Nous pensons que le phénomène important dans la formation et les propriétés de cette phase est la mise en ordre dans les plans d'empilement, comme le suggèrent les résultats obtenus à haute température. La propagation de cet ordre sur une période de 27 plans pose un problème non résolu à ce jour.

Sato *et al.* (1967) ont lié les modulations d'empilement périodiques aux modulations d'ordre des antiphases périodiques, ces deux phénomènes apparaissant simultanément dans les exemples qu'ils traitent. Dans le cas de $Au_{11}Mn_4$, à aucun moment n'intervient le phénomène d'antiphase. Il n'y a donc pas de raison d'invoquer le même mécanisme de stabilisation pour ces deux types de structure qui peuvent être parfaitement indépendants.

Nous remercions M G. Jéhanno qui nous a fait profiter de son expérience sur les alliages or–manganèse et est à l'origine de ce travail pour la composition $Au_{11}Mn_4$. Nous remercions également M P. Vérine pour sa collaboration dans l'élaboration des échantillons, ainsi que M P. Pério avec qui nous avons eu de nombreuses et fructueuses discussions. Pour la diffraction de neutrons, nous remercions particulièrement MM Mériel, Sougi et Allain.

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Anisotropic Corrections of Measured Integrated Bragg Intensities for Thermal Diffuse Scattering. II

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The method of evaluation for the contribution of TDS to Bragg reflexions is given on the basis of the general formalism developed in the previous paper [Harada & Sakata, *Acta Cryst.* (1974), A**30**, 77–82]. TDS tensor $\Delta\boldsymbol{\beta}$ is expressed by a matrix product as $\tilde{\boldsymbol{\sigma}}\mathbf{T}\boldsymbol{\sigma}$, where $\mathbf{T}$ is the tensor that characterizes the anisotropy of TDS in reciprocal space and $\boldsymbol{\sigma}$ is the transformation matrix of scattering vector from Cartesian axes to crystallographic reciprocal axes. All the components of $\mathbf{T}$ and $\boldsymbol{\sigma}$ are listed in a table for the nine groups of elastic constants for practical use. It is, however, found that there are only seven matrix forms of $\Delta\boldsymbol{\beta}$ corresponding to the seven crystallographic systems. Two different approximations proposed previously for Nillson's formalism in the estimation of the scan area of Bragg reflexion are shown to be available also for the general formula. The numerical calculations of the TDS correction for an NaCl single crystal are made with these approximations and they are compared with the experimental measurements by Renninger and with the results of calculations given with other approximations. No substantial difference is seen among the results of calculations and they are in good agreement with experiments.

1. Introduction

In a kinematical approximation in X-ray and neutron diffraction theory, the first-order thermal diffuse scattering, TDS, due to acoustic lattice vibrations is known to produce sharp maxima at reciprocal-lattice points in addition to the Bragg peaks. If a smooth background is subtracted in the normal way, the observed integrated intensity for the Bragg scattering $I(\text{obs})$ is given in the form

$$I(\text{obs}) = I(\text{Bragg})\,(1+\alpha_1-\alpha_1') \qquad (1)$$

where $\alpha_1 I(\text{Bragg})$ is the contribution from the first-order TDS under the Bragg peak and $\alpha_1' I(\text{Bragg})$ the TDS already corrected in the course of the background subtraction.

Recently it has been shown by the present authors (Harada & Sakata, 1974) that the TDS correction α_1

can be written in a quadratic form in terms of the Miller indices h,k,l as

$$\alpha_1=\Delta\beta_{11}h^2+\Delta\beta_{22}k^2+\Delta\beta_{33}l^2+2\Delta\beta_{12}hk+2\Delta\beta_{23}kl+2\Delta\beta_{13}hl\,, \quad (2)$$

or in an abbreviated matrix notation as

$$\alpha_1=\tilde{\mathbf{h}}\boldsymbol{\Delta\beta}\mathbf{h}\,, \quad (2')$$

where $\mathbf{h}$ is a column vector consisting of the three elements h,k,l, and $\tilde{\mathbf{h}}$ the transpose of the vector $\mathbf{h}$. The anisotropy of TDS among the reciprocal-lattice points is characterized by the tensor $\boldsymbol{\Delta\beta}$ in equation (2), which has 3×3 elements and is symmetric. The form of the tensor $\boldsymbol{\Delta\beta}$ is closely related to the crystallographic system.

Since this formula is quite general, the TDS contribution to the observed integrated Bragg intensity can be estimated for a general crystal without any restrictions due to the crystal symmetry. For practical use of this formula, however, it is necessary to establish a method for evaluation of the tensor $\boldsymbol{\Delta\beta}$. It is the purpose of the present paper to describe a method and then to show the relations existing between the $\boldsymbol{\Delta\beta}$ and the symmetry of the crystal.

2. Expression for tensor $\boldsymbol{\Delta\beta}$

The TDS which contaminates the Bragg scattering is mainly due to acoustic lattice vibrations of small wave vector, which are very well approximated by the elastic waves of long wavelength. Since the nature of such elastic waves can be described by giving a set of elastic constants C_{ij},* the lattice nature of the crystal does not appear in the TDS in this limit. It is, therefore, usual and convenient to describe such TDS with respect to the Cartesian coordinate axes for which the elastic constants are given, instead of the crystallographic axes.

The intensity distribution of the first-order TDS in reciprocal space is given in a quadratic form in terms of the three components of the scattering vector $\mathbf{Q}$ along the orthogonal axes (Harada & Sakata, 1974),

$$J_1(\mathbf{q})=\frac{k_BT}{q^2}\sum_{lm}(\mathbf{A}^{-1})_{lm}Q_lQ_m \quad (3)$$

where $(\mathbf{A}^{-1})_{lm}$ is the element of the inverse matrix of $\mathbf{A}$ which is obtained from the elastic constants C_{ij} and the direction cosines of wave vector $\mathbf{q}$; *i.e.*

