intensités intégrées des réflexions de Bragg permet de déterminer le module des coefficients de Fourier de $f(\mathbf{r})$. La détermination de la structure se fait par approximations successives: on cherche une fonction dont les coefficients de Fourier ont même module que ceux de $f(\mathbf{r})$, et cela revient à résoudre l'équation

$$f(\mathbf{r})*f(-\mathbf{r})=P(\mathbf{r})\,,$$

$P(\mathbf{r})$ étant la fonction de Patterson. Si le cristal n'est pas parfaitement ordonné, on ne peut plus définir les coefficients de Fourier de sa densité électronique. La mesure des intensités intégrées des réflexions sélectives permet de construire la fonction de Patterson apparente, $P_a(\mathbf{r})$; c'est une fonction périodique qui contient toutes les données expérimentales; elle s'identifie à la fonction de Patterson quand le cristal est ordonné; elle peut varier en fonction de la largeur du domaine d'intégration au voisinage de chaque noeud: les domaines d'intégration doivent être assez larges pour que $P_a(\mathbf{r})$ soit indépendante d'une petite variation du volume des domaines d'intégration. Si la structure n'est pas très simple, il faut commencer par la déterminer grossièrement en appliquant les méthodes classiques, c'est-à-dire en résolvant l'équation

$$P_a(\mathbf{r})=f(\mathbf{r})*f(-\mathbf{r})\,.$$

La solution trouvée $f(\mathbf{r})$ est périodique et ne représente pas exactement la structure étudiée. Pourtant, elle permet d'obtenir des indications nombreuses sur la structure réelle, et dans les cas, fréquents, où l'ordre est à grande distance, elle représente une structure 'moyenne'. Si l'ordre est à 'moyenne distance', $P_a(\mathbf{r})$ apparaît comme la superposition des fonctions de Patterson des divers types de structure que l'on peut trouver localement dans un domaine ordonné. $f(\mathbf{r})$ peut alors contenir des anomalies (probabilités de présence négatives par exemple) qui interdisent de la considérer comme une 'structure moyenne'. L'interprétation de ces anomalies permet d'obtenir des indications sur l'état d'ordre réel du cristal. La variation de $P_a(\mathbf{r})$ en fonction des dimensions des domaines d'intégration de l'intensité dans l'espace réciproque permet l'étude de la répartition des fautes dans certains cas: nous avons montré, sur un modèle simple à deux dimensions comment on pouvait rendre compte de certaines extinctions ou de l'élargissement d'un groupe donné de réflexions et nous avons retrouvé certains résultats classiques concernant les fautes d'empilement dans les assemblages hexagonaux compacts. Enfin, nous avons montré comment l'étude de la fonction $P_a(\mathbf{r})$ permettait d'interpréter les résultats d'une détermination de la structure d'un composé qui présente une surstructure et dont la symétrie n'est pas connue avec certitude; en particulier, nous avons établi dans quelle mesure la valeur finale du facteur R était un test de validité de la symétrie du modèle utilisé.

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The Correction of Measured Integrated Bragg Intensities for Anisotropic Thermal Diffuse Scattering

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The correction of measured integrated Bragg intensities for first-order thermal diffuse scattering was considered in an earlier paper [Cooper & Rouse, *Acta Cryst.* (1968). A**24**, 405] using an approximate method, valid for pseudo-isotropic materials. A method is now derived for the evaluation of the correction for a crystal of any symmetry, allowing for the contributions from first- and second-order scattering for X-rays or neutrons. Allowance for the effects of experimental resolution is also considered.

Introduction

In an earlier paper (Cooper & Rouse, 1968) we have considered the correction of measured integrated Bragg intensities for first-order thermal diffuse scattering (TDS) in the isotropic approximation. It was assumed that the TDS contribution to the integrated intensity can be averaged over a sphere before integration over the appropriate volume in reciprocal space, in which case the TDS correction becomes directly proportional to a function of the elastic constants which is the same for all reflexions. This approximation is valid only for crystals in which the elastic anisotropy is small, and the appropriate function of the elastic constants was given for a pseudo-isotropic cubic crystal. In the present paper we therefore consider the extension of the analysis to the general case for a crystal of any symmetry.

The evaluation of a correction for TDS can be considered in two parts, the derivation of the relevant scattering cross-section and the integration of this over the volume in reciprocal space appropriate to the scan used (see, *e.g.* Cooper, 1969; Cochran, 1963; Willis, 1969). In deriving the cross-section we shall make the following assumptions:

1. Optical modes and processes involving three or more phonons are assumed to be corrected for adequately by the normal background correction.
2. We assume that only low frequency modes are important and that we can therefore ignore dispersion effects, taking the frequency of a mode to be proportional to its wave vector:

$$\omega_j(\mathbf{q}) = |V_j(\mathbf{q})| q \tag{1}$$

where $\omega_j(\mathbf{q})$, $V_j(\mathbf{q})$ and q are the frequency, velocity and wave vector respectively of the mode $(j, \mathbf{q})$.

3. We consider only the classical, high temperature region for which each mode has an energy k_BT, where k_B is Boltzmann's constant and T is the absolute temperature.

