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Anisotropic Corrections of Measured Integrated Bragg Intensities for Thermal Diffuse Scattering–General Formula

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The correction of measured integrated intensities for the first-order thermal diffuse scattering (TDS) is considered on the basis of the existing theory of X-ray thermal diffuse scattering for an elastic wave of long wave length. Generalized formula for the TDS correction α is found to be represented by a quadratic form in the Miller indices h,k,l and a tensor $\mathbf{\Delta\beta}$, as $\alpha=\Delta\beta_{11}h^2+\Delta\beta_{22}k^2+\Delta\beta_{33}l^2+2\Delta\beta_{12}hk+2\Delta\beta_{23}kl+2\Delta\beta_{31}lh$. $\mathbf{\Delta\beta}$ is a tensor introduced in this paper which characterizes the anisotropy of the TDS correction. The form of the tensor $\mathbf{\Delta\beta}$ is shown to depend only on the crystallographic system. The relation between $\mathbf{\Delta\beta}$ and the temperature-parameter tensor is presented.

Introduction

Recently remarkable progress has been made in the accuracy of crystal structure analysis by means of X-ray diffraction from single-crystal specimens. Even for organic crystals and minerals, if they are not too complicated, it is becoming possible to investigate bonding electrons between atoms and lone-pair electrons (*e.g.* Iwata & Saito, 1972) by analysis of charge-density distributions. In such analysis the reliability of the result depends on the accuracy of the observed structure factors and a significant point in the discussion is whether deconvolution of thermal and bonding effects is properly treated.

In order to obtain the structure factors with sufficient accuracy, several corrections to the observed intensities are required. These are for Lorentz–polarization, absorption, extinction and thermal diffuse scattering (TDS) effects. Among them TDS correction is usually neglected except in some specific cases where accurate determination of the temperature parameter is the purpose of the studies. The correction involves the subtraction of the thermal diffuse scattering contributions, which contaminate, as sharp maxima, the measured integrated Bragg intensities. The effect of such TDS on a structure investigation with a single-crystal specimen was first studied by Nilsson (1957) and it was shown that the temperature parameters B_j in the temperature factors $\exp\{-B_j(\sin\theta/\lambda)^2\}$ so obtained are apparently small if the correction is neglected. The amount of the correction in the temperature parameter has been shown to depend on the softness of the crystal and has been estimated to be 15% for example in the case of KCl. Thus one cannot neglect the TDS correction, as has been realized by a number of authors, especially in the detailed structure analysis of soft materials like molecular crystals.

It has been pointed out, as one of the reasons for not applying the TDS correction, that the existing formulae for the TDS correction are restrictive in that they are applicable only to crystals of the cubic system. Furthermore, an assumption of elastic isotropy is made to avoid complex numerical calculation. In this situation, generalization of the theory has recently been considered by Skelton & Katz (1969) and Rouse & Cooper (1969). From their studies it became possible to evaluate the TDS correction for all crystallographic systems. However, there still remains some difficulty in deriving from their formulae a relation between the anisotropy of the TDS correction and the crystallographic system.

In this paper we consider this problem in order to make clear such a relation on the basis of the assumption that the TDS which contributes to the measured Bragg intensity is only first-order thermal diffuse scattering due to acoustic modes of small wave number. We then show that the general formula is expressed as quadratic in the three indices h,k,l of the reciprocal lattice. In the formula a 3×3 symmetric tensor is introduced, the characteristics of which are determined by the crystallographic system. This tensor is closely related to the temperature-parameter tensor in the Debye–Waller factor. With the use of the formula the effect of the anisotropic TDS correction on the structure analysis is discussed.

TDS correction

In the treatment of X-ray scattering from an ideally mosaic single crystal, the measured integrated intensity of the Bragg reflexion, $I(\mathrm{Obs})$, is given by the sum of a contribution from the true Bragg reflexion, $I(B)$, and contributions from the TDS, $I(\mathrm{TDS})$; *i.e.*

$$I(\mathrm{Obs})=I(B)+\sum_j I_j(\mathrm{TDS}) \tag{1}$$

where $I_j(\mathrm{TDS})$ indicates jth order TDS, representing the scattering where j phonons are involved in the scattering process. Equation (1) can be written alternatively as

$$I(\mathrm{Obs})=I(B)\{1+\sum_{j\geq 1}{}'\alpha_j\}, \tag{2}$$

if we define α_j as a ratio of the two components $I_j(\mathrm{TDS})$ and $I(B)$.

