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Table 1.1.1
Types of scattering from a sample

Type of scattering	Coherent	Incoherent
Elastic	Bragg scattering Magnetic Bragg scattering Bragg scattering from ferroelectric/magnetic order Diffuse scattering from static defects Diffuse signal from small nanoparticles (<10 nm) Scattering from amorphous material (except excitations) Multiple scattering (coherent)	Laue monotonic diffuse scattering Neutron incoherent scattering Multiple scattering (incoherent)
Inelastic	Thermal diffuse scattering Spin-wave scattering Paraelectric/paramagnetic scattering Scattering from liquids	Compton scattering Fluorescence Incoherent scattering from hydrogen

leading to

$$\mathrm{d}d = -\frac{n\lambda}{2\sin\theta}\frac{\cos\theta}{\sin\theta}\mathrm{d}\theta + \frac{n}{2\sin\theta}\mathrm{d}\lambda \qquad (1.1.77)$$

and finally

$$\frac{\mathrm{d}d}{d} = -\frac{\mathrm{d}\theta}{\tan\theta} + \frac{\mathrm{d}\lambda}{\lambda}. \qquad (1.1.78)$$

When a crystal is strained, the d-spacings vary. A *macroscopic* strain changes the interplanar spacing by Δd_{hkl}, giving rise to a shift of $\Delta\theta$ in the *average* position of the diffraction peak. On the other hand, *microscopic* strains result in a distribution of d-spacings of width δd_{hkl}, which has the effect of *broadening* the diffraction peak by $\delta\theta$. Equation (1.1.78) gives an expression for the amount of Bragg-peak broadening that occurs for a given δd_{hkl}.

1.1.5. The background

1.1.5.1. *Information content in the background*

As discussed above, the elastic scattering from a crystalline powder consists of sharp rings, or peaks, of scattering at the 2θ angles where the Bragg or von Laue laws are satisfied. In general these sharp peaks sit on top of a 'background' which is broad and somewhat featureless. There are two components to this background, illustrated in Fig. 1.1.1: extraneous counts in the detector from things other than the sample, and non-Bragg scattering from the sample itself. The former are rarely of interest scientifically and the objective of a good experimental design is to minimize them as far as possible, or explicitly measure and subtract them, and then account well in any model or data interpretation for the part that cannot be eliminated from the measurement. Historically, the diffuse-scattering signals from the sample itself were also considered to be an inconvenience to be minimized and removed, and indeed in many cases this is still the best course of action (for example, sample fluorescence can be eliminated by choosing to work at an X-ray energy that lies below the absorption edge of a constituent atom). However, the diffuse 'background' from the sample can contain crucial information about defects, disorder and nanoscale order in the sample, and increasingly we are interested in studying it in order to understand the properties of the material that is under investigation. In some cases, such as glasses, liquids and samples of small nanoparticles, there is no Bragg scattering at all and only a diffuse scattering signal (see Chapter 5.6).

All the intensity scattered by the sample can be categorized as either coherent or incoherent and as elastic or inelastic, which are defined as follows. The coherency of the signal derives from whether or not the scattered waves interfere with each other constructively, and the resulting intensities are different in each case. For coherent scattering, the waves contributing to the signal are all summed first, before the wave amplitude is squared, to find the intensity distribution, which is the modulus squared of the resulting wave. For incoherent waves, one simply squares the amplitude of each wave to get its intensity and sums these together to get the total intensity. Switching to a consideration of the elasticity of the scattering, we define the scattering as elastic if the incident and scattered waves have the same energy, in which case no energy was exchanged during the scattering process between the incident wave and the sample, and inelastic scattering as the opposite. Inelastic scattering may result in a gain or a loss of energy of the scattered particle depending on the nature of the scattering, which results in a change in the wavelength of the scattered particle. There are also some non-scattering processes that can take place, such as absorption and fluorescence, but emissions resulting from these processes can also be categorized by whether or not they are coherent and elastic. It should be noted that the total energy of the system must be conserved during the scattering process, and so when a scattered wave gains or loses energy it exchanges it with the sample. This is used as a way of probing excitations in a material. Table 1.1.1 summarizes many of the types of diffuse scattering coming from a sample and categorizes them by their coherency and elasticity.

