Nanoscale structural order from the atomic pair distribution function (PDF): There's plenty of room in the middle

Simon J.L. Billinge [a,b,*]

[a] Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027, USA
[b] Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, NY 11973, USA

ABSTRACT

Emerging materials of scientific and technological interest are generally complex and often nanostructured: they have atomic orderings that extend on nanometer length-scales. These can be discrete nanoparticles; bulk crystals with nanoscale chemical or displacive order within them; mesoporous materials that are bulk materials containing nanoscale holes; and nanocomposites that are intimate heterogeneous mixtures of nano-sized constituents. As always, a quantitative knowledge of the atomic structure within these materials is a prerequisite to understanding and engineering their properties. Traditional crystallographic methods for obtaining this information break down at the nanoscale, sometimes referred to as "the nanostructure problem". We describe here some emerging methods for studying nanoscale structure. We present some examples of recent successes. Finally, we discuss future directions and opportunities and draw attention to limitations and potential problems.

© 2008 Elsevier Inc. All rights reserved.

1. Introduction

Richard Feynman's visionary lecture, "There is Plenty of Room at the Bottom", given at the American Physical Society meeting at Caltech on December 29th 1959, is often quoted as giving birth to the concept of nanotechnology: controlling matter at the nanometer length-scale. It is a highly readable, but remarkably prescient account of the promise of nanoscience and technology and well worth reading [1]. The key point of the talk is that the nanoscale is small enough for extreme minimization, but large enough (hence "there is plenty of room") to accommodate sufficient atoms to produce interesting complexity, if we could just learn how to control it. Nanotechnology also opens a new playground for scientists, a *terra incognita* with enormous possibilities, and there is plenty of room for multitudes of scientists to stretch their imaginations.

A significant impediment to the vision is the "nanostructure problem" [2]: the fact that we do not have robust broadly applicable quantitative methods for solving structure at the nanoscale. Crystallography, the foundation of structural science for almost 100 years, breaks down for structures that extend only over a few nanometers. We have incredibly powerful tools to image nanoscale structures (scanning probe microscopies, transmission electron microscopy) but not to yield quantitative 3D structures of individual nanoparticles (or ensembles of identical nanoparticles). In the world of structural science, we have powerful tools for studying long-range structure (crystallography) and local structure (EXAFS, NMR), but very little for probing structure "in the middle" or on the scale of 1–10 nm. This is emerging as an exciting field.

One very valuable approach, which is gaining popularity for nanostructure studies, is total scattering and the atomic pair distribution function (PDF) analysis of X-ray and neutron scattering data [3,4]. This approach has been around for more than 70 years [5,6] and has been widely applied to liquids and amorphous materials [7,8]. Now, with the advent of high power X-ray and neutron facilities and the availability of high power computing, the PDF is proving to be a valuable and powerful tool for studying structure on the nanoscale [4]. Total scattering refers to the fact that all (structure-relevant) scattering from a sample is collected, including both Bragg and diffuse components, over a wide range of reciprocal space where coherent scattering exists. The PDF is obtained when the properly corrected and normalized total scattering signal is Fourier transformed to real-space. The data are then modeled quantitatively to obtain the structural information. It is one of the only techniques to give quantitative structural information as a function of length-scale on the nanoscale [9]. In this paper we will give examples that illustrate the kind of information that is available from the PDF. We will highlight recent developments that extend the applicability and power of the technique. Finally, we will look ahead to some future directions that the field is headed in and discuss some of the challenges that lie ahead.

* Corresponding author at: Department of Applied Physics and Applied Mathematics, Columbia University, 500 West 120th Street, Room 200 Mudd, MC 4701, New York, NY 10027, USA.
E-mail address: sb2896@columbia.edu

2. Atomic PDF method

The PDF method can yield precise structure and size information, provided that special care is applied to the measurement and to the method used for analyzing the data. Details of the method can be found in Egami and Billinge [3] and in Ref. [10]. Here we give a brief background to the theory.

The atomic PDF, $G(r)$, is defined as

$$G(r) = 4\pi r[\rho(r) - \rho_0], \qquad (1)$$

where $\rho(r)$ is the atomic pair-density, ρ_0 is the average atomic number density and r is the radial distance [6]. The PDF yields the probability of finding pairs of atoms separated by a distance r. It is obtained by a sine Fourier transformation of the reciprocal space total scattering structure function $S(Q)$, according to

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

where $S(Q)$ is the corrected, normalized, diffracted intensity from the sample and Q is the magnitude of the scattering vector, $Q = 4\pi \sin\theta/\lambda$. Data corrections are described in detail in [3], but briefly, extraneous contributions to the scattering (from such sources as sample mounts, sample fluorescence, Compton scattering and multiple scattering) are subtracted and multiplicative aberrations such as detector dead-time and absorption are corrected. Finally the data are normalized by incident flux and number of atoms to get the scattering in units of intensity per atom. In practice, the last normalization is done in an *ad hoc* way such that the scattering intensity at high-Q, which is mostly incoherent, asymptotically approaches the average scattering cross-section of the sample. In the case of X-rays, this is the average form-factor squared $\langle f(Q)\rangle^2$.