Among the $I_j(\mathrm{TDS})$'s, the TDS which has a pronounced maximum under the Bragg reflexion is the first-order TDS, $I_1(\mathrm{TDS})$, due to accoustic modes of small wave number $\mathbf{q}$. The TDS due to optic modes is less important, because the frequencies of these modes are high and the dispersion curves are usually flat in the vicinity of the Brillouin-zone centre. The higher-order TDS, $I_j(\mathrm{TDS})$ ($j>1$), also does not form appreciable peaks at the reciprocal-lattice points. For these reasons we shall neglect components due to such scattering and, therefore, consider in this paper α_1 due to acoustic modes only.

The corresponding cross sections for Bragg scattering and for first-order TDS due to acoustic modes of small $\mathbf{q}$ are well known (*e.g.* James, 1949), and the total intensity for the two types of scattering integrated over the vicinity of a reciprocal-lattice point are expressed as (Cochran, 1969)

$$I(B)=\frac{N\lambda^3}{v\Omega\sin 2\theta}|F(\mathbf{B})|^2\int\delta(\mathbf{Q}-\mathbf{B})\mathrm{d}^3Q \tag{3}$$

$$I_1(\mathrm{TDS})=\frac{\lambda^3}{v^2\Omega\sin 2\theta}|F(\mathbf{B})|^2 \times\int\sum_{\mathbf{q}}\sum_j\frac{[\mathbf{Q}\cdot\mathbf{e}_j(\mathbf{q})]^2}{\varrho\cdot\omega_j^2(\mathbf{q})}\times E_j(\mathbf{q})\cdot\delta(\mathbf{Q}+\mathbf{q}-\mathbf{B})\mathrm{d}^3Q\,, \tag{4}$$

where the following notations are used;

N: number of unit cells in crystal
v: volume of unit cell
λ: wavelength of X-rays
Ω: angular velocity for recording the intensities
2θ: scattering angle
$\mathbf{B}$: reciprocal-lattice vector
$\mathbf{Q}$: scattering vector ($|\mathbf{Q}|=4\pi\sin\theta/\lambda$). This is related to $\mathbf{B}$ as $\mathbf{Q}=\mathbf{B}+\mathbf{q}$.
$F(\mathbf{B})$: crystal structure factor at the reciprocal lattice point $\mathbf{B}$
$\mathbf{e}_j(\mathbf{q})$: polarization vector of mode $(j,\mathbf{q})$
$\omega_j(\mathbf{q})$: circular frequency of mode $(j,\mathbf{q})$
$E_j(\mathbf{q})$: energy of mode $(j,\mathbf{q})$
ϱ: density of crystal.

Integrating the δ-functions in equations (3) and (4), and substituting into equation (2), we have

$$\alpha_1 = \frac{1}{Nv}\sum_{\mathbf{q}}\sum_{j} \frac{[\mathbf{Q}\,.\,\mathbf{e}_j(\mathbf{q})]^2}{\varrho\omega_j^2(\mathbf{q})} E_j(\mathbf{q})\,. \tag{5}$$

Here the summation with respect to $\mathbf{q}$ is to be taken over the range of measurement and can be replaced by an integral

$$\sum_{\mathbf{q}} \rightarrow \frac{Nv}{(2\pi)^3}\int \mathrm{d}^3q\,. \tag{6}$$

Thus, we have

$$\alpha_1 = \frac{1}{(2\pi)^3}\int J_1(\mathbf{q})\mathrm{d}^3q \tag{7}$$

with

$$J_1(\mathbf{q}) = \sum_{j} \frac{[\mathbf{Q}\,.\,\mathbf{e}_j(\mathbf{q})]^2}{\varrho\omega_j^2(\mathbf{q})} E_j(\mathbf{q})\,, \tag{8}$$

where the summation over j is a summation over all possible acoustic branches: $j=1,2,3$. $J_1(\mathbf{q})$ gives the intensity distribution in the vicinity of a reciprocal lattice point **B**. This is the most basic equation for the TDS correction due to acoustic modes (Cochran, 1969). The anisotropy of the TDS correction can be derived from this basic equation.

