BONSE, U., SPIEKER, P., HEIN, J.-T. & MATERLIK, G. (1980). *Nucl. Instrum. Methods*, **172**, 223-226.

CROMER, D. T. & LIBERMAN, D. A. (1981). *Acta Cryst.* A**37**, 267-268.

HART, M. & SIDDONS, D. P. (1981). *Proc. R. Soc. London Ser. A*, **376**, 465-482.

HART, M. & SIDDONS, D. P. (1982*a*). *Nucl. Instrum. Methods*, **204**, 219-221.

HART, M. & SIDDONS, D. P. (1982*b*). *EXAFS and Near Edge Structure*, edited by A. BIANCONI, L. INCOCCIA & S. STIPCICH, pp. 373-375. Berlin: Springer.

RODRIGUES, A. R. D. & SIDDONS, D. P. (1979). *J. Phys. E*, **12**, 403-406.

Acta Cryst. (1986). A**42**, 464-469

Secondary Extinction in an Anisotropic Crystal

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Abstract

The formalism for secondary extinction developed by Kato [*Acta Cryst.* (1976), A**32**, 453-457, 458-466] is extended to apply to a crystal with anisotropic strain. If an anisotropic correlation for the lattice phase factors is assumed, the formalism can be developed in the same way as for an isotropic crystal. If the geometric average of the correlation lengths of the phase factors is sufficiently smaller than the extinction distance, the ensemble averages of the intensity fields satisfy a set of energy-transfer equations of the same form as in an isotropic crystal. The distribution function of the deviation angle from the exact Bragg condition for the misorientation model of a crystal is given using the notation introduced by Coppens & Hamilton [*Acta Cryst.* (1970), A**26**, 71-83].

1. Introduction

By using the approximation of secondary extinction developed by Zachariasen (1967), Coppens & Hamilton (1970) have shown that anisotropic extinction is often significant in the refinement of a crystal structure. They presented the formalism for two extreme cases: an anisotropic Gaussian mosaic spread distribution function was assumed for a crystal in which extinction is dominated by mosaic spread, and the average particle shape was described as an ellipsoid for a crystal in which extinction was dominated by particle size.

Becker & Coppens (1973, 1974*a*,*b*) developed a formalism for extinction to remove several inadequacies of the theory of Zachariasen, and then (Becker & Coppens, 1975) extended it to include a crystal of non-spherical shape and also to take into account the anisotropy of mosaic spread and particle size introduced by Coppens & Hamilton.

Becker & Coppens assumed incoherent manyfold rescattering of the beams inside a crystal as an approximation in their theory, but extinction theory is based on the dynamical theory of waves in a crystal, and incoherence is treated by taking a statistical average over the crystal. Assuming that the intensity was given by an ensemble average of the intensity field over a statistical ensemble of distorted crystals, Kato (1976*a*,*b*) proposed a formalism to take the statistical nature of lattice distortions into account. The intensity field in his formalism is calculated from the dynamical theory for a distorted crystal developed by Takagi (1962, 1969).

The formalism developed by Kato is extended to include anisotropy in a crystal in the present paper. If an anisotropic and homogeneous correlation of the lattice phase factors is assumed, the formalism can be developed in the same way from the dynamical theory. The distribution function of the deviation angle from the exact Bragg condition for the misorientation model for a crystal which has elastic strains is given using the notation introduced by Coppens & Hamilton (1970).

2. The correlation of the lattice phase factors

We can calculate the wave field of X-rays in a deformed crystal by a pair of partial differential equations derived by Takagi (1962, 1969),

$$\partial d_o/\partial s_o = i\kappa_{-g} \exp(iG) d_g, \qquad (1a)$$

$$\partial d_g/\partial s_g = i\kappa_g \exp(-iG) d_o, \qquad (1b)$$

where d_o and d_g are the wave fields of the transmitted and diffracted waves, respectively, which will be called o and g waves hereafter, s_o and s_g are the oblique coordinates in real space, the axes of which are taken along the directions of the o and g beams, respectively, and κ_g is the reflection strength,

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proportional to the structure factor F_g,

$$\kappa_g = (\lambda C/v)(e^2/mc^2)F_g, \tag{2}$$

where λ is the wavelength, C is the polarization factor, v is the unit-cell volume, e is the electronic charge, m the electronic mass and c the velocity of light. The phase G is given by

$$G(s_o, s_g) = 2\pi \mathbf{g} \cdot \mathbf{u}(s_o, s_g), \tag{3}$$

where $\mathbf{g}$ is the reflection vector and $\mathbf{u}$ is the displacement of the lattice point from its position in a perfect crystal. The factor $\exp(\pm iG)$ is called a lattice phase factor.

