

1. INTRODUCTION

obtained by taking the atomic density of the molecule or cluster (which are the atoms at their respective positions) and convoluting it with a replica of the same thing. This object is then orientationally averaged to obtain the PDF. It is not a particularly intuitive object, but it is straightforward to calculate it from a given structural model. The inverse problem, calculating the structure from a PDF, is not possible directly, although in favourable cases, as with structure solution from powder diffraction, it is possible to obtain a unique structure solution from a PDF (Juhás *et al.*, 2006).

We described above how to obtain $G(r)$ from powder data. Here we briefly describe how to calculate a PDF from a structural model. To do this we have to introduce a related function to the PDF, the radial distribution function (RDF), $R(r)$, which is related to $G(r)$ by

$$G(r) = \frac{R(r)}{r} - 4\pi r \rho_0, \quad (1.1.85)$$

where ρ_0 is the atomic number density (Egami & Billinge, 2013).

The function $R(r)$ is important because it is more closely related to the physical structure than $G(r)$, since $R(r) dr$ gives the number of atoms in an annulus of thickness dr at distance r from another atom. For example, the coordination number (or the number of neighbours) of an atom, N_C , is given by

$$N_C = \int_{r_1}^{r_2} R(r) dr, \quad (1.1.86)$$

where r_1 and r_2 define the start and end positions of the RDF peak corresponding to the coordination shell in question. This suggests a scheme for calculating PDFs from atomic models. Consider a model consisting of a large number of atoms situated at positions \mathbf{r}_ν with respect to some origin. Expressed mathematically, this amounts to a series of delta functions, $\delta(\mathbf{r} - \mathbf{r}_\nu)$. The RDF is then given as

$$R(r) = \frac{1}{N} \sum_\nu \sum_\mu \delta(r - r_{\nu\mu}), \quad (1.1.87)$$

where $r_{\nu\mu} = |\mathbf{r}_\nu - \mathbf{r}_\mu|$ is the magnitude of the separation of the ν th and μ th ions, and the double sum runs twice over all atoms in the sample. In Chapter 5.7 on PDF analysis we address explicitly samples with more than one type of atom, but for completeness we give here the expression for $R(r)$ in this case:

$$R(r) = \frac{1}{N} \sum_\nu \sum_\mu \frac{f_\nu f_\mu}{\langle f \rangle^2} \delta(r - r_{\nu\mu}), \quad (1.1.88)$$

where f_ν and f_μ are the form factors, evaluated at $Q = h = 0$, for the ν th and μ th atoms, respectively, and $\langle f \rangle$ is the sample-average form factor.

1.1.5.3.3. Inelastic coherent diffuse scattering

Scattering events must conserve energy and momentum. When a wave is scattered it changes direction and therefore changes its momentum. To satisfy conservation, this momentum, $\mathbf{Q} = 2\pi\mathbf{h} = 2\pi(\mathbf{s} - \mathbf{s}_0)$, must be transferred to the material. When radiation is scattered by a crystal, the mass of the crystal is so large that this produces a negligible acceleration and the scattering is elastic. However, scattering from free atoms or fluids will produce a recoil, which results from a transfer of energy to the atom and the scattering is strictly inelastic. Even within a bulk crystal, there are lattice excitation modes (phonons) which may be created during a particular scattering event and the resulting scattering is

inelastic. In an X-ray experiment, the energy resolution of the measurement usually is much too poor to separate this from the elastic scattering and it all appears mixed together (and is often simply referred to as ‘elastic scattering’). As the excitation energies of internal modes of the system have energies of the order of meV (10^{-3} eV) and the X-ray energy is of the order of keV (10^3 eV), resolving the inelastic modes would require an energy resolution of $\Delta E/E = 10^{-6}$, which is often unachievable. Nonetheless, such experiments are now carried out at synchrotron sources and provide important scientific insights, although the experiments are very slow and very specialized (Burkel, 1991).