One-phonon scattering

X-rays

In a one-phonon scattering process the wave vector of the phonon is related to the scattering vector $\mathbf{Q}$ by the equation corresponding to the conservation of momentum, *viz.*

$$\mathbf{B} - \mathbf{q} = \mathbf{Q} = \mathbf{k} - \mathbf{k}_0 \tag{2}$$

where $\mathbf{k}_0$ is the wave vector of the incident radiation $(=2\pi/\lambda_0)$, $\mathbf{k}$ is the wave vector of the scattered radiation and $\mathbf{B}$ is a reciprocal lattice vector for Bragg reflexion.

The energy of the phonon is given by:

$$\hbar\omega_j(\mathbf{q}) = \pm \hbar c(k - k_0) \tag{3}$$

where c is the velocity of light and the + and − signs refer to phonon absorption and phonon emission respectively. In the case of X-ray scattering this is negligible compared with the energy of the X-rays and we can therefore consider $k = k_0$.

The cross-section for one-phonon scattering of X-rays associated with low energy acoustic modes is given by Cooper (1969), equation (12), and if we equate $E_j(\mathbf{q})$, the energy of the mode $(j, \mathbf{q})$, to k_BT we can write the cross-section as:

$$\left(\frac{\mathrm{d}\sigma(q)}{\mathrm{d}\Omega}\right)_1 = \frac{NQ^2}{mq^2} k_BT |F(\mathbf{Q})|^2 \sum_{j=1}^{3} \frac{\cos^2 \alpha_j(\mathbf{q})}{V_j^2(\mathbf{q})}, \tag{4}$$

where N is the number of unit cells in the crystal, m is the mass per unit cell, $F(\mathbf{Q})$ is the structure factor for Bragg scattering, and $\alpha_j(\mathbf{q})$ is the angle between the polarization direction of the mode $(j, \mathbf{q})$ and $\mathbf{Q}$.

To obtain the TDS contribution to the integrated intensity we must integrate this cross-section over the volume in reciprocal space which is swept out during the scan. If we further assume that, since only low frequency modes are important, $q \ll Q$ and we can therefore replace $\mathbf{Q}$ by $\mathbf{B}$, the TDS intensity can be written as:

$$I_1 = \frac{Nk_BT}{m} |F(\mathbf{B})|^2 B^2 \int \frac{1}{q^2} \sum_{j=1}^{3} \frac{\cos^2 \alpha'_j(\mathbf{q})}{V_j^2(\mathbf{q})} \,\mathrm{d}u\,\mathrm{d}v\,\mathrm{d}w, \tag{5}$$

where du is an element of angle through which the crystal is rotated during a scan and dv and dw are elements of vertical and horizontal divergence angles respectively in the scattered beam (see Cooper & Rouse, 1968), and $\alpha'_j(\mathbf{q})$ is the angle between the polarization direction of the mode $(j, \mathbf{q})$ and $\mathbf{B}$.

Neutrons

For thermal neutron scattering the energy of the neutrons is comparable with that of the phonons:

$$\hbar\omega_k(\mathbf{q}) = \pm \frac{\hbar^2}{2m_n}(k^2 - k_0^2) \tag{6}$$

where m_n is the mass of the neutron.

The cross-section for one phonon scattering is then:

$$\left(\frac{\mathrm{d}\sigma(\mathbf{q})}{\mathrm{d}\Omega}\right)_1 = \frac{NQ^2}{2mq^2}\frac{k}{k_0} |F(\mathbf{Q})|^2 \times \sum_{j=1}^{3} \frac{E_j(\mathbf{q}) \pm \frac{1}{2}\hbar\omega_j(\mathbf{q})}{|J_j(\mathbf{q})|} \frac{\cos^2 \alpha_j(\mathbf{q})}{V_j^2(\mathbf{q})} \tag{7}$$

[see Cooper (1969), equation (19)] where

$$|J_j(\mathbf{q})| = \left.\frac{\mathrm{d}[E_n \pm \hbar\omega_j(\mathbf{q})]}{\mathrm{d}E_n}\right|_{E_n \pm \hbar\omega_j(\mathbf{q}) = 0} \tag{8}$$

E_n is the change in energy of the neutron and the + and − signs in equations (7) and (8) refer to phonon emission and phonon absorption respectively.

The Jacobian $|J_j(\mathbf{q})|$ can be expressed in terms of the velocity of the neutrons and the velocity of the mode concerned:

$$|J_j(\mathbf{q})| = 1 \pm V_n^{-2}\mathbf{V}_n \cdot \mathbf{V}_j(\mathbf{q}) \tag{9}$$

where the signs have the same significance as in equation (8).

It should, however, be emphasised that in this equation $\mathbf{V}_n$ is the velocity of the scattered neutrons (Waller, 1964), since this fact has apparently been overlooked by a number of authors.

