Measuring Correlated Atomic Motion Using X-ray Diffraction

Il-Kyoung Jeong,* Thomas Proffen, Farida Mohiuddin-Jacobs, and Simon J. L. Billinge

Department of Physics and Astronomy and Center for Fundamental Materials Research,
Michigan State University, East Lansing, Michigan 48824-1116

The atomic motions in crystals are correlated. In this paper we demonstrate that information about the correlated motion of atoms, and consequently about the bonding within the crystal, can be obtained by analyzing the peak width of the atomic pair distribution function (PDF). We have measured the PDFs of Ni and InAs using synchrotron X-ray diffraction. The analysis of the Ni data allowed us to determine the Debye temperature which is in good agreement with values found in the literature. In contrast to the isotropic metallic bonding in Ni resulting in a relatively weak correlation between the motion of neighboring atoms, we found a very strong correlation in InAs as one might expect from the covalent bond between In and As. The results are compared with theoretical predictions by Chung and Thorpe (*Phys. Rev. B* **1977,** *55,* 1545).

1. Introduction

The atomic motions in crystals are correlated. For example, near-neighbor atoms tend to move in-phase with each other. This *correlated* movement of neighboring atoms contains detailed information about the bonding and the atomic potential in the materials. Thus, empirical potential parameters can be determined from studies of atomic motions.

There are various ways to study correlated movements of atoms in crystalline materials. The most detailed information can be obtained from phonon dispersion curves determined using inelastic neutron diffraction. However, those measurements require large single crystals and considerable neutron beamtime. Other experimental techniques include Raman or IR scattering, which can only extract frequencies of zone center phonons, but no information about phonon dispersion or zone edge behavior. Correlated motion can be measured in X-ray absorption fine structure (XAFS) experiments,[1] which directly probe the relative motion of near neighbors. In these measurements the information available about the relative motion of far neighbor pairs is very limited and uncorrelated thermal parameters are not available.

We have taken the approach of extracting correlated thermal motion from powder diffraction data. This approach yields extensive information, yet the experiments are straightforward and do not require single crystals. First we review how atomic motion affects the scattered intensity in a diffraction experiment. In a simple Einstein model with *uncorrelated* motions (Figure 1a) each atom vibrates independently of its neighbors and the Bragg peak intensity is attenuated as a function of scattering angle by the well-known Debye−Waller factor.[2] The "remaining" intensity shows up as uniform diffuse scattering. If correlated motions (Figure 1b) are taken into account, the behavior of the intensities of the Bragg reflections is unchanged, but so-called thermal diffuse scattering (TDS) appears centered around Bragg positions. Thus, by measuring the attenuation of Bragg-peak intensity it is possible to find the mean-square atomic displacement amplitude, $\langle u^2 \rangle$, which corresponds to the uncorrelated value of the thermal motion. However, to learn about the correlated motion of atoms, *all* diffraction data including TDS must be used.
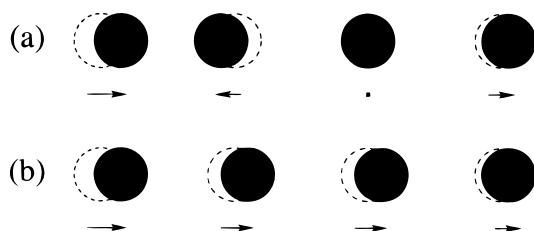
* To whom correspondence should be addressed. Phone: 517-432-0042. Fax: 517-353-4500. E-mail: jeong@pa.msu.edu.

Figure 1. Schematic representation of (a) uncorrelated and (b) correlated movement of atoms.

A convenient and relatively fast method to achieve this goal is powder diffraction using neutrons or X-rays. The TDS is evident in powder diffraction data.[3] Although directional information is lost, it is still possible to extract significant information about the correlation of thermal motions. A representation of powder diffraction data, which emphasizes the correlated atomic motions, is to Fourier transform it to real-space and consider the atomic pair distribution function (PDF). This gives information about the correlation of the atomic motion since the PDF peak width is a measure of the amplitude of relative motions of atom pairs. At low r_{ij} the PDF peaks are relatively sharpened because of the tendency for near-neighbor atoms to move in-phase with each other, where r_{ij} is the separation distance of the pair of atoms. This behavior was first analyzed by Kaplow in a series of papers[3−5] and interatomic potentials were determined directly from the PDF for a number of elemental metals. With the advent of modern synchrotron X-ray and neutron sources and high-speed computing, the reliability and utility of this technique has dramatically improved from these early investigations.

