

Local Atomic Structure Analysis Using the Atomic Pair Distribution Method

Jennifer Niedziela*

*Course: Solid State II, Spring 2010 Semester; Instructor: Elbio Dagotto,
Department of Physics, University of Tennessee - Knoxville*

(Dated: May 2, 2010)

Abstract

Powder diffraction is a major component of any condensed matter scientist's arsenal, providing the investigator a way to directly map the location of atoms inside of a material. The most common diffraction experiments provide insights into the average atomic structure of materials, which can break down when materials have lowered local symmetry, or are disordered. Analysis of the pair distribution function (PDF) was already an important tool in the study of liquids and glassy structures when it was shown that it can be applied to crystalline materials to gain insight into local disorder and dynamics. This paper will discuss powder diffraction analysis of crystalline materials, comparing standard powder diffraction analysis and PDF methods, and discuss the relevant differences in these techniques. The paper concludes with a discussion of experimental concerns for conducting PDF measurements.

*jniedzie@utk.edu

I. POWDER DIFFRACTION

Powder diffraction is a very powerful tool in crystallography and condensed matter sciences which allows direct determination of the crystalline structure of materials. It is often used as a first tool in characterizing a new material, and can reveal important information about the behavior of material as external environments (ie, temperature, pressure) change.

A powder diffraction experiment begins with a crystalline material that is ground up (or created as) a fine powder, typically on the order of tens of microns in size. The experimental set up is a beam of particles (most commonly photons or neutrons) incident upon a sample, which scatter into a detector array. The incident particles are scattered from the sample from the electronic cloud (in the case of photons), or by the nuclear interaction (neutrons), in accordance with Bragg's Law[1], $\lambda = 2d\sin\theta$, where d is the space between lattice planes, λ is the wavelength of the incident beam, and 2θ is the angle between the incident and the scattered beam (see fig(1)). The particulars of the incident beam are important for the analysis, but the crux of the issue arises in the momentum transfer of the incident beam. For elastically scattered particles, the momentum transfer $Q = 4\pi \frac{\sin\theta}{\lambda}$ [2].

II. PAIR DISTRIBUTION FUNCTION

A neutron powder diffraction measurement measures the coherent scattering cross section from the sample:

$$\frac{d\sigma_c(Q)}{d\Omega} = \frac{\langle b \rangle^2}{N} |\Psi(Q)|^2 = \frac{1}{N} \left(\sum_{\nu, \mu} b_\nu b_\mu e^{iQ(R_\nu - R_\mu)} \right) \quad (1)$$

which is proportional to the square of the sample scattering amplitude. The sample scattering amplitude is a direct result from scattering analysis, and can be directly compared to the result from the Born approximation[3].

The total scattering function ($S(Q)$) is the intensity of the scattering in Q space, and the PDF is determined by the Fourier transform of the total scattering function[3].

$$g(r) = \frac{2}{\pi} \int_0^{Q_{max}} Q [S(Q) - 1] \sin(Qr) dQ \quad (2)$$

This fourier transform takes us back to real space, showing that what the PDF physically represents is a real space map of the atomic positions within a solid; a probability distri-

