1.1. OVERVIEW AND PRINCIPLES
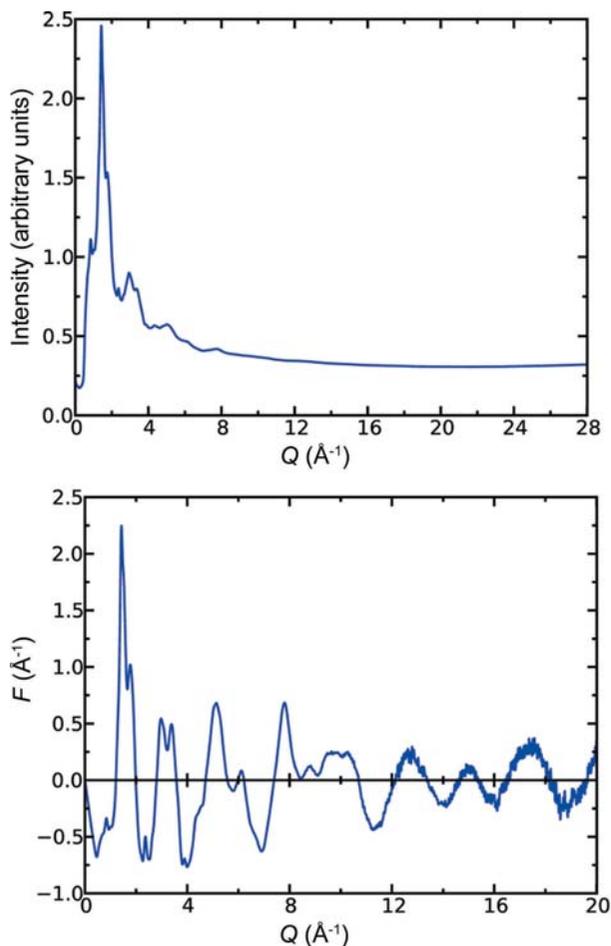

Figure 1.1.22

Comparison of raw data and the normalized reduced total-scattering structure function $F(Q) = Q[S(Q) - 1]$. The sample is a powder of 2 nm diameter CdSe nanoparticles and the data are X-ray data from beamline 6ID-D at the Advanced Photon Source at Argonne National Laboratory. The raw data are shown in the top panel. The high-Q data in the region $Q > 9\,\text{Å}^{-1}$ appear smooth and featureless. However, after normalizing and dividing by the square of the atomic form factor, important diffuse scattering is evident in this region of the diffraction pattern (bottom panel).
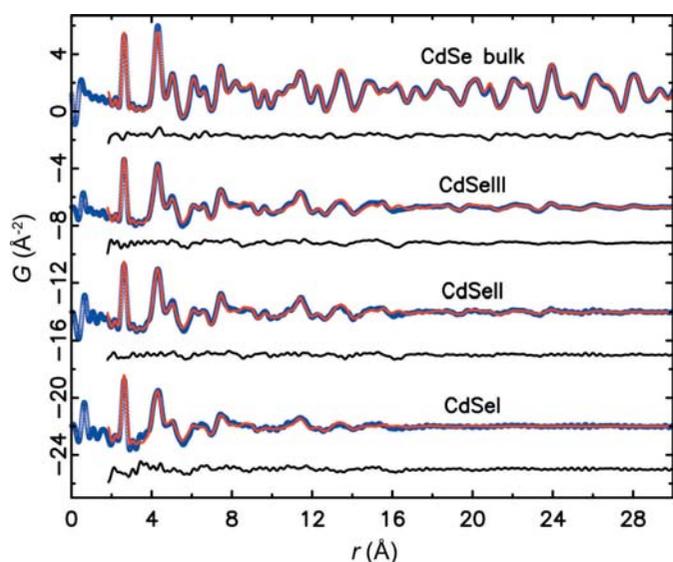

Figure 1.1.23

PDFs in the form of $G(r)$ from bulk CdSe and from a series of CdSe nanoparticles. The blue curve at the bottom is the PDF obtained from the data shown in Figure 1.1.22. The blue symbols are from the data and the thin red lines on top are from models of the local structure in these nanoparticles. Offset below are difference curves between the model and the data. [Reprinted with permission from Masadeh *et al.* (2007). Copyright (2007) by the American Physical Society.]

has been corrected for experimental artifacts and suitably normalized (Egami & Billinge, 2013).

Measuring over a wide range of Q values yields better resolution in real space, as well as yielding more information, and is desirable. The coherent intensity (the features) in $S(Q)$ dies out with increasing Q because of the Debye–Waller factor (which comes from thermal and quantum zero-point motion of the atoms), as well as any static displacive disorder in the material and, for X-ray measuerments, because of the X-ray form factor. In a neutron measurement, the atomic displacement effects are still present, but the neutron has no form factor and the scattering length is constant in Q. By a Q value of 30–50 Å^{-1} (depending on the temperature and the stiffness of the bonding in the sample) there are no more features in $S(Q)$ and there is no need to measure data to higher Q. Still, this is a much higher maximum value of Q than is measured in conventional powder diffraction experiments using laboratory X-rays or reactor neutrons. The maximum value of Q attainable in back scattering from a Cu $K\alpha$ tube is around 8 Å^{-1} and from an Mo $K\alpha$ tube it is around 16 Å^{-1}. Routine total-scattering measurements can be made using laboratory sources with Mo or Ag tubes; however, for the highest real-space resolution, and the smallest statistical uncertainties, synchrotron data are preferred. In the case of neutron scattering, spallation neutron sources are ideal for total-scattering experiments.

The total-scattering function $S(Q)$ appears to be different from the function measured in a standard powder diffraction experiment because of the Q range studied, and also because of an important aspect of the normalization: the measured intensity is divided by the total scattering cross section of the sample. In the case of X-ray scattering, the sample scattering cross section is the square of the atomic form factor, $\langle f(Q) \rangle^2$, which becomes very small at high Q. Thus, during the normalization process the data at high Q are amplified (by being divided by a small number), which has the effect that even rather weak intensities at high Q, which are totally neglected in a conventional analysis of the data, become rather important in a total-scattering experiment. Because the signal at high Q is weak it is important to collect the data in that region with good statistics. This is illustrated in Fig. 1.1.22.

The Fourier transform of the total-scattering data is the reduced pair distribution function, $G(r)$, which is related to $S(Q)$ through a sine Fourier transform according to

$$G(r) = \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} Q[S(Q) - 1]\sin(Qr)\,\mathrm{d}Q. \qquad (1.1.84)$$

Examples of $G(r)$ functions from small nanoparticles of CdSe are shown in Fig. 1.1.23.

$G(r)$ has peaks at positions, r, that separate pairs of atoms in the solid with high probability. For example, there are no physically meaningful peaks below the nearest-neighbour peak at ~2.5 Å, which is the Cd–Se separation in CdSe. However, in addition to the nearest-neighbour information, valuable structural information is contained in the pair correlations that extend to much higher values of r. In fact, with data to a high resolution in Q, PDFs can be measured out to hundreds of nanometres (*i.e.*, thousands of ångströms) and the structural information that can be obtained from the data remains quantitatively reliable (Levashov *et al.*, 2005).

The function $G(r)$ is related to the atomic density. However, it is not the atomic density itself, but its autocorrelation. This is