High real-space resolution measurement of the local structure of Ga$_{1-x}$In$_x$As using x-ray diffraction

V. Petkov$^1$, I-K. Jeong$^1$, J. S. Chung$^1$, M. F. Thorpe$^1$, S. Kycia$^2$ and S. J. L. Billinge$^1$

$^1$Department of Physics and Astronomy and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI 48824-1116. $^2$Cornell High Energy Synchrotron Source, Cornell University, Ithaca, NY 14853

(March 24, 2022)

High real-space resolution atomic pair distribution functions (PDF)s from the alloy series Ga$_{1-x}$In$_x$As have been obtained using high-energy x-ray diffraction. The first peak in the PDF is resolved as a doublet due to the presence of two nearest neighbor bond lengths, Ga-As and In-As, as previously observed using XAFS. The widths of nearest, and higher, neighbor pairs are analyzed by separating the strain broadening from the thermal motion. The strain broadening is five times larger for distant atomic neighbors as compared to nearest neighbors. The results are in agreement with model calculations.

The average atomic arrangement of crystalline semiconductor alloys is usually obtained from the position and intensities of the Bragg peaks in a diffraction experiment, and the actual nearest neighbor and sometimes next nearest neighbor distances for various pairs of atoms by XAFS measurements. In this Letter we show how high energy x-ray diffraction and the resulting high-resolution atomic pair distribution functions (PDF)s can be used for studying the internal strain in Ga$_{1-x}$In$_x$As alloys. We show that the first peak in the PDFs can be resolved as a doublet and, hence, the mean position and also the widths of the Ga-As and In-As bond length distributions determined. The detailed structure in the PDF can be followed out to very large distances and the widths of the various peaks obtained. We use the concentration dependence of the peak widths to separate the strain broadening from the thermal broadening. At large distances the strain broadening is shown to be about five times larger than for nearest neighbor pairs. Using a simple valence force field model, we get good agreement with the experimental results.

Ternary semiconductor alloys, in particular Ga$_{1-x}$In$_x$As, have technological significance because they allow important properties, such as band-gaps, to be tuned continuously between the two end-points by varying the composition $x$. Surprisingly, there is no complete experimental determination of the microscopically strained structure of these alloys. On average, both GaAs and InAs form in the zinc-blende structure where Ga or In and As atoms occupy two inter-penetrating face-centered-cubic lattices and are tetrahedrally coordinated to each other. However, both extended x-ray absorption fine structure (XAFS) experiments and theory have shown that Ga-As and In-As bonds do not take some average value but remain close to their natural lengths of $L_{\text{Ga-As}}^{0} = 2.437$ Å and $L_{\text{In-As}}^{0} = 2.610$ Å in the alloy. Due to the two considerably different bond lengths present, the zinc-blende structure of Ga$_{1-x}$In$_x$As alloys becomes locally distorted. A number of authors have proposed distorted local structures but there has been limited experimental data available to date. The fully distorted structure is a prerequisite as an input for accurate band structure and phonon dispersion calculations.

The technique of choice for studying the local structure of semiconductor alloys has been XAFS. However, XAFS provides information only about the immediate atomic ordering (first and sometimes second coordination shells) and all longer-ranged structural features remain hidden. To remedy this shortcoming we have taken the alternative experimental approach of obtaining high-resolution PDFs of these alloys from high energy x-ray diffraction data.