In this paper we present the PDFs from two different systems: Ni with isotropic metallic bonding and InAs with strongly directional covalent bonding.[6] Both PDFs were obtained using synchrotron X-ray diffraction.

2. Experimental Section

The experiments were performed in flat plate, transmission geometry for InAs and reflection geometry for Ni, at beam line X7A at the National Synchrotron Light Source at Brookhaven
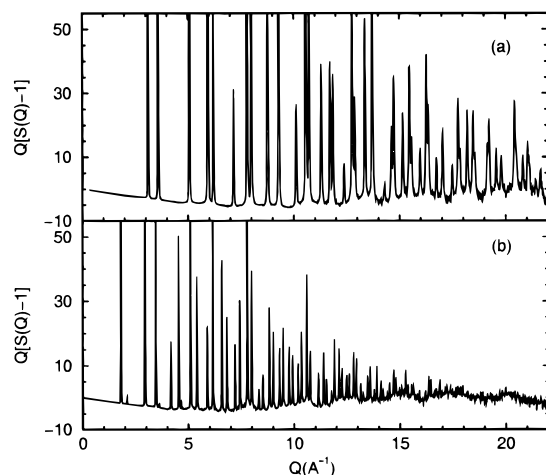
Figure 2. Reduced structure factors $F(Q) = Q[S(Q) - 1]$ for (a) Ni and (b) InAs.
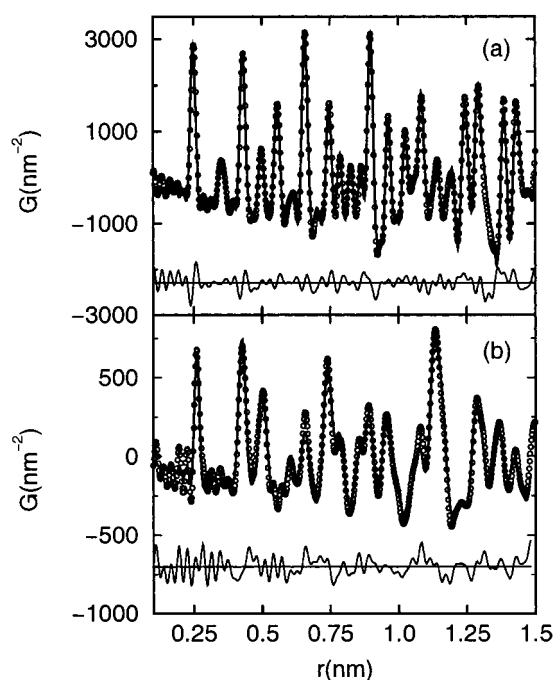

Figure 3. Experimental PDF (circles) and model PDF (solid line) of Ni (a) and InAs (b) for refinement B. Difference curves are plotted below the data.

National Laboratory using a wavelength of $\lambda = 0.5$ Å. Both measurements were carried out at room temperature.

The sample dependent single scattering, $S(Q)$, was obtained using standard procedures.[2,7] The data were corrected for absorption, multiple scattering, and polarization effects. Background and Compton scattering were removed and the data were normalized for flux and number of scatterers. The reduced structure factor $F(Q) = Q[S(Q) - 1]$ for the Ni and InAs data are shown in Figure 2a,b, respectively.