Formulation of α_1

In the measurement of the Bragg reflexion the volume swept out in reciprocal space is in the vicinity of a reciprocal-lattice point, so that the lattice vibrations involved in the integral of equation (7) are only of small wave number. Such vibrations can be approximated very well by those of the elastic-continuum model for which the dispersion relation can be written as

$$\omega_j(\mathbf{q}) = \mathbf{V}_j\,.\,\mathbf{q}\,, \tag{9}$$

where $\mathbf{V}_j$ is the velocity of elastic wave with polarization vector $\mathbf{e}_j$ and is given in terms of the elastic constants C_{ij} as a solution of the following equation of motion for propagation of the elastic wave through the medium:

$$\begin{aligned} e_x(A_{11}-\varrho V^2)+e_yA_{12}+e_zA_{13}&=0\\ e_xA_{12}+e_y(A_{22}-\varrho V^2)+e_zA_{23}&=0\\ e_xA_{13}+e_yA_{23}+e_z(A_{33}-\varrho V^2)&=0\,, \end{aligned} \tag{9}$$

where A_{lm} is the lm component of a 3×3 symmetric matrix **A**. If $\hat{q}_p$ and $\hat{q}_q$ are the direction cosines of vector $\mathbf{q}$ referring to orthogonal axes x,y,z, A_{lm} is given in terms of the elastic constant $C_{pl,qm}$* by

$$A_{lm} = \sum_{pq} C_{pl,qm}\hat{q}_p\hat{q}_q\,. \tag{10}$$

The full description of A_{lm} is given in the Appendix for the most general crystallographic system. The associated polarization vector $\mathbf{e}_j(\mathbf{q})$ is also given by substituting the solution $\mathbf{V}_j^2$ back into the equations (9), but it becomes independent of $\mathbf{q}$ in this approximation. We shall therefore drop $\mathbf{q}$ from the notation of $\mathbf{e}_j(\mathbf{q})$, leaving simply $\mathbf{e}_j$. Besides, we can equate $E_j(\mathbf{q})$ to k_BT in this classical treatment of lattice vibrations.

The anisotropy of α can be obtained by decomposing the scalar product $(\mathbf{Q}\,.\,\mathbf{e}_j)$ in equation (8) into components. We set up coordinate axes with reference to which components of both polarization and scattering vectors are given. The polarization vector can be specified with respect to the above set of orthogonal x,y,z axes for which the elastic constants are usually given. We shall thus employ this set of axes, so that

$$\begin{aligned} \mathbf{e}_j&=e_{jx}\mathbf{i}+e_{jy}\mathbf{j}+e_{jz}\mathbf{k}\\ \mathbf{Q}&=Q_x\mathbf{i}+Q_y\mathbf{j}+Q_z\mathbf{k} \end{aligned} \tag{11}$$

where **i**, **j**, **k** are the unit vectors along the axes. Decomposing the scalar product $(\mathbf{Q}\,.\,\mathbf{e}_j)$ and substituting it into equation (8), we obtain

$$J_1(\mathbf{q}) = \frac{k_BT}{q^2}\sum_{l}\sum_{m} Q_lQ_m \sum_{j} \frac{(e_{jl}\,.\,e_{jm})}{\varrho V_j^2}\,. \tag{12}$$

In this expression we see that the summation over j forms a 3×3 symmetric tensor and in fact, with the use of the orthonormality relation

$$\sum_{j} e_{jl}e_{jm} = \delta_{lm}\,, \tag{13}$$

we can easily derive the relation

$$\sum_{j} \frac{(e_{jl}\,.\,e_{jm})}{\varrho V_j^2} = (\mathbf{A}^{-1})_{lm}\,, \tag{14}$$

where $(\mathbf{A}^{-1})_{lm}$ is the lm component of the inverse of matrix **A**. Equation (14) is the well known relation representing the anisotropy of the TDS in the theory of X-ray scattering (*e.g.* Takagi, 1961; Wooster, 1962). Substituting this relation into equation (12), we can immediately see that equation (12) is quadratic in Q_l $(l=x,y,z)$:

$$J_1(\mathbf{q}) = \frac{k_BT}{q^2}\sum_{lm}(\mathbf{A}^{-1})_{lm}Q_lQ_m\,. \tag{15}$$