The PDF is the instantaneous atomic density-density correlation function which describes the local arrangement of atoms in a material. It is the sine Fourier transform of the experimentally observable total structure function obtained from powder diffraction measurements. PDF analysis yields the real local structure whereas an analysis of the Bragg scattering alone yields the average crystal structure. Determining the PDF has been the approach of choice for characterizing glasses, liquids and amorphous materials for a long time. However, its widespread application to study crystalline materials has been relatively recent. Very high real-space resolution is required to differentiate the distinct Ga-As and In-As bond lengths present in Ga$_{1-x}$In$_x$As. High real-space resolution is obtained by measuring the structure function, $S(Q)$ ($Q$ is the amplitude of the wave vector), to a very high value of $Q$ ($Q_{\text{max}} \geq 40$ Å$^{-1}$). An indium neutron absorption resonance rules out neutron measurements in the Ga$_{1-x}$In$_x$As system. We therefore carried out x-ray powder diffraction measurements. To access $Q$ values in the vicinity of $40-50$ Å$^{-1}$ it is necessary to use x-rays with energies $\geq 50$ keV. The experiments were carried out at the A2 56 pole wiggler beamline at Cornell High Energy Synchrotron Source (CHESS) which is capable of delivering intense x-rays of energy 60 keV. Six powder samples of Ga$_{1-x}$In$_x$As, with $x = 0.0, 0.17, 0.5, 0.67, 0.83$ and $1.0$, were measured. The samples were made by standard methods and the details of the sample preparation will be reported elsewhere. All measurements were done in symmetric transmission geometry at 10K. Low temperature was used to minimize thermal vi-
The data were normalized for flux, corrected for background scattering, detector deadtime and absorption and divided by the average form factor to obtain the total ground scattering. Detector deadtime and absorption and the shortness atomic distances in GaAs and InAs were determined the positions of the two subcomponents of the first PDF peak, i.e. the mean Ga-As and In-As bond lengths, and the results are shown in Fig. 3. Also shown is the room temperature result previously obtained in the XAFS study of Mikkelson and Boyce [2]. There is clearly good agreement. The PDF-based bond lengths are shifted to smaller lengths by about 0.012 ˚A since our data were measured at 10K, whereas the XAFS experiments were at room temperature. The nearest neighbor peak is the only peak which is sharp in the experimental PDFs as can be seen in Fig. 2. From the second-neighbor onwards the significant strain in the alloy samples results in broad atom-pair distributions without any resolvable splitting. Model calculations show that this broadening is intrinsic and not due to any experimental limitations. The strain in Ga1-xInxAs was quantified by fitting the individual peaks in experimental PDFs. We used Gaussians convoluted with Sinc functions which account for the experimental resolution coming from the finite Q max. The FWHM of the resolution function is 0.086 ˚A. This is significant for the near-neighbor peaks as shown in Fig. 3, but is much smaller than the width of the high-r peaks. The high-r peaks are fit using the PDFFIT modeling program [6] assuming the virtual crystal zinc-blende structure and refining displacement parameters. The resulting
The strain peaks at a composition $x=0.5$ and affects the common (As) more than the mixed (metal) sublattice. In order to better understand these results, we have modeled the static and thermal disorder in the alloy by using a Kirkwood potential \cite{14}. The key element in this potential is the central force term that connects nearest neighbor atoms and would like to keep each bond at its natural (unstrained) length. The potential contains nearest neighbor bond stretching force constants $\alpha$ and force constants $\beta$ that couple to the change in the angle between adjacent nearest neighbor bonds. We choose these parameters to fit the end members \cite{3} with $\alpha_{Ga-As} = 96N/m$, $\alpha_{In-As} = 97N/m$, $\beta_{Ga-As-Ga} = \beta_{As-Ga-As} = 10N/m$ and $\beta_{In-As-In} = \beta_{As-In-As} = 6N/m$. The additional angular force constant required in the alloy are taken to be the geometrical mean, so that $\beta_{Ga-As-In} = \sqrt{(\beta_{Ga-As-Ga}\beta_{In-As-In})}$. We have constructed a series of cubic 512 atom periodic supercells in which the Ga and In atoms are distributed randomly according to the composition $x$. The system is relaxed using the Kirkwood potential to find the displacements from the virtual crystal positions. The volume of the supercell is also adjusted to find the minimum energy. Using this strained static structure, a dynamical matrix has been constructed and the eigenvalues and eigenvectors found numerically. From this the Debye-Waller factors for all the individual atoms in the supercell can be found and hence the PDF of the model by including the Gaussian broadening of all the subpeaks. We have shown previously \cite{13} that this is the correct procedure within the harmonic approximation. The model-PDF is plotted with the data in the inset to Fig. 2 and in Fig. 5. The agreement at higher-$r$ is comparable to that in the $r$-range shown. All the peaks shown in the Figures consist of many Gaussian subpeaks. The overall fit to the experimental $G(r)$ is excellent and the small discrepancies in Fig. 5 between theory and experiment are probably due to small residual experimental errors. Note that in comparing with experiment, the theoretical PDF has been convoluted with a sinc function to incorporate the truncation of the experimental data at $Q_{max} = 45 \text{Å}^{-1}$. The technique discussed above could be extended using a better force constant model with more parameters, but does not seem necessary at this time.

The thermal and strain contributions to the widths of the individual peaks in the reduced PDF act independently, as expected and as confirmed by our supercell calculations described in the previous paragraph. We therefore expect the squared width $\Delta$ to be a sum of the two parts. The thermal part $\sigma$ is almost independent of the concentration and we fit $\sigma^2$ by a linear function of the composition $x$ between the two end points in Fig. 4. To better understand the strain model it is convenient to assume that all the force constants are the same and independent of chemical species. Then it can be shown \cite{16} for any such model that

$$\Delta_i^2 = \sigma_{ij}^2 + A_{ij}x(1-x)(L_{0}^0_{In-As} - L_{0}^0_{Ga-As})^2$$