$$A_{11}=C_{11}\hat{q}_x^2+C_{66}\hat{q}_y^2+C_{55}\hat{q}_z^2+2C_{56}\hat{q}_y\hat{q}_z+2C_{15}\hat{q}_z\hat{q}_x+2C_{16}\hat{q}_x\hat{q}_y$$
$$A_{22}=C_{66}\hat{q}_x^2+C_{22}\hat{q}_y^2+C_{44}\hat{q}_z^2+2C_{24}\hat{q}_y\hat{q}_z+2C_{46}\hat{q}_z\hat{q}_x+2C_{26}\hat{q}_x\hat{q}_y$$
$$A_{33}=C_{55}\hat{q}_x^2+C_{44}\hat{q}_y^2+C_{33}\hat{q}_z^2+2C_{34}\hat{q}_y\hat{q}_z+2C_{35}\hat{q}_z\hat{q}_x+2C_{45}\hat{q}_x\hat{q}_y$$
$$A_{12}=C_{16}\hat{q}_x^2+C_{26}\hat{q}_y^2+C_{45}\hat{q}_z^2+(C_{25}+C_{46})\hat{q}_y\hat{q}_z+(C_{14}+C_{56})\hat{q}_z\hat{q}_x+(C_{12}+C_{66})\hat{q}_x\hat{q}_y$$
$$A_{13}=C_{15}\hat{q}_x^2+C_{46}\hat{q}_y^2+C_{35}\hat{q}_z^2+(C_{36}+C_{45})\hat{q}_y\hat{q}_z+(C_{13}+C_{55})\hat{q}_z\hat{q}_x+(C_{14}+C_{56})\hat{q}_x\hat{q}_y$$
$$A_{23}=C_{56}\hat{q}_x^2+C_{24}\hat{q}_y^2+C_{34}\hat{q}_z^2+(C_{23}+C_{44})\hat{q}_y\hat{q}_z+(C_{36}+C_{45})\hat{q}_z\hat{q}_x+(C_{25}+C_{46})\hat{q}_x\hat{q}_y\,. \quad (4)$$

Thus, $(\mathbf{A}^{-1})$ forms a 3×3 symmetric tensor and describes the anisotropy of TDS in reciprocal space due to the anisotropic properties of crystals.

The contribution of the TDS to Bragg scattering is given by the integration of equation (3) with respect to $\mathbf{q}$ for the range of measurement in reciprocal space. If we thus introduce a tensor $\mathbf{T}$, the components of which are defined by

$$T_{lm}=\frac{k_BT}{(2\pi)^3}\int\frac{(\mathbf{A}^{-1})_{lm}}{q^2}\,\mathrm{d}^3q\,, \quad (5)$$

we see that the ratio of the TDS to the Bragg intensity, α_1, is also written in a quadratic form by using this tensor,

$$\alpha_1=\sum_l\sum_m T_{lm}Q_lQ_m\,. \quad (6)$$

If the range of the integral in equation (5) is modified so as to be applicable for the background region, the background correction α_1' in equation (1) is also represented by the same form as expression (6).

In the treatment of the Bragg scattering, however, it is extremely useful to express the scattering vector $\mathbf{Q}$ in terms of the Miller indices hkl defined in the crystallographic reciprocal lattice. We then transform the coordinates from the Cartesian axes to the crystallographic reciprocal-lattice axes. By this coordinate transformation expression (6) is rewritten into the quadratic form of expression (2). The tensor $\boldsymbol{\Delta\beta}$ in the expression (2), therefore, is given by

$$\Delta\beta_{lm}=\frac{k_BT}{(2\pi)^3}\sum_p\sum_q\sigma_{lp}\sigma_{mq}\int\frac{(\mathbf{A}^{-1})_{pq}}{q^2}\,\mathrm{d}^3q\,, \quad (7)$$

where $\boldsymbol{\sigma}$ is the 3×3 matrix to transform the scattering vector $\mathbf{Q}$ in the Cartesian axes to the crystallographic reciprocal-lattice axes. In matrix notation $\boldsymbol{\Delta\beta}$ is expressed as

$$\boldsymbol{\Delta\beta}=\tilde{\boldsymbol{\sigma}}\mathbf{T}\boldsymbol{\sigma} \quad (8)$$

where $\tilde{\boldsymbol{\sigma}}$ is the transpose of $\boldsymbol{\sigma}$. In order to evaluate $\boldsymbol{\Delta\beta}$, therefore, it is required to provide all the components of the matrices $\boldsymbol{\sigma}$ and $\mathbf{T}$ for crystals with symmetries.

3. Matrix form of $\boldsymbol{\sigma}$

The definition of the transformation matrix $\boldsymbol{\sigma}$ in equation (7) is the following, *i.e.* in terms of this matrix $\boldsymbol{\sigma}$ and the Miller indices hkl, we can write the three components of the scattering vector $\mathbf{Q}$ along the orthogonal axes as,

* For the expression of elastic constants, two suffices are used for convenience.

$$Q_x = \sigma_{11}h + \sigma_{12}k + \sigma_{13}l$$
$$Q_y = \sigma_{21}h + \sigma_{22}k + \sigma_{23}l$$
$$Q_z = \sigma_{31}h + \sigma_{32}k + \sigma_{33}l \,. \tag{9}$$

Thus, if the direction cosines of the reciprocal-lattice vector $\mathbf{a}^*$ to the Cartesian axes are denoted by d_{11}, d_{21}, d_{31} and of $\mathbf{b}^*$ and $\mathbf{c}^*$ by d_{12}, d_{22}, d_{32} and d_{13}, d_{23}, d_{33}, $\boldsymbol{\sigma}$ is expressed by

$$\boldsymbol{\sigma} = \begin{pmatrix} a^*d_{11} & b^*d_{12} & c^*d_{13} \\ a^*d_{21} & b^*d_{22} & c^*d_{23} \\ a^*d_{31} & b^*d_{32} & c^*d_{33} \end{pmatrix}, \tag{10}$$

where we have a simple relation among the direction cosines

$$d_{1j}^2 + d_{2j}^2 + d_{3j}^2 = 1 \,. \tag{11}$$

According to Nye (1957), the x axis of the Cartesian system is taken to be parallel to the crystallographic a axis and the z axis is in the ac plane. In this geometry the y axis becomes parallel to the b^* axis. This geometry gives directly $d_{12}=0$, $d_{22}=1$ and $d_{32}=0$. Since the c^* axis is normal to the ab plane, $d_{13}=0$ is also obtained. The relation between the Cartesian axes xyz and the crystallographic axes abc is illustrated in Fig. 1(a) for the triclinic system. From Fig. 1(a) it is seen that the components of $\boldsymbol{\sigma}$ can be written as

$$\boldsymbol{\sigma} = \begin{bmatrix} \dfrac{\delta}{\sin\alpha} a^* & 0 & 0 \\ \dfrac{\cos\alpha\cos\beta - \cos\gamma}{\sin\alpha\sin\beta} a^* & b^* & \dfrac{\cos\beta\cos\gamma - \cos\alpha}{\sin\beta\sin\gamma} c^* \\ \dfrac{-\delta\cos\beta}{\sin\alpha\sin\beta} a^* & 0 & \dfrac{\delta}{\sin\beta\sin\gamma} c^* \end{bmatrix}, \tag{12}$$

where $\delta^2 = 1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma$. If we substitute appropriate angles for α, β and γ in the expression (12), the transformation matrix for any other crystallographic system with higher symmetry except the trigonal system can be easily obtained.