1.1.5.2. *Background from extraneous sources*

The most commonly observed extraneous, or parasitic, scattering is from the sample container (such as a capillary) that holds the sample during the measurement. Another large contribution may come from air scattering, which originates principally from scattering of the direct beam by molecules in the air in the beam path, both before and after the sample. Air-scattering effects can be minimized by enclosing as much of the beam path as possible in a tube which may be evacuated or where the air is replaced by a weakly scattering gas (such as He in the case of X-rays). Air scattering that is detected by the detector can also be reduced by careful collimation of the beams and then shielding the detector from detecting radiation that does not originate from the sample position. Collimating the incident beam is straightforward and results in a big reduction in air scattering. For point detectors it is also straightforward to collimate the scattered beam, but the modern trend towards using linear and area detectors makes this more difficult. There is sometimes a trade-off between collimating the scattered beam to reduce background and having uniform backgrounds that do not vary with angle because of incomplete angle-dependent collimation. Incomplete angle-dependent collimation can be very difficult to correct when trying to measure diffuse scattering quantitatively and the current trend is to have minimal secondary collimation.

There is increasing interest in carrying out *in situ* experiments under extreme conditions of pressure, temperature, magnetic field and so on (see Chapters 2.6 to 2.8). These experiments inevitably introduce additional scattering from the environment. Again, there is a balance between finding creative ways to reduce these backgrounds, and simply making them less problematic in the data analysis. For example, in a diamond-anvil cell, where the beam accesses the sample through the diamond, one can drill a hole part way through the diamond to accommodate the direct beam and make the direct beam small enough to fit in the hole. This increases the complexity of the measurement as alignment becomes harder, but it is usually worth it. Shielding structural parts of the environment cell with an absorbing material, such as lead for X-rays or a borated material for neutrons, can help to reduce unwanted background intensity a lot, as can making thin, transparent windows for the incident and scattered beams.

An additional source of background in the signal does not come from scattering at all, but from electrical noise in the detector electronics. For some types of detectors it may be important to measure 'dark' exposures with the X-rays turned off and subtract these carefully from the experimental data. It is also possible to detect signals from cosmic rays, which can leave tracks in two-dimensional detector signals.

1.1.5.3. *Sources of background from the sample*

1.1.5.3.1. *Elastic coherent diffuse scattering*

As discussed in Section 1.1.4.1.1, decreasing the size of a crystal leads to an increase in the width of the Bragg peaks. When the size of the crystallite becomes very small, as a rule of thumb below 10 nm in diameter for typical unit cells, the widths of the Bragg peaks become so large that they merge and overlap, and it does not make sense to use delta-function Bragg peaks as the starting point for the analysis. At this point the coherent diffraction is completely diffuse in nature. Nonetheless, it still contains structural information. To see this we begin again with the Laue equation before we assumed periodicity [equation (1.1.39)]. For the simple case of a diatomic gas such as N_2, the sum would be taken only over two atoms, since scattering from a single molecule will be coherent but that from different molecules will be incoherent. In that case we have

$$\begin{aligned} A(\mathbf{h}) &= \sum_{j=1}^{2} f_j(h)\exp(2\pi i\mathbf{h}\cdot\mathbf{r}_j),\\ A(\mathbf{h}) &= f_1\exp(2\pi i\mathbf{h}\cdot\mathbf{r}_1) + f_2\exp(2\pi i\mathbf{h}\cdot\mathbf{r}_2), \end{aligned} \quad (1.1.79)$$

and the intensity is proportional to

$$\begin{aligned} I(\mathbf{h}) &= (f_1f_1^* + f_2f_2^*) + f_1f_2^*\exp\left(2\pi i\mathbf{h}\cdot\mathbf{r}_{12}\right)\\ &\quad + f_2f_1^*\exp\left(-2\pi i\mathbf{h}\cdot\mathbf{r}_{12}\right), \end{aligned} \quad (1.1.80)$$

where $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$. For a diatomic molecule where both atoms are the same $f_1 = f_2$ and

$$I(\mathbf{h}) = f^*f\cos^2(\pi\mathbf{h}\cdot\mathbf{r}_{12}). \quad (1.1.81)$$