In the classical region we can equate $E_j(\mathbf{q})$ to k_BT and ignore the $\frac{1}{2}\hbar\omega_j(\mathbf{q})$ in equation (8). If we then sum the cross-sections for phonon emission and phonon absorption and assume as before that $q \ll Q$ so that $k \to k_0$ and $\mathbf{Q} \to \mathbf{B}$, the integrated TDS intensity can be written as

$$I_1 = \frac{Nk_BT}{m} |F(\mathbf{B})|^2 B^2 \int \frac{1}{q^2} \times \sum_{j=1}^{3} \frac{\cos^2 \alpha'_j(\mathbf{q})}{V_j^2(\mathbf{q})} \frac{1}{1-\varepsilon_j^2(\mathbf{q})} \, \mathrm{d}u \, \mathrm{d}v \, \mathrm{d}w \,, \tag{10}$$

where $\varepsilon_j(\mathbf{q}) = V_n^{-2} \mathbf{V}_n \,.\, \mathbf{V}_j(\mathbf{q})$.

Comparing equation (10) with equation (5) we see that this intensity differs from that for X-ray scattering only in the insertion of the $[1-\varepsilon_j^2(\mathbf{q})]$ terms and that in the limit as $V_n \gg V_j(\mathbf{q})$ it becomes identical. However, if the velocity of the scattered neutrons is comparable to the velocities of the phonons we must retain these terms in equation (10) which is then valid for $V_n > V_j(\mathbf{q})$, except when $V_n \to V_j(\mathbf{q})$.

For slower than sound neutrons the scattering corresponds to phonon absorption only when the crystal setting is on one side of the Bragg position and to phonon emission only when the setting is on the other side. As the crystal setting approaches the Bragg position the scattering surface contracts and, to a rough approximation, the total cross-section is essentially constant. In this case no correction, other than the normal background correction, will be necessary (Willis, 1969).

We should note, however, that for faster than sound neutrons as $V_n \to V_j(\mathbf{q})$, $\varepsilon_j^2(\mathbf{q}) \to 1$ and the cross-section for phonons travelling in directions close to that of the scattered neutrons will become very large. This will give rise to apparently anomalous integrated intensities which will be difficult to correct reliably, particularly as some of the approximations involved in deriving equation (10) will no longer be valid, and it is therefore important that the neutron wavelength for a given experiment should be chosen to avoid this condition.

Two-phonon scattering

X-rays

The conditions for scattering of X-rays in a two-phonon process are

$$\mathbf{Q} = \mathbf{k} - \mathbf{k}_0 = \mathbf{B} - \mathbf{q}$$

$$\hbar\omega_j(\mathbf{q}_1) \pm \hbar\omega_j(\mathbf{q}-\mathbf{q}_1) = \pm \hbar c(k-k_0) \tag{11}$$

where $\mathbf{q}_1$ and $\mathbf{q}-\mathbf{q}_1$ are the wave vectors of the two phonons concerned.

The scattering cross-section for this process is then:

$$\left(\frac{\mathrm{d}\sigma(\mathbf{q})}{\mathrm{d}\Omega}\right)_2 = \frac{NQ^4}{2m^2} \sum_{i,j} \sum_{\mathbf{q}_1} \frac{E_j(\mathbf{q}_1)E_i(\mathbf{q}-\mathbf{q}_1)}{\omega_j^2(\mathbf{q}_1)\omega_i^2(\mathbf{q}-\mathbf{q}_1)} \times |F(\mathbf{Q}) \cos \alpha_j(\mathbf{q}_1) \cos \alpha_i(\mathbf{q}-\mathbf{q}_1)|^2 \,. \tag{12}$$

The major contribution to this cross-section arises when the wave-vectors of the two phonons concerned are collinear and we can therefore approximate this to:

$$\left(\frac{\mathrm{d}\sigma(\mathbf{q})}{\mathrm{d}\Omega}\right)_2 = \frac{\pi^3}{2} \frac{NQ^4}{m^2 q V_c} |F(\mathbf{Q})|^2 \sum_{j=1}^{3} \frac{E_j^2(\mathbf{q}) \cos^4 \alpha_j(\mathbf{q})}{V_j^4(\mathbf{q})} \tag{13}$$

where V_c is the volume of the unit cell (see Wooster, 1962).

If we assume, as before, that $q \ll Q$ then the contribution to the integrated intensity from two-phonon processes is given by:

$$I_2 = \frac{\pi^3}{2} \frac{N(k_BT)^2}{m^2 V_c} |F(\mathbf{B})|^2 B^4 \int \frac{1}{q} \times \sum_{j=1}^{3} \frac{\cos^4 \alpha'_j(\mathbf{q})}{V_j^4(\mathbf{q})} \, \mathrm{d}u \, \mathrm{d}v \, \mathrm{d}w \tag{14}$$

which we can compare with equation (5) for one-phonon scattering.

Except at high temperature the two-phonon scattering cross-section is, in general, much less than that for one-phonon scattering and since it is proportional to q^{-1} the peaking is considerably less. Hence, in many cases we may be justified in neglecting the two-phonon scattering.

Neutrons

For thermal neutron scattering involving two-phonons the energy equation is

$$\hbar\omega_j(\mathbf{q}_1) \pm \hbar\omega_j(\mathbf{q}-\mathbf{q}_1) = \pm \frac{\hbar^2}{2m_n}(k^2 - k_0^2) \tag{15}$$

and we must again introduce the Jacobian into the scattering cross-section.