The equations (1) can be written in recurrence form as equations (I-11),*

$$d_o(m+1, n) = d_o(m, n) + i(\kappa_{-g}a)\exp[iG(m, n)]d_g(m, n), \tag{4a}$$

$$d_g(m, n+1) = d_g(m, n) + i(\kappa_g a)\exp[-iG(m, n)]d_o(m, n), \tag{4b}$$

where the arguments (m, n), which may be called position coordinate numbers, are the abbreviations of the coordinates $(s_o, s_g) = (ma, na)$ and a is unit increment of the coordinates, which will be made infinitesimal in the final expression. The intensity is calculated from the wave field above. Kato postulated that the observed intensity was the average of the intensity over a statistical ensemble of displacements from a perfect crystal, and obtained the observed intensity written with the second-order correlation functions of the lattice phase factor, the correlation of which was assumed isotropic and homogeneous.

We shall assume an anisotropic and homogeneous correlation of the phase factors. The distribution function to calculate the ensemble average of the correlation function may have different values for the different directions, and the correlation functions f_o and f_g for o and g directions, respectively, may have different values.

$$f_o(z) = \langle \exp[iG(m+z, n)]\exp[-iG(m, n)]\rangle, \tag{5a}$$

$$f_g(z) = \langle \exp[iG(m, n+z)]\exp[-iG(m, n)]\rangle. \tag{5b}$$

The above functions are complex.

The second-order correlation lengths for the o and g directions are defined by

$$\tau_2^o = \tfrac{1}{2}a\sum_{z=-\infty}^{\infty}|f_o(z)|^2 = \tfrac{1}{2}\int_{-\infty}^{\infty}|f_o(s)|^2\,ds, \tag{6a}$$

$$\tau_2^g = \tfrac{1}{2}a\sum_{z=-\infty}^{\infty}|f_g(z)|^2 = \tfrac{1}{2}\int_{-\infty}^{\infty}|f_g(s)|^2\,ds, \tag{6b}$$

where $f_o(s)$ and $f_g(s)$ are the smoothed functions of $f_o(z)$ and $f_g(z)$.

The terminologies defined by Kato in his paper (II), isolate kink (IK) and kink pair (KP), will be used for the o and g directions, and separation numbers Δ_o and Δ_g are defined for each direction, which are small enough but

$$\Delta_o > \tau_2^o/a, \qquad \Delta_g > \tau_2^g/a, \tag{7}$$

so that $f_o(\Delta)$ and $f_g(\Delta)$ are practically zero. The separation numbers Δ_o and Δ_g are greater than $\bar{x}_i$ and $\bar{y}_i$ in Fig. II-1.

As in (II), we shall describe the details of calculations only for $\langle I_o\rangle$ in the following

3. IK approximation

We consider a pair of routes R_o and R_o' composed of IK's. Their kink points (n_i, m_i) and (n_i', m_i') are assumed to differ by the numbers $(\bar{x}_i, \bar{y}_i)$ which are less than (Δ_o, Δ_g) as mentioned above.

The boundary conditions are given by $\bar{x}_o = \bar{y}_o = \bar{y}_r = 0$ for d_o and $\bar{x}_o = \bar{y}_o = \bar{x}_{r+1} = 0$ for d_g. The phases for the wave fields in equation (I-13) are given by equation (I-15), and the phase factor for the pair of routes R_o and R_o' is given by equation (II-4). Then, it is assumed that

$$\langle \exp i[G(n+x, m+y) - G(n, m)]\rangle = f_o(x)f_g(y). \tag{8}$$

Thus, one obtains

$$\langle \exp i(P_{R_o} - P'_{R_o})\rangle = \prod_{i=1}^{r}|f_o(\bar{x}_i)|^2\prod_{i=1}^{r-1}|f_g(\bar{y}_i)|^2. \tag{9}$$