For the trigonal system, it is much easier to choose the Cartesian axes another way, as illustrated in Fig. 1(b): the z axis is taken to be along the [111] direction and the x axis parallel to the projection of the a axis on the (111) plane. In this geometry, as seen from Fig. 1(b), $\boldsymbol{\sigma}$ is expressed by

$$\boldsymbol{\sigma} = \begin{pmatrix} a^*\sin\chi^* & (b^*/2)\sin\chi^* & -(c^*/2)\sin\chi^* \\ 0 & (\sqrt{3}b^*/2)\sin\chi^* & -(\sqrt{3}c^*/2)\sin\chi^* \\ a^*\cos\chi^* & b^*\cos\chi^* & c^*\cos\chi^* \end{pmatrix} \tag{13}$$

where

$$a^* = b^* = c^*$$
$$\sin\chi^* = \sqrt{2(1-\cos a^*)/3}$$
$$\cos\chi^* = \sqrt{(1+2\cos\alpha^*)/3} \,.$$

By using the two expressions (12) and (13), the transformation matrix $\boldsymbol{\sigma}$ can be obtained for crystals of any crystallographic system. For practical use fuller descriptions of $\boldsymbol{\sigma}$ are listed in Table 1 for all the seven crystallographic systems.

4. Integration of T_{lm} for scan volume

In the integral (5) of the expression for T_{lm}, $(\mathbf{A}^{-1})_{lm}$ is given as a function of the direction cosines of wave vector, $\hat{q}_x, \hat{q}_y, \hat{q}_z$. The integral with ıespect to $\mathbf{q}$ is to be taken for the small volume swept out around the reciprocal-lattice point by a counter in the measurement. The region of the integration thus depends on the size of the counter aperture used and also on how the integrated intensity of the Bragg scattering is measured; *i.e.* Ω or θ–2θ scans *etc.* In Fig. 2 the regions of the

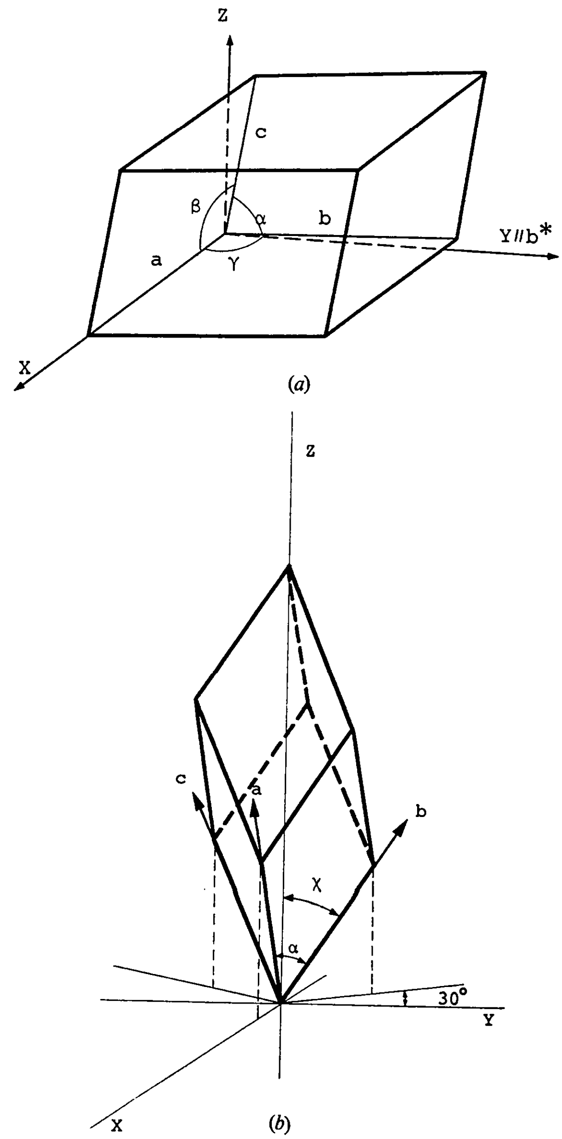

Fig. 1. Relation between the Cartesian axes x,y,z and the crystallographic axes a,b,c; (a) for the triclinic system and (b) for the trigonal system.

Table 1. *The matrices of σ_{pq}, C_{ij}, T_{lm} and $\Delta\beta_{ij}$ for the seven crystallographic systems*

