$$
\begin{aligned}
A_{11} &= c_{11}\widehat{q}_1^2 + c_{66}\widehat{q}_2^2 + c_{55}\widehat{q}_3^2 + 2c_{56}\widehat{q}_2\widehat{q}_3 \\
&\quad + 2c_{15}\widehat{q}_3\widehat{q}_1 + 2c_{16}\widehat{q}_1\widehat{q}_2, \\
A_{22} &= c_{66}\widehat{q}_1^2 + c_{22}\widehat{q}_2^2 + c_{44}\widehat{q}_3^2 + 2c_{24}\widehat{q}_2\widehat{q}_3 \\
&\quad + 2c_{46}\widehat{q}_3\widehat{q}_1 + 2c_{26}\widehat{q}_1\widehat{q}_2, \\
A_{33} &= c_{55}\widehat{q}_1^2 + c_{44}\widehat{q}_2^2 + c_{33}\widehat{q}_3^2 + 2c_{34}\widehat{q}_2\widehat{q}_3 \\
&\quad + 2c_{35}\widehat{q}_3\widehat{q}_1 + 2c_{45}\widehat{q}_1\widehat{q}_2, \\
A_{12} &= c_{16}\widehat{q}_1^2 + c_{26}\widehat{q}_2^2 + c_{45}\widehat{q}_3^2 + (c_{25} + c_{46})\widehat{q}_2\widehat{q}_3 \\
&\quad + (c_{14} + c_{56})\widehat{q}_3\widehat{q}_1 + (c_{12} + c_{66})\widehat{q}_1\widehat{q}_2, \\
A_{13} &= c_{15}\widehat{q}_1^2 + c_{46}\widehat{q}_2^2 + c_{35}\widehat{q}_3^2 + (c_{36} + c_{45})\widehat{q}_2\widehat{q}_3 \\
&\quad + (c_{13} + c_{55})\widehat{q}_3\widehat{q}_1 + (c_{14} + c_{56})\widehat{q}_1\widehat{q}_2, \\
A_{23} &= c_{56}\widehat{q}_1^2 + c_{24}\widehat{q}_2^2 + c_{34}\widehat{q}_3^2 + (c_{23} + c_{44})\widehat{q}_2\widehat{q}_3 \\
&\quad + (c_{36} + c_{45})\widehat{q}_3\widehat{q}_1 + (c_{25} + c_{46})\widehat{q}_1\widehat{q}_2.
\end{aligned}
$$

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

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

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

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

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

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

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

$$\alpha = \mathbf{H}^T \mathbf{T} \mathbf{H}, \tag{7.4.2.11}$$

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

$$\mathbf{H} = \mathbf{S}\mathbf{h}, \tag{7.4.2.12}$$

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

$$\alpha = \mathbf{h}^T \mathbf{S}^T \mathbf{T} \mathbf{S} \mathbf{h}. \tag{7.4.2.13}$$

This is the basic formula for the TDS correction factor.

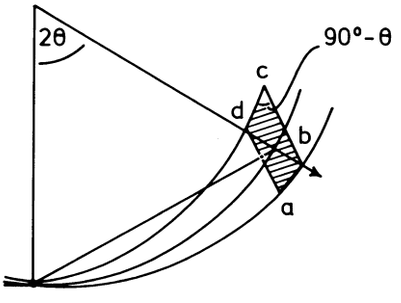
We have assumed that the entire one-phonon TDS under the Bragg peak contributes to the measured integrated intensity, whereas some of it is removed in the background subtraction. This portion can be calculated by taking the range of integration in (7.4.2.10) as that corresponding to the region of reciprocal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

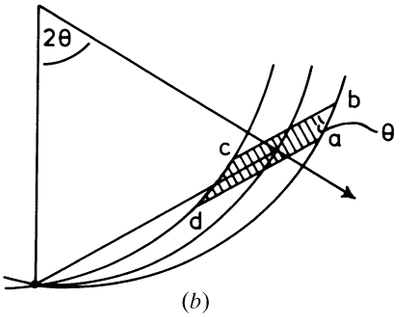
Computer programs for calculating the anisotropic TDS correction for crystals of any symmetry have been written by Rouse & Cooper (1969), Stevens (1974), Merisalo & Kurittu (1978), Helmholdt, Braam & Vos (1983), and Sakata, Stevenson & Harada (1983). To simplify the calculation, further approximations 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

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

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.

references