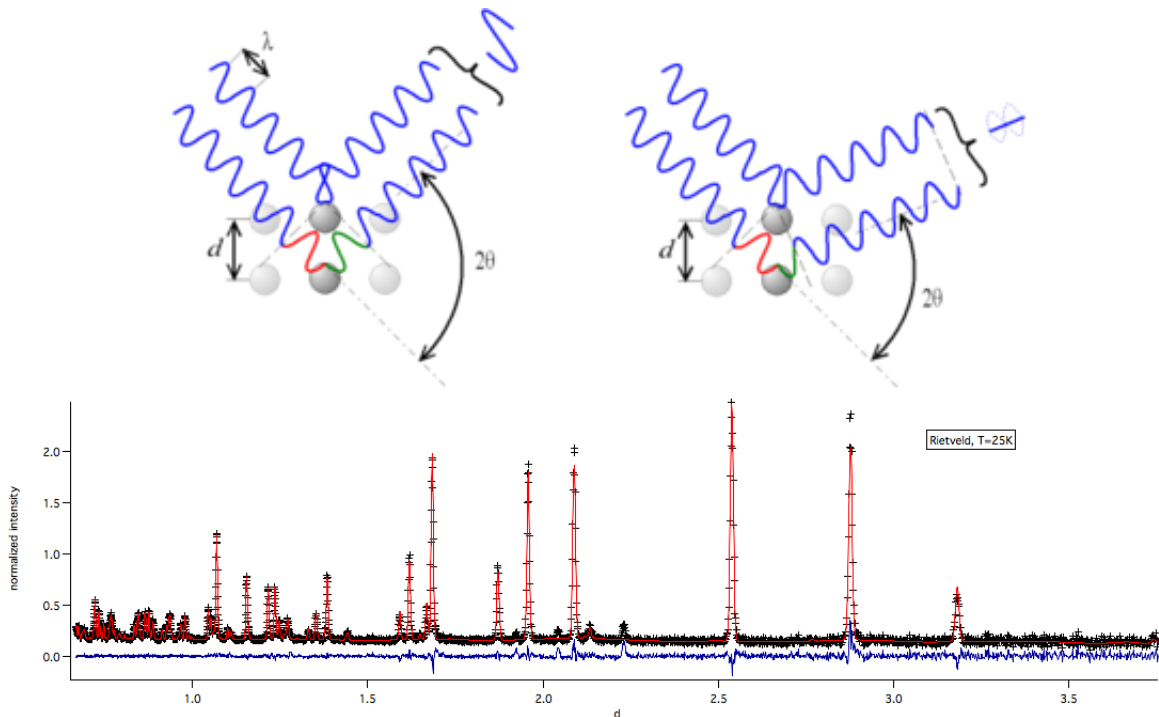


FIG. 1: Schematic illustration of Bragg’s law. An incident beam of particles is scattered off of lattice planes satisfying the Bragg condition. Waves that interfere constructively appear as peaks in the diffraction pattern, which destructively interfering waves are extinct in the resulting diffraction pattern. (lower) illustrative diffraction pattern of $BaFe_2(As_{0.66}P_{0.33})_2$ generated with neutrons.

bution function providing the probability of finding two atoms a distance r apart within a material (see fig. 2). This has two important consequences. The first is that the transformation to r allows a direct analysis of real space, rather than reciprocal space, which is conceptually easier to visualize. Further, the PDF retains *all information* collected by the powder diffraction experiment, including diffuse scattering and inelastic scattering[3]. This notion is what sets the PDF method apart from other powder refinement methods, where diffuse scattering is typically discarded as background and only the contributions from the Bragg peaks are included[4].

The value of Q_{max} in the upper limit of the integral in eq. 2 needs to be as large as possible to prevent termination ripples from appearing in the final PDF (demonstrated in fig. 3. This constraint is apparent in the construction of instruments capable of performing a PDF measurement, and the current practical limit is a momentum transfer of 60\AA^{-1} . Further, the value of the total scattering function ($S(Q)$) tends to 1 as $Q \rightarrow \infty$, so the

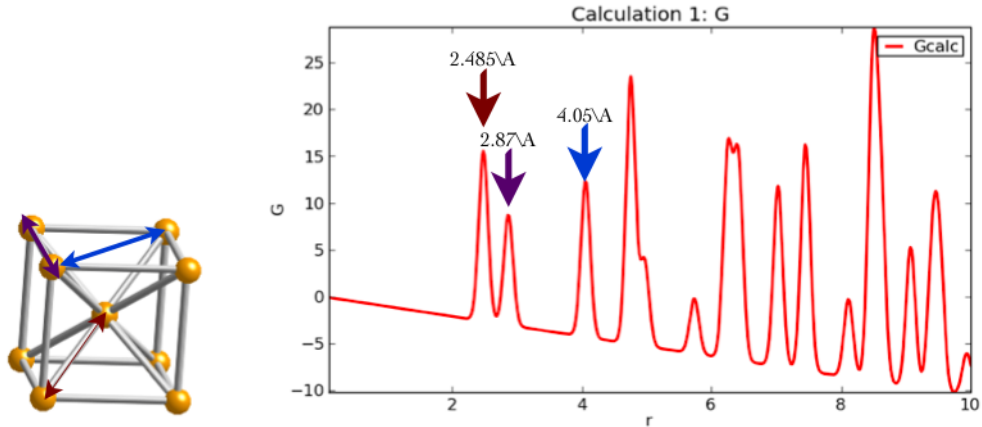


FIG. 2: (left) illustration of the atomic arrangement of iron atoms in *bcc* iron with three nearest neighbor pairs highlighted. (right) Calculated PDF of the iron structure, with three nearest neighbor peaks illustrated. Since the PDF represents a probability of finding two atoms a distance r apart, peaks in the PDF show the distribution of atomic pair distances in a material. The height of the peak corresponds to the relative probability of finding an atomic pair at that distance (i.e., there is zero likelihood of finding a pair before the nearest neighbor peak at 2.485 \AA). PDF shown at right generated with PDFGui[5].

