

1. INTRODUCTION

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 N₂, 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

$$A(\mathbf{h}) = \sum_{j=1}^2 f_j(h) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j),$$

$$A(\mathbf{h}) = f_1 \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_1) + f_2 \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_2), \quad (1.1.79)$$

and the intensity is proportional to

$$I(\mathbf{h}) = (f_1 f_1^* + f_2 f_2^*) + f_1 f_2^* \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_{12}) + f_2 f_1^* \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}_{12}), \quad (1.1.80)$$

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

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

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