The experiments to obtain data for PDF analysis are straightforward powder diffraction measurements. The sample is made up of disordered fine crystallites or nanocrystals of the material under study. In synchrotron X-ray experiments this is often in a 0.5 mm ID capillary or a disk of thickness 0.5–1 mm and diameter a few millimeters [11]. On laboratory sources the geometry is often Bragg Brentano [12] with the sample mounted on a flat plate. In the case of neutrons cylindrical vanadium sample cans are used, but more sample is needed, typically a few grams to 10 g at current sources, though trial experiments have been carried out with samples as small as a few tens of milligrams [13]. The advent of high flux sources such as the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL) will hopefully allow X-ray sized samples to be measured routinely with neutrons.

An important aspect of experimental design is that data must be collected over a wide Q-range. Low real-space resolution, a consequence of measurements made over a limited Q-range, is often sufficient in studies of glasses and liquids and many such studies exist in the literature using laboratory X-rays and reactor neutron sources [7,8]. However, in more ordered materials such as crystals and nanocrystals, there are significant advantages of having the best real-space resolution possible [14,15]. Q-ranges up to Q_{max} values of 30–50 Å^{-1} are desirable. This requires short wavelength X-rays or neutrons. Such measurements were made possible with the advent of SNSs and hard X-ray synchrotron sources. Neutrons have a natural advantage in that there is no decreasing atomic form factor that kills the intensity of coherent scattering at high-Q. However, it was shown that the high fluxes of X-rays at modern synchrotrons amply compensate for the intensity loss and very high quality X-ray measurements whose real-space resolution is limited by intrinsic properties of the sample and not the measurement are not only possible, but straightforward [14–16]. The use of 2D detectors with very hard (>70 keV) X-rays, sometimes known as the rapid acquisition PDF (RAPDF) method, allow quantitatively reliable data-sets to be determined in a single shot [11], with the current record of <50 ms [17] though more typically a few seconds or minutes are needed to get sufficient statistics. This development opens the door to time-resolved measurements [17], *in situ* measurements under different temperature and gas environments [18] and pressures [19], high throughput measurements of phase diagrams [20], and so on. When coupled with quantitative data analysis methods described below, real nanomaterials problems in chemistry, physics, earth science and engineering can be studied. The first dedicated X-ray beamline is X11-ID-B at the Advanced Photon Source (APS) (www.aps.anl.gov) at Argonne National Laboratory (ANL), with the development of beamlines at other facilities around the world being planned. A number of neutron diffractometers are optimized for PDF measurements, notably NPDF at Los Alamos National Laboratory (LANL) (www.lansce.lanl.gov) [21] and the GEM diffractometer at the ISIS facility (www.isis.rlac.uk) [22]. Time at facilities is given out free but based on a competitive proposal system. For first time users the best way to begin is to contact instrument scientists at the above mentioned beamlines. Contact information can be obtained at the facility websites.

Raw data are processed to obtain the PDF using freely available software. The theory is described in detail in Egami and Billinge [3]. Examples of commonly used programs for data reduction from 2D to 1D are Fit2D [23] and Powder3D [24]. The most commonly used data reduction program is PDFgetX2 [25]. Once a PDF is obtained it can be analyzed directly by considering the positions widths and intensities of peaks, or by fitting models to the data. The peak position yields a bond-length, assuming that a correct assignment of an atom pair can be made to the peak [3,10]. The width is a measure of the thermal motion, and where present, static disorder, associated with that bond or atom pair. Finally the intensity measures the multiplicity and type of atoms involved in pair.

It is fairly trivial to calculate the PDF from a known model [3,26]. A commonly used program for this is PDFgui [27] which replaces its forerunner PDFfit [26]. This program is applicable to calculating the structure from crystals and has recently been extended to nanocrystals where the finite extent is modeled as a shape function that terminates the signal at higher-r. The calculation is then included in a regression loop so that structural parameters are updated automatically by the program in such a way as to improve the fit to the data: the real-space analog of Rietveld refinement. An alternative is to do big-box modeling, where thousands of atoms are placed in a box and moved, usually using a Monte Carlo simulated annealing approach in such a way as to give a good fit to the data. This approach is often called reverse Monte Carlo (RMC) [28,29]. Traditionally this was used for more disordered systems such as glasses [30], but recent developments allow it to be used to study nanostructure in crystals using the program RMCProfile [31]. Another recent development couples geometric modeling [32] to Monte Carlo regression allowing fits to be carried out where the local chemistry is included as a constraint in a very computationally efficient way [33]. For discrete structures, such as small nanoparticles, fits can be done by calculating the Debye function directly and avoiding the Fourier transform altogether [34], and alternative regression approaches using genetic algorithms are also under development [35].

