Anomalous X-Ray Scattering

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Unlike gases, liquids and glasses are *condensed matter*, with atomic densities almost equal to those in crystalline solids. Each atom interacts strongly with its neighbors, and tries to set up an environment most comfortable to that atom. This creates "short-range order (SRO)" which is both physical and chemical. In other words where the neighbors are and what neighbor you have. The total scattering tells you mostly the physical SRO, not the chemical, or compositional, SRO (CSRO), except that the bond lengths are so distinct that each peak in the pair-distribution function (PDF) can be assigned chemical identity. But such cases are exceptions than the norm. Often peaks with different chemical identities overlap and cannot be resolved.

Anomalous x-ray scattering (AXS) is the technique of choice to resolve CSRO with x-rays. It takes advantage of the strong energy dependence of the atomic scattering factor near the absorption edge. The x-ray scattering factor of an atom is energy independent, most of the time. But when the incident energy of x-ray is equal to the absorption edge, say of the *K*-shell, the incident x-ray photon resonates with the $1s$-$2p$ excitation, and induces emission which is out-of phase. The consequence is the reduced scattering factor, in the close vicinity of the absorption edge. For this reason this technique is also called the resonant elastic x-ray scattering (REXS). In a multi-component system, since the x-ray scattering factor of other elements do not change much in a narrow energy range near the absorption edge of one element, measuring the scattering intensities at two incident energies just below the absorption edge of one element isolates the structure factor involving that element, and yields the differential PDF (DDF) [1] as shown below. AXS is also a powerful technique when combined with small angle x-ray scattering (SAXS). SAXS is sensitive to mesoscopic density fluctuation. When combined with AXS (SAAXS) it can probe the mesoscopic compositional fluctuation.

Whereas the theory of AXS appears straightforward, the practice of AXS is not. First, the energy of the absorption edge is fixed by atomic physics. The energy of the incident x-ray, E_i, is directly related to the scattering vector, Q, by $Q = 2k\sin\theta = (2E_i/c\hbar)\sin\theta$, where θ is the diffraction angle. Since $\sin\theta \leq 1$, $Q \leq 2E_i/c\hbar$; the energy of the absorption edge limits the range of Q. For light elements it is too low to gain sufficient information, except for SAAXS.

The second reason is the so-called x-ray Raman effect, induced electronic transition below the absorption edge. If the incident energy is above the absorption edge the sample strongly absorbs x-ray and emits fluorescence, emission of the characteristic x-ray from the sample, which interferes with the measurement. Thus we have to choose the incident energy *below* the absorption edge. But even below the edge fluorescence occurs because of the x-ray Raman effect. Therefore the AXS setup has to be made to exclude the fluorescent radiation. This, in principle, can be done by using an analyzer crystal. Now, most of the x-ray diffraction measurements are done to determine the position of the Bragg peaks in *Q*-space with high accuracy, and the accuracy of the intensity measurement is secondary in importance. Thus the analyzer crystal is customarily used in high-resolution diffraction measurement. However, in

practice it is not easy to align the analyzer correctly with respect to the sample over a wide range of scattering angle, particularly because a crystal analyzer is very sensitive to aberration in angle. Consequently the intensity measurements become compromised, and DDF becomes inaccurate.

The best setup is to use an energy sensitive semiconductor detector, such as a pure Ge detector. Pure Ge detector typically has the energy resolution of the order of 2%. Thus it can differentiate the K_α fluorescence from the elastic line, but not the K_β radiation. We measure both the intensities of elastic scattering, including K_β fluorescence, and K_α fluorescence, knowing the K_β/K_α ratio calculate the intensity of K_β fluorescence from the K_β fluorescence intensity with the absorption correction, and subtract it from the elastic intensity [2]. Examples of the DDF in glasses will be discussed [3,4].

Derivation of the differential PDF:

Near the absorption edge the x-ray scattering factor, $f(Q)$, depends on the x-ray energy, E: $f(Q) = f_0(Q) + f'(E) + if''(E)$. The cross terms involving both Q and E are very small. Now the structure function, $S(Q)$,

$$S(Q) = \frac{1}{\langle f \rangle^2} \sum_{i,j} f_i f_j e^{i\mathbf{Q}\cdot(\mathbf{r_i}-\mathbf{r_j})} \tag{1}$$

can be grouped into compositionally resolved functions,

$$S(Q) = \frac{1}{\langle f \rangle^2} \sum_{\alpha,\beta} f_\alpha f_\beta S_{\alpha\beta}(Q), \quad S_{\alpha\beta}(Q) = \sum_{i(\alpha),j(\beta)} e^{i\mathbf{Q}\cdot(\mathbf{r_i}-\mathbf{r_j})}, \tag{2}$$

and its Fourier-transform,

$$G(r) = \frac{1}{\langle f \rangle^2} \sum_{\alpha,\beta} f_\alpha f_\beta G_{\alpha\beta}(r), \quad G_{\alpha\beta}(r) = \int S_{\alpha\beta}(Q)\sin(Qr)QdQ. \tag{3}$$

By differentiating (2) by the scattering factor of an element ,

$$S_\alpha(Q) = \langle f \rangle \frac{dS(Q)}{df_\alpha} = \frac{1}{\langle f \rangle} \sum_{\alpha,\beta} f_\beta S_{\alpha\beta}(Q), \tag{4}$$

we obtain the compositionally differential PDF;

$$G_\alpha(r) = \int \left[S_\alpha(Q)-1 \right] \sin(Qr)QdQ, \tag{5}$$

which is the PDF with an element α at the origin. In order to obtain the compositionally resolved PDF we have to differentiate this again, but to carry out such a practice with accuracy is extremely difficult. Thus most of the time we stop the analysis at the level of the DDF, which still carries a lot of information.

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