Crystallographic System	Point group	Transformation Matrix $\underset{\sim}{\sigma}$		Elastic Stiffness Constant Tensor $\underset{\sim}{C}$	Expression of $\underset{\sim}{T}$	Expression of $\underset{\sim}{\Delta\beta}$
		Selection of Axes	Expression of $\underset{\sim}{\sigma}$			
Triclinic	1, $\bar{1}$	X // a* Y // b* Z: on the a-c plane	$\begin{pmatrix} \frac{\delta^{+}}{\sin\alpha}a^* & 0 & 0 \\ \frac{\cos\alpha\cos\beta-\cos\gamma}{\sin\alpha\sin\beta}a^* & b^* & \frac{\cos\beta\cos\gamma-\cos\alpha}{\sin\beta\sin\gamma}c^* \\ \frac{-\delta\cos\beta}{\sin\alpha\sin\beta}a^* & 0 & \frac{\delta}{\sin\beta\sin\gamma}c^* \end{pmatrix}$ + $\delta^2 = 1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma$	$\begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ & & C_{33} & C_{34} & C_{35} & C_{36} \\ & & & C_{44} & C_{45} & C_{46} \\ & & & & C_{55} & C_{56} \\ & & & & & C_{66} \end{pmatrix}$	$\begin{pmatrix} T_{11} & T_{12} & T_{13} \\ & T_{22} & T_{23} \\ & & T_{33} \end{pmatrix}$	$\begin{pmatrix} \Delta\beta_{11} & \Delta\beta_{12} & \Delta\beta_{13} \\ & \Delta\beta_{22} & \Delta\beta_{23} \\ & & \Delta\beta_{33} \end{pmatrix}$
Monoclinic	m 2 2/m	X // a Y // b Z // c*	$\begin{pmatrix} a^*\sin\beta & 0 & 0 \\ 0 & b^* & 0 \\ -a^*\cos\beta & 0 & c^* \end{pmatrix}$	$\begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & C_{15} & 0 \\ & C_{22} & C_{23} & 0 & C_{25} & 0 \\ & & C_{33} & 0 & C_{35} & 0 \\ & & & C_{44} & 0 & C_{46} \\ & & & & C_{55} & 0 \\ & & & & & C_{66} \end{pmatrix}$	$\begin{pmatrix} T_{11} & 0 & T_{13} \\ & T_{22} & 0 \\ & & T_{33} \end{pmatrix}$	$\begin{pmatrix} \Delta\beta_{11} & 0 & \Delta\beta_{13} \\ & \Delta\beta_{22} & 0 \\ & & \Delta\beta_{33} \end{pmatrix}$
Trigonal	3, $\bar{3}$	X: on the (111) and (011) planes. Y: on the (111) plane Z // <111>	$\begin{pmatrix} a^*\sin\chi^* & -\frac{b^*}{2}\sin\chi^* & -\frac{c^*}{2}\sin\chi^* \\ 0 & \frac{\sqrt{3}b^*}{2}\sin\chi^* & -\frac{\sqrt{3}c^*}{2}\sin\chi^* \\ a^*\cos\chi^* & b^*\cos\chi^* & c^*\cos\chi^* \end{pmatrix}$ where $a^* = b^* = c^*$ $\sin\chi^* = \sqrt{2(1-\cos\alpha^*)/3}$ $\cos\chi^* = \sqrt{2(0.5+\cos\alpha^*)/3}$	$\begin{pmatrix} C_{13} & C_{12} & C_{13} & C_{14} & -C_{15} & 0 \\ & C_{11} & C_{13} & -C_{14} & C_{15} & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 2C_{15} \\ & & & & C_{44} & 2C_{14} \\ & & & & & (C_{11}-C_{12})/2 \end{pmatrix}$	$\begin{pmatrix} T_{11} & T_{12} & T_{13} \\ & T_{22} & T_{23} \\ & & T_{33} \end{pmatrix}$	$\begin{pmatrix} \Delta\beta_{11} & \Delta\beta_{12} & \Delta\beta_{13} \\ & \Delta\beta_{22} & \Delta\beta_{23} \\ & & \Delta\beta_{33} \end{pmatrix}$
	$\bar{3}$m, 32, 3m			$\begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ & C_{11} & C_{13} & -C_{14} & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 2C_{14} \\ & & & & & (C_{11}-C_{12})/2 \end{pmatrix}$	$\begin{pmatrix} T_{11} & 0 & 0 \\ & T_{11} & T_{23} \\ & & T_{33} \end{pmatrix}$	
Hexagonal	6, $\bar{6}$, 6/m, $\bar{6}$m2, 6mm, 622, 6/mmm	X // a Y // b* Z // c	$\begin{pmatrix} \frac{2}{3}a^* & 0 & 0 \\ \frac{1}{2}a^* & b^* & 0 \\ 0 & 0 & c^* \end{pmatrix}$	$\begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{11} & C_{13} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & (C_{11}-C_{12})/2 \end{pmatrix}$	$\begin{pmatrix} T_{11} & 0 & 0 \\ & T_{11} & 0 \\ & & T_{33} \end{pmatrix}$	$\begin{pmatrix} \Delta\beta_{11} & \frac{1}{2}\Delta\beta_{11} & 0 \\ & \Delta\beta_{11} & 0 \\ & & \Delta\beta_{33} \end{pmatrix}$
Orthorhombic	mm2, 222, mmm	X // a Y // b Z // c	$\begin{pmatrix} a^* & 0 & 0 \\ 0 & b^* & 0 \\ 0 & 0 & c^* \end{pmatrix}$	$\begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{22} & C_{23} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{55} & 0 \\ & & & & & C_{66} \end{pmatrix}$	$\begin{pmatrix} T_{11} & 0 & 0 \\ & T_{22} & 0 \\ & & T_{33} \end{pmatrix}$	$\begin{pmatrix} \Delta\beta_{11} & 0 & 0 \\ & \Delta\beta_{22} & 0 \\ & & \Delta\beta_{33} \end{pmatrix}$
Tetragonal	4, $\bar{4}$, 4/m	X // a Y // b Z // c	$\begin{pmatrix} a^* & 0 & 0 \\ 0 & a^* & 0 \\ 0 & 0 & c^* \end{pmatrix}$	$\begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ & C_{11} & C_{13} & 0 & 0 & -C_{16} \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & C_{66} \end{pmatrix}$	$\begin{pmatrix} T_{11} & 0 & 0 \\ & T_{11} & 0 \\ & & T_{33} \end{pmatrix}$	$\begin{pmatrix} \Delta\beta_{11} & 0 & 0 \\ & \Delta\beta_{11} & 0 \\ & & \Delta\beta_{33} \end{pmatrix}$
	$\bar{4}$2m, 4mm, 422, 4/mmm			$\begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{11} & C_{13} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & C_{66} \end{pmatrix}$		
Cubic	23, m3, $\bar{4}$3m, 432, m3m	X // a Y // b Z // c	$\begin{pmatrix} a^* & 0 & 0 \\ 0 & a^* & 0 \\ 0 & 0 & a^* \end{pmatrix}$	$\begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ & C_{11} & C_{12} & 0 & 0 & 0 \\ & & C_{11} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & C_{44} \end{pmatrix}$	$\begin{pmatrix} T_{11} & 0 & 0 \\ & T_{11} & 0 \\ & & T_{11} \end{pmatrix}$	$\begin{pmatrix} \Delta\beta_{11} & 0 & 0 \\ & \Delta\beta_{11} & 0 \\ & & \Delta\beta_{11} \end{pmatrix}$

integrations are shown schematically for Ω and θ–2θ scans. As seen from the figures, the regions around the reciprocal-lattice point are not simple and convenient forms for the evaluation, so that it is necessary to make approximations.