version of the $S(Q)$ to be transformed has a 1 subtracted from it to subtract contributions from the average continuum, since there is no diffraction in the infinite limit of uniform material density[3].

III. BRIEF HISTORY

The notion of fourier transformation of the powder diffraction pattern was first demonstrated by Warren in the 1930's [6] with X-rays. The problem with X-rays is that the structure factor drops off very rapidly in Q , which limits the resolution of the measurement. Further, the method fell out of use for two reasons. The first of these was that the computation of Fourier transforms was done using Beavers-Lipson strips, which were awkward to work with, the second being the rising popularity of the Rietveld Method[4] in the late 1960's[7], which made it possible to very rapidly analyze crystal structures in reciprocal space. The use of the PDF as a crystalline modeling tool was revitalized in the late 1980's with the rise in pulsed neutron sources capable of reaching high enough energies that

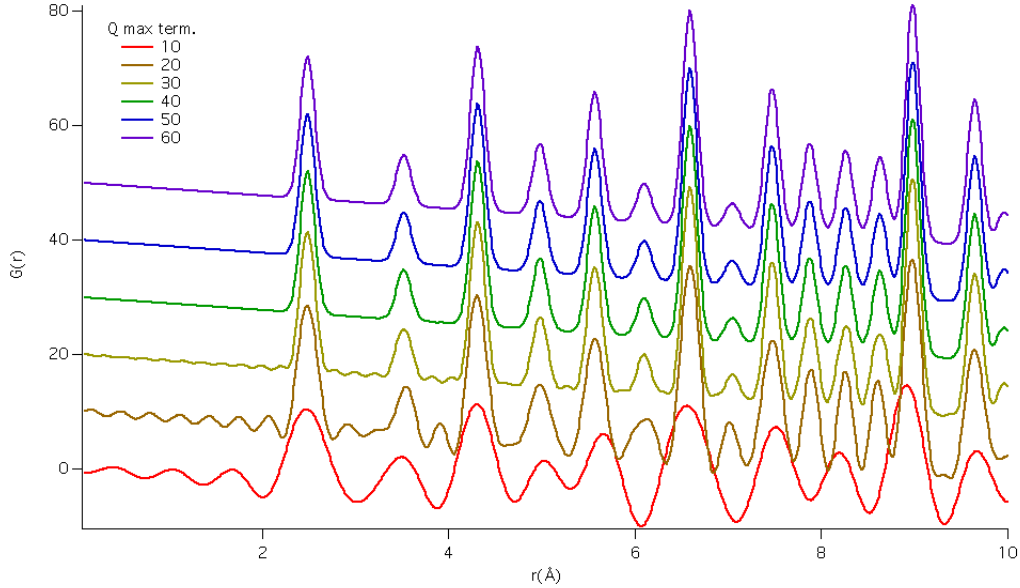


FIG. 3: Demonstration of the impact of the Q_{max} parameter on the PDF. Data shown here are calculated PDFs of nickel, with Q_{max} increasing from 10-60 \AA^{-1} . A clear effect of the Q_{max} can be seen, in both reduction in termination ripples, and the appearance of spurious peaks. The first real peak is the nickel nearest neighbor peak, located at $r = 2.50\text{\AA}$. Calculated PDFs generated with PDFGui[5].

crystalline analysis was again possible[8].

IV. EXAMPLES

Now that the basic groundwork is established, a few important examples are discussed. The real strength of the PDF lies in the ability to create a structural model that allows analysis of real space without any *a priori* assumptions about the crystal structure. PDF analysis is the most useful in situations where there is known or suspected disorder in materials, which can be hinted at by anomalous powder diffraction patterns or larger than predicted Debye-Waller factors in Rietveld analysis[8]. The PDF is able to detect local distortions, and can determine the point of crossover to an average long range order[3]. In a high- r limit, the results of the PDF refinement should agree with the Rietveld refinement for crystalline data, as in this situation, one is looking at the long range, average ordered state of a material, and the effects of local distortion are minimized[3].