These experiments are rarely carried out on powders. If the inelastic scattering is not resolved during the measurement, as is usually the case, it appears as a diffuse-scattering component in the signal from the powder or single crystal and it can be interpreted and modelled to extract information. In powder diffraction, when the scattering occurs from lattice vibrations, or phonons, the diffuse signal is called ‘thermal diffuse scattering’ or TDS (Warren, 1990). Over the last 50–60 years, a number of attempts have been made to extract information about phonon energies and phonon dispersions from TDS with varying amounts of success (Warren, 1990; Jeong *et al.*, 1999; Graf *et al.*, 2003; Goodwin *et al.*, 2005). In the case of PDF analysis, the information in the TDS manifests itself in real space as correlated motion, and it is observed that the low- r peaks are sharper than the high- r peaks. This is because closely bonded atoms tend to move together: if an atom moves to the right it tends to push its neighbour also over to the right, so the motion is correlated. There is useful information in the TDS and the r dependence of the PDF peak broadening, but this is at best a very indirect way of measuring lattice-dynamical effects.

When the energy transfer is not resolved it is hard to separate the cases of scattering arising from phonons (which are dynamic atomic displacements) and scattering arising from static atomic displacements. To some extent these can be disentangled by studying the temperature dependence of the atomic displacement parameters (ADPs) obtained from modelling the data either in reciprocal space or real space (Billinge *et al.*, 1991). This is often done by using a Debye model (Debye, 1912), where the temperature dependence of the mean-square ADP is given by

$$\overline{u^2} = \left(\frac{3h^2 T}{4\pi^2 M k_B \theta_D^2} \right) \left[\varphi\left(\frac{\theta_D}{T}\right) + \frac{1}{4} \frac{\theta_D}{T} \right] + A_{\text{offset}}, \quad (1.1.89)$$

where

$$\varphi\left(\frac{\theta_D}{T}\right) = \frac{T}{\theta_D} \int_0^{\theta_D/T} \left[\frac{x}{\exp(x) - 1} \right] dx, \quad (1.1.90)$$

is the Debye integral. Here, θ_D is the Debye temperature, which is a measure of the stiffness of the bonding, h and k_B are Planck’s and Boltzmann’s constants, respectively, and M is the mass of the oscillating atom. The constant A_{offset} is a temperature-independent offset that is generally needed in the model to account for static distortions. The Debye model is rather crude but surprisingly useful and works well in many cases.

As in the case of phonons, if the scatterer couples to something else in the solid that has an excitation spectrum, this can be studied too. The case of neutrons scattered by magnetic moments is the best known example. Inelastic scattering gives direct information about the magnon dispersion curves. Information about magnetic excitations may also be obtained indirectly from

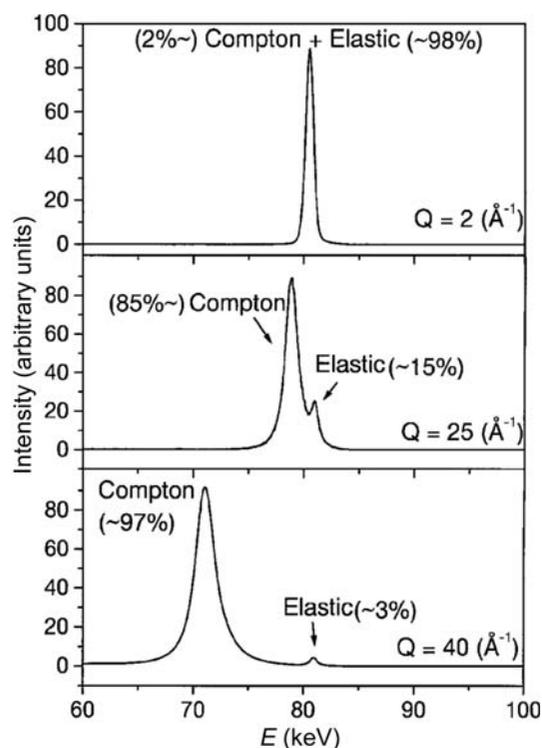


Figure 1.1.24

Spectrum from an energy-resolving detector that shows the elastic and Compton signals as a function of scattering vector Q . [Reprinted with permission from Petkov *et al.* (2000). Copyright (2007) by the American Physical Society.]

the non-energy-resolved magnetic diffuse scattering signal. Magnetic PDF is now possible (Frandsen & Billinge, 2015) as described in Chapter 5.7, as well as reciprocal-space studies of magnetic diffuse scattering (Paddison & Goodwin, 2012).