If we assume that the approximations involved in deriving equations (13) and (14) are valid for the neutron case then the Jacobian will be the same as that for the one-phonon scattering, given by equations (8) and (9), and the two-phonon TDS intensity will be:

$$I_2 = \frac{\pi^3}{2} \frac{N(k_BT)^2}{m^2 V_c} |F(\mathbf{B})|^2 B^4 \int \frac{1}{q} \times \sum_{j=1}^{3} \frac{\cos^4 \alpha'_j(\mathbf{q})}{V_j^4(\mathbf{q})} \frac{1}{1-\varepsilon_j^2(\mathbf{q})} \, \mathrm{d}u \, \mathrm{d}v \, \mathrm{d}w \tag{16}$$

where $\varepsilon_j(\mathbf{q}) = V_n^{-2} \mathbf{V}_n \,.\, \mathbf{V}_j(\mathbf{q})$.

However, it should be noted that some of these approximations may not be valid if the velocity of the neutrons is close to that of one or more acoustic modes.

Evaluation of the TDS correction

The contributions to the integrated intensity due to TDS are given in equations (5) and (14) for X-rays and equations (10) and (16) for neutrons.

The Bragg integrated intensity I_0 is given by

$$I_0 = N|F(\mathbf{B})|^2 \lambda^3 \operatorname{cosec} 2\theta_B / V_c \,, \tag{17}$$

where θ_B is the Bragg scattering angle.

If we write the total integrated intensity in the form:

$$I = I_0(1 + \alpha_1 + \alpha_2) \tag{18}$$

then we have, for X-rays:

$$\alpha_1 = \frac{I_1}{I_0} = \frac{k_BT}{\lambda^3 \operatorname{cosec} 2\theta_B} B^2 \int \frac{1}{q^2} \times \sum_{j=1}^{3} \frac{\cos^2 \alpha'_j(\mathbf{q})}{\varrho V_j^2(\mathbf{q})} \, du \, dv \, dw \tag{19}$$

where ϱ is the density of the crystal, and:

$$\alpha_2 = \frac{I_2}{I_0} = \frac{\pi^3}{3} \frac{(k_BT)^2}{\lambda^3 \operatorname{cosec} 2\theta_B} B^4 \int \frac{1}{q} \times \sum_{j=1}^{3} \frac{\cos^4 \alpha'_j(\mathbf{q})}{\varrho^2 V_j^4(\mathbf{q})} \, du \, dv \, dw \tag{20}$$

and B has the value $4\pi \sin \theta_B/\lambda$.

For neutron scattering the expressions for α_1 and α_2 are identical except that each term in the summations must be multiplied by $1/[1-\varepsilon_j^2(\mathbf{q})]$.

We shall define a set of orthogonal axes x,y,z as before (Cooper & Rouse, 1968), *i.e.* with y perpendicular to the plane containing the wave vectors of the incident and scattered radiation, and z parallel to the wave vector of the scattered radiation (see Fig. 1).

We then have that

$$du \, dv \, dw = \frac{\lambda^3 \operatorname{cosec} 2\theta_B}{8\pi^3} \, dx \, dy \, dz \tag{21}$$

so that we can rewrite equations (19) and (20) in the form:

$$\alpha_1 = \frac{2k_BT}{\pi} \left(\frac{\sin \theta_B}{\lambda}\right)^2 \int \frac{1}{q^2} \times \sum_{j=1}^{3} \frac{\cos^2 \alpha'_j(\mathbf{q})}{\varrho V_j^2(\mathbf{q})} \, dx \, dy \, dz \tag{22}$$

$$\alpha_2 = \frac{(k_BT)^2}{24} \left(\frac{4\pi \sin \theta_B}{\lambda}\right)^4 \int \frac{1}{q} \times \sum_{j=1}^{3} \frac{\cos^4 \alpha'_j(\mathbf{q})}{\varrho^2 V_j^4(\mathbf{q})} \, dx \, dy \, dz \tag{23}$$

We can define the polarization direction of the mode $(j, \mathbf{q})$ by its direction cosines l_j, m_j, n_j with respect to the x,y,z axes respectively. The direction cosines of $\mathbf{B}$ are $\cos \theta_B$, 0, $\sin \theta_B$ so that

$$\cos \alpha'_j(\mathbf{q}) = l_j \cos \theta_B + n_j \sin \theta_B \, . \tag{24}$$

The equations of motion for a plane elastic wave propagating in a direction $\mathbf{q}$ in a medium lead to the following equations (Jahn, 1942):

$$l_j = A_{11} \frac{l_j}{\varrho V_j^2(\mathbf{q})} + A_{12} \frac{m_j}{\varrho V_j^2(\mathbf{q})} + A_{13} \frac{n_j}{\varrho V_j^2(\mathbf{q})} \tag{25a}$$

$$m_j = A_{12} \frac{l_j}{\varrho V_j^2(\mathbf{q})} + A_{22} \frac{m_j}{\varrho V_j^2(\mathbf{q})} + A_{23} \frac{n_j}{\varrho V_j^2(\mathbf{q})} \tag{25b}$$

$$n_j = A_{13} \frac{l_j}{\varrho V_j^2(\mathbf{q})} + A_{23} \frac{m_j}{\varrho V_j^2(\mathbf{q})} + A_{33} \frac{n_j}{\varrho V_j^2(\mathbf{q})} \, , \tag{25c}$$

where A_{kl} is given by

$$A_{kl} = a_j a_m c'_{jklm} \, , \tag{26}$$

a_j, a_m being the direction cosines of $\mathbf{q}$ ($j,m = 1$, 2 or 3) and c'_{jklm} the elastic constants of the medium referred to the x,y,z axes, *i.e.*

$$c'_{jklm} = b_{jn} b_{kp} b_{lq} b_{mr} c_{npqr} \, , \tag{27}$$

where b_{jn} *etc.* are direction cosines of the x,y,z axes referred to the orthogonal axes for which the elastic constants c_{npqr} are given.