The scattering from a diatomic molecule of an element is simply a single-component cosine wave with a wavelength that depends on the separation of the atoms in the molecule. In an actual experiment there will be scattering from all the molecules that have every orientation with equal probability, so it is necessary to take an orientational average of the scattering. How this is done is shown in Chapter 5.7 on PDF analysis, but the result is the Debye equation (Debye, 1915),

$$I(h) = \frac{1}{N\langle f\rangle^2}\sum_{i,j} f_j^* f_i\left[\frac{\sin(Qr_{ij})}{Qr_{ij}}\right], \quad (1.1.82)$$

where N is the total number of atoms. For our diatomic molecule this becomes

$$I(h) = \frac{1}{N}\left[\frac{\sin(Qr_{ij})}{Qr_{ij}}\right]. \quad (1.1.83)$$

For clusters of atoms such as larger molecules or small nanoparticles that are intermediate in size between a diatomic molecule and a small chunk of crystal, the Debye equation is exact and may be used to calculate the intensity of the scattering. As the clusters get larger and the structure more periodic, such as small chunks of crystal, the scattering calculated from the Debye equation crosses smoothly to that obtained from the periodic Laue equation. The finite size broadened crystallographic model works well as a starting point for calculating scattering from well ordered crystals down to nanoparticle sizes of 10 nm, but loses accuracy rapidly below this particle size. The Debye equation is accurate for all particle sizes, but becomes computationally intractable for larger clusters much above 10 nm.

1.1.5.3.2. *Total-scattering and atomic pair distribution function analysis*

An alternative approach to the analysis of diffuse scattering from nanostructures is to Fourier transform the data to obtain the atomic pair distribution function, or PDF. In fact, the Fourier transform does not depend on whether the structure is periodic or not, and it is also possible to Fourier transform the Bragg scattering from crystals. If there is no nanoscale disorder in the crystal there are few real benefits in doing this rather than using the powerful crystallographic methods described elsewhere in this chapter. However, the PDF approach utilizes both the Bragg *and* diffuse components, and yields additional information about the structure that is particularly valuable when the crystal contains some kind of nanoscale domains. The presence of such domains was rarely considered in the past, but we now know that they are often found in materials. In the sense that both Bragg and diffuse scattering data are used without prejudice, and also that the data are measured over a wide range of the scattering vector so that, as far as possible, the coherent scattering in all of the reciprocal space is measured, this method is known as 'total-scattering analysis', and as 'PDF analysis' when the data are Fourier transformed and studied in real space.

The powder diffraction data for total-scattering studies are measured in much the same way as in a regular powder diffraction experiment. However, explicit corrections are made for extrinsic contributions to the background intensity from such effects as Compton scattering, fluorescence, scattering from the sample holder and so on. The resulting coherent scattering function $I(Q)$ is a continuous function of $Q = |\mathbf{Q}| = 2h = 4\pi\sin\theta/\lambda$, with sharp peaks where there are Bragg reflections and broad features in between. In general it is usual to work with a normalized version of this scattering intensity, $S(Q)$. This is the intensity normalized by the incident flux per atom in the sample. $S(Q)$ is called the total-scattering structure function. It is a dimensionless quantity and the normalization is such that the average value $\langle S(Q)\rangle = 1$. In short, $S(Q)$ is nothing other than the powder diffraction pattern that

references