7.4. CORRECTION OF SYSTEMATIC ERRORS

$$A_{11} = c_{11}\widehat{q}_1^2 + c_{66}\widehat{q}_2^2 + c_{55}\widehat{q}_3^2 + 2c_{56}\widehat{q}_2\widehat{q}_3$$
$$+ 2c_{15}\widehat{q}_3\widehat{q}_1 + 2c_{16}\widehat{q}_1\widehat{q}_2,$$

$$A_{22} = c_{66}\widehat{q}_1^2 + c_{22}\widehat{q}_2^2 + c_{44}\widehat{q}_3^2 + 2c_{24}\widehat{q}_2\widehat{q}_3$$
$$+ 2c_{46}\widehat{q}_3\widehat{q}_1 + 2c_{26}\widehat{q}_1\widehat{q}_2,$$

$$A_{33} = c_{55}\widehat{q}_1^2 + c_{44}\widehat{q}_2^2 + c_{33}\widehat{q}_3^2 + 2c_{34}\widehat{q}_2\widehat{q}_3$$
$$+ 2c_{35}\widehat{q}_3\widehat{q}_1 + 2c_{45}\widehat{q}_1\widehat{q}_2,$$

$$A_{12} = c_{16}\widehat{q}_1^2 + c_{26}\widehat{q}_2^2 + c_{45}\widehat{q}_3^2 + (c_{25} + c_{46})\widehat{q}_2\widehat{q}_3$$
$$+ (c_{14} + c_{56})\widehat{q}_3\widehat{q}_1 + (c_{12} + c_{66})\widehat{q}_1\widehat{q}_2,$$

$$A_{13} = c_{15}\widehat{q}_1^2 + c_{46}\widehat{q}_2^2 + c_{35}\widehat{q}_3^2 + (c_{36} + c_{45})\widehat{q}_2\widehat{q}_3$$
$$+ (c_{13} + c_{55})\widehat{q}_3\widehat{q}_1 + (c_{14} + c_{56})\widehat{q}_1\widehat{q}_2,$$

$$A_{23} = c_{56}\widehat{q}_1^2 + c_{24}\widehat{q}_2^2 + c_{34}\widehat{q}_3^2 + (c_{23} + c_{44})\widehat{q}_2\widehat{q}_3$$
$$+ (c_{36} + c_{45})\widehat{q}_3\widehat{q}_1 + (c_{25} + c_{46})\widehat{q}_1\widehat{q}_2.$$

The setting up of the matrix $\mathbf{A}$ is a fundamental first step in calculating the TDS correction factor. This implies a knowledge of the elastic constants, whose number ranges from three for cubic crystals to twenty one for triclinic crystals. The measurement of elastic stiffness constants is described in Section 4.1.6 of *IT* B (1992).

For each direction of propagation $\widehat{\mathbf{q}}$, there are three values of ρv_j^2 ($j = 1, 2, 3$), given by the eigenvalues of $\mathbf{A}$. The corresponding eigenvectors of $\mathbf{A}$ are the polarization vectors $\mathbf{e}_j(\mathbf{q})$. These polarization vectors are mutually perpendicular, but are not necessarily parallel or perpendicular to the propagation direction.

The function $J(\mathbf{q})$ in equation (7.4.2.7) is related to the inverse matrix $\mathbf{A}^{-1}$ by

$$J(\mathbf{q}) = \frac{k_B T}{q^2} \sum_{m=1}^{3} \sum_{n=1}^{3} (\mathbf{A}^{-1})_{mn} H_m H_n, \qquad (7.4.2.8)$$

where H_1, H_2, H_3 are the x, y, z components of the scattering vector $\mathbf{H}$, and classical equipartition of energy is assumed [$E_j(\mathbf{q}) = k_B T$]. Thus $\mathbf{A}^{-1}$ determines the anisotropy of the TDS in reciprocal space, arising from the anisotropic elastic properties of the crystal.