For a crystal of general symmetry the values of A_{kl} are:

$$A_{11} = a_1^2 c'_{11} + a_2^2 c'_{66} + a_3^2 c'_{55} + 2a_2a_3c'_{56} + 2a_1a_3c'_{15} + 2a_1a_2c'_{16} \tag{28a}$$

$$A_{22} = a_1^2 c'_{66} + a_2^2 c'_{22} + a_3^2 c'_{44} + 2a_2a_3c'_{24} + 2a_1a_3c'_{46} + 2a_1a_2c'_{26} \tag{28b}$$

$$A_{33} = a_1^2 c'_{55} + a_2^2 c'_{44} + a_3^2 c'_{33} + 2a_2a_3c'_{34} + 2a_1a_3c'_{35} + 2a_1a_2c'_{45} \tag{28c}$$

$$A_{12} = a_1^2 c'_{16} + a_2^2 c'_{26} + a_3^2 c'_{45} + a_2a_3(c'_{25} + c'_{46}) + a_1a_3(c'_{14} + c'_{56}) + a_1a_2(c'_{12} + c'_{66}) \tag{28d}$$

$$A_{13} = a_1^2 c'_{15} + a_2^2 c'_{46} + a_3^2 c'_{35} + a_2a_3(c'_{36} + c'_{45}) + a_1a_3(c'_{13} + c'_{55}) + a_1a_2(c'_{14} + c'_{56}) \tag{28e}$$

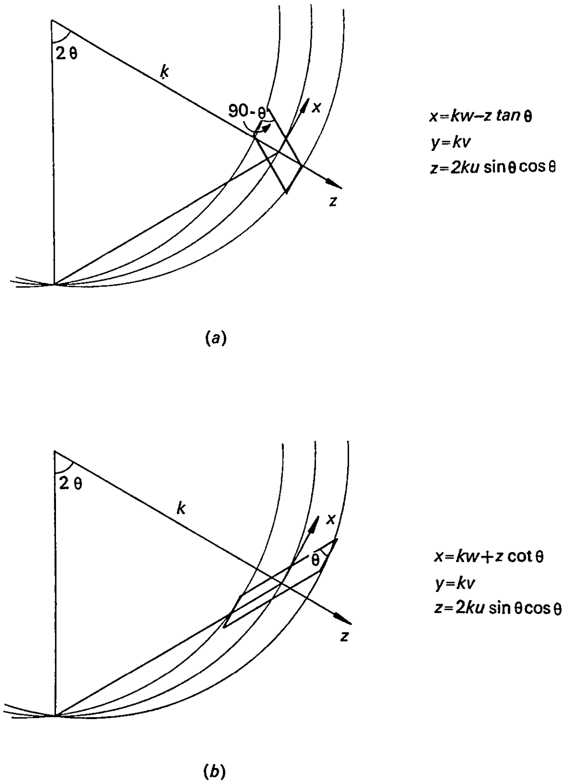

Fig. 1. Diagrams in reciprocal space illustrating the volume swept out for (*a*) ω scan, (*b*) $\theta-2\theta$ scan and showing the system of axes used.

$$A_{23}=a_1^2c'_{56}+a_2^2c'_{24}+a_3^2c'_{34}+a_2a_3(c'_{23}+c'_{44})$$
$$+a_1a_3(c'_{36}+c'_{45})+a_1a_2(c'_{25}+c'_{46})\,, \quad (28f)$$

where the standard two-suffix notation is used for the elastic constants (Nye, 1957).

From equations (25) we obtain the condition for non-zero solutions for l_j, m_j and n_j:

$$\begin{vmatrix} A_{11}-\varrho V_j^2(\mathbf{q}) & A_{12} & A_{13} \\ A_{12} & A_{22}-\varrho V_j^2(\mathbf{q}) & A_{23} \\ A_{13} & A_{23} & A_{33}-\varrho V_j^2(\mathbf{q}) \end{vmatrix}=0\,, \quad (29)$$

which is a cubic equation in $V_j^2(\mathbf{q})$ leading to the three solutions for l_j, m_j and n_j corresponding to the three polarization modes for a given $\mathbf{q}$. These solutions are given from the velocities by the relation:

$$l_j:m_j:n_j=\frac{1}{A_{23}(\varrho V_j^2(\mathbf{q})-A_{11})+A_{12}A_{13}}:$$
$$\frac{1}{A_{13}(\varrho V_j^2(\mathbf{q})-A_{22})+A_{23}A_{12}}:$$
$$\frac{1}{A_{12}(\varrho V_j^2(\mathbf{q})-A_{33})+A_{13}A_{23}}. \quad (30)$$

It is necessary, in general, to solve equations (29) and (30) before integrating the TDS over the scanned volume. However, if a correction is required only for one-phonon X-ray scattering we can use a much more straightforward method which we outline below.

