6. INTERPRETATION OF DIFFRACTED INTENSITIES

tion in incident-beam intensity is many times larger than the sum of the squares of the individual atomic scattering powers.

An extreme case occurs in a perfect crystal, for which total reflection is possible. There is destructive interference with the incident beam producing a marked change in the index of refraction from its normal value of

$$n = 1 - \frac{\lambda^2 e^2}{2\pi mc^2} \sum_a N_a f_a(0), \qquad (6.3.1.4)$$

where e and m are the charge and mass of the electron. $f_a(0)$ is the scattering factor in the forward direction for an atom of type a and N_a is the number of atoms of that type per unit volume.

Thus, for strong reflections in near-perfect crystals, the Rayleigh scattering is affected by both crystal texture and beam direction. This reduction of primary-beam intensity due to the Rayleigh scattering is usually included, along with other specimen-dependent factors affecting diffracted-beam intensity, in the analysis of extinction.

6.3.1.4. *Attenuation (mass absorption) coefficients*

Since the reduction of intensity depends on the quantity of matter traversed by the beam, the absorption coefficient is often expressed on a mass basis by dividing by the density ρ_m. μ/ρ_m defines the attenuation coefficient.

The determination of attenuation coefficients to high precision is possible only when contributions from all different scattering processes are analysed in detail. To a level of accuracy appropriate to most experiments, however, the coefficient can be determined from the atomic cross sections for scattering and photoelectric absorption. Ideally, absorption corrections for scattering from single crystals in the absence of extinction should be evaluated using the Rayleigh cross section for a crystal in the non-reflecting position. However, as Rayleigh scattering is a minor contribution to the total absorption except for the lighter elements, no large error is made by applying the absorption correction appropriate to an assembly of isolated atoms to a single crystal.

Likewise, μ/ρ_m is, to a good approximation, given by the sum of the attenuation coefficients for each constituent element $(\mu/\rho_m)_a$, weighted by the mass fraction g_a for that element, *i.e.*

$$\frac{\mu}{\rho_m} = \sum_a g_a(\mu/\rho_m)_a, \qquad (6.3.1.5)$$

where the sum is over the elements. The atomic cross section for attenuation is given by

$$\sigma_a = (\mu/\rho_m)_a A_a/N_A = \mu/N_a, \qquad (6.3.1.6)$$

where A_a is the atomic weight and N_a is Avogadro's number. The evaluation of the attenuation coefficients is described in Section 4.2.4.

6.3.2. Dispersion

In the wavelength regime associated with anomalous scattering, where

$$f = f^0 + f' + f'', \qquad (6.3.2.1)$$

the refractive index becomes complex, its imaginary component contributing an additional term to the absorption.

f^0 is the scattering factor for ideal elastic scattering. The dispersion corrections f' and f'' are related to the absorption since (James, 1962; Wagenfeld, 1975)

$$f''(\omega) = mc\omega\sigma(\omega)/4\pi e^2, \quad \omega = 2\pi c/\lambda \qquad (6.3.2.2)$$

$$f'(\omega) = \frac{2}{\pi} \int_0^\infty [\omega' f''(\omega')/(\omega^2 - \omega'^2)] \, d\omega'. \qquad (6.3.2.3)$$

That is, the dispersion corrections are determined by the absorption cross sections. The relationships (6.3.2.2) and (6.3.2.3) can be used in measuring absorption coefficients, as described in Section 4.2.4. The dispersion terms change rapidly near the absorption edge, especially on the short-wavelength side. The changes are anisotropic, sensitive to structure and to the direction of polarization. Details are given by Templeton & Templeton (1980, 1982, 1985).

In near-perfect crystals, the changes near the absorption edge are also sensitive to temperature (Karamura & Fukamachi, 1979; Fukamachi, Karamura, Hayakawa, Nakano & Koh, 1982). The effective absorption coefficient can also be altered by the Borrmann effect (Azaroff, Kaplow, Kato, Weiss, Wilson & Young, 1974).

6.3.3. Absorption corrections

The reduction in the intensity of an X-ray reflection from a uniform beam due to absorption is given by the transmission coefficient

$$A = \frac{1}{V} \int \exp(-\mu T) \, dV, \qquad (6.3.3.1)$$

where the integration is over the volume of the crystal. The absorption correction

$$A^* = 1/A. \qquad (6.3.3.2)$$

T, the path length of the X-ray beam in the crystal, is the sum of the path lengths for the incident and diffracted beams. A technique for measuring crystals for absorption measurements is described in Subsection 6.3.3.6.

Any least-squares analysis involving variation of the linear absorption coefficient, or equivalently an isotropic variation in crystal size, requires the weighted mean path length

$$\bar{T} = -A^{-1} \frac{\partial A}{\partial \mu} = \frac{1}{A^*} \frac{\partial A^*}{\delta \mu}. \qquad (6.3.3.3)$$

This path length is also required in some analyses of extinction (Zachariasen, 1968; Becker & Coppens, 1974).

6.3.3.1. *Special cases*

For special cases, the integral can be solved analytically, and in some of these the expression reduces to closed form. These are listed in Table 6.3.3.1.

6.3.3.2. *Cylinders and spheres*

For diffraction in the equatorial plane of a cylinder of radius R within the X-ray beam, the expression for the transmission coefficient reduces to

$$A = \frac{1}{A^*} = \frac{1}{\pi R^2} \int_0^R \int_0^{2\pi} \exp\Big(-\mu\{[R^2 - r^2\sin^2(\theta + \varphi)]^{1/2}$$

$$+ [R^2 - r^2\sin^2(\theta - \varphi)]^{1/2}\}\Big)$$

$$\times \cosh(2\mu r\sin\theta\sin\varphi) r \, dr \, d\varphi. \qquad (6.3.3.4)$$

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