All these methods solve the forward problem: given a structure, what does the PDF look like. A major success of crystallography is that the inverse problem has been solved. Given a diffraction pattern, what is the crystal structure that gave rise to it. One could argue that RMC solves the inverse problem as atoms may be put randomly into a box and arrange themselves to give a

good fit. However, this only works in highly disordered systems where there is a large degeneracy or nearly equivalent solutions. The Monte Carlo algorithm turns out to be too inefficient to find the global minimum in problems where there is a unique or nearly unique solution. However, the first demonstration of an *ab initio* nanostructure solution from PDF data was made recently when the structure of C_{60} was reconstructed from PDF data alone [36]. This was done both with an adapted genetic algorithm [37] and a novel cluster build-up algorithm [36], which is named LIGA because of the similarity of the heuristic with the promotion and relegation process of European soccer leagues such as La Liga in Spain. There is still much work to be done to make this approach useful, and there is a large number of cases which are not amenable to this kind of structure solution, for example, where the structure of the cluster is not rigid or is of very low symmetry, but this will undoubtedly be an active area of research in the upcoming years.

3. Recent scientific applications of the PDF

Here by way of illustration we briefly describe a number of recent successful PDF studies. Because of my greater familiarity I have picked examples from the work of my group, though many excellent examples exist in the literature from other groups [38–42].

3.1. Nanoparticle structure solution by trial and error

As we discussed, *ab initio* structure solution is still difficult, but in favorable cases the structure of nano-sized objects can be determined through a process of trial and error. This is done by finding a portfolio of structural analogs and trying to refine each one to the data. Earlier examples include exfoliated MoS_2 [43] and WS_2 [44], vanadium oxide xerogel [45], and more recently titania [41]. Here we describe an example, a study [46] of the recently discovered novel $Mo_6S_{9−x}I_x$ nanowires [47,48]. RAPDF data were collected at beamline 6ID-D at APS on a sample of nanowires obtained from the group of Dragan Mihailovic in Ljubljana, Slovenia. The material structure had been studied by EXAFS, but its nanocrystallinity prevented successful attempts at solving the structure using crystallographic methods [49]. In Fig. 1(a) we show the PDF obtained from the X-ray diffraction data (circles) with the fit of the final model shown as a solid line over the data with the difference curve offset below. Despite the material being nanocrystalline and having broad features in reciprocal space, the features in the real-space are sharp indicating a well defined structure over short length-scales. This was quantitatively fit using the PDF refinement program PDFfit [26] to obtain the agreement shown in the figure. The quantitative refinement results in a structural solution shown in Fig. 1(b). This is an example where, in favorable circumstances, a nanoparticle structure can be solved by a trial and error approach.

3.2. Nanointercalates

An important area of study is that of mesoporous materials where a host matrix contains pores that have nanometer dimensions [50]. These have uses as molecular sieves, sponges and catalyst supports. Even when the host is crystalline, as in zeolites [51], and can be studied using crystallographic methods, the important local environment of intercalants cannot be studied in this way in general. PDF yields important additional information in this case, and is not restricted to cases where the host is crystalline. For example, the use of a disordered silica host as a
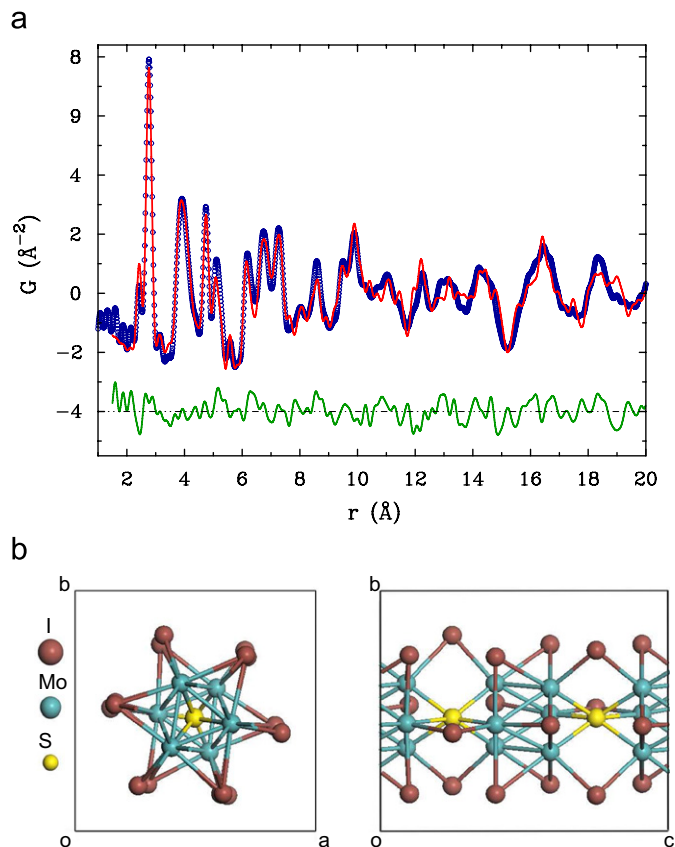