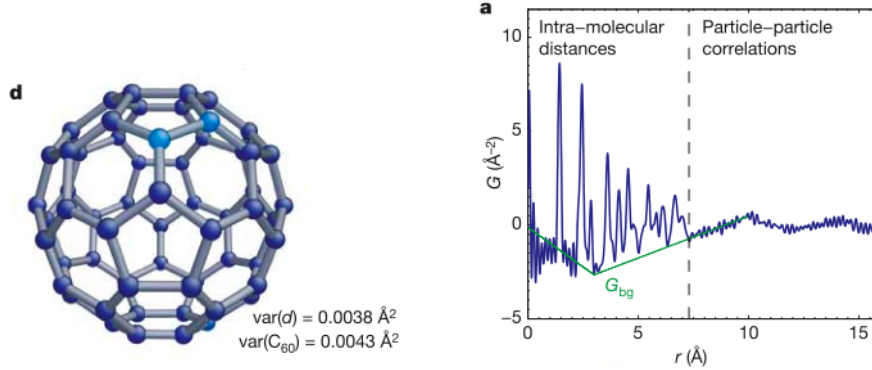


FIG. 4: Structure of a C_{60} molecule, and experimentally determined PDF. This example is striking due to the distinction in short and long range atomic neighbor distances. Up to $r=7.1\text{\AA}$, the PDF shows contributions from the nearest atomic neighbors in the molecule, while above $r=7.1\text{\AA}$, the PDF is dominated by inter-particle interactions between buckyballs, which are smoothed out due to the relative rotational movements of the buckyballs. Figure from [10]

The first example will be a discussion of the fullerene C_{60} molecule, a carbon allotrope that was one of the first stable, nanoscale configuration of atoms discovered [9]. These complex nanostructures have been intensely studied, due to their unique stability, and interesting material properties. The fullerene molecules form what could be termed a face centered cubic lattice, with the center of the molecules on the lattice points. PDF studies of the C_{60} *fcc* structure can resolve the local structure of the fullerene up to the radius of the molecule (fig(4)), showing that the individual atoms in the molecule were highly correlated, while the different fullerene molecules in the arrangement were not well correlated[3] [10]. It is important to note that this structural information is *local* in character, and is not obtainable from average crystallographic analysis. Recent work building on the lack of requirement of a rigid crystallographic model has recently paved the way to determine *ab initio* methods of structural determination derived from PDF measurements. This was demonstrated in the particular case of the fullerenes, which is important because nanomaterials are a particular case where crystallographic analysis breaks down entirely[10].

Another recent example is that provided a study regarding local atomic distortions in the $FeTe_{1-x}Se_x$ group of pnictide superconductors. In the crystallographic analysis of these materials, the Te and Se atoms necessarily share the same site, however, the PDF indicates that

