7.4. Correction of systematic errors

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7.4.1. Absorption

The positions and intensities of X-ray diffraction maxima are affected by absorption, the magnitude of the effect depending on the size and shape of the specimen. Positional effects are treated as they are encountered in the chapters on experimental techniques.

In structure determination, the effect of absorption on intensity may sometimes be negligible, if the crystal is small enough and the radiation penetrating enough. In general, however, this is not the case, and corrections must be applied. They are simplest if the crystal is of a regular geometric shape, produced either through natural growth or through grinding or cutting. Expressions for reflection from and transmission through a flat plate are given in Table 6.3.3.1, for reflection from cylinders in Table 6.3.3.2, and for reflection from spheres in Table 6.3.3.3. The calculation for a crystal bounded by arbitrary plane faces is treated in Subsection 6.3.3.3.

The values of mass absorption (attenuation) coefficients required for the calculation of corrections are given as a function of the element and of the radiation in Table 4.2.4.3.

7.4.2. Thermal diffuse scattering
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7.4.2.1. *Glossary of symbols*

$\widehat{e}_j$	Direction cosines of $\mathbf{e}_j(\mathbf{q})$
$\mathbf{e}_j(\mathbf{q})$	Polarization vector of normal mode ($j\mathbf{q}$)
$E_j(\mathbf{q})$	Energy of mode ($j\mathbf{q}$)
E_{meas}	Total integrated intensity measured under Bragg peak
E_0	Integrated intensity from Bragg scattering
E_1	Integrated intensity from one-phonon scattering
$F(\mathbf{h})$	Structure factor
$\hbar$	Planck's constant h divided by 2π
$2\pi\mathbf{h}$	Reciprocal-lattice vector
$\mathbf{H}$	Scattering vector
j	Label for branch of dispersion relation
$\mathbf{k}_0$	Wavevector of incident radiation
$\mathbf{k}$	Wavevector of scattered radiation
k_B	Boltzmann's constant
m_n	Neutron mass
m	Mass of unit cell
N	Number of unit cells in crystal
$\mathbf{q}$	Wavevector of normal mode of vibration
q_m	Radius of scanning sphere in reciprocal space
V	Volume of unit cell
$\mathbf{v}_j$	Elastic wave velocity for branch j
$\mathbf{v}_L$	Mean velocity of elastic waves
α	TDS correction factor
2θ	Scattering angle
θ_B	Bragg angle
$\left(\dfrac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)^{(0)}$	Differential cross section for Bragg scattering
$\left(\dfrac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)^{(1)}$	Differential cross section for one-phonon scattering
ρ	Density of crystal
$\omega_j(\mathbf{q})$	Frequency of normal mode ($j\mathbf{q}$)

Thermal diffuse scattering (TDS) is a process in which the radiation is scattered inelastically, so that the incident X-ray photon (or neutron) exchanges one or more quanta of vibrational energy with the crystal. The vibrational quantum is known as a phonon, and the TDS can be distinguished as one-phonon (first-order), two-phonon (second-order), ... scattering according to the number of phonons exchanged.

The normal modes of vibration of a crystal are characterized as either acoustic modes, for which the frequency $\omega(\mathbf{q})$ goes to zero as the wavevector $\mathbf{q}$ approaches zero, or optic modes, for which the frequency remains finite for all values of $\mathbf{q}$ [see Section 4.1.1 of *IT* B (1992)]. The one-phonon scattering by the acoustic modes rises to a maximum at the reciprocal-lattice points and so is not entirely subtracted with the background measured on either side of the reflection. This gives rise to the 'TDS error' in estimating Bragg intensities. The remaining contributions to the TDS – the two-phonon and multphonon acoustic mode scattering and all kinds of scattering by the optic modes – are largely removed with the background.