If we define a tensor T_{lm} as

$$T_{lm} = \frac{k_BT}{(2\pi)^3}\int \frac{(\mathbf{A}^{-1})_{lm}}{q^2}\mathrm{d}^3q\,, \tag{16}$$

the TDS correction α_1 reduces to the similar quadratic expression;

$$\alpha_1 = \sum_{lm} T_{lm}Q_lQ_m\,. \tag{17}$$

In this treatment we have represented the scattering vector **Q** in terms of the Cartesian axes. However, it is rather inconvenient to represent it by this set of axes, because the scattering vector **Q** can always be represented with a crystallographic reciprocal-lattice point for the case of the Bragg scattering. Thus, we

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* The four suffices of C's are used in this expression but can be reduced to two.

need to transform the Cartesian axes to the crystallographic reciprocal-lattice axes which, however, are not always mutually perpendicular. Introducing a linear transformation matrix $\boldsymbol{\sigma}$, we can write

$$Q_1 = \sum_{p} \sigma_{lp} h_p \,, \tag{18}$$

where h_p is the abbreviated notation for the Miller indices h, k, l. By substitution of this relation (18) into equation (17), α_1 is given as

$$\alpha_1 = \sum_{lp} \sum_{qm} \sigma_{lp} \sigma_{mq} T_{lm} h_p h_q \,. \tag{19}$$

Since it is possible to define a tensor as

$$\Delta\beta_{pq} = \sum_{lm} \sigma_{lp} \sigma_{mq} T_{lm} \,, \tag{20}$$

equation (19) can be reduced again to a simple quadratic form in the three indices h, k, l, namely

$$\alpha_1 = \sum_{pq} \Delta\beta_{pq} h_p h_q \,. \tag{21}$$

This is the most fundamental formula from which the TDS contribution to the measured Bragg intensities can be estimated for any type of Bragg point for any crystallographic system, if all the tensor components of $\boldsymbol{\Delta\beta}$ are evaluated. It should be noticed that the TDS contribution depends not only on $\sin\theta/\lambda$, but also on the type of the reciprocal lattice point h, k, l; the anisotropy of the TDS correction among the reciprocal-lattice points is characterized by the tensor $\boldsymbol{\Delta\beta}$.

Cubic crystal

If the crystal lattice is orthogonal, the Cartesian axes for which the elastic constants are given can be taken as parallel to the three crystallographic ones. Thus, the transformation matrix $\boldsymbol{\sigma}$ is reduced to

$$\boldsymbol{\sigma} = \begin{pmatrix} a^* & 0 & 0 \\ 0 & b^* & 0 \\ 0 & 0 & c^* \end{pmatrix} , \tag{22}$$

where a^*, b^* and c^* are the reciprocal cell parameters. Obviously, $a^* = b^* = c^*$ for the case of a cubic lattice, so that we have

$$\Delta\beta_{lm} = \frac{k_B T}{(2\pi)^3} a^{*2} \iiint \frac{(\mathbf{A}^{-1})_{lm}}{q^2} \, \mathrm{d}^3 q \,. \tag{23}$$

Furthermore, since the elastic constants are reduced to three independent non-zero values C_{11} $(=C_{22}=C_{33})$, C_{12} $(=C_{13}=C_{23})$ and C_{44} $(=C_{55}=C_{66})$ in this case, $\mathbf{A}_{lm}$ which is given in the Appendix is reduced simply to

$$\begin{aligned} A_{11} &= C_{11}\hat{q}_x^2 + C_{44}\hat{q}_y^2 + C_{44}\hat{q}_z^2 \\ A_{22} &= C_{44}\hat{q}_x^2 + C_{11}\hat{q}_y^2 + C_{44}\hat{q}_z^2 \\ A_{33} &= C_{44}\hat{q}_x^2 + C_{44}\hat{q}_y^2 + C_{11}\hat{q}_z^2 \\ A_{12} &= (C_{12} + C_{44})\hat{q}_x\hat{q}_y \\ A_{13} &= (C_{12} + C_{44})\hat{q}_x\hat{q}_z \\ A_{23} &= (C_{12} + C_{44})\hat{q}_y\hat{q}_z \end{aligned} \tag{24a}$$