It should be noticed, however, that the integration is very similar to that encountered in Nillson's (1957) formalism for the TDS correction of the cubic system, for which several approximations have so far been considered for the evaluation. These approximations can be applied to the present general form.

(a) Spherical-volume approximation

Pryor (1966) proposed replacing the region of the integral by a sphere of appropriate volume. With this approximation the radial part of the integral (5) can be evaluated separately and then the triple integral is reduced to a surface integral;

$$T_{lm}=\frac{k_BT}{(2\pi)^3}\,q_m\iint(\mathbf{A}^{-1})_{lm}\mathrm{d}S\,, \tag{15}$$

where q_m is the radius of the sphere and $\mathrm{d}S$ is an element of area on the surface. The double integral in expression (15) can be easily evaluated if the numerical Gauss method is employed with the use of an electronic computor.

Cochran (1969) has suggested replacing the volume swept out in reciprocal space by a sphere of the same volume. By the use of this approximation, the radius q_m is given in the form

$$\frac{4\pi}{3}\,q_m{}^3=(2\pi/\lambda)^3\,(\sin 2\theta)\Omega\psi_1\psi_2 \tag{16}$$

for the Ω scan, where ψ_1 and ψ_2 are the horizontal and vertical divergence angles of the counter aperture subtended at a specimen position and Ω the angle rotated around the vertical axis in the measurement. We can easily extend this method to the case of a θ–2θ scan and we have

$$\frac{4\pi}{3}\,q_m{}^3=\left(\frac{2\pi}{\lambda}\right)^3\sin 2\theta\left(2\sin\frac{\Omega}{2}\right)\psi_1\psi_2\,. \tag{17}$$

The geometrical relations between scan volume and the sphere replacing it are illustrated also in Figs. 2(*a*) and (*b*) for the two scan modes.

(b) Approximation by taking average value of $(\mathbf{A}^{-1})_{lm}$

In the formulation for a cubic crystal Nillson (1957) has replaced the quantity corresponding to the $(\mathbf{A}^{-1})_{lm}$ in the present formula (5) by its average value and taken it out of the integral. When this approximation is extended to the present general case, T_{lm} can be written as

$$T_{lm}=\frac{k_BT}{(2\pi)^3}\,\langle(\mathbf{A}^{-1})_{lm}\rangle\int\frac{1}{q^2}\,\mathrm{d}^3q\,, \tag{18}$$

where $\langle(\mathbf{A}^{-1})_{lm}\rangle$ is the average value of $(\mathbf{A}^{-1})_{lm}$. It has been also shown by Nillson (1957) that for an Ω scan the integration can be performed analytically, if the height of a counter aperture is taken to be infinite. For the more practical case where the counter aperture has a finite size, Cooper & Rouse (1968) have shown that the triple integral is reduced to the double integral for which numerical calculation can be made by computer.*

Since, in principle, the average value $\langle(\mathbf{A}^{-1})_{lm}\rangle$ is represented by

$$\langle(\mathbf{A}^{-1})_{lm}\rangle=\frac{1}{4\pi}\iint(\mathbf{A}^{-1})_{lm}\mathrm{d}S\,, \tag{19}$$

expression (18) is rewritten as

$$T_{lm}=\frac{k_BT}{(2\pi)^3}\,\varrho\,\frac{1}{4\pi}\iint(\mathbf{A}^{-1})_{lm}\mathrm{d}S\,, \tag{20}$$

where the integral of $(1/q^2)$ for the scan volume is denoted by ϱ. It should be noticed that the expression

* Different approximations have been considered by Skelton & Katz (1969) and Jennings (1970). All these approximations may also be available for the present integration (18), without many modifications.

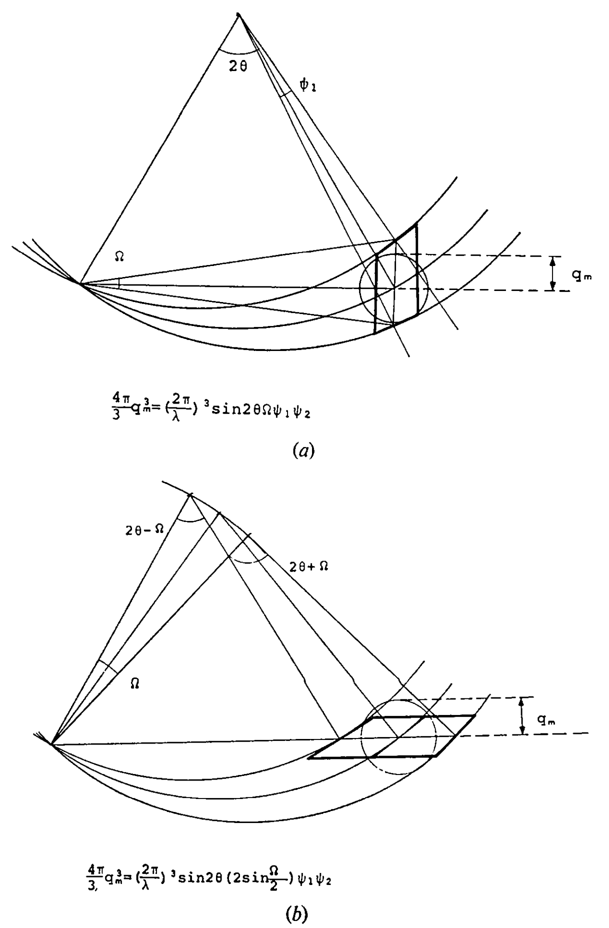

Fig. 2. Integral regions in reciprocal space swept out by the counter in measurement; (*a*) for the Ω scan and (*b*) for the θ–2θ scan.

(15) coincides with (20), if the integral ϱ is replaced by $4\pi q_m$.