Fig. 1. (a) PDFs of $Mo_6S_{9−x}I_x$. Nanowire data (circles) and model (solid line) are shown with the difference curve offset below. (b) Schematic of the resulting $Mo_6S_{9−x}I_x$ structure. Reproduced from [46] with permission.

sponge for sequestering mercury has been demonstrated in the laboratory [52]. PDF was able to show the local environment of the mercury in the disordered pores [53]. The silica host material is amorphous and has disordered "wormhole-like" pores running through it. These can be functionalized with an organic, mercaptan, which contains a thiol group that binds to the mercury. However, the local bonding and environment of the Hg in the pores is not known and could yield information to help understand the very high loadings that are possible. PDFs from a series of samples with different loadings were measured at 6ID-D at APS [53]. These are shown in Fig. 2. A number of features appear with increasing Hg loading and are clearly Hg correlations. Comparison with crystalline analogs, cinnabar (HgS) and HgO clearly show what these features are and tell us that the sulphur atom on the mercaptan thiol group binds two Hg ions forming a triangle with the Hg–Hg second neighbor distance being clearly present. There is no evidence for any HgO which could come about if oxygen in the silica host were closely coordinating the Hg.

Other similar studies on clusters intercalated inside mesoporous hosts include the passivation of reactive reducing agents [54] and the detection of the local environment of hydrogen intercalated in a cyanide host [40].

3.3. Nanoparticle crystallography

Obtaining the internal atomic arrangement in nanoparticles is a challenge. In general they cannot be made into an orientationally ordered array and solved crystallographically as is done for proteins (and, to-date, one case for inorganic nanoparticles [55]). Still, using the PDF method, a significant amount of quantitative information can be extracted from data collected from an
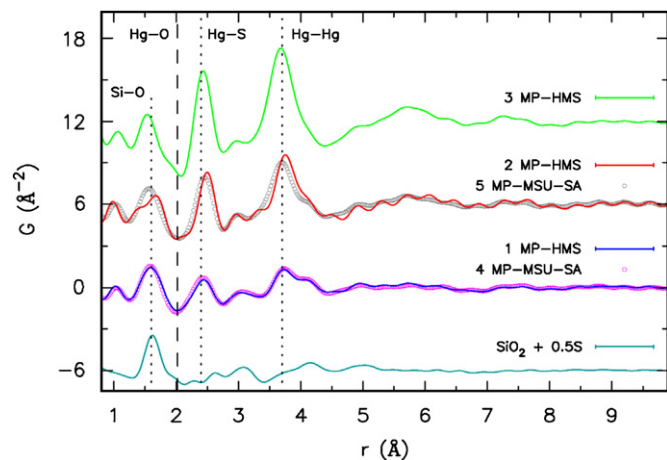
Fig. 2. PDFs of various mercaptan functionalized mesoporous silica hosts (denoted MP-HMS and MP-MSU and described in more detail in Ref. [53]) with various loadings of Hg from unloaded at the bottom through moderate and high loadings at the top. Samples with different loadings are offset from each other. Different data-sets with the same Hg loadings are plotted on top of each other. The vertical dotted lines indicate the positions of Hg–S and Hg–Hg peaks in the PDFs of crystalline HgS (cinnabar). The vertical dashed line is the position where a Hg–O peak would be expected if it were present (it is not). Reproduced from [53] with permission.