and $(\mathbf{A}^{-1})_{lm}$ is given as

$$\begin{aligned} (\mathbf{A}^{-1})_{11} &= (A_{22}A_{33} - A_{23}A_{23})/\Delta \\ (\mathbf{A}^{-1})_{22} &= (A_{11}A_{33} - A_{13}A_{13})/\Delta \\ (\mathbf{A}^{-1})_{33} &= (A_{11}A_{22} - A_{12}A_{12})/\Delta \\ (\mathbf{A}^{-1})_{12} &= (A_{23}A_{13} - A_{12}A_{33})/\Delta \\ (\mathbf{A}^{-1})_{13} &= (A_{12}A_{23} - A_{22}A_{13})/\Delta \\ (\mathbf{A}^{-1})_{23} &= (A_{12}A_{13} - A_{11}A_{23})/\Delta \end{aligned} \tag{24b}$$

where $\Delta = \det|\mathbf{A}|$.

It is easily seen from the relations (24) that $(\mathbf{A}^{-1})_{lm}$ has the following characteristics with respect to $\hat{q}_x$, $\hat{q}_y$ and $\hat{q}_z$:

(1) For all $l=m$

$$\begin{aligned} \mathbf{A}^{-1}(-\hat{q}_x,\hat{q}_y,\hat{q}_z)_{11} &= \mathbf{A}^{-1}(\hat{q}_x,-\hat{q}_y,\hat{q}_z)_{11} \\ &= \mathbf{A}^{-1}(\hat{q}_x,\hat{q}_y,-\hat{q}_z)_{11} \\ &= \mathbf{A}^{-1}(\hat{q}_x,\hat{q}_y,\hat{q}_z)_{11} \,. \end{aligned} \tag{25a}$$

(2) For all $l \neq m$

$$\begin{aligned} \mathbf{A}^{-1}(-\hat{q}_x,\hat{q}_y,\hat{q}_z)_{lm} &= -\mathbf{A}^{-1}(\hat{q}_x,\hat{q}_y,\hat{q}_z)_{lm} \\ \mathbf{A}^{-1}(\hat{q}_x,-\hat{q}_y,\hat{q}_z)_{lm} &= -\mathbf{A}^{-1}(\hat{q}_x,\hat{q}_y,\hat{q}_z)_{lm} \\ \mathbf{A}^{-1}(\pm\hat{q}_x,0,0)_{lm} &= \mathbf{A}^{-1}(0,\pm\hat{q}_y,0)_{lm} \\ &= \mathbf{A}^{-1}(0,0,\pm\hat{q}_z)_{lm} = 0 \,. \end{aligned} \tag{25b}$$

If we substitute these relations into equation (23) and then perform the integral over a volume which is symmetrical around a reciprocal-lattice point, we find that $\boldsymbol{\Delta\beta}_{lm} = 0$ unless $l=m$ so that $\boldsymbol{\Delta\beta}$ is given in matrix notation as

$$\begin{pmatrix} \beta_{11} & 0 & 0 \\ 0 & \beta_{22} & 0 \\ 0 & 0 & \beta_{33} \end{pmatrix} . \tag{26}$$

The relation that all the off-diagonal components are zero arises from the characteristics of the tensor $(\mathbf{A}^{-1})_{lm}$ [see relations (25)]. We can also see from the relations (24) that all the diagonal components $\boldsymbol{\Delta\beta}_{ll}$ are identical in the case of a cubic system. Thus, we obtain a formula for the cubic system,

$$\alpha_1 = \beta_{11}(h^2 + k^2 + l^2) \,. \tag{27}$$

In general, the integral of $\Delta\beta_{11}$ is not easy to evaluate analytically since it involves the triple integral, as can be seen from equation (23). Therefore, several approximations have been considered (Nilsson, 1957; Pryor, 1967; Cooper & Rouse, 1968; Jennings, 1970). If the approximation replacing the volume swept out in reciprocal space by a sphere of radius q_m (Pryor, 1967) is adopted, the radial part of the integral can be performed separately. Thus, the triple integral is reduced to a surface integral:

$$\Delta\beta_{11} = \frac{k_B T}{(2\pi)^3} a^{*2} q_m \iint_{\text{surface}} (\mathbf{A}^{-1})_{11} \mathrm{d}\Omega \tag{28}$$

where q_m is the radius of the sphere and $d\Omega$ is $\sin\theta d\theta d\varphi$. If the isotropic approximation for the elastic constants $C_{11}=C_{12}+2C_{44}$ is available, we have

$$(\mathbf{A}^{-1})_{11}=\frac{1}{C_{11}}+\left(\frac{1}{C_{44}}-\frac{1}{C_{11}}\right)(\hat{q}_y^2+\hat{q}_z^2) \tag{29}$$

and the surface integral can be immediately performed as

$$\iint\limits_{\text{surface}}(\mathbf{A}^{-1})_{11}d\Omega=\frac{4\pi}{3}\left(\frac{1}{C_{11}}+\frac{2}{C_{44}}\right). \tag{30}$$