Isodiffusion surfaces, giving the locus in reciprocal space for which the intensity $J(\mathbf{q})$ is constant for elastic waves of a given wavelength, were first plotted by Jahn (1942). These surfaces are not spherical even for cubic crystals (unless $c_{11} - c_{12} = c_{44}$), and their shapes vary from one reciprocal-lattice point to another.

7.4.2.2.2. *Calculation of* α

Inserting (7.4.2.8) into (7.4.2.6) gives the TDS correction factor as

$$\alpha = \sum_{m=1}^{3} \sum_{n=1}^{3} T_{mn} H_m H_n, \qquad (7.4.2.9)$$

where T_{mn}, an element of a 3×3 symmetric matrix $\mathbf{T}$, is defined by

$$T_{mn} = \frac{k_B T}{8\pi^3} \int \frac{(\mathbf{A}^{-1})_{mn}}{q^2} \, d\mathbf{q}. \qquad (7.4.2.10)$$

Equation (7.4.2.9) can also be written in the matrix form

$$\alpha = \mathbf{H}^T \mathbf{T} \mathbf{H}, \qquad (7.4.2.11)$$

with $\mathbf{H}^T = (H_1, H_2, H_3)$ representing the transpose of $\mathbf{H}$.

The components of $\mathbf{H}$ relate to orthonormal axes, whereas it is more convenient to express them in terms of Miller indices hkl and the axes of the reciprocal lattice. If $\mathbf{S}$ is the 3×3 matrix that transforms the scattering vector $\mathbf{H}$ from orthonormal axes to reciprocal-lattice axes, then

$$\mathbf{H} = \mathbf{Sh}, \qquad (7.4.2.12)$$

where $\mathbf{h}^T = (h, k, l)$. The final expression for α, from (7.4.2.11) and (7.4.2.12), is

$$\alpha = \mathbf{h}^T \mathbf{S}^T \mathbf{T} \mathbf{S} \mathbf{h}. \qquad (7.4.2.13)$$

This is the basic formula for the TDS correction factor.

We have assumed that the entire one-phonon TDS under the Bragg peak contributes to the measured integrated intensity, whereas some of it is removed in the background subtraction. This portion can be calculated by taking the range of integration in (7.4.2.10) as that corresponding to the region of reciprocal space covered in the background measurement.

To evaluate $\mathbf{T}$ requires the integration of the function $\mathbf{A}^{-1}$ over the scanned region in reciprocal space (see Fig. 7.4.2.2). Both the function itself and the scanned region are anisotropic about the reciprocal-lattice point, and so the TDS correction is anisotropic too, *i.e.* it depends on the direction of the diffraction vector as well as on $\sin\theta/\lambda$.

Computer programs for calculating the anisotropic TDS correction for crystals of any symmetry have been written by Rouse & Cooper (1969), Stevens (1974), Merisalo & Kurittu (1978), Helmholdt, Braam & Vos (1983), and Sakata, Stevenson & Harada (1983). To simplify the calculation, further approximations can be made, either by removing the anisotropy associated with $\mathbf{A}^{-1}$ or that associated with the scanned region. In the first case, the element T_{mn} is expressed as

$$T_{mn} = \frac{k_B T}{8\pi^3} \langle (\mathbf{A}^{-1})_{mn} \rangle \int \frac{1}{q^2} \, dq,$$

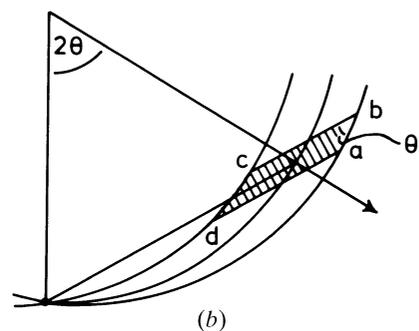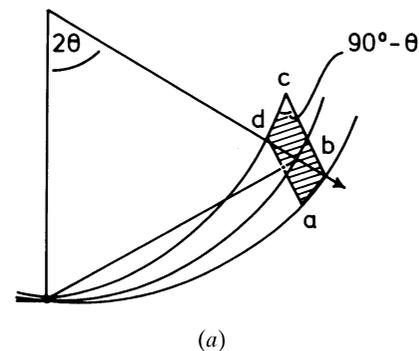where the angle brackets indicate the average value over all directions. In the second case,