5. Symmetry of the crystal and tensor T_{lm}

It is seen from equations (15) and (20) that the matrix form of the tensor T_{lm} depends very much upon the average value of $(\mathbf{A}^{-1})_{lm}$ for both the approximations. If all the components of the elastic-constant tensor are known, $(\mathbf{A}^{-1})_{lm}$ can be easily obtained as a function of $\hat{q}_x, \hat{q}_y$ and $\hat{q}_z$. The matrix form of the elastic constants is classified into nine groups as listed in Table 1; there are two forms for the trigonal and the tetragonal systems and one for each of the other systems, *i.e.* triclinic, monoclinic, hexagonal, orthorhombic and cubic systems. However, there are eight forms of T_{lm} for these nine groups, since T_{lm} for the two groups of the tetragonal system can be reduced to one. This can be proved as follows.

One of the subgroups belonging to the tetragonal system has point-group symmetry $4/m$, 4 or $\bar{4}$ and the other 42, $4mmm$, $4/mmm$ or $\bar{4}2m$. The elastic constant matrix of the former subgroup is represented as

$$\begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ & C_{11} & C_{13} & 0 & 0 & -C_{16} \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & C_{66} \end{pmatrix} . \quad (21)$$

Then, we have

$$\begin{aligned} A_{11} &= C_{11}\hat{q}_x^2 + C_{66}\hat{q}_y^2 + C_{44}\hat{q}_z^2 + 2C_{16}\hat{q}_x\hat{q}_y \\ A_{22} &= C_{66}\hat{q}_x^2 + C_{11}\hat{q}_y^2 + C_{44}\hat{q}_z^2 - 2C_{16}\hat{q}_x\hat{q}_y \\ A_{33} &= C_{44}\hat{q}_x^2 + C_{44}\hat{q}_y^2 + C_{33}\hat{q}_z^2 \\ A_{12} &= C_{16}\hat{q}_x^2 - C_{16}\hat{q}_y^2 + (C_{12}+C_{66})\hat{q}_x\hat{q}_y \\ A_{13} &= (C_{13}+C_{44})\hat{q}_z\hat{q}_x \\ A_{23} &= (C_{13}+C_{44})\hat{q}_y\hat{q}_z . \end{aligned} \quad (22)$$

From the definition of the inverse matrix, $(\mathbf{A}^{-1})_{lm}$ is given as

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

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

We see from equations (22) and (23) that the following relations exist for the diagonal components;

$$\begin{aligned} (\mathbf{A}^{-1})_{11} &= f(\hat{q}_x, \hat{q}_y, \hat{q}_z) - 2C_{16}\hat{q}_x\hat{q}_y g(\hat{q}_x, \hat{q}_y, \hat{q}_z) \\ (\mathbf{A}^{-1})_{22} &= f(\hat{q}_y, \hat{q}_x, \hat{q}_z) - 2C_{16}\hat{q}_x\hat{q}_y g(\hat{q}_x, \hat{q}_y, \hat{q}_z) \\ (\mathbf{A}^{-1})_{33} &= h(\hat{q}_x, \hat{q}_y, \hat{q}_z) + 2C_{16}\hat{q}_x\hat{q}_y\{i(\hat{q}_x, \hat{q}_y, \hat{q}_z) \\ &\quad - i(\hat{q}_y, \hat{q}_x, \hat{q}_z)\} + C_{16}(\hat{q}_x^2 - \hat{q}_y^2)(\hat{q}_x^2 + \hat{q}_y^2 + 1) \end{aligned} \quad (24)$$

where $f(\hat{q}_x, \hat{q}_y, \hat{q}_z)$, $g(\hat{q}_x, \hat{q}_y, \hat{q}_z)$, $h(\hat{q}_x, \hat{q}_y, \hat{q}_z)$ and $i(\hat{q}_x, \hat{q}_y, \hat{q}_z)$ are all the even functions of $\hat{q}_x$, $\hat{q}_y$ and $\hat{q}_z$. Since the surface integral of $(\mathbf{A}^{-1})_{lm}$ of equations (15) and (20) is equivalent to taking the summation of $(\mathbf{A}^{-1})_{lm}$ for all the directions of $\hat{\mathbf{q}}$, we see that

$$\begin{aligned} \sum_{\text{all } \mathbf{q}} f(\hat{q}_x, \hat{q}_y, \hat{q}_z) &= \sum f(\hat{q}_y, \hat{q}_x, \hat{q}_z) \\ \sum i(\hat{q}_x, \hat{q}_y, \hat{q}_z) &= \sum i(\hat{q}_y, \hat{q}_x, \hat{q}_z) \end{aligned} \quad (25)$$

and $\sum 2C_{16}\hat{q}_x\hat{q}_y \times g(\hat{q}_x, \hat{q}_y, \hat{q}_z)$ is zero, because this is the odd function with respect to q_x and q_y. It should be noted that the function $h(\hat{q}_x, \hat{q}_y, \hat{q}_z)$ is different from $f(\hat{q}_x, \hat{q}_y, \hat{q}_z)$; C_{12} is involved as an off-diagonal component of elastic constants in the function $h(\hat{q}_x, \hat{q}_y, \hat{q}_z)$, while C_{13} in the $f(\hat{q}_x, \hat{q}_y, \hat{q}_z)$. Thus we have

$$T_{11} = T_{22} \neq T_{33} . \quad (26)$$

On the other hand, for the off-diagonal components of $(\mathbf{A}^{-1})_{lm}$, we have

$$\begin{aligned} (\mathbf{A}^{-1})_{12} &= j(\hat{q}_x, \hat{q}_y, \hat{q}_z) + C_{16}k(\hat{q}_x, \hat{q}_y, \hat{q}_z)(\hat{q}_x^2 - \hat{q}_y^2) \\ (\mathbf{A}^{-1})_{23} &= l(\hat{q}_x, \hat{q}_y, \hat{q}_z) + C_{16}m(\hat{q}_x, \hat{q}_y, \hat{q}_z)(\hat{q}_x^2 - \hat{q}_y^2) \\ &\quad - 2C_{16}\hat{q}_x\hat{q}_y m(\hat{q}_y, \hat{q}_x, \hat{q}_z) \\ (\mathbf{A}^{-1})_{13} &= l(\hat{q}_x, \hat{q}_y, \hat{q}_z) + C_{16}m(\hat{q}_x, \hat{q}_y, \hat{q}_z)(\hat{q}_x^2 - \hat{q}_y^2) \\ &\quad + 2C_{16}\hat{q}_x\hat{q}_y m(\hat{q}_y, \hat{q}_x, \hat{q}_z) \end{aligned} \quad (27)$$