Therefore, we obtain

$$\Delta\beta_{11}=\frac{k_BT}{2\pi^2}\frac{q_m}{3}\left(\frac{1}{C_{11}}+\frac{2}{C_{44}}\right)a^{*2} \tag{31}$$

and the TDS correction α can be written as

$$\alpha=\frac{Q^2k_BTq_m}{2\pi^2C} \tag{32}$$

where

$$Q=a^*\sqrt{h^2+k^2+l^2}$$

and

$$\frac{3}{C}=\frac{1}{C_{11}}+\frac{2}{C_{44}}.$$

This is the formula given by Cochran (1969) for the case of a cubic crystal having isotropic elastic constants. It will be clear that the formulae (27) and (32) are described as a special case of the present expression (21).

Characteristics of $\Delta\boldsymbol{\beta}$

It was shown that the TDS correction α_1 can be given as quadratic in h, k, l and a new tensor $\Delta\boldsymbol{\beta}$ introduced. In this section general properties of this tensor $\Delta\boldsymbol{\beta}$ will be presented.

As seen in the Appendix the matrix $\mathbf{A}$ is symmetric, so that inverse of this, $\mathbf{A}^{-1}$, is necessarily symmetric. Referring to equation (16), it is easily seen that tensor $\mathbf{T}$ is also symmetric. This property ensures that the tensor $\Delta\boldsymbol{\beta}$ given by equation (20) is also symmetric, even if the transformation matrix $\boldsymbol{\sigma}$ is not. Thus, we have $\Delta\beta_{pq}=\Delta\beta_{qp}$ as a general property of $\Delta\boldsymbol{\beta}$.

In above section it was shown that $\Delta\boldsymbol{\beta}$ reduces to a diagonal tensor with $\Delta\beta_{11}=\Delta\beta_{22}=\Delta\beta_{33}$ if the crystal is cubic. This diagonal property of $\Delta\boldsymbol{\beta}$ is also found for the case of the orthorhombic system, although the three components $\Delta\beta_{11}$, $\Delta\beta_{22}$, $\Delta\beta_{33}$ are no longer identical. For the case of tetragonal system, for example, $\Delta\beta_{33}$ is different from the other two. This characteristic comes from the fact that $(\mathbf{A}^{-1})_{33}$ is not identical with $(\mathbf{A}^{-1})_{11}$, since the elastic stiffness constants C_{13}, C_{33} and C_{66} are not equal to C_{12}, C_{11} and C_{44}, respectively, in the case of the tetragonal system.

It is easy to see from this example that tensor $\Delta\beta$ is strongly related to the matrix form of the elastic stiffness constants. We see that such a relation originates in the fact that the TDS contribution to the Bragg intensity comes mainly from the first-order thermal diffuse scattering due to acoustic waves of long wavelength, the velocity of which is completely described by a set of the elastic stiffness constants. In general, with the use of similar considerations the relations in Table 1 are found to exist between the tensor form $\Delta\boldsymbol{\beta}$ and the crystallographic systems. Detailed verification of these relations will be presented in a separate paper.

Table 1. *The tensor* $\Delta\boldsymbol{\beta}$ *for the different crystallographic systems*