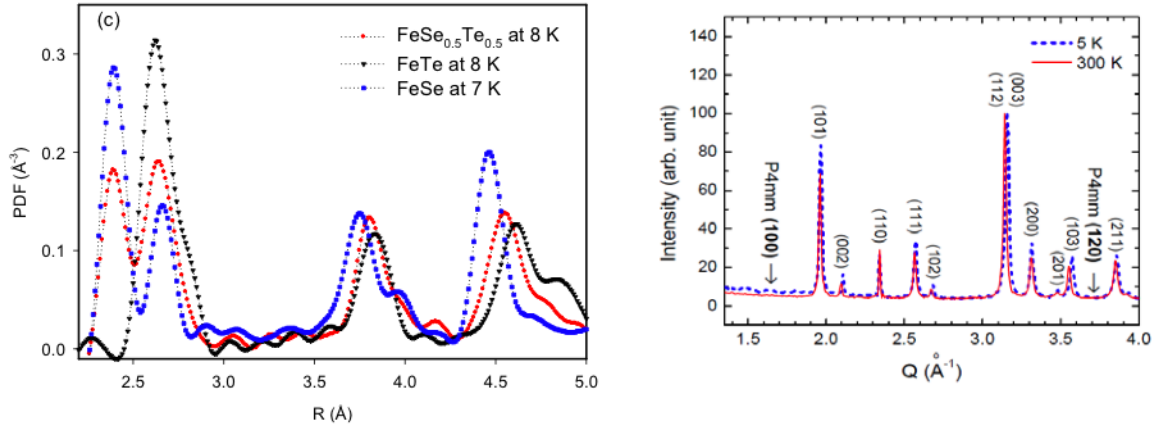


FIG. 5: The PDF of $\text{Fe}(\text{Te},\text{Se})$ compounds at different compositions, and the diffraction pattern of the superconducting version at low temperatures, showing that there are no peaks that would remove the crystalline structure symmetry[13].

these atoms have distinct positions in the structure. This has important implications for the magnetism and superconductivity in these materials, as there are significant demonstrations of the dependence of the superconductivity on details of the lattice [11][12].

V. EXPERIMENTAL CONSIDERATIONS

As noted, in order to collect a PDF, one needs a machine with a very large momentum transfer range. As the Fourier transform in eq. 2 indicates, the Fourier transform ideally extends to $Q = \infty$, but in reality we are limited by available particle energies. A machine suitable for PDF analysis is typically constructed as a powder diffractometer, with energies able to provide sufficient momentum to provide the probability that a scattered particle will be placed into a high momentum transfer bin (epithermal neutrons, high energy x-rays). Currently, there are three neutron powder diffractometers in the US - two at the Lujan Center at Los Alamos, and one Spallation Neutron Source with the native capability to measure the PDF. Other machines at the SNS, including the ARCS spectrometer and the SNAP single crystal diffractometer are capable of making such measurements. There are several X-ray beamlines available at light sources like the Advanced Photon Source at Argonne National Lab which can produce data suitable for PDF refinement. X-ray measurements

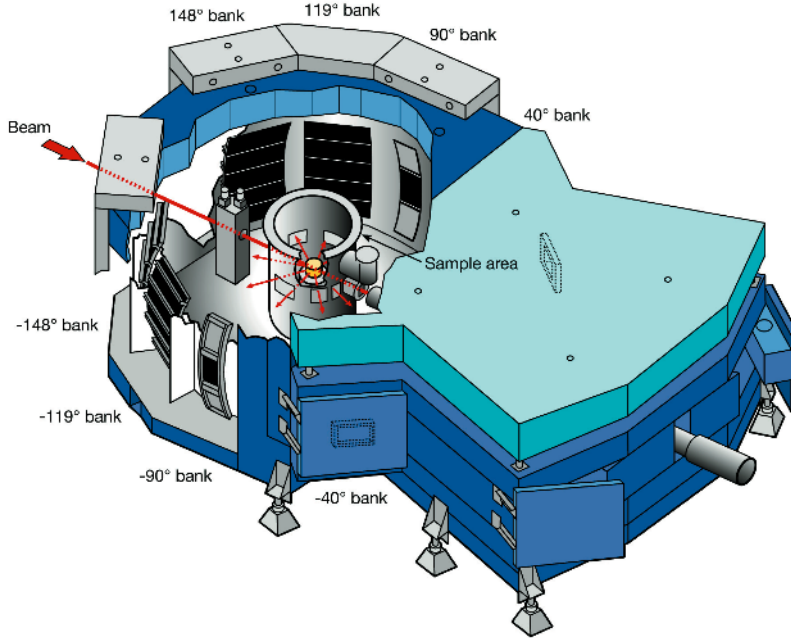


FIG. 6: Schematic of the Neutron Powder Diffractometer (NPDF) beamline, which completed construction in 2003 at the Lujan Center at Los Alamos. The diffractometer has four detector banks, covering an angular spread from 40 to 148 degrees, providing a maximum momentum transfer of 51.1\AA^{-1} [15].

are much faster, on the order of seconds to minutes for a data set, allowing rapid acquisition measurements for time-resolution of physical processes [14]. However X-rays suffer from a reduction in scattering power at higher momentum transfer resulting from limitations of the sample structure factor on the scattering, and reductions in PDF resolution [3].