Evaluation of one-phonon X-ray scattering

From equations (22) and (24) we can see that for one-phonon X-ray scattering we need to evaluate, for each value of $\mathbf{q}$, the summation

$$S_{\mathbf{q}}=\sum_{j=1}^{3}\frac{\cos^2\alpha'_j(\mathbf{q})}{\varrho V_j^2(\mathbf{q})} \quad (31a)$$
$$=\sum_{j=1}^{3}\frac{(l_j\cos\theta_B+n_j\sin\theta_B)^2}{\varrho V_j^2(\mathbf{q})} \quad (31b)$$
$$=\cos^2\theta_B\sum_{j=1}^{3}\frac{l_j^2}{\varrho V_j^2(\mathbf{q})}+\sin^2\theta_B\sum_{j=1}^{3}\frac{n_j^2}{\varrho V_j^2(\mathbf{q})}$$
$$+\sin 2\theta_B\sum_{j=1}^{3}\frac{l_jn_j}{\varrho V_j^2(\mathbf{q})} \quad (31c)$$

The individual summations in equation (31*c*) can now be evaluated by the method given by Jahn (1942).

Since the polarization vectors are orthogonal we can write from equations (25):

$$\sum_{j=1}^{3}l_j^2=A_{11}\sum_{j=1}^{3}\frac{l_j^2}{\varrho V_j^2(\mathbf{q})}+A_{12}\sum_{j=1}^{3}\frac{l_jm_j}{\varrho V_j^2(\mathbf{q})}$$
$$+A_{13}\sum_{j=1}^{3}\frac{l_jn_j}{\varrho V_j^2(\mathbf{q})}=1 \quad (32a)$$

$$\sum_{j=1}^{3}l_jm_j=A_{12}\sum_{j=1}^{3}\frac{l_j^2}{\varrho V_j^2(\mathbf{q})}+A_{22}\sum_{j=1}^{3}\frac{l_jm_j}{\varrho V_j^2(\mathbf{q})}$$
$$+A_{23}\sum_{j=1}^{3}\frac{l_jn_j}{\varrho V_j^2(\mathbf{q})}=0 \quad (32b)$$

$$\sum_{j=1}^{3}l_jn_j=A_{13}\sum_{j=1}^{3}\frac{l_j^2}{\varrho V_j^2(\mathbf{q})}+A_{23}\sum_{j=1}^{3}\frac{l_jm_j}{\varrho V_j^2(\mathbf{q})}$$
$$+A_{33}\sum_{j=1}^{3}\frac{l_jn'_j}{\varrho V_j^2(\mathbf{q})}=0. \quad (32c)$$

Hence

$$\sum_{j=1}^{3}\frac{l_j^2}{\varrho V_j^2(\mathbf{q})}=\begin{vmatrix} A_{22} & A_{23} \\ A_{23} & A_{33} \end{vmatrix}\Big/\Delta=(A^{-1})_{11} \quad (33a)$$

$$\sum_{j=1}^{3}\frac{l_jn_j}{\varrho V_j^2(\mathbf{q})}=\begin{vmatrix} A_{12} & A_{22} \\ A_{13} & A_{23} \end{vmatrix}\Big/\Delta=(A^{-1})_{13}, \quad (33b)$$

where

$$\Delta=\begin{vmatrix} A_{11} & A_{12} & A_{13} \\ A_{12} & A_{22} & A_{23} \\ A_{13} & A_{23} & A_{33} \end{vmatrix} \quad (34)$$

is the Christoffel determinant and $(A^{-1})_{kl}$ denotes an element of the matrix A^{-1} inverse to A.

In a similar way we obtain

$$\sum_{j=1}^{3}\frac{n_j^2}{\varrho V_j^2(\mathbf{q})}=\begin{vmatrix} A_{11} & A_{12} \\ A_{12} & A_{22} \end{vmatrix}\Big/\Delta=(A^{-1})_{33} \quad (35)$$

and we can rewrite equation (31) as

$$S_{\mathbf{q}}=\cos^2\theta_B(A^{-1})_{11}+\sin^2\theta_B(A^{-1})_{33}+\sin 2\theta_B(A^{-1})_{13} \quad (36)$$

which can be evaluated directly.

The isotropic approximation

In the isotropic approximation we assume that we can consider average velocities for the acoustic modes, independent of direction. In deriving these average velocities we need therefore consider only the case in which the x,y,z axes coincide with those for which the elastic constants are given and it is not necessary to carry out the transformation given in equation (27).