where $l(\hat{q}_x, \hat{q}_y, \hat{q}_z)$ and $m(\hat{q}_x, \hat{q}_y, \hat{q}_z)$ are both odd functions of $\hat{q}_z$ and $j(\hat{q}_x, \hat{q}_y, \hat{q}_z)$ an odd function of $\hat{q}_x, \hat{q}_y$, while $k(\hat{q}_x, \hat{q}_y, \hat{q}_z)$ is an even function of $\hat{q}_x, \hat{q}_y, \hat{q}_z$. Summations of these functions over all directions lead to the following relations,

$$\begin{aligned} &\sum_{\text{all } \mathbf{q}} k(\hat{q}_x, \hat{q}\ , \hat{q}_z)(q_x^2 - q_y^2) = 0 \\ &\sum j(\hat{q}_x, \hat{q}_y, \hat{q}_z) = \sum l(\hat{q}_x, \hat{q}_y, \hat{q}_z) = 0 \\ &\sum m(\hat{q}_x, \hat{q}_y, \hat{q}_z) = 0 . \end{aligned} \quad (28)$$

Therefore, we have

$$T_{12} = T_{23} = T_{13} = 0 . \quad (29)$$

For the latter subgroup of the tetragonal system, the elastic-constant matrix is the same as matrix (21) except that $C_{16} = 0$. Under this condition, it is comparatively easy to find the following relations for the elements of the inverse matrix $(\mathbf{A}^{-1})_{lm}$,

$$\begin{aligned} (\mathbf{A}^{-1})_{11} &= f(\hat{q}_x, \hat{q}_y, \hat{q}_z) \\ (\mathbf{A}^{-1})_{22} &= f(\hat{q}_y, \hat{q}_x, \hat{q}_z) \\ (\mathbf{A}^{-1})_{33} &= h(\hat{q}_x, \hat{q}_y, \hat{q}_z) \\ (\mathbf{A}^{-1})_{12} &= j(\hat{q}_x, \hat{q}_y, \hat{q}_z) \\ (\mathbf{A}^{-1})_{23} &= l(\hat{q}_x, \hat{q}_y, \hat{q}_z) \\ (\mathbf{A}^{-1})_{13} &= l(\hat{q}_x, \hat{q}_y, \hat{q}_z) . \end{aligned} \quad (30)$$

By taking the surface integral of these functions, we have

$$T_{11} = T_{22} \neq T_{33} \quad \text{and} \quad T_{12} = T_{23} = T_{13} = 0 .$$

Thus we see that the matrix forms of these two subgroups belonging to the tetragonal system are the same, *i.e.*

$$\begin{pmatrix} T_{11} & 0 & 0 \\ 0 & T_{11} & 0 \\ 0 & 0 & T_{33} \end{pmatrix} . \qquad (31)$$

With the use of a similar consideration, it can be confirmed that the matrix forms of **T** for other groups are those listed in Table 1. An exceptional case can be seen in the trigonal system, where the matrix forms of T_{lm} are different for the two subgroups belonging to this system.

6. Symmetry of the crystal and the tensor $\Delta\boldsymbol{\beta}$

Once the matrix forms of T_{lm} and σ_{pq} are known, the matrix form of $\Delta\beta_{ij}$ can easily be obtained with the relation $\Delta\boldsymbol{\beta}=\tilde{\boldsymbol{\sigma}}\mathbf{T}\boldsymbol{\sigma}$. They are also listed in Table 1. We see that the matrix forms of $\Delta\beta_{ij}$ are the same for the two subgroups of the trigonal system, although the **T** are different. Thus, we see that the matrix form of $\Delta\beta_{ij}$ depends only on the crystallographic system.

7. Background correction term

It should be mentioned here that the background correction α_1' of equation (1) has the same quadratic form as α_1, because the tensor form of T_{lm}' involved in α_1' is determined by the averaged value of $(\mathbf{A}^{-1})_{lm}$ and is not different from that of T_{lm}. It is therefore possible to factorize T_{lm} from α_1' and equation (1) can be reduced to

$$I(\text{obs})=I(\text{Bragg})\,(1+k\alpha_1)\,, \qquad (32)$$

where $k=1-\varrho'/\varrho$, ϱ' being the integral of $\int(1/q^2)\mathrm{d}^3q$ for the range of scan measured in estimating the background. Several methods to estimate k have been proposed for the case of isotropic correction for TDS. These methods can be applied to the present general case without any modifications. No reasonable value of k, however, seems to have been estimated yet. We are tentatively using 0·72 since the value 0·67 proposed by Willis (1969) seems to be a little low.

8. Comparison with experiments

Renninger (1966) has measured the TDS correction $k\alpha_1$ in equation (32) for 820 and 10,2,0 Bragg reflexions of a NaCl single crystal with the use of a perfect-crysta monochromator. It is interesting to compare these with the results of the calculations in the present work and the results of other calculations. In the calculations, ϱ and ϱ' were estimated by the use of Rouse & Cooper's (1968) program for the approximation in which the average value of $(\mathbf{A}^{-1})_{lm}$ is taken and $k=0{\cdot}72$ was employed for the spherical-volume approximation. The results are shown in Fig. 3. As expected, no substantial difference can be seen between the different approaches. All the results are in good agreement with the experiments, although Skelton & Katz's values are a little lower than those from the present calculations. It should be noticed that rather good agreement with the experimental results can be seen in the spherical-volume approximation, in spite of its simplicity.

9. Discussion

According to the general formalism, the TDS correction α_1 is given in a quadratic form in terms of **h**, by introducing the new TDS tensor $\Delta\boldsymbol{\beta}$. However, $\Delta\boldsymbol{\beta}$ must be evaluated for all the reciprocal-lattice points under consideration, because $\Delta\beta_{ij}$ involves an integral over

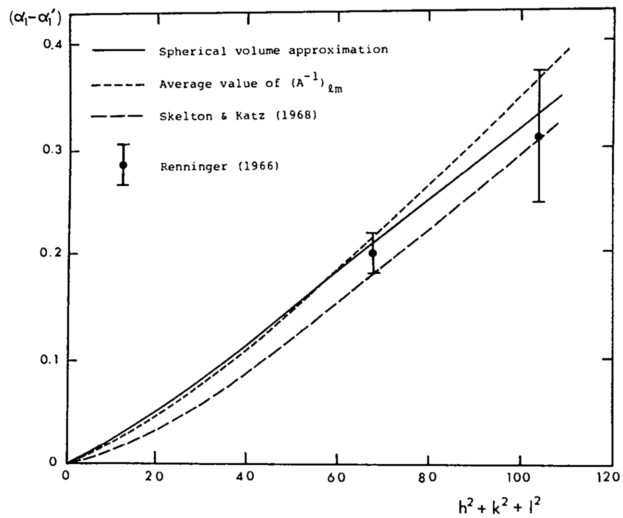

Fig. 3. Comparison of calculated values of $\alpha_1-\alpha_1'$ using the present two approximations with Skelton & Katz's (1968) calculations and Renninger's (1966) measurements for NaCl.