The experimental PDF, $G(r)$, is obtained by taking the Fourier transform of the reduced structure factor $F(Q)$ according to the following equation:

$$G(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1]\sin(Qr)\, dQ \qquad (1)$$

The resulting PDFs are shown in Figures 3 and 4 as open circles. One notable aspect of these powder diffraction patterns is that the data were collected up to a high momentum transfer $Q =$
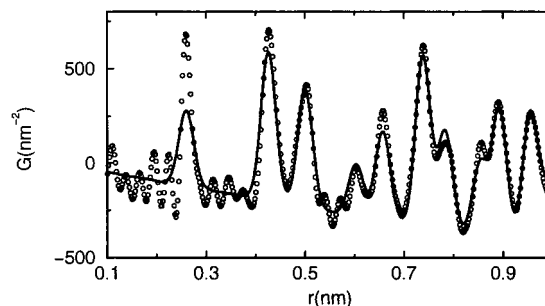

Figure 4. Experimental PDF (circles) and model PDF (solid line) of InAs for refinement A.

22 Å^{-1} corresponding to a d spacing of 0.29 Å. This is necessary to obtain a high-resolution PDF.

3. Modeling

In principle one can imagine various ways to extract the width of the individual peaks from the experimental PDF. However, the task is not as straightforward as it might seem. One of the problems is the contribution of termination ripples. These ripples appear in the PDF from the Fourier transform due to a finite data range. They are well understood[8] but may cause conventional fitting or integration procedures to fail.

A model independent way to extract PDF widths taking those experimental effects into account is currently being developed by the authors of this paper. Here we have used the "real-space" Rietveld program RESPAR,[8] which contains a correction for these effects, to fit a model PDF, $G_m(r)$, to the observed PDF. The model PDF, $G_m(r)$, is defined as

$$G_m(r) + 4\pi r\rho_0 = \frac{1}{r}\sum_i \sum_j \frac{f_i f_j}{\langle f \rangle^2}\delta(r - r_{ij}) \qquad (2)$$

The sums are over all atoms within the sample. The number density of the sample is given by ρ_0. The value f_i is the scattering power of atom i evaluated at $Q = 0$, in other words the number of electrons Z for atom i. The sample average scattering power is $\langle f \rangle$. Additionally, each atomic pair correlation, $\delta(r - r_{ij})$, is convoluted with a Gaussian to account for thermal motion. Atomic positions, site occupancies, displacement parameters, and lattice parameters are refined similar to conventional Rietveld refinement[9] to obtain a match between the observed and calculated PDF. Furthermore, some sample independent parameters (e.g., scale factor) are refined. Details of the procedure are given by Billinge.[8]

The result of the initial refinement (A) of the InAs data is shown in Figure 4. It is immediately obvious that although the agreement at large values of r is good, the first peak of the model PDF, $G_m(r)$, is too broad compared to the experimental PDF. This directly shows the effect of correlated motion for the nearest neighbor due to the strong covalent bond between In and As. In refinement A the sharpening of the PDF peaks at low values of r was not taken into account to illustrate this point. Thus, the calculated PDF we see in Figure 4 corresponds to the case of completely *uncorrelated* motion.

The effect of *correlated* motion is taken into account in our modeling by describing the r dependence of the PDF peak width, σ_c, by the following empirical equation

$$\sigma_c = \sigma_0 - \frac{\delta}{r_{ij}^2} \qquad (3)$$

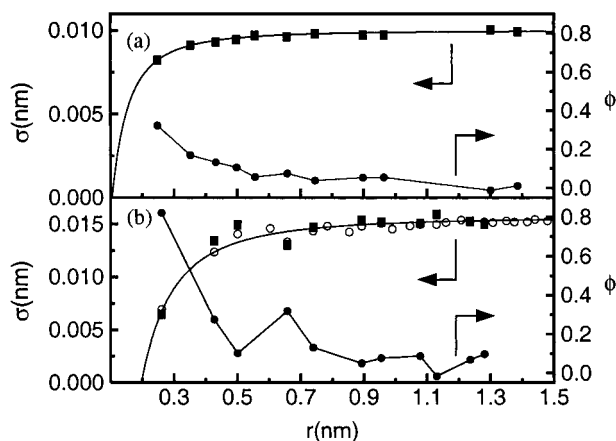The parameter σ_0 corresponds to the uncorrelated thermal motion

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Figure 5. (a) Ni: PDF peak width σ_{ij} (filled square) and correlation ϕ (filled circle) as a function of r. The solid line marks the empirical relation in eq 3. (b) InAs: PDF peak width σ_{ij} (filled square) and correlation ϕ (filled circle) as function of r. Empty circles mark the theoretical values by Chung and Thorpe. The solid line marks the empirical relation in eq 3.