For a crystal of cubic symmetry the elastic constants reduce to three independent non-zero values: c_{11} $(=c_{22}=c_{33})$, c_{12} $(=c_{13}=c_{23})$ and c_{44} $(=c_{55}=c_{66})$. Equations (28) therefore reduce to

$$A_{11}=a_1^2c_{11}+(a_2^2+a_3^2)c_{44} \quad (37a)$$
$$A_{22}=a_2^2c_{11}+(a_1^2+a_3^2)c_{44} \quad (37b)$$
$$A_{33}=a_3^2c_{11}+(a_1^2+a_2^2)c_{44} \quad (37c)$$
$$A_{12}=a_1a_2(c_{12}+c_{44}) \quad (37d)$$
$$A_{13}=a_1a_3(c_{12}+c_{44}) \quad (37e)$$
$$A_{23}=a_2a_3(c_{12}+c_{44}) \quad (37f)$$

from which we obtain

$$(A^{-1})_{11}=[a_4^1c_{44}^2+(a_2^4+a_3^4)c_{11}c_{44}+(a_1^2a_2^2+a_1^2a_3^2)\ (c_{11}c_{44}+c_{44}^2)$$
$$+a_2^2a_2^3(c_{11}^2-c_{12}^2-2c_{12}c_{44})]/\Delta \quad (38a)$$

$$(A^{-1})_{33}=[(a_1^4+a_2^4)c_{11}c_{44}+a_3^4c_{44}+a_1^2a_2^2(c_{11}^2-c_{12}^2-2c_{12}c_{44}) \\ +(a_1^2a_3^2+a_2^2a_3^2)\,(c_{11}c_{44}+c_{44}^2)]/\Delta \tag{38b}$$

$$(A^{-1})_{13}=[a_1^2a_3(a_2^2-a_1^2-a_3^2)c_{44}^2+a_1a_3(2a_2^2-a_3^2-a_1^2)c_{12}c_{44} \\ -a_1a_2^2a_3c_{11}(c_{12}+c_{44})+a_1a_2^2a_3c_{12}^2)]/\Delta\,, \tag{38c}$$

where

$$\Delta=a_1^2a_2^2a_3^2(c_{11}^3+2c_{12}^3+4c_{44}^3-3c_{11}c_{12}^2-3c_{11}^2c_{44}+12c_{12}c_{44}^2 \\ +9c_{12}^2c_{44}-6c_{11}c_{12}c_{44})+(a_1^2a_2^2+a_1^2a_3^2+a_2^2a_3^2)\,(c_{11}^2c_{44} \\ -2c_{11}c_{44}^2-c_{12}^2c_{44}-2c_{12}c_{44}^2)+c_{11}c_{44}^2\,. \tag{39}$$

If we take the mean value of the numerator and denominator separately for each $(A^{-1})_{kl}$ we find that

$$\overline{(A^{-1})_{11}}=\overline{(A^{-1})_{33}}$$

and \hfill (40)

$$\overline{(A^{-1})_{13}}=0\,,$$

and substituting the mean values in equation (36) we obtain:

$$S_{\mathbf{q}}=\tfrac{1}{3}\cdot\frac{\tfrac{1}{5}b_1(c_{11}+c_{12})+c_{44}(2c_{11}+c_{44})}{\tfrac{1}{105}b_1^2b_2+\tfrac{1}{5}b_1(c_{11}+c_{12})c_{44}+c_{11}c_{44}^2}\,, \tag{41}$$

with

$$b_1=c_{11}-c_{12}-2c_{44}$$

$$b_2=c_{11}+2c_{12}+c_{44}$$

and the integral for the TDS intensity becomes that used in the isotropic approximation (Cooper & Rouse, 1968).

A value for $S_{\mathbf{q}}$ could be derived similarly for a pseudo-isotropic crystal of any symmetry. However, this would require, in the general case, the evaluation of over 1000 separate terms. In order to use an isotropic approximation in this case it would therefore seem preferable to estimate effective values of c_{11}, c_{12} and c_{44} for use in equation (41), thus assuming a quasi-cubic symmetry for the elastic properties of the crystal. However, it should be emphasized that extreme care should be taken when an isotropic approximation is used for non-cubic crystals.

Experimental resolution

If we ignore the divergence of the incident beam and the mosaic spread of the sample then the volume of integration is defined directly by the ranges of the angles u, v and w defined by the scan range and the detector aperture. Both of these factors, however, will cause a reduction in the TDS contribution to the integrated intensity and we should replace the integration over the detector aperture by a weighted integration over the resolution function.

The resolution function can be considered as the probability of detection of the radiation as a function of $\mathbf{\Delta Q}$ when the instrument has been set to measure a scattering process corresponding to the scattering vector $\mathbf{Q}_0$. The determination of the resolution function of a conventional two-crystal neutron diffractometer and its application to diffuse scattering have been considered by Cooper & Nathans (1968*a*,*b*). These authors show that if a Gaussian approximation for the mosaic and collimation functions is valid the resolution function $R(\mathbf{Q}_0+\mathbf{\Delta Q})$ can be considered very conveniently in terms of a resolution matrix M_{kl} such that:

$$R(\mathbf{Q}_0+\mathbf{\Delta Q})=R_0\exp\left\{-\tfrac{1}{2}\sum_{k=1}^{3}\sum_{j=1}^{3}M_{kl}X_kX_l\right\}\,, \tag{43}$$

where $X_1=\Delta Q_x$, $X_2=\Delta Q_y$, $X_3=\Delta Q_z$ (Cooper & Nathans, 1968*a*).