1.1.5.3.4. Incoherent scattering

Incoherent scattering does not contain any structural information, and cannot be used to study structure in a diffraction experiment since the intensities of the scattered waves do not depend on the position of the scatterers. This does not mean that all incoherent scattering intensity is useless. The fluorescence intensity is incoherent, but may be used in EXAFS experiments to yield structural information. This is because coherent scattering of the photoexcited electron during an absorption event modulates the absorption cross section and therefore the incoherent fluorescence intensity, so a coherent scattering process leaves a measurable response in an incoherent intensity. Incoherent scattering can also be used to measure excitations, although all momentum-transfer information is lost so it is not possible to measure, for example, dispersions of excitations such as phonons and magnons. Even if the scattering process is incoherent, the energy exchanged between the probe and the sample can be measured by the change in wavelength of the scattered wave, and the amplitude of the scattering at each energy transfer is proportional to the density of states of the excitation being probed. In the case of neutrons, the very large incoherent cross section for scattering by hydrogen ($\sim 100\times$ the scattering cross section of most atoms) provides a strong signal for studying low-probability inelastic scattering events. Measuring inelastic scattering from powders can be a rapid way of determining the density of states of phonons, magnons and so on, which is very useful for determining the thermodynamic properties of materials, even though it is less precise than measurement of the full set of dispersion curves.

Another type of incoherent scattering that can be observed in X-ray experiments is Compton scattering (Compton, 1923; Cooper *et al.*, 2004), which is an inelastic incoherent process where the scattering atom recoils during the scattering event. An example of Compton scattering measured in the spectrum from an energy-resolving detector is shown in Fig. 1.1.24.

The Compton scattering is strong in this experiment because the incident X-ray energy is high (80 keV) and the sample is a low-atomic-number alumina-silicate glass. Both the high X-ray energy and the low atomic numbers of the atoms in the sample increase the Compton cross section with respect to the coherent elastic scattering. As the magnitude of the scattering vector, Q , is increased the Compton scattering moves to lower energy and increases in intensity, but the elastic line stays fixed in energy and its intensity decreases because of form-factor and Debye–Waller effects. Momentum as well as energy is conserved in this process and the Compton scattering can be used to measure the momentum distribution of electrons in a material, although this kind of experiment is not widespread these days.

Elastic incoherent scattering provides no information about the sample, and simply degrades the signal-to-noise ratio of the measurement. As such, it is just inconvenient and cannot be easily removed. Monotonic Laue diffuse scattering originates from different chemical species with different scattering powers residing on different sites in the crystal, and when a destructive interference condition is satisfied the resulting intensity does not go to zero but is proportional to $[f_i(h) - f_j(h)]^2$ (Warren, 1990). In pure elements in an X-ray experiment, the atoms on every site are the same and there is no Laue diffuse scattering. This is not true in neutron experiments where different nuclei have different scattering powers and most elements contain a range of isotopes in their natural form (the ‘natural abundance’; Squires, 1996). This results in Laue diffuse scattering even in an element, although it is normally not referred to in these terms but is encompassed by a so-called ‘incoherent neutron cross section’ that is defined and tabulated (see Table 4.4.4.1 in *International Tables for Crystallography*, Volume C) for each element. This is not the only source of incoherent scattering in neutron diffraction, since the scattering power also depends on the relative orientation of the neutron and nuclear spins. In general these spins are all orientationally disordered (and fluctuating) and the result is an additional scattering-event-dependent contribution to the incoherent scattering from the sample, again encompassed by the ‘incoherent neutron cross section’ of the element. Where necessary, it may be possible to make isotopically enriched samples for neutron experiments so that the proportion of isotopes with large incoherent scattering cross sections is minimized (or the isotopes are removed altogether), and the range of isotopes can also be reduced, which further reduces the incoherent component of the signal. However, the cost and difficulty of doing this means that it is rarely done.

1.1.6. Local and global optimization of crystal structures from powder diffraction data

1.1.6.1. Rietveld refinement

More than 40 years have passed since the publication of the pioneering papers by Hugo Rietveld (Rietveld, 1967, 1969), in which he described a method for the refinement of crystal structures from neutron powder diffraction data. Neutron data sets from reactor sources were more amenable than X-ray data sets to this method because the line profiles are quite Gaussian.