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cone. Generally, only a small fraction of this power is recorded by the detector. Thus, the useful quantity is the power per unit length of the diffraction circle on the receiving surface, $P'_{\mathbf{h}}$. At a distance r from the sample, the circumference of the diffraction circle is $2\pi r \sin 2\theta_0$ and one has (constants omitted)

$$P'_{\mathbf{h}} \propto r^{-1} V N_c^2 [i_0(E) j d^2 |F|^2]_{\mathbf{h}} \frac{C_p(E, \theta_0) \Delta\theta_0}{\sin\theta_0}. \qquad (2.5.1.7)$$

The peak areas in an XED powder spectrum are directly proportional to the $P'_{\mathbf{h}}$ of equation (2.5.1.7).

Quantitative structural analysis requires the knowledge of $i_0(E)$ and $P(E)$. As mentioned above, these quantities are not known with sufficient accuracy for *Bremsstrahlung*. For synchrotron radiation they can be calculated, but they will nevertheless contribute to the total uncertainty in the analysis. Accordingly, XED is used rather for identification of a known or assumed structure than for a full structure determination.

2.5.1.5. *Corrections*

(*a*) *Temperature effects*

The effect of thermal vibrations on the integrated intensities is expressed by the Debye–Waller factor in the same way as for standard angle-dispersive methods. Notice that $(\sin\theta)/\lambda = 1/2d$ irrespective of the method used. The contribution of the thermal diffuse scattering to the measured integrated intensities can be calculated if the elastic constants of the sample are known (Uno & Ishigaki 1975).

(*b*) *Absorption*

The transmission factor $A(E, \theta_0)$ for a small sample bathed in the incident beam and the factor $A_c(E, \theta_0)$ for a large sample intercepting the entire incident beam are the same as for monochromatic methods (Table 6.3.3.1). However, when they are applied to energy-dispersive techniques, one has to note that the absorption corrections are strongly varying with energy. In the special case of a symmetrical reflection where the incident and diffracted beams each make angles θ_0 with the face of a thick sample (powder or imperfect crystal), one has

$$A_c(E) = \frac{1}{2\mu(E)}, \qquad (2.5.1.8)$$

where $\mu(E)$ is the linear attentuation coefficient evaluated at the energy associated with the Bragg reflection.

(*c*) *Extinction and dispersion*

Extinction and dispersion corrections are applied in the same way as for angle-dispersive monochromatic methods. However, in XED, the energy dependence of the corrections has to be taken into account.

(*d*) *Geometrical aberrations*

These are distortions and displacements of the line profile by features of the geometry of the apparatus. Axial aberrations as well as equatorial divergence contribute to the angular range $\Delta\theta_0$ of the Bragg reflections. There is a predominance of positive contributions to $\Delta\theta_0$, so that the diffraction maxima are slightly displaced to the low-energy side, and show more tailing on the low-energy side than the high-energy side (Wilson, 1973).

(*e*) *Physical aberrations*

Displacements due to the energy-dependent absorption and reflectivity of the sample tend to cancel each other if the incident intensity, $i_0(E)$, can be assumed to be constant within the energy range of Bragg reflection. With synchrotron radiation, $i_0(E)$ varies rapidly with energy and its influence on the peak positions should be checked. Also, the detector response function will influence the line profile. Low-energy line shapes are particularly sensitive to the deadlayer absorption, which may cause tailing on the low-energy side of the peak. Integrated intensities, measured as peak areas in the diffraction spectrum, have to be corrected for detector efficiency and intensity losses due to escape peaks.

2.5.1.6. *The Rietveld method*

The Rietveld method (see Chapter 8.6) for refining structural variables has only recently been applied to energy-dispersive powder data. The ability to analyse diffraction patterns with overlapping Bragg peaks is particularly important for a low-resolution technique, such as XED (Glazer, Hidaka & Bordas, 1978; Buras, Gerward, Glazer, Hidaka & Olsen, 1979; Neuling & Holzapfel, 1992). In this section, it is assumed that the diffraction peaks are Gaussian in energy. It then follows from equation (2.5.1.7) that the measured profile y_i of the reflection k at energy E_i corresponding to the ith channel of the multichannel analyser can be written

$$y_i = \frac{c'}{H_k} i_0(E_i) A(E_i) j_k d_k^2 |F_k|^2 \exp\{-4\ln 2[(E_k - E_i)^2/H_k^2]\}, \qquad (2.5.1.9)$$

where c' is a constant, $i_0(E_i)$ is evaluated at the energy E_i, and H_k is the full width (in energy) at half-maximum of the diffraction peak. $A(E_i)$ is a factor that accounts for the absorption in the sample and elsewhere in the beam path. The number of overlapping peaks can be determined on the basis of their position and half-width. The full width at half-maximum can be expressed as a linear function of energy:

$$H_k = UE_k + V, \qquad (2.5.1.10)$$

where U and V are the half-width parameters.

2.5.1.7. *Single-crystal diffraction*

Energy-dispersive diffraction is mainly used for powdered crystals. However, it can also be applied to single-crystal diffraction.

A two-circle system for single-crystal diffraction in a diamond-anvil high-pressure cell with a polychromatic, synchrotron X-ray beam has been devised by Mao, Jephcoat, Hemley, Finger, Zha, Hazen & Cox (1988).

Formulae for single-crystal integrated intensities are well known from the classical Laue method. Adaptations to energy-dispersive work have been made by Buras, Olsen, Gerward, Selsmark & Lindegaard-Andersen (1975).

2.5.1.8. *Applications*

The unique features of energy-dispersive diffraction make it a complement to rather than a substitute for monochromatic angle-dispersive diffraction. Both techniques yield quantitative structural information, although XED is seldom used for a full structure determination. Because of the fixed geometry, energy-dispersive methods are particularly suited to *in situ* studies of samples in special environments, *e.g.* at high or low temperature and/or high pressure. The study of anomalous scattering and forbidden reflections is facilitated by the possibility of shifting the diffraction peaks on the energy scale by changing the scattering angle. Other applications are studies of Debye–Waller factors, determinative mineralogy, attenuation-coefficient measurements, on-stream measurements, particle-size and -strain

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