(a)

(b)

Fig. 7.4.2.2. Diagrams in reciprocal space illustrating the volume *abcd* swept out for (*a*) an ω scan, and (*b*) a $\theta/2\theta$, or $\omega/2\theta$, scan. The dimension of *ab* is determined by the aperture of the detector and of *bc* by the rocking angle of the crystal.

$$T_{mn} = \frac{k_B T}{8\pi^3} q_m \int \int (\mathbf{A}^{-1})_{mn} \, \mathrm{d}S,$$

where q_m is the radius of the sphere that replaces the anisotropic region (Fig. 7.4.2.2) actually scanned in the experiment, and $\mathrm{d}S$ is a surface element of this sphere. q_m can be estimated by equating the volume of the sphere to the volume swept out in the scan.

If *both* approximations are employed, the correction factor is isotropic and reduces to

$$\alpha = \frac{H^2 k_B T q_m}{3\pi^2 \rho \mathbf{v}_L^2}, \qquad (7.4.2.14)$$

with $\mathbf{v}_L$ representing the mean velocity of the elastic waves, averaged over all directions of propagation and of polarization.

Experimental values of α have been measured for several crystals by γ-ray diffraction of Mössbauer radiation (Krec & Steiner, 1984). In general, there is good agreement between these values and those calculated by the numerical methods, which take into account anisotropy of the TDS. The correction factors calculated analytically from (7.4.2.14) are less satisfactory.

The principal effect of *not* correcting for TDS is to underestimate the values of the atomic displacement parameters. Writing $\exp\alpha \approx 1 + \alpha$, we see from (7.4.2.14) that the overall

displacement factor is increased from B to $B + \Delta B$ when the correction is made. ΔB is given by

$$\Delta B = \frac{8 k_B T q_m}{3\pi^2 \rho \mathbf{v}_L^2}.$$

Typically, $\Delta B / B$ is 10–20%. Smaller errors occur in other parameters, but, for accurate studies of charge densities or bonding effects, a TDS correction of all integrated intensities is advisable (Helmholdt & Vos, 1977; Stevenson & Harada, 1983).

7.4.2.3. *TDS correction factor for thermal neutrons (single crystals)*

The neutron treatment of the correction factor lies along similar lines to that for X-rays. The principal difference arises from the different topologies of the one-phonon 'scattering surfaces' for X-rays and neutrons. These surfaces represent the locus in reciprocal space of the end-points of the phonon wavevectors $\mathbf{q}$ (for fixed crystal orientation and fixed incident wavevector $\mathbf{k}_0$) when the wavevector $\mathbf{k}$ of the scattered radiation is allowed to vary. We shall not discuss the theory for pulsed neutrons, where the incident wavelength varies (see Popa & Willis, 1994).

The scattering surfaces are determined by the conservation laws for momentum transfer,

$$\mathbf{H} = \mathbf{k} - \mathbf{k}_0 = 2\pi\mathbf{h} + \mathbf{q},$$

and for energy transfer,

$$\hbar^2 (k^2 - k_0^2)/2m_n = -\varepsilon \hbar \omega_j(\mathbf{q}), \qquad (7.4.2.15)$$

where m_n is the neutron mass and $\hbar \omega_j(\mathbf{q})$ is the phonon energy. ε is either $+1$ or -1, where $\varepsilon = +1$ corresponds to phonon emission (or phonon creation) in the crystal and a loss in energy of the neutrons after scattering, and $\varepsilon = -1$ corresponds to phonon absorption (or phonon annihilation) in the crystal and a gain in neutron energy. In the X-ray case, the phonon energy is negligible compared with the energy of the X-ray photon, so that (7.4.2.15) reduces to