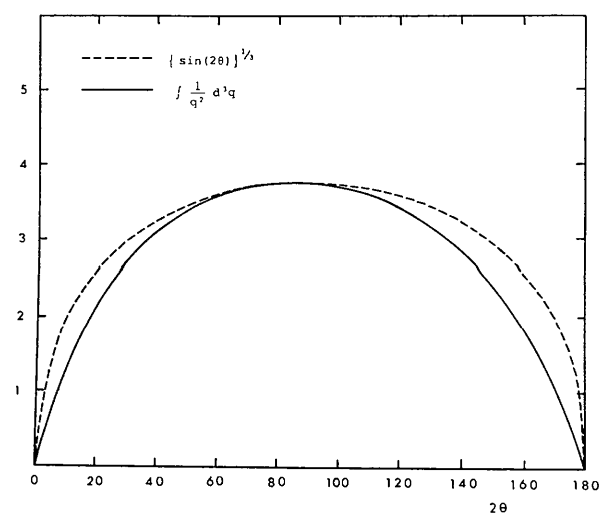

Fig. 4. 2θ-dependence of $\Delta\beta_{ij}$; Solid curve for $(\sin 2\theta)^{1/3}$ and dashed curve for numerical calculation of the integral $\int \mathrm{d}^3q/q^2$. Both curves are normalized at $2\theta=90°$.

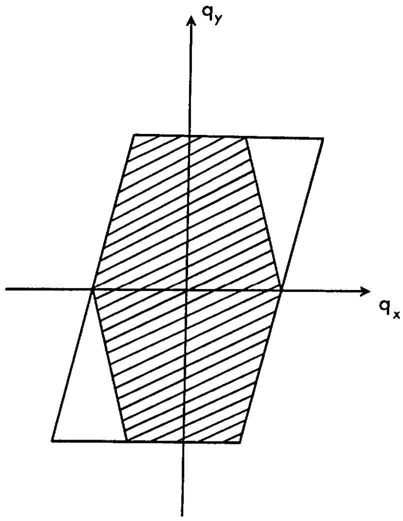

Fig. 5. Schematic illustration of the section of the scan region on the q_xq_y plane. The shaded area has symmetry with respect to both q_x and q_y axes but the parallelogram does not have such symmetry.

an appropriate volume scanned around the reciprocal-lattice point, which depends on the scattering angle 2θ. If we adopt the spherical-volume approximation for the evaluation of $\Delta\beta_{ij}$, we see that $\Delta\beta_{ij}$ depends on 2θ as $(\sin 2\theta)^{1/3}$. In the case of an approximation in which the average of $(\mathbf{A}^{-1})_{lm}$ is taken, however, such simple 2θ dependence is not obtained. In order to show the 2θ dependence of $\Delta\beta_{ij}$ in this approximation and to compare it with $(\sin 2\theta)^{1/3}$ for the spherical-volume approximation, numerical evaluations of the integral $\int d^3q/q^2$ have been made using Rouse & Cooper's (1968) program. The result is shown in Fig. 4. There are some differences between the two, particularly in the low- and high-angle regions.

In § 6, we have shown that the form of matrix $\Delta\beta_{ij}$ depends only on the crystallographic system. It should be noticed that in deriving this result we have implicitly assumed that the three-dimensional integral with respect to $\mathbf{q}$ is rewritten in terms of equations (15) and (18), that is, the surface integral $\iint(\mathbf{A}^{-1})_{lm}dS$ may be taken out of the volume integral $\int(\mathbf{A}^{-1})_{lm}/q^2d^3q$. However, the characteristic feature of T_{lm} is, in principle, given by the integration of $(\mathbf{A}^{-1})_{lm}/q^2$ over the region scanned by the counter near the reciprocal-lattice point. The shape of region does not always have the same symmetry around the reciprocal-lattice point as that of $(\mathbf{A}^{-1})_{lm}$, as shown in Fig. 5. If only the shaded area is taken into acount, off-diagonal components of T_{lm} vanish in the case of cubic and orthorhombic systems, for example, and the matrix form of T_{lm} would be the same as in Table 1. If the integral of the remaining area is taken into acount, however, the integral of the off-diagonal component $\{(\mathbf{A}^{-1})_{lm}/q^2\}$ will not be zero. Thus, it should be understood that matrix forms of T_{lm} or $\Delta\beta_{ij}$ also depend on the shape of the scan volume, in the strict sense. It would, however, be safe to ignore this effect, since the contribution from the non-shaded area in Fig. 5 to the integral $\int[(\mathbf{A}^{-1})_m/q^2]d^3q$ can be regarded as very small, because q is large. In this sense, to compute rigorously the integral of $1/q^2$ over the scan volume may not be a better approximation.

Recently, the advent of energy-dispersive diffractometry, *i.e.* the time-of-flight neutron diffraction technique and the white X-ray diffraction method with SSD (Solid State Detector) has enabled us to measure integrated Bragg intensities. It is easy to extend the present method for TDS correction to these cases by simply modifying the scan volume. In the limit of the spherical-volume approximation this can be done if the quantity q_m defined by the following relation is substituted into equation (15);

$$\frac{4\pi}{3}q_m^3=\left(\frac{2\pi}{\lambda}\right)\frac{\Delta\lambda}{\lambda}2\sin^2\theta\psi_1\psi_2\,,$$

where $\Delta\lambda$ is the width of the wavelength profile with which the Bragg reflexion is observed.

Calculations in the present work were carried out on the FACŌM 230-60 computer of Nagoya University Computation Centre.

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