Fig. 3. Illustrating how strain information as a function of nanoparticle size can be extracted from PDFs of CdSe nanoparticles. (a) Cadmium to selenium bond PDF peak from (•) bulk CdSe, (○) 3.7 nm CdSe nanoparticles, (□) 3.1 nm CdSe nanoparticles and (△) 2.7 nm CdSe nanoparticles fitted with one Gaussian (—). The dashed line represents the position of first PDF peak in the bulk data. (b) (▲) The first PDF peak width vs. nanoparticle size, obtained from a single Gaussian fit. The dashed line represents the width of first PDF peak in the bulk data. (c) Strain in Cd–Se bond ($\Delta r/r$) (%) vs. nanoparticle size. (■) Strain values obtained from PDFgui fit and (•) from single Gaussian fits, respectively, to the first PDF peak. Dotted curves are guides for the eye. Reproduced from [58] with permission.

ensemble of nanoparticles [35,36,38,39,56,57]. This is illustrated here with a study of CdSe nanoparticles where the data were quantitatively modeled to extract the internal structure, including a quantification of the stacking-fault density, the size, and the internal strain of the particle [58]. The measurement of the strain is shown in Fig. 3. The precision of the PDF measurement was sufficient to allow a small bond-strain of $<0.5\%$ to be measured, where the bond-strain is defined as $\delta r/r$ and r is the Cd–Se bond length. Panel (b) also shows that the PDF can be used to measure the inhomogeneous strain, or the distribution of Cd–Se bond-lengths in the sample. This shows a small variation in this particular case. This kind of study can be applied broadly to study the strain state of nanoparticles down to the sub-nanometer length-scale.

3.4. Nanostructure in bulk crystals

There is an increasing realization that crystalline materials often support nanoscale structures beyond the average structure. These nanoscale structures can have significant implications for the materials properties. This was shown, for example, in the manganites where charge localization and polaron formation was seen in PDF measurements [59] and short-range charge (or polaron) ordering observed in single-crystal diffuse scattering measurements [60]. Here we show an extension of the PDF work where the local correlations of short-range ordered Jahn–Teller (JT) distortions in $LaMnO_3$ were studied as a function of temperature through the "quadrupole melting" transition [9,33]. To model these data a new modeling approach was developed [33] that combined geometric modeling [32] and simulated annealing. The idea is that the structure is made up of JT distorted corner-shared octahedra which arrange themselves in space to minimize the free energy. At low temperature they arrange in an ordered checkerboard pattern, but at high temperature the JT distortion persists locally [9,61] but the quadrupole moments (the elongations of the octahedra) become disordered [9] and no JT distortion is measured in the crystallographic structure. Information about the short-range order of the quadrupole moments is contained in the PDF and could be extracted by
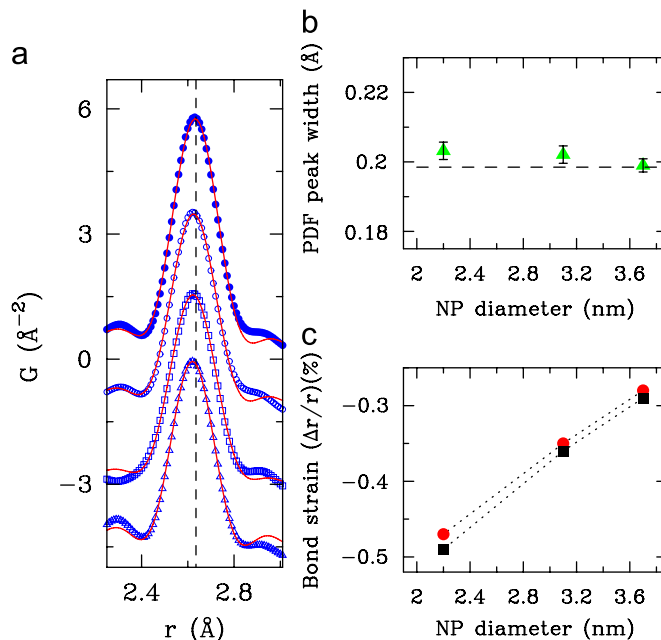
the geometric modeling approach mentioned above. The fit to the data is shown in Fig. 4(a) and projections of the resulting models for low and high temperature are shown in Fig. 4(b). The measured PDFs were from neutron diffraction data collected at the NPDF diffractometer at LANL.

The advent of accessible PDF measurements is allowing the short-range order to be studied in crystalline materials in a routine way. We expect that, in the future, many crystalline systems will be revisited in this way with potentially fruitful results.