$$k = k_0,$$

and the scattering surface is the Ewald sphere. For neutron scattering, $\hbar \omega_j(\mathbf{q})$ is comparable with the energy of a thermal neutron, and so the topology of the scattering surface is more complicated. For one-phonon scattering by long-wavelength acoustic modes with $q \ll k_0$, (7.4.2.15) reduces to

$$k = k_0 - \varepsilon \beta q,$$

where β ($= \mathbf{v}_L/\mathbf{v}_n$) is the ratio of the sound velocity in the crystal and the neutron velocity. If the Ewald sphere in the neighbourhood of a reciprocal-lattice point is replaced by its tangent plane, the scattering surface becomes a conic section with eccentricity $1/\beta$. For $\beta < 1$, the conic section is a hyperboloid of two sheets with the reciprocal-lattice point P at one focus. The phonon
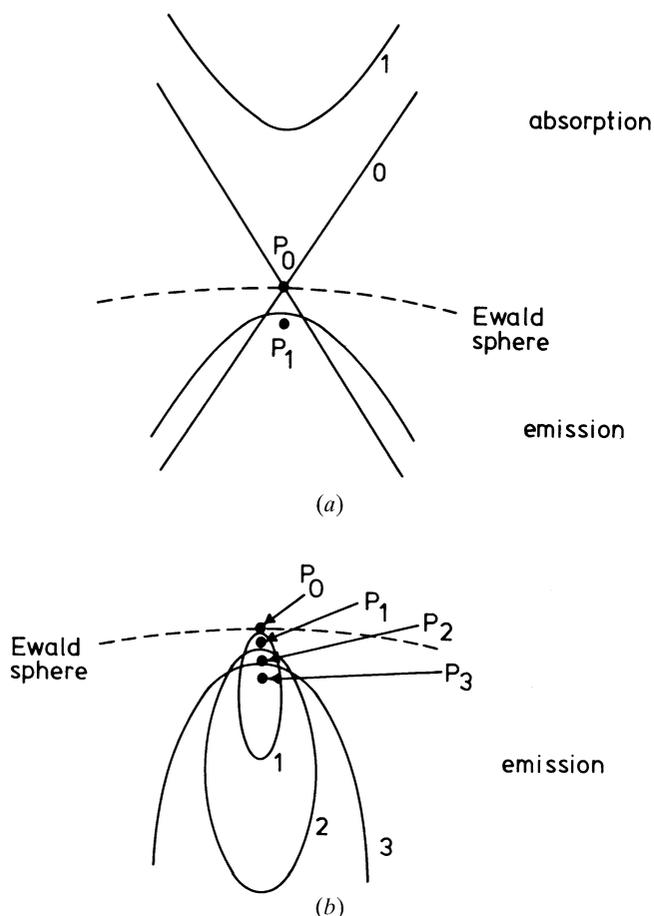

Fig. 7.4.2.3. Scattering surfaces for one-phonon scattering of neutrons: (*a*) for neutrons faster than sound ($\beta < 1$); (*b*) for neutrons slower than sound ($\beta > 1$). The scattering surface for X-rays is the Ewald sphere. P_0, P_1, *etc.* are different positions of the reciprocal-lattice point with respect to the Ewald sphere, and the scattering surfaces are numbered to correspond with the appropriate position of P.
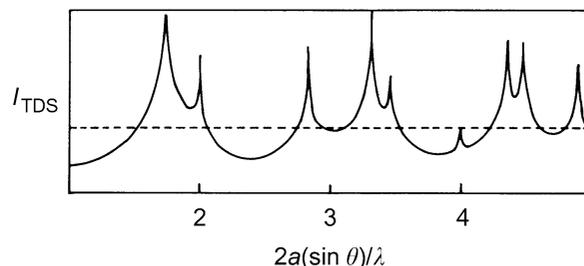

Fig. 7.4.2.4. One-phonon scattering calculated for polycrystalline nickel of lattice constant a (after Suortti, 1980).