Figure 6. Schematic drawing of the unit cell of InAs. The marked distances, r_1 to r_5 are discussed in the text.

of atom pairs and is given by $\sigma_0^2 = \sigma_i^2 + \sigma_j^2$, where σ_i and σ_j are the amplitude of uncorrelated thermal motion ($\sqrt{\langle u^2 \rangle}$) of atoms i and j and δ is an empirical parameter describing the sharpening of the PDF peaks. The parameters σ_0 and δ are refined in the modeling process. Figure 3 shows the results of refinement B for the Ni and InAs data. Here the parameter δ was refined, and we observe a good agreement between experimental and calculated PDF over the complete r range.

To actually extract the peak width, σ_c, as a function of r, we carried out the following two steps: First, all parameters were refined using the complete r range of the experimental PDF. In a second step, multiple refinements were carried out, using only a small region in r around each PDF peak. All parameters except lattice parameters and the thermal motion parameters were kept fixed. This way reliable widths for individual peaks could be extracted.

4. Results

To describe correlation more quantitatively, a correlation parameter ϕ can be defined using the following equation.[1]

$$\sigma_c^2 = \sigma_i^2 + \sigma_j^2 - 2\sigma_i\sigma_j\phi \qquad (4)$$

It can be seen from eq 4 that $\phi = 0$ corresponds to completely uncorrelated motion. Positive values of ϕ describe a situation where the atoms move in phase, thus the resulting value of σ_c is smaller than for the uncorrelated case. Negative values of ϕ stand for neighboring atoms moving in opposite directions. Using eq 4 the correlation parameter ϕ can be calculated from the PDF results as

$$\phi = \frac{\sigma_0^2 - \sigma_c^2}{2\sigma_i\sigma_j} \qquad (5)$$

The peak widths and correlation parameters, ϕ, as a function of the separation distance r are shown in Figure 5 for the Ni and InAs crystals.

4.1. Ni. The r dependence of the PDF peak width and the correlation ϕ for Ni is shown in Figure 5a. Even in this close-packed compound with isotropic metal bonding we observe a weak correlation of the motion of neighboring atoms; e.g., the correlation parameter for the nearest neighbor is $\phi = 0.32$ corresponding to a value of $\sigma_c = 0.00823(2)$ nm. Fitting the
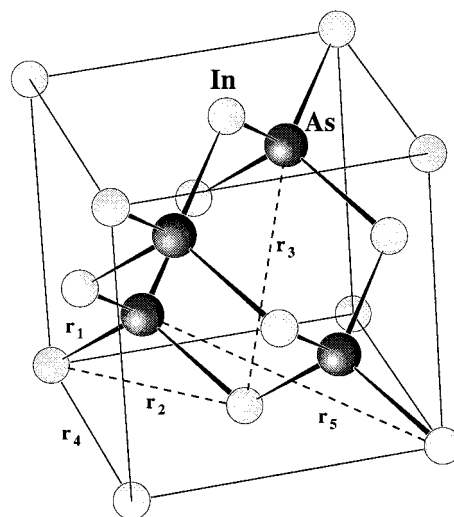
expression given in eq 3 to the data points in Figure 5, we find the following values: $\sigma_0 = 0.010(3)$ nm and $\delta = 0.00011(4)$ nm^3. Here the width of the PDF peak is only determined by thermal broadening and zero-point motion, and no static disorder or strain is present in the crystal.

The value for the uncorrelated thermal motion of $\sigma_0 = 0.010-(3)$ nm determined in this analysis can directly be compared to the theoretical value for nickel of $\sigma_{Ni} = 0.01045$ nm calculated from the Debye temperature of Ni.[10] The good agreement of the observed and theoretical value indicates that the PDF analysis allows one to extract thermal parameters on an absolute scale.

