4.2. DISORDER DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS
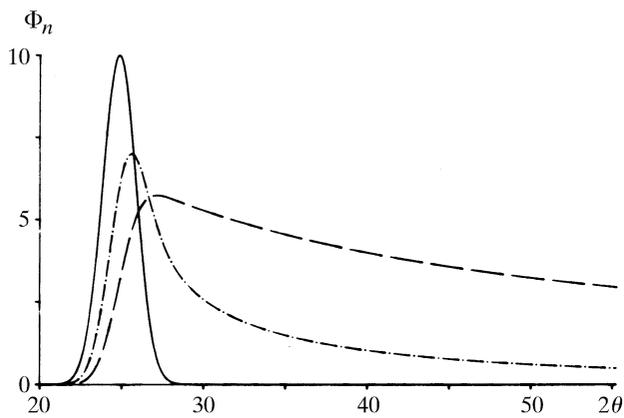

Fig. 4.2.8.2. Line profiles in powder diffraction for diffuse peaks (full line), continuous streaks (dot–dash lines) and continuous planes (broken lines). For explanation see text.

P denotes a scaling factor that depends on the instrumental luminosity, T is the shortest distance to the origin of the reciprocal lattice, $m(T)$ is the corresponding symmetry-induced multiplicity, A_n contains the structure factor of the structural units and the type of disorder, and Φ_n describes the characteristic modulation of the diffuse phenomenon of dimension n in the powder pattern. These expressions are given below with the assumption of Gaussian line shapes of width D for the narrow extension(s). The formulae depend on a factor $M = A_{1/2}(4k_1^2 - H_0^2)/(32 \ln 2)$, where $A_{1/2}$ describes the dependence of the Bragg peaks on the instrumental parameters U, V and W (see Caglioti *et al.*, 1958),

$$A_{1/2}^2 = U \tan^2 \theta + V \tan \theta + W, \qquad (4.2.8.13)$$

and $k_1 = 1/\lambda$.

(*a*) *Isotropic diffuse peak around T*

$$\Phi_0 = [2\pi(M^2 + D^2)]^{-1/2}(1/T^2)$$
$$\times \exp\{-(H_0 - T)^2/2(M^2 + D^2)\}. \qquad (4.2.8.14)$$

The moduli $|\mathbf{H}_0|$ and T enter the exponential, *i.e.* the variation of $d\sigma/d\Omega$ along $|\mathbf{H}_0|$ is essential. For broad diffuse peaks ($M \ll D$) the angular dependence is due to $1/T^2$, *i.e.* proportional to $1/\sin^2 \theta$. This result is valid for diffuse peaks of any shape.

(*b*) *Diffuse streak*

$$\Phi_1 = [2\pi(M^2 + D^2)]^{-1/2} \int_{-\infty}^{\infty} (T^2 + H^2)^{-1/2}$$
$$\times \exp\{-H_0 - (T^2 + H^2)^{1/2}/2(M^2 + D^2)\}\,dH. \qquad (4.2.8.15)$$

The integral has to be evaluated numerically. If $(M^2 + D^2)$ is not too large, the term $1/(T^2 + H^2)$ varies only slowly compared to the exponential term and may be kept outside the integral, setting it approximately to $1/H_0^2$.

(*c*) *Diffuse plane* (with $R^2 = H_x^2 + H_y^2$)

$$\Phi_2 = (M^2 + D^2)^{-1/2} \int R^2/(T^2 + R^2)$$
$$\times \exp\{-H_0 - (T^2 + R^2)^{1/2}/2(M^2 + D^2)\}\,dR. \qquad (4.2.8.16)$$

With the same approximation as in (*b*) the expression may be simplified to

$$\Phi_2 = \pi/H_0[1 - \text{erf}\{(T - H_0)/[2(M^2 + D^2)]^{1/2}\}$$
$$+ 1/H_0^2[2\pi(M^2 + D^2)]^{1/2}$$
$$\times \exp\{-(H_0 - T)^2/2(M^2 + D^2)\}]. \qquad (4.2.8.17)$$

(*d*) *Slowly varying diffuse scattering in three dimensions*

Φ_3 = constant. Consequently, the intensity is directly proportional to the cross section. The characteristic functions Φ_0, Φ_1 and Φ_2 are shown in Fig. 4.2.8.2 for equal values of T and D. Note the relative peak shifts and the high-angle tail.

4.2.8.3. Total diffraction pattern

As mentioned in Section 4.2.7.3.2, the atomic pair-distribution function (PDF), which is classically used for the analysis of the atomic distributions in liquids, melts or amorphous samples, can also be used to gain an understanding of disorder in crystals. The PDF is the Fourier transform of the total scattering. The measurement of total scattering is basically similar to recording X-ray or neutron powder patterns. The success of the method depends, however, decisively on various factors: (i) The availability of a large data set, *i.e.* reliable intensities up to high H values, in order to get rid of truncation ripples, which heavily influence the interpretation. Currently, values of $H_{\max}$ of more than 7 Å^{-1} can be achieved either with synchrotron X-rays [at the European Synchrotron Radiation Facility (ESRF) or Cornell High Energy Synchrotron Source (CHESS)] or with neutrons from reactors (*e.g.* instrument D4 at the ILL) and spallation sources [at ISIS or at LANSCE (instrument NPDF)]. (ii) High H resolution. (iii) High intensities, in particular at high H values. (iv) Low background of any kind which does not originate from the sample. High-quality intensities are therefore to be extracted from the raw data by taking care of an adequate absorption correction, correction of multiple-scattering effects, separation of inelastically scattered radiation (*e.g.* Compton scattering) and careful subtraction of 'diffuse' background which is not the 'true' diffuse scattering from the sample. These conditions are in practice rather demanding. A further detailed discussion is beyond the scope of this chapter, but a more thorough discussion is given, *e.g.*, by Egami (2004), and some examples are given by Egami & Billinge (2003).

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