6.3. X-ray absorption

By E. N. Maslen

6.3.1. Linear absorption coefficient

When a monochromatic X-ray beam of intensity I_o travels a distance T through a homogeneous isotropic material, the intensity is reduced to a value

$$I = I_o \exp(-\mu T), \tag{6.3.1.1}$$

where μ is the total linear absorption coefficient. This expression can also be applied to X-ray absorption in crystalline solids provided the absorption is insensitive to the arrangement of the atoms in the unit cell. This holds to a good approximation in most cases. If it is assumed that the absorption processes are additive,

$$\mu = \frac{1}{V_c} \sum_{n=1}^{N_n} \sigma_n, \tag{6.3.1.2}$$

where V_c is the cell volume and there are N_n contributions to absorption per cell. σ_n is the absorption cross section for the nth contribution.

Of the processes that reduce the intensity of X-rays passing through matter, described in detail by Anderson (1984), photoelectric absorption, scattering, and extinction are important for the X-ray wavelengths used in crystallography.

6.3.1.1. *True or photoelectric absorption*

In photoelectric absorption, X-ray photons disappear completely. The absorption of each photon results in the ejection from the atom of an electron that carries excess energy away as kinetic energy. The corresponding linear photoelectric absorption cross section σ_{ph} is occasionally termed the cross section for 'fluorescence'.

Excitation of an electron from a low to a higher bound state also occurs. Such an electron can be excited only if the photon energy exceeds the gap to the nearest unoccupied level. For this reason, σ_{ph} varies abruptly in the manner shown in Fig. 6.3.1.1.

The probability of ejection of an electron is largest for a photon energy just sufficient for excitation. It is small if the energy greatly exceeds that required. With increasing atomic number Z, the absorption edges shift to shorter wavelengths. The ratio of the value of σ_{ph} for λ just below and just above the edge decreases with increasing Z, especially for the K edge.

The natural width of the resulting core-vacancy state sets a lower limit to the sharpness of the absorption edge (James, 1962). In some cases, such as the K edges for certain metals, the edge is substantially less sharp than that limit (Beeman &
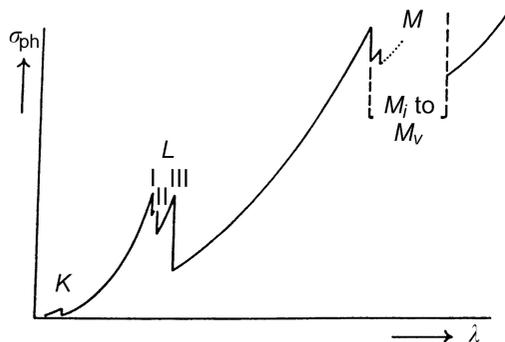

Fig. 6.3.1.1. Idealized diagram showing the variation of the photo-electric absorption coefficient σ_{ph} with wavelength λ.

Friedman, 1939). Natural level widths are tabulated by Krause & Oliver (1979).

The wavelength of the absorption edge for a given element shifts slightly with changes in the chemical environment of the absorbing atom. There is also fine structure in the absorption coefficient that depends, especially on the short-wavelength side, both on chemical composition and on temperature. The range of the larger effects in the fine structure is of the order of 10^{-3} Å for X-ray wavelengths of approximately 1 Å. This corresponds to a photon-energy range of tens of electron volts, whereas X-ray photon energies are of the order of 10 keV. Smaller effects in the fine structure cover a far greater range. These are observed in extended X-ray absorption fine structure (EXAFS) spectra up to 1 keV from the edge (see Section 4.2.3). However, these small terms are of limited relevance when measuring X-ray diffraction intensities.

6.3.1.2. *Scattering*

The X-ray photon is deflected from the original beam by collisions with atoms or electrons, the linear scattering cross section being σ_{sc}. The total cross section

$$\sigma = \sigma_{ph} + \sigma_{sc} + \sigma', \tag{6.3.1.3}$$

where σ' is the combined cross section for all processes other than photoelectric absorption or scattering.

There are two types of scattering process, coherent (Rayleigh) scattering and incoherent (Compton) scattering as described in Section 6.1.1. Rayleigh scattering may be regarded as resulting from a collision between a photon and an atom as a whole. Because the effective mass of a photon is far less than that of an atom, the photon retains its original energy. In a frame with the atom at rest, the scattering is elastic – *i.e.* the photon wavelength is essentially unmodified.

Rayleigh scattering by isolated atoms increases monotonically with Z – the cross section is proportional to the square of the integral of the atomic scattering factor f. However, the photoelectric absorption cross section increases far more rapidly, so Rayleigh scattering is relatively more important for atoms with low atomic number.

The atomic Rayleigh cross sections decrease with λ. Although there are anomalies near absorption edges, these have a limited effect on σ because the Rayleigh scattering in these regions is small compared with the photoelectric cross section except for the lightest elements.

The cross section for Compton scattering depends on the state of the electrons involved in the collision, but for very short wavelengths the atomic Compton cross section is approximately proportional to the atomic number. It varies far more slowly with λ than either the photoelectric or the Rayleigh cross section.

6.3.1.3. *Extinction*

Because Rayleigh scattering is elastic, the scattering from different atoms may combine coherently, giving rise to interference, and hence to Bragg reflection from crystals.

For a crystal oriented so that there is no Bragg reflection, the interference reduces the scattered intensity far below the sum of the intensities that would be scattered by the atoms individually. For a strong Bragg reflection, on the other hand, the atomic scattering amplitudes add approximately in phase. The reduc-

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

$$A = \frac{1}{A^*} = \frac{1}{\pi R^2} \int_0^R \int_0^{2\pi} \exp\Big(-\mu\{[R^2 - r^2\sin^2(\theta + \varphi)]^{1/2}$$
$$+ [R^2 - r^2\sin^2(\theta - \varphi)]^{1/2}\}\Big)$$
$$\times \cosh(2\mu r\sin\theta\sin\varphi)r \, dr \, d\varphi. \qquad (6.3.3.4)$$