4.2. InAs. InAs crystallizes in the zinc blende structure and shows strong covalent bonding. The r dependence of the PDF peak width and the correlation parameter ϕ are displayed in Figure 5b. It should be noted that for some separation distances r only a theoretical value is present since no meaningful peak width could be extracted from the experimental PDF at those points due to PDF peak overlap. The correlation parameter for the nearest neighbor (In–As) of $\phi = 0.82$ is much larger than in Ni, reflecting the differences in the bonding of the nearest neighbors. The corresponding value of σ_c is 0.0064(2) nm. The resulting values from the empirical relation given in eq 3 are $\sigma_0 = 0.0160(7)$ nm and $\delta = 0.00061(9)$ nm^3.

In contrast to the Ni results, we can observe a deviation from the empirical behavior given in eq 3 for low values of r_{ij}. A tentative explanation of this behavior can be given as follows: First we assume all bonds to be rigid; thus the first neighboring atoms separated by $r_1 \approx 0.26$ nm would move completely in phase, i.e., $\sigma_c = 0$. This is obviously an approximation since we only observe $\sigma_c = 0.0064(2)$ nm for the first neighbor. In our simple model all broadening of subsequent PDF peaks would be caused by bond bending. The structure of InAs is illustrated in Figure 6. The first to fifth nearest neighbors are marked by r_1 to r_5, respectively. From Figure 5 we can see that the PDF peak width for neighbors separated by r_3 is larger whereas for r_5 the width is smaller than given by eq 3. To understand this, we need to consider the bond bending motion at the two intermediate atoms in both cases. For neighbors separated by r_3, both bending motions result in almost parallel displacements along the vector r_3 and the correlation is determined by *two* bending motions, resulting in a weaker correlation or broader PDF peak. For neighbors separated by r_5, however, the bending motions at the intermediate atoms lead

to roughly orthogonal displacements; thus the combined motion can be considered as a *single* bond bending. Subsequently, the correlation should be of the same magnitude as for neighbors separated by r_2 connected by just a single bond bending motion. This is in good agreement with the observed correlation parameters of 0.27 and 0.31 for neighbors separated by r_2 and r_5, respectively, but only 0.10 for neighbors separated by r_3. For large separation distances r_{ij}, the PDF peak width converges to its uncorrelated limit σ_0 and the correlation ϕ goes to zero.

Chung and Thorpe[11,12] have calculated the r dependence of the PDF peak width theoretically using the Kirkwood model.[13] They adjusted the force constants of their model to match the PDF peak width of the first and last peak of the experimental data presented in this paper[11] and obtained the bond stretching ($\alpha = 80$ N/m) and bond bending ($\beta = 10.3$ N/m) force constants. As one might expect, the bond stretching force is larger than the bond bending force. The theoretical PDF peak widths are shown as open circles in Figure 5b. For more details about these calculations, see refs 11 and 12. The experimental and theoretical values show a good agreement. Even the deviations of the experimental data from the behavior described by eq 3 are reproduced by these theoretical calculations.

5. Conclusions

In this paper we have demonstrated that information about correlated motion of pairs of atoms can be extracted from powder X-ray diffraction data measured at a synchrotron source. We have shown that we can extract thermal motion parameters on an absolute scale from the measured PDFs. To study bonds within a crystal, it is important to obtain vibrational parameters that take correlated motion into account. For large values of r the thermal parameters obtained by the PDF analysis described here converge to the uncorrelated value. Note that conventional Rietveld analysis will only give thermal parameters in the uncorrelated limit.

In this paper we have assumed that the width of the PDF peaks is only determined by thermal and zero-point motion. However, in many compounds there will be a static disorder component or strain as well. In these cases one might measure the PDF as a function of temperature to distinguish between both components.

Finally, it should be mentioned that it might not be necessary to use a neutron or synchrotron source to collect data suitable for this kind of analysis. Recently, we have started to collect data using a conventional X-ray tube source and first attempts to model those PDF data look promising.

References and Notes

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