It is not easy in an X-ray experiment to separate the elastic (Bragg) and the inelastic thermal scattering by energy analysis, as the energy difference is only a few parts per million. However, this has been achieved by Dorner, Burkel, Illini & Peisl (1987) using extremely high energy resolution. The separation is also possible using Mössbauer spectroscopy. Fig. 7.4.2.1 shows the elastic and inelastic components from the 060 reflection of LiNbO$_3$ (Krec, Steiner, Pongratz & Skalicky, 1984), measured with γ-radiation from a ^{57}Co Mössbauer source. The TDS makes a substantial contribution to the measured integrated intensity; in Fig. 7.4.2.1, it is 10% of the total intensity, but it can be much larger for higher-order reflections. On the other hand, for the extremely sharp Bragg peaks obtained with synchrotron radiation, the TDS error may be reduced to negligible proportions (Bachmann, Kohler, Schulz & Weber, 1985).
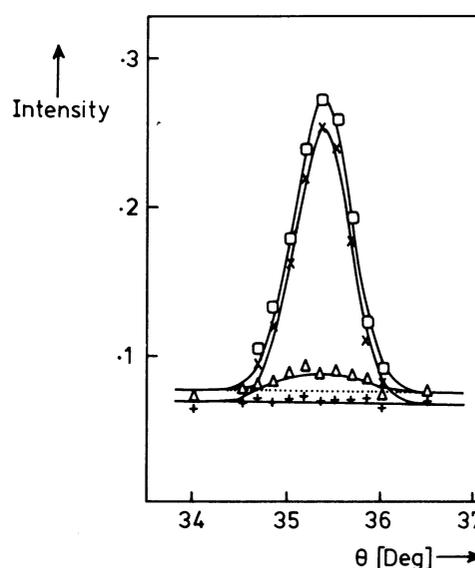

Fig. 7.4.2.1. 060 reflection of LiNbO$_3$ (Mössbauer diffraction). Inelastic (triangles), elastic (crosses), total (squares) and background (pluses) intensity (after Krec, Steiner, Pongratz & Skalicky, 1984).

Let E_{meas} represent the *total* integrated intensity measured in a diffraction experiment, with E_0 the contribution from Bragg scattering and E_1 that from (one-phonon) TDS. Then,

$$E_{\text{meas}} = E_0 + E_1 = E_0(1 + \alpha), \qquad (7.4.2.1)$$

where α is the ratio E_1/E_0 and is known as the 'TDS correction factor'. α can be evaluated in terms of the properties of the crystal (elastic constants, temperature) and the experimental conditions of measurement. In the following, it is implied that the intensities are measured using a single-crystal diffractometer with incident radiation of a fixed wavelength We shall treat separately the calculation of α for X-rays and for thermal neutrons.

7.4.2.2. TDS correction factor for X-rays (single crystals)

The differential cross section, representing the intensity per unit solid angle for Bragg scattering, is

$$\left(\frac{d\sigma}{d\Omega}\right)^{(0)} = \frac{N(2\pi)^3}{V}|F(\mathbf{h})|^2 \delta(\mathbf{H} - 2\pi\mathbf{h}),$$

where N is the number of unit cells, each of volume V, and $F(\mathbf{h})$ is the structure factor. $\mathbf{H}$ is the scattering vector, defined by

$$\mathbf{H} = \mathbf{k} - \mathbf{k}_0,$$

with $\mathbf{k}$ and $\mathbf{k}_0$ the wavevectors of the scattered and incident beams, respectively. (The scattering is elastic, so $k = k_0 = 2\pi/\lambda$, where λ is the wavelength.) $2\pi\mathbf{h}$ is the reciprocal-lattice vector and the delta function shows that the scattered intensity is restricted to the reciprocal-lattice points.

The integrated Bragg intensity is given by

$$E_0 = \int \int \left(\frac{d\sigma}{d\Omega}\right)^{(0)} d\Omega \, dt$$
$$= N\frac{(2\pi)^3}{V}|F(\mathbf{h})|^2 \int \int \delta(\mathbf{H} - 2\pi\mathbf{h}) \, d\Omega \, dt, \qquad (7.4.2.2)$$

where the integration is over the solid angle Ω subtended by the detector at the crystal and over the time t spent in scanning the reflection. Using

$$\int \delta(\mathbf{H}) \, d\mathbf{H} = 1,$$

with $d\mathbf{H} = H \, d\theta$, equation (7.4.2.2) reduces to the familiar result (James, 1962)

$$E_0 = \frac{N\lambda^3|F(\mathbf{h})|^2}{V\omega_0 \sin 2\theta}, \qquad (7.4.2.3)$$

where ω_0 is the angular velocity of the crystal and 2θ the scattering angle.