4. Future directions

The PDF method is developing rapidly and growing in popularity. This is in part due to improvements in the methodology, but also demand fueled by our need to study complex and nanostructured materials. Future developments are expected to increase the impact of PDF style studies. There is an increasing desire to study materials not only *in situ*, but in *operando*. In the case of *in situ* studies materials are studied under non-ambient conditions of temperature, pressure, gas environment, electric or magnetic field. This is the domain where functional materials really function. For example, there is a big difference between studying a catalyst structure under ambient conditions, and under operational conditions [62]. The use of high flux pulsed neutron sources and high energy X-ray studies make this kind of study particularly amenable and a big push in the future will be to match special environments to facility beamlines. Taking this idea to its logical conclusion is the idea to look at real operating devices, for example, to study the local structure of an electrode in an operating fuel cell or a discharging battery. In
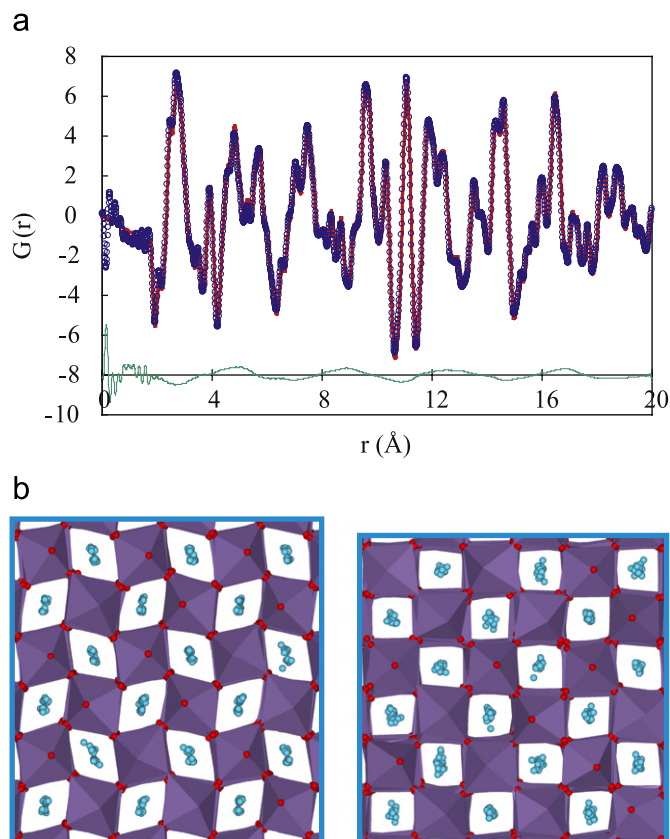
a

b

Fig. 4. (a) PDFs from LaMnO$_3$ at 300 K (circles) and the fitted model (line). Difference curve is shown offset. (b) Projections of the models for 300 K (left) and 1050 K (right) showing MnO$_6$ octahedra in purple, oxygen atoms in red and La atoms in cyan. At 300 K—the JT distortions and octahedral rotations are ordered resulting in a zig-zag pattern of the octahedra with La atoms relatively ordered in the channels. At 1050 K the octahedral rotations are disordered, which results in a cubic appearance in the projection and the La ions are more disordered in the channels. Reproduced from [33] with permission.

such studies materials are being measured in *operando*. They have very much the same characteristics as *in situ* studies except that the "samples" under study are inherently heterogeneous and small beams need to be positioned accurately to get the required information, and the measurements are inherently time-sensitive. The special challenges that will flow from *operando* studies will be addressed with the next generation of X-ray sources. Just as in biology where studies can be *in vitro* and *in vivo*, we see a shift over the next 10 years or so from Materials Science v1.0 (*in vitro*), where materials are studied in glass capillaries under ambient conditions, through Materials Science v2.0 (*in situ*), to Materials Science v3.0 (*in operando*). *In vitro* studies will never lose their value, but a powerful development is to have a suite of tools allowing all three types of studies to be carried out together.

A significant bottleneck in PDF studies currently is the limitation brought by inadequate data analysis software tools. We very much hope that this issue will also be addressed in a systematic way in the upcoming years. New algorithms are needed [36] to address unsolved problems such as the nanostructure problem [2], and also to handle the demands of enormously high (and growing) data-rates from high-throughput studies. A fundamental issue is the robustness and uniqueness of structural solutions which will, in general, require data from more than one source to constrain a structure solution, something that has been called "Complex Modeling" [2]. A start

has already been made but significant investment is needed in software, which can be expected to pay big dividends.