However, whatever the form of the resolution function, it can be determined experimentally by means of a series of suitable scans through the relevant Bragg peak (Cooper & Nathans, 1968*b*). The diffuse intensity observed at a given setting of the diffractometer is then given by:

$$I(\mathbf{Q}_0)=\int\{\int\sigma(\mathbf{Q}_0+\mathbf{\Delta Q}+\mathbf{q}_m) \\ \times M(\mathbf{q}_m)\mathbf{dq}_m\}R(\mathbf{Q}_0+\mathbf{\Delta Q})\mathbf{\Delta Q} \tag{44}$$

where the scattering cross-section is integrated over the mosaic spread of the sample $M(\mathbf{q}_m)$, $\mathbf{q}_m$ being the reciprocal lattice vector defining translation from the point of optimum Bragg reflexion.

The nature of the resolution function for an X-ray diffractometer has been discussed by Cochran (1969). In this case it is complicated somewhat by the $K\alpha_1$–$K\alpha_2$ doublet but its determination and application are similar to those for the neutron case.

It is clear that integration over the resolution function at each point on the scan considerably complicates the evaluation of the TDS correction. However, since the aperture of the detector will usually be the most significant factor we can, in general, calculate the TDS contribution ignoring the other factors and then allow for these by repeating the calculation with the centre of the scan at different points in a partial resolution function centred on the original centre of the scan.

Discussion

In the present paper we have outlined the method of evaluation of the correction of measured integrated intensities for thermal diffuse scattering for a crystal of any symmetry, allowing for the contributions from one-phonon and two-phonon processes and allowing for experimental resolution effects. A computer program has been written to evaluate the special case of one-phonon scattering of X-rays for which the analysis is somewhat simpler. Although the extension of this program to the general case is relatively straightforward the computation involved becomes considerable. In addition the allowance for resolution effects requires a detailed experimental determination of the resolution function of the instrument.

TDS corrections evaluated by the procedures described here for typical experimental situations will be discussed in a later paper.

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The use of Neutron Resonance Scattering in the Structure Determination of $Sm(BrO_3)_3.9H_2O$

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The structure of $Sm(BrO_3)_3.9H_2O$ has been solved by the neutron anomalous-dispersion method, with the use of data collected at two wavelengths. Five out of eight atoms in the asymmetric unit were located from the 'anomalous difference Patterson' synthesis, and the remaining three from a Fourier synthesis. The structure is centrosymmetric, and the signs of 78% of the reflexions were determined correctly from the differences in the F_{obs} values at the two wavelengths.

1. Introduction

It has been known for some time that certain isotopes (especially ^{113}Cd and ^{149}Sm) when present in crystals, give rise to resonance scattering of thermal neutrons and this can be used to solve the phase problem in a structure analysis from neutron diffraction intensity data (Peterson & Smith, 1962; Ramaseshan, 1966; Dale & Willis, 1966). In the first reported application of this technique (Macdonald & Sikka, 1969), anomalous scattering from the Cd atom was utilized to solve the structure of $Cd(NO_3)_2.4D_2O$. Macdonald & Sikka showed that the 'direct phase' method of Ramachandran & Raman (1956) and the sine Patterson approach of Okaya, Saito & Pepinsky (1955) can be directly applied in neutron diffraction. These methods were devised originally for X-ray diffraction, where the intensities are measured at one wavelength. This paper is concerned with the third approach, that of the use of data at two wavelengths. Peterson & Smith (1962) pointed out that the real and imaginary parts of the scattering amplitude for ^{113}Cd and ^{149}Sm vary with the wavelength of the neutrons; the measurement of data at two different wavelengths would then correspond to the replacement of one atom of the crystal by an atom of different scattering amplitude. In this way the isomorphous replacement method can be used in neutron diffraction.

The substance chosen to test the suitability of the two wavelength method was $Sm(BrO_3)_3.9H_2O$. This choice was dictated largely by the need to obtain a large single crystal, suitable for a neutron study and containing Sm as the anomalous scatterer. From an experimental point of view, Sm is preferable to Cd as the anomalous scatterer since the range of wavelength, over which the real (b'_{Sm}) and imaginary (b''_{Sm}) parts of the scattering amplitude for the Sm atom vary, lies well within the experimentally useful region of the thermal neutron spectrum from a reactor. (For Sm, resonance occurs at 0·92 Å; for Cd it occurs at 0·67 Å and on the lower wavelength side of the Cd resonance the neutron flux is extremely low.) At the start of this study, it was thought that this crystal would be isomorphous with $Nd(BrO_3)_3.9H_2O$, whose X-ray structure is non-centrosymmetric (Helmholz, 1939). Later, as no Bijvoet differences could be observed from $Sm(BrO_3)_3.9H_2O$, it was realized that the crystal structure was centrosymmetric and belonged to a different space group, $P6_3/mmc$, in the hexagonal system.

2. Experimental

Single crystals of $Sm(BrO_3)_3.9H_2O$ were grown by slow evaporation of an aqueous solution of samarium bromate. The crystals were pink hexagonal prisms, bounded by {100} and {101} faces.

Three-dimensional neutron intensity measurements were made at two wavelengths with the Mark I auto-

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