When collecting powder diffraction data for a PDF measurement, the required background characterization runs are important. First, one has to run an empty vanadium can, then the empty sample environment (if used), and finally the empty scattering chamber. These values are included in the data analysis to reduce spurious effects in the PDF that are caused by the instrument background. Subtraction of these effects is important, as they will appear in both the elastic and inelastic channels of the detector, and will increase uncertainty in the PDF[16].

VI. DATA ANALYSIS

In principle, the PDF requires no *a priori* development of a structural model. In practice, the initial refinements on crystalline data are performed by another powder diffraction method, such as a Rietveld refinement, and are then forwarded to the PDF analysis. This method allows the retention of information about the crystalline symmetry, and provides a good basis for beginning the refinement. Performing data analysis on PDF measurements has been streamlined significantly through the production of software packages, such as PDFGetN[17] or PDFGetX2[18], which calculate the PDF from the experimental data, and PDFGui[5], which allows the analysis of the PDF through creation and refinement of a structural model.

VII. CONCLUSION

This paper has barely scratched the surface on the application of the atomic pair distribution function to crystalline and nanostructural analysis. The reader is highly encouraged to investigate this material in greater detail, and the author would suggest the text of Egami and Billinge[3] as a starting point. There is also an edition of *Zeitschrift für Physik* dedicated to this topic, which has several accessible articles on the history and application of this method([19], [7]).

-
- [1] W. L. Bragg, *Proc. Cambridge Phil. Soc.* **17** (1913).
 - [2] S. J. L. Billinge and M. F. Thorpe, *Local Structure from Diffraction* (Fundamental Materials Research, 1998).
 - [3] T. Egami and S. J. L. Billinge, *Underneath the Bragg Peaks* (Pergamon Press, 2003).
 - [4] H. M. Rietveld, *J. Appl. Cryst.* **2**, 65 (1969), URL <http://www.ccp14.ac.uk/ccp/web-mirrors/hugorietveld/xtal/paper2/paper2.html>.
 - [5] C. Farrow, P. Juhas, J. Liu, D. Bryndin, E. S. Bozin, J. Bloch, T. Proffen, and S. Billinge, *J. Phys.: Condens. Matter* **19**, 335219 (2007).
 - [6] B. Warren and N. Gingrich, *Physical Review* **46**, 368 (1934).
 - [7] S. J. L. Billinge, *Zeitschrift für Kristallographie* **219**, 117 (2004).

- [8] W. Dmowski, B. Toby, T. Egami, M. Subramanian, J. Gopalakrishnan, and A. Sleight, *Phys. Rev. Lett.* **61**, 2608 (1988).
- [9] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature* **318**, 162 (1985).
- [10] P. Juhás, D. M. Cherba, P. M. Duxbury, W. F. Punch, and S. J. L. Billinge, *Nature* **440**, 655 (2006).
- [11] T. Yildirim, *Phys. Rev. Lett.* **102**, 037003 (2009).
- [12] C.-H. Lee, A. Iyo, H. Eisaki, H. Kito, M. T. Fernandez-Diaz, T. Ito, K. Kihou, H. Matsuhata, M. Braden, and K. Yamada, *J. Phys. Soc. Jpn.* **77**, 083704 (2008).
- [13] M. C. Lehman, D. Louca, K. Horigane, A. Llobet, R. Arita, N. Katayama, S. Konbu, K. Nakamura, P. Tong, T.-Y. Koo, et al., *arXiv cond-mat.supr-con* (2009), 0909.0480v1, URL <http://arxiv.org/abs/0909.0480v1>.
- [14] P. J. Chupas, X. Qiu, J. C. Hanson, P. L. Lee, C. P. Grey, and S. J. L. Billinge, *J. Appl. Cryst.* **36**, 1342 (2003).
- [15] T. Proffen, T. Egami, S. Billinge, A. Cheetham, D. Louca, and J. Parise, *Applied Physics A: Materials Science & Processing* **74**, s163 (2002).
- [16] B. H. Toby and S. J. L. Billinge, *Acta Crystallogr A Found Crystallogr* **60**, 315 (2004).
- [17] P. Peterson, M. Gutmann, T. Proffen, and S. J. L. Billinge, *J. Appl. Cryst.* **33**, 1192 (2000).
- [18] X. Qiu, J. Thompson, and S. J. L. Billinge, *J. Appl. Cryst.* **37**, 678 (2004).
- [19] T. Egami, *Zeitschrift für Kristallographie* **219**, 122 (2004).