where the subscripts $ij$ refer to the two atoms that lead to a given peak in the reduced PDF. For the Kirkwood model the $A_{ij}$ are functions of the ratio of force constants $\beta/\alpha$ only. It further turns out that the $A_{ij}$ are independent of whether a site in one sublattice is Ga or In, so we will just refer to that as the metal site. Taking mean values from the force constants used in the simulation we find that $\beta/\alpha = 0.83$, and that for nearest neighbor pairs $A_{ij} = 0.0712$. For more distant pairs the motion of the two atoms becomes incoherent so that $A_{ij} = A_i + A_j$ and we find that for the metal site $A_i = 0.375$ and for the As site $A_j = 1.134$. The validity of the approximation of using mean values for the force constants was shown to be accurate by calculating the model-PDF for all compositions as described above and comparing to the prediction of Eq. (2) \cite{16}. Equation 2 shows good agreement with the data for near and far neighbor PDF peaks, and for the different sublattices, over the whole alloy range, as shown in Fig. 4, using only parameters taken from fits to the end-members. There is a considerably larger width associated with the As-As peak in Fig. 4 when compared to the Me-Me peak, because the As atom is surrounded by four metal cations, providing five distinct first-neighbor environments \cite{16}. The theoretical curve in the lower panel of Fig. 4 is predicted to
be the same for the Ga-As and In-As bond length distribution, using the simplified approach. The Kirkwood model seems adequate to describe the experimental data at this time, although further refinement of the error bars may require the use of a better potential containing more parameters.

In summary, we report for the first time a high-real-space-resolution measurement of the PDF of Ga$_{1-x}$In$_x$As ($0 < x < 1$) alloys. The PDF allows the local distortions away from the average structure over a wide range of $r$ to be determined in disordered crystals such as these. The nearest-neighbor Ga-As and In-As bond lengths in the alloys are clearly resolved. Significantly greater disorder exists in the more distant neighbor length distributions in the alloys. The experimental results are well fit over a wide range or $r$ using a Kirkwood model. Because the agreement between theory and experiment is good at both short and large distances, the Kirkwood model can be used with some confidence to generate strained alloy structures for use in the calculation of electronic band structure and phonon dispersion curves.

We would like to thank Rosa Barabash for discussions and help with the analysis of the static strains and Andrea Perez and the support staff at CHESS for help with data collection and analysis. This work was supported by DOE through grant DE FG02 97ER45651. CHESS is operated by NSF through grant DMR97-13424.

[1] R. W. G. Wyckoff, *Crystal Structures*, volume 1, Wiley, New York, 2 edition, 1967.
[2] J. C. Mikkelsen and J. B. Boyce, Phys. Rev. Lett. 49, 1412 (1982); J. C. Mikkelsen and J. B. Boyce, Phys. Rev. B 28, 7130 (1983).
[3] Y. Cai and M. F. Thorpe, Phys. Rev. B 46, 15879 (1992).
[4] J. L. Martins and A. Zunger, Phys. Rev. B 30, 6217 (1984); M. C. Schabel and J. L. Martins, Phys. Rev. B 43, 11873 (1991).
[5] A. Balzarotti et al., Phys. Rev. B 31, 7526 (1985); H. Oyanagi et al., Solid State Commun. 67, 453 (1988).
[6] A. Zunger et al., Phys. Rev. Lett. 65, 353 (1990).
[7] B. E. Warren, *X-ray Diffraction*, Dover, New York, 1990.
[8] Y. Waseda, *The structure of non-crystalline materials*, McGraw-Hill, New York, (1980).
[9] T. Egami, Mater. Trans. 31, 163 (1990); T. Egami, in *Local Structure from Diffraction*, edited by S. J. L. Billinge and M. F. Thorpe, page 1, New York, 1998, Plenum.
[10] I-K. Jeong, F. Mohiuddin-Jacobs, V. Petkov and S. J. L. Billinge, unpublished.
[11] H. P. Klug and L. E. Alexander, *X-ray Diffraction Procedures for Polycrystalline Materials*, Wiley, New York, 2nd edition, 1974.
[12] V. Petkov, J. Appl. Cryst. 22, 387 (1989).
[13] Th. Proffen and S. J. L. Billinge, J. Appl. Cryst., to be published.
[14] J. G. Kirkwood, J. Chem. Phys. 7, 506 (1939).
[15] Jean S. Chung and M. F. Thorpe, Phys. Rev. B 55, 1545 (1997); M. F. Thorpe, et al., in *Local Structure from Diffraction*, edited by S. J. L. Billinge and M. F. Thorpe, page 157, New York, 1998, Plenum.
[16] J. S. Chung, R. I. Barabash and M. F. Thorpe, unpublished, 1999.