Acknowledgments

References

[1] R.P. Feynman, There is plenty of room at the bottom ⟨http://www.its.caltech.edu/~feynman/plenty.html⟩.
[2] S.J.L. Billinge, I. Levin, Science 316 (2007) 561.
[3] T. Egami, S.J.L. Billinge, Underneath the Bragg Peaks: Structural Analysis of Complex Materials, Pergamon Press, Elsevier, Oxford, England, 2003.
[4] S.J.L. Billinge, M.G. Kanatzidis, Chem. Commun. 2004 (2004) 749.
[5] P. Debye, H. Menke, Phys. Z. 31 (1930) 797.
[6] B.E. Warren, X-ray Diffraction, Dover, New York, 1990.
[7] A.C. Wright, Glass. Phys. Chem. 24 (1998) 148.
[8] A.C. Barnes, H.E. Fischer, P.S. Salmon, J. Phys. IV 111 (2003) 59.
[9] X. Qiu, Th. Proffen, J.F. Mitchell, S.J.L. Billinge, Phys. Rev. Lett. 94 (2005) 177203.
[10] S.J.L. Billinge, in: R.E. Dinnebier, S.J.L. Billinge (Eds.), Powder Diffraction: Theory and Practice, Royal Society of Chemistry, London, England, 2008.
[11] P.J. Chupas, X. Qiu, J.C. Hanson, P.L. Lee, C.P. Grey, S.J.L. Billinge, J. Appl. Crystallogr. 36 (2003) 1342.
[12] H.P. Klug, L.E. Alexander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, second ed., Wiley, New York, 1974.
[13] T. Proffen, S.J.L. Billinge, T. Egami, D. Louca, Z. Kristallogr. 218 (2003) 132.
[14] V. Petkov, S.J.L. Billinge, S.D. Shastri, B. Himmel, Phys. Rev. Lett. 85 (2000) 3436.
[15] I.-K. Jeong, F. Mohiuddin-Jacobs, V. Petkov, S.J.L. Billinge, S. Kycia, Phys. Rev. B 63 (2001) 205202.
[16] K. Laaziri, S. Kycia, S. Roorda, M. Chicoine, J.L. Robertson, J. Wang, S.C. Moss, Phys. Rev. Lett. 82 (1999) 3460.
[17] P.J. Chupas, K.W. Chapman, P.L. Lee, J. Appl. Crystallogr. 40 (2007) 463.
[18] F. Zhang, P.J. Chupas, S.L.A. Lui, J.C. Hanson, W.A. Caliebe, P.L. Lee, S.-W. Chan, Chem. Mater. 19 (2007) 3118.
[19] L. Ehm, S.M. Antao, J. Chen, D.R. Locke, F.M. Michel, C.D. Martin, T. Yu, J.B. Parise, S.M. Antao, P.L. Lee, P.J. Chupas, S.D. Shastri, Q. Guo, Powder Diffr. 22 (2007) 108.
[20] E.S. Božin, M. Schmidt, A.J. DeConinck, G. Paglia, J.F. Mitchell, T. Chatterji, P.G. Radaelli, T. Proffen, S.J.L. Billinge, Phys. Rev. Lett. 98 (2007) 137203.
[21] T. Proffen, T. Egami, S.J.L. Billinge, A.K. Cheetham, D. Louca, J.B. Parise, Appl. Phys. A 74 (2002) s163.
[22] W.G. Williams, R.M. Ibberson, P. Day, J.E. Enderby, Physica B 241–243 (1998) 234.
[23] A.P. Hammersley, S.O. Svenson, M. Hanfland, D. Hauserman, High Pressure Res. 14 (1996) 235.
[24] B. Hinrichsen, R.E. Dinnebier, M. Jansen, Z. Kristallogr. (Part 1 Suppl. 23) (2006) 231.
[25] X. Qiu, J.W. Thompson, S.J.L. Billinge, J. Appl. Crystallogr. 37 (2004) 678.
[26] T. Proffen, S.J.L. Billinge, J. Appl. Crystallogr. 32 (1999) 572.
[27] C.L. Farrow, P. Juhás, J.W. Liu, D. Bryndin, E.S. Božin, J. Bloch, T. Proffen, S.J.L. Billinge, J. Phys. Condens. Matter 19 (2007) 335219.
[28] R.L. McGreevy, J. Phys. Condens. Matter 13 (2001) R877.
[29] A.K. Soper, Chem. Phys. 258 (2000) 121.
[30] D.A. Keen, R.L. McGreevy, J. Phys. Condens. Matter 3 (1991) 7383.
[31] M.G. Tucker, M.T. Dove, D.A. Keen, J. Appl. Crystallogr. 34 (2001) 630.
[32] S.A. Wells, M.T. Dove, M.G. Tucker, J. Phys. Condens. Matter 14 (2002) 4567.