Cubic	Tetragonal
$\begin{pmatrix}\Delta\beta_{11} & 0 & 0\\ 0 & \Delta\beta_{11} & 0\\ 0 & 0 & \Delta\beta_{11}\end{pmatrix}$	$\begin{pmatrix}\Delta\beta_{11} & 0 & 0\\ 0 & \Delta\beta_{11} & 0\\ 0 & 0 & \Delta\beta_{33}\end{pmatrix}$
Orthorhombic	Hexagonal
$\begin{pmatrix}\Delta\beta_{11} & 0 & 0\\ 0 & \Delta\beta_{22} & 0\\ 0 & 0 & \Delta\beta_{33}\end{pmatrix}$	$\begin{pmatrix}\Delta\beta_{11} & \frac{1}{2}\Delta\beta_{11} & 0\\ \frac{1}{2}\Delta\beta_{11} & \Delta\beta_{11} & 0\\ 0 & 0 & \Delta\beta_{33}\end{pmatrix}$
Monoclinic	Triclinic and trigonal
$\begin{pmatrix}\Delta\beta_{11} & 0 & \Delta\beta_{13}\\ 0 & \Delta\beta_{22} & 0\\ \Delta\beta_{13} & 0 & \Delta\beta_{33}\end{pmatrix}$	$\begin{pmatrix}\Delta\beta_{11} & \Delta\beta_{12} & \Delta\beta_{13}\\ \Delta\beta_{12} & \Delta\beta_{22} & \Delta\beta_{23}\\ \Delta\beta_{13} & \Delta\beta_{23} & \Delta\beta_{33}\end{pmatrix}$

Influence of TDS on structure analysis

As Nilsson (1957) predicted, neglect of the TDS correction in structure analysis has an effect on the temperature parameters. A qualitative idea of the effects can easily be gained from the characteristics of the tensor $\Delta\boldsymbol{\beta}$.

In equation (2) the TDS correction α can usually be considered to be a small quantity compared with one, so that, neglecting the higher-order correction terms, equation (2) can be replaced by

$$I(B)=I(\text{Obs})\exp(-\tilde{\mathbf{h}}\Delta\boldsymbol{\beta}\mathbf{h}), \tag{33}$$

where α is represented in matrix notation as $\tilde{\mathbf{h}}\Delta\boldsymbol{\beta}\mathbf{h}$, $\tilde{\mathbf{h}}$ and $\mathbf{h}$ being row and column matrices with three components h, k, l respectively. If the observed intensity data $I(\text{Obs})$ are not corrected for the TDS and then they are applied to the crystal structure analysis, the intensities themselves are treated as proportional to the squares of the structure factors. Thus

$$I(\text{Obs})=s|\sum_k f_k\exp(-w_k)\,.\,\exp\{i(\mathbf{Q}\,.\,\mathbf{r}_k)\}|^2 \tag{34}$$

where s is the scale factor, f_k and $\mathbf{r}_k$ are the structure amplitude and the position vector of kth atom, and w_k is the exponent of the temperature factor for the kth atom. Using the temperature parameter tensor $\boldsymbol{\beta}_k$, w_k can be represented in matrix notation as

$$w_k=\tilde{\mathbf{h}}\boldsymbol{\beta}_k\mathbf{h}. \tag{35}$$

Substituting into equation (32), we immediately see that the temperature factor is modified to be

$$\exp\{-(\tilde{\mathbf{h}}\boldsymbol{\beta}_k+\tfrac{1}{2}\Delta\boldsymbol{\beta})\mathbf{h}\}. \tag{36}$$

This means that the true temperature-parameter tensor $\boldsymbol{\beta}_k^{\text{true}}$ is given by the sum of the tensor $\boldsymbol{\beta}_k$ and half of the TDS tensor $\Delta\boldsymbol{\beta}$ as

$$\boldsymbol{\beta}_k^{\text{true}} = \boldsymbol{\beta}_k + \tfrac{1}{2}\Delta\boldsymbol{\beta}. \qquad (37)$$

It should be noticed that the tensor forms of $\boldsymbol{\beta}_k$ and $\Delta\boldsymbol{\beta}$ are different in general. $\boldsymbol{\beta}_k$ is regarded as depending on the symmetry of the position in which the kth atom is located and is obtained from the least-squares analysis, while $\Delta\boldsymbol{\beta}$ depends only on the crystallographic system. This indicates that the thermal ellipsoid $\boldsymbol{\beta}_k$ is modified from the true ellipsoid $\boldsymbol{\beta}_k^{\text{true}}$ by an amount of $\frac{1}{2}\Delta\boldsymbol{\beta}$, if the TDS contribution to the Bragg intensity is not considered. A change in the directions of the principal axes of the thermal ellipsoid is also conceivable.

The magnitude of $\Delta\boldsymbol{\beta}$ will be largest for materials with low elastic constants, such as molecular crystals. Thus, for these soft materials it is particularly important to correct for TDS in the accurate analysis of the electron-density distribution.