The differential cross section for one-phonon scattering by acoustic modes of small wavevector $\mathbf{q}$ is

$$\left(\frac{d\sigma}{d\Omega}\right)^{(1)} = \frac{(2\pi)^3}{V}|F(\mathbf{h})|^2$$
$$\times \sum_{j=1}^{3} \frac{\mathbf{H} \cdot \mathbf{e}_j(\mathbf{q})}{m\omega_j^2(\mathbf{q})}E_j(\mathbf{q})\delta(\mathbf{H} \pm \mathbf{q} - 2\pi\mathbf{h}) \qquad (7.4.2.4)$$

[see Section 4.1.1 of *IT* B (1992)]. Here, $\mathbf{e}_j(\mathbf{q})$ is the polarization vector of the mode $(j\mathbf{q})$, where j is an index for labelling the acoustic branches of the dispersion relations, m is the mass of the unit cell and $E_j(\mathbf{q})$ is the mode energy. The delta function in (7.4.2.4) shows that the scattering from the mode $(j\mathbf{q})$ is confined to the points in reciprocal space displaced by $\pm\mathbf{q}$ from the reciprocal-lattice point at $\mathbf{q} = 0$. The acoustic modes

involved are of small wavenumber, for which the dispersion relation can be written

$$\omega_j(\mathbf{q}) = \mathbf{v}_j|\mathbf{q}|, \qquad (7.4.2.5)$$

where $\mathbf{v}_j$ is the velocity of the elastic wave with polarization vector $\mathbf{e}_j(\mathbf{q})$. Substituting (7.4.2.5) into (7.4.2.4) shows that the intensity from the acoustic modes varies as $1/q^2$, and so peaks strongly at the reciprocal-lattice points to give rise to the TDS error.

Integrating the delta function in (7.4.2.4) gives the integrated one-phonon intensity

$$E_1 = \frac{\lambda^3}{V^2\omega_0 \sin 2\theta_B}H^2|F(\mathbf{h})|^2$$
$$\times \sum_q \sum_j \frac{[\mathbf{H} \cdot \mathbf{e}_j(\mathbf{q})]^2}{\rho\omega_q^2(\mathbf{q})}E_j(\mathbf{q}),$$

with ρ the crystal density. The sum over the wavevectors $\mathbf{q}$ is determined by the range of $\mathbf{q}$ encompassed in the intensity scan. The density of wavevectors is uniform in reciprocal space [see Section 4.1.1 of *IT* B (1992)], and so the sum can be replaced by an integral

$$\sum_q \rightarrow \frac{NV}{(2\pi)^3}\int d\mathbf{q}.$$

Thus, the correction factor (E_1/E_0) is given by

$$\alpha = \frac{1}{8\pi^3}\int J(\mathbf{q}) \, d\mathbf{q}, \qquad (7.4.2.6)$$

where

$$J(\mathbf{q}) = \sum_j \frac{\mathbf{H} \cdot \mathbf{e}_j(\mathbf{q})^2}{\rho\omega^2(\mathbf{q})}E_j(\mathbf{q}). \qquad (7.4.2.7)$$

The integral in (7.4.2.6) is over the range of measurement, and the summation in (7.4.2.7) is over the three acoustic branches. Only long-wavelength elastic waves, with a linear dispersion relation, equation (7.4.2.5), need be considered.

7.4.2.2.1. Evaluation of J(q)

The frequencies $\omega_j(\mathbf{q})$ and polarization vectors $\mathbf{e}_j(\mathbf{q})$ of the elastic waves in equation (7.4.2.7) can be calculated from the classical theory of Voigt (1910) [see Wooster (1962)]. If $\widehat{e}_1$, $\widehat{e}_2$, $\widehat{e}_3$ are the direction cosines of the polarization vector with respect to orthogonal axes x, y, z, then the velocity $\mathbf{v}_j$ is determined from the elastic stiffness constants c_{ijkl} by solving the following equations of motion.

$$\widehat{e}_1(A_{11} - \rho v_j^2) + \widehat{e}_2 A_{12} + \widehat{e}_3 A_{13} = 0,$$
$$\widehat{e}_1 A_{12} + \widehat{e}_2(A_{22} - \rho v_j^2) + \widehat{e}_3 A_{23} = 0,$$
$$\widehat{e}_1 A_{13} + \widehat{e}_2 A_{23} + \widehat{e}_3(A_{33} - \rho v_j^2) = 0.$$

Here, A_{km} is the km element of a 3×3 symmetric matrix $\mathbf{A}$; if $\widehat{q}_1$, $\widehat{q}_2$, $\widehat{q}_3$ are the direction cosines of the wavevector $\mathbf{q}$ with reference to x, y, z, the km element is given in terms of the elastic stiffness constants by

$$A_{km} = \sum_{l=1}^{3}\sum_{n=1}^{3} c_{klmn}\widehat{q}_l\widehat{q}_n.$$

The four indices $klmn$ can be reduced to two, replacing 11 by 1, 22 by 2, 33 by 3, 23 and 32 by 4, 31 and 13 by 5, and 12 and 21 by 6. The elements of $\mathbf{A}$ are then given explicitly by