[33] A. Sartbaeva, S.A. Wells, M.F. Thorpe, E.S. Božin, S.J.L. Billinge, Phys. Rev. Lett. 99 (2007) 155503.
[34] A. Cervellino, C. Giannini, A. Guagliardi, J. Comput. Chem. 27 (2006) 995.
[35] R.B. Neder, V.I. Korsunskiy, J. Phys. Condens. Matter 17 (2005) S125.
[36] P. Juhás, D.M. Cherba, P.M. Duxbury, W.F. Punch, S.J.L. Billinge, Nature 440 (2006) 655.
[37] D.M. Deaven, K.M. Ho, Phys. Rev. Lett. 75 (1995) 288.
[38] B. Gilbert, F. Huang, H. Zhang, G.A. Waychunas, J.F. Banfield, Science 305 (2004) 651.
[39] K. Page, T. Proffen, H. Terrones, M. Terrones, L. Lee, Y. Yang, S. Stemmer, R. Seshadri, A.K. Cheetham, Chem. Phys. Lett. 393 (2004) 385.
[40] K.W. Chapman, P.J. Chupas, E.R. Maxey, J.W. Richardson, Chem. Commun. (2007) 4013.
[41] S.K. Pradhan, Y. Mao, S.S. Wong, P. Chupas, V. Petkov, Chem. Mater. 19 (2007) 6180.
[42] F.M. Michel, L. Ehm, S.M. Antao, P.L. Lee, P.J. Chupas, G. Liu, D.R. Strongin, M.A.A. Schoonen, B.L. Phillips, J.B. Parise, Science 316 (2007) 1726.
[43] V. Petkov, S.J.L. Billinge, P. Larson, S.D. Mahanti, T. Vogt, K.K. Rangan, M.G. Kanatzidis, Phys. Rev. B 65 (2002) 092105.
[44] V. Petkov, S.J.L. Billinge, J. Heising, M.G. Kanatzidis, J. Am. Chem. Soc. 122 (2000) 11571.
[45] V. Petkov, P.N. Trikalitis, E.S. Božin, S.J.L. Billinge, T. Vogt, M.G. Kanatzidis, J. Am. Chem. Soc. 124 (2002) 10157.
[46] G. Paglia, E.S. Božin, D. Vengust, D. Mihailovic, S.J.L. Billinge, Chem. Mater. 18 (2006) 100.
[47] M. Remskar, A. Mrzel, Z. Skraba, A. Jesih, M. Ceh, J. Demsar, P. Stadelmann, F. Levy, D. Mihailovic, Science 292 (2001) 479.
[48] D. Vrbanič, M. Remskar, A. Jesih, A. Mrzel, P. Umek, M. Ponikar, B. Jancar, A. Meden, B. Novosel, S. Pejovnik, P. Venturini, J.C. Coleman, D. Mihailovic, Nanotechnology 15 (2004) 635.
[49] A. Meden, A. Kodre, J. Padežnick Gomilšek, I. Arčon, I. Vilfan, D. Vrbanič, A. Mrzel, D. Mihailovic, Nanotechnology 16 (2005) 1578.
[50] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T. Chu, D.H. Olson, E.W. Sheppard, B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[51] A.K. Cheetham, G. Ferey, T. Loiseau, Angew. Chem. Int. Ed. 38 (1999) 3268.
[52] L. Mercier, T.J. Pinnavaia, Adv. Mater. 9 (1997) 500.
[53] S.J.L. Billinge, E.J. McKimmey, M. Shatnawi, H.J. Kim, V. Petkov, D. Wermeille, T.J. Pinnavaia, J. Am. Chem. Soc. 127 (2005) 8492.
[54] M. Shatnawi, G. Paglia, J.L. Dye, K.D. Cram, M. Lefenfeld, S.J.L. Billinge, J. Am. Chem. Soc. 129 (2007) 1386.
[55] P.D. Jadzinsky, G. Calero, C.J. Ackerson, D.A. Bushnell, R.D. Kornberg, Science 318 (2007) 430.
[56] H.Z. Zhang, B. Gilbert, F. Huang, J.F. Banfield, Nature 424 (2003) 1025.
[57] V. Petkov, Y. Peng, G. Williams, B. Huang, D. Tomalia, Y. Ren, Phys. Rev. B 72 (2005) 195402.
[58] A.S. Masadeh, E.S. Božin, C.L. Farrow, G. Paglia, P. Juhás, A. Karkamkar, M.G. Kanatzidis, S.J.L. Billinge, Phys. Rev. B 76 (2007) 115413.
[59] S.J.L. Billinge, R.G. DiFrancesco, G.H. Kwei, J.J. Neumeier, J.D. Thompson, Phys. Rev. Lett. 77 (1996) 715.
[60] B. Campbell, R. Osborn, D. Argyriou, L. Vasiliu-Doloc, J. Mitchell, S. Sinha, U. Ruett, C. Ling, Z. Islam, J. Lynn, Phys. Rev. B 65 (2002).
[61] M.C. Sanchez, G. Subias, J. Garcia, J. Blasco, Phys. Rev. Lett. 90 (2003) 045503.
[62] J.A. Kaduk, Crystallogr. Rev. 11 (2005) 1.