Discussion

We have shown that the general expression for the correction of measured integrated intensities for thermal diffuse scattering is expressed by relation (21) for a crystal of any symmetry, if only the first-order TDS due to acoustic modes is considered as a significant contribution. As discussed by Cochran (1969) and Rouse & Cooper (1969), however, the effect of experimental resolution is important, although this correction is too laborious to make in practice. In the present formulation this may be performed by replacing the TDS tensor $\Delta\beta_{lm}$ by

$$\Delta\beta_{lm}^{(R)} = \frac{k_BT}{(2\pi)^3} \sum_{i=l}^{3} \sum_{j=l}^{3} \sigma_{il} \cdot \sigma_{jm} \times \iint_{\mathbf{q}\,\mathbf{q}'} R(\mathbf{q}') \,\frac{\{A^{-1}(\mathbf{q}-\mathbf{q}')\}_{lm}}{|\mathbf{q}-\mathbf{q}'|^2}\, \mathrm{d}^3q'\mathrm{d}^3q\ , \qquad (38)$$

where $R(\mathbf{q}')$ is the resolution function (Als-Nielsen & Dietrich, 1967; Cooper & Nathans, 1968).

In the present paper we have been concerned with the case of X-ray diffraction only, but the whole theory can be also applied to the neutron-diffraction case, provided that the incident neutrons are faster than the velocity of sound in the crystal, as has been pointed out by Willis (1969, 1970).

For the application of the present TDS formula to practical analysis the triple integration of equation (16) has to be evaluated, even if we neglect the effect of the instrumental resolution. This is a laborious task and therefore several approximate methods have been proposed for the case of the cubic crystal. These approximations will be applicable for the general case, but the approximation replacing the volume swept out in reciprocal space by a sphere of the same volume seems to be the most convenient in the present formula. The practical method of evaluation and comparison with other calculations and observations will be given in a separate paper.

APPENDIX

$$A_{lm} = \sum_{pq} C_{pl,qm} \cdot \hat{q}_p \cdot \hat{q}_q$$

A is a symmetric 3 × 3 matrix and the independent six elements of **A** are given in the explicit formulation as follows:

$$A_{11} = C_{11}\hat{q}_x^2 + C_{66}\hat{q}_y^2 + C_{55}\hat{q}_z^2 + 2C_{56}\hat{q}_y\hat{q}_z + 2C_{15}\hat{q}_z\hat{q}_x + 2C_{16}\hat{q}_x\hat{q}_y$$

$$A_{22} = C_{66}\hat{q}_x^2 + C_{22}\hat{q}_y^2 + C_{44}\hat{q}_z^2 + 2C_{24}\hat{q}_y\hat{q}_z + 2C_{46}\hat{q}_z\hat{q}_x + 2C_{26}\hat{q}_x\hat{q}_y$$

$$A_{33} = C_{55}\hat{q}_x^2 + C_{44}\hat{q}_y^2 + C_{33}\hat{q}_z^2 + 2C_{34}\hat{q}_y\hat{q}_z + 2C_{35}\hat{q}_z\hat{q}_x + 2C_{45}\hat{q}_x\hat{q}_y$$

$$A_{12} = C_{16}\hat{q}_x^2 + C_{26}\hat{q}_y^2 + C_{45}\hat{q}_z^2 + (C_{25} + C_{46})\hat{q}_y\hat{q}_z + (C_{14} + C_{56})\hat{q}_z\hat{q}_x + (C_{12} + C_{66})\hat{q}_x\hat{q}_y$$

$$A_{13} = C_{15}\hat{q}_x^2 + C_{46}\hat{q}_y^2 + C_{35}\hat{q}_z^2 + (C_{36} + C_{45})\hat{q}_y\hat{q}_z + (C_{13} + C_{55})\hat{q}_z\hat{q}_x + (C_{14} + C_{56})\hat{q}_x\hat{q}_y$$

$$A_{23} = C_{56}\hat{q}_x^2 + C_{24}\hat{q}_y^2 + C_{34}\hat{q}_z^2 + (C_{23} + C_{44})\hat{q}_y\hat{q}_z + (C_{36} + C_{45})\hat{q}_z\hat{q}_x + (C_{25} + C_{46})\hat{q}_x\hat{q}_y\ .$$

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