $2a_0$ ). The calculated nn and nnn distances for this pseudo chalcopyrite are in good agreement with the observed alloy distances. This suggests that the local tetrahedral distortions in the chalcopyrite structure provide an analogous description of local bonding in pseudo-binary zinc-blende alloys.

Our experimental results can be compared with two classes of alloy models, first, a two-dimensional force-constant model applied to pseudo-binary alloys<sup>10</sup> and, second, the continuum<sup>3</sup> and discrete-lattice<sup>11</sup> elastic models applied to binary metal alloys. In the first model a bimodal nn distribution was postulated to explain the S-shaped bowing of the lattice constant as a function of composition observed in some zinc-blende ternary solid solutions. Since we find a bimodal nn distribution in  $\text{Ga}_{1-x}\text{In}_x\text{As}$ , but the lattice constant strictly follows Vegard's Law, a bimodal distribution may be necessary, but is not a *sufficient*, condition for an S-shaped lattice constant. In addition, this model predicts that each nn distribution will be broadened by  $\sim \frac{1}{4}$  the splitting, or 0.04 Å in the case of  $\text{Ga}_{1-x}\text{In}_x\text{As}$ . This was not observed. The second class of models has been used to describe binary metal alloys, with the most studied system being dilute Cu in Al. Both the continuum and discrete models underestimated by a factor of 3 one of the measured differences ( $\Delta = 0.13$  Å)<sup>3</sup> between the impurity Al-Cu and the host Al-Al distances. However, another measurement<sup>12</sup> on Cu-Al alloys obtained  $\Delta = 0.06$  Å, in good agreement with both elastic models. The application of either elastic model to  $\text{Ga}_{1-x}\text{In}_x\text{As}$  alloys is further complicated by the fact that the covalent bonding of the open zinc-blende structure (only 4 nn) is characterized by strong noncentral forces and the substitution is on second-neighbor sites.

We find that the atomic-scale structure of  $\text{Ga}_{1-x}\text{In}_x\text{As}$  alloys is characterized by a nn distribution which is composed of two well-defined distances, whereas the mixed (cation) nnn distances exhibit a single broadened distribution, while the common (anion) nnn distribution is bimodal. We, therefore, conclude that  $\text{Ga}_{1-x}\text{In}_x\text{As}$  alloys are not virtual crystals at the atomic level, but that the cation sublattice does approach a virtual crystal beyond the second-neighbor distance. It is probably for this reason that the virtual-crystal model works so well in band-structure calculations. Indeed, in the analogous chalcopyrite compounds, the tetragonal distortion affects the band structure much more than the displacement of anions from a face-centered sublattice.<sup>9</sup>

We thank C. Herring for useful comments on this work. The Stanford Synchrotron Radiation Laboratory is supported by the National Science Foundation through the Division of Materials Research.

<sup>1</sup>See, for example, J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973), p. 214.

<sup>2</sup>L. Vegard, *Z. Phys.* **5**, 17 (1921).

<sup>3</sup>See D. Raoux, A. Fontaine, P. Lagarde, and A. Sado, *Phys. Rev. B* **24**, 5547 (1981), and references therein.

<sup>4</sup>J. C. Mikkelsen, Jr., and J. B. Boyce, *Phys. Rev. B* **24**, 5999 (1981).

<sup>5</sup>J. B. Boyce, R. M. Martin, J. W. Allen, and F. Holtzberg, in *Valence Fluctuations in Solids*, edited by L. M. Falicov, W. Hanks, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 427.

<sup>6</sup>J. Azoulay, E. A. Stern, D. Shaltiel, and A. Grayevski, *Phys. Rev. B* **25**, 5627 (1982).

<sup>7</sup>J. C. Wooley and B. C. Smith, *Proc. Phys. Soc. London* **72**, 241 (1958).

<sup>8</sup>J. B. Boyce, T. M. Hayes, and J. C. Mikkelsen, Jr., *Phys. Rev. B* **23**, 2876 (1981).

<sup>9</sup>J. L. Shay and J. H. Wernick, *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties, and Applications* (Pergamon, Oxford, 1975), p. 85.

<sup>10</sup>C. Y. Fong, W. Weber, and J. C. Phillips, *Phys. Rev. B* **12**, 5387 (1976).

<sup>11</sup>Sverre Froyen and Conyers Herring, *J. Appl. Phys.* **52**, 7165 (1981).

<sup>12</sup>B. Lengeler and P. Eisenberger, *Phys. Rev. B* **21**, 4507 (1980).