International Tables for Crystallography (2006). Vol. C, Figure 7.4.2.1, p. 653.

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 (By B. T. M. Willis)

7.4.2.1. *Glossary of symbols*

$\hat{e}_j$	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 $(j\mathbf{q})$
$E_{\rm meas}$	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
$\left(\frac{{\rm d}\sigma}{{\rm d}\Omega}\right)^{(0)}$	Differential cross section for Bragg scattering
$\left(\frac{{\rm d}\sigma}{{\rm d}\Omega}\right)^{(1)}$	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).

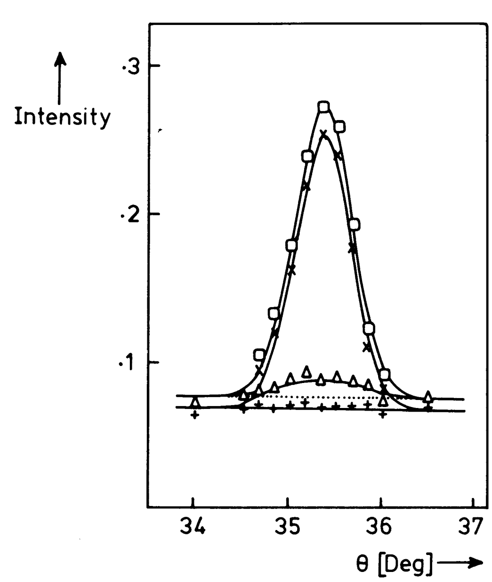

Fig. 7.4.2.1. 060 reflection of $LiNbO_3$ (Mössbauer diffraction). Inelastic (triangles), elastic (crosses), total (squares) and background (pluses) intensity (after Krec, Steiner, Pongratz & Skalicky, 1984).

references