If the amplitude of the routes R_o and R_o' given in (I-14a) and the phase given in (9) are substituted into (I-16a), the averaged intensity is given by

$$\langle I_o\rangle = |A|^2\sum_{r=1}^{\infty}\alpha_r|\kappa_g\kappa_{-g}|^{2r}a^{4r-2} \times \prod_{i=1}^{r}\mathrm{S}_{\bar{x}_i}|f_o(\bar{x}_i)|^2\prod_{i=1}^{r-1}\mathrm{S}_{\bar{y}_i}|f_g(\bar{y}_i)|^2, \tag{10}$$

where α_r is given by (I-20a) and the sum S is taken over $(-\Delta_o, \Delta_o)$ for f_o and $(-\Delta_g, \Delta_g)$ for f_g. From the definition of the correlation lengths τ_2^o and τ_2^g, we obtain

$$\langle I_o\rangle = |A|^2\sum_{r=1}^{\infty}\frac{1}{r!(r-1)!}|\kappa_g\kappa_{-g}|^{2r} \times (2\tau_2^o s_o)^r(2\tau_2^g s_g)^{r-1} \tag{11a}$$

$$= |A|^2|\kappa_g\kappa_{-g}|(\tau_2^o s_o/\tau_2^g s_g)^{1/2} \times I_1[4|\kappa_g\kappa_{-g}|(\tau_2^o\tau_2^g s_o s_g)^{1/2}], \tag{11b}$$

where I_1 is the modified Bessel function of the first order.

* The equations and figures of the papers by Kato (1976a,b) are referred to by Roman numbers I and II, respectively.

The average distances* between IK's for a single route R_o containing r isolated kinks are estimated to be

$$\tilde{l}_o = s_o/r, \qquad \tilde{l}_g = s_g/r. \tag{12}$$

The sum of terms of higher order than $r \gg \bar{r}$ in (11a) can be neglected provided that

$$\bar{r} \gg 2|\kappa_g \kappa_{-g}|(\tau_2^o \tau_2^g s_o s_g)^{1/2}. \tag{13a}$$

The requirements for the IK approximation

$$\tilde{l}_o > \Delta_o a > \tau_2^o, \qquad \tilde{l}_g > \Delta_g a > \tau_2^g, \tag{13b}$$

must be

$$s_o/\tau_2^o > \bar{r}, \qquad s_g/\tau_2^g > \bar{r}. \tag{13c}$$

Combining conditions (13a) and (13c), one finds that the necessary and sufficient condition for the IK approximation is

$$\begin{aligned} s_o/s_g &\gg 4|\kappa_g \kappa_{-g}|^2 (\tau_2^o)^3 \tau_2^g, \\ s_g/s_o &\gg 4|\kappa_g \kappa_{-g}|^2 \tau_2^o (\tau_2^g)^3. \end{aligned} \tag{13d}$$

Discussion of (13d) will be postponed to the next section because the routes with KP's are of significance in the region where condition (13d) fails.

By using similar procedures one can calculate $\langle I_g \rangle$ as

$$\langle I_g \rangle = |A|^2 |\kappa_g|^2 \sum_{r=0}^{\infty} \frac{1}{r!\,r!} |\kappa_g \kappa_{-g}|^2 (2\tau_2^o s_o)^r (2\tau_2^g s_g)^r \tag{14a}$$

$$= |A|^2 |\kappa_g|^2 I_0[4|\kappa_g \kappa_{-g}|(\tau_2^o \tau_2^g s_o s_g)^{1/2}], \tag{14b}$$

where I_0 is the modified Bessel function of the zeroth order.

4. The improvement by taking KP's into account

We shall consider the associated routes R which have kink pairs in the vicinity of the route R_o. It is assumed that KP's on a route R are mutually independent, and also that a KP is independent of IK's. The assumption is justified if KP's are sufficiently rare. Thus, we take the ensemble averages $\langle \exp(iP_R) \rangle_P$ and $\langle \exp(iP_{R'}) \rangle_P$ over KP's first, then the ensemble average $\langle\ \rangle_k$ over IK's. By definition, $\langle \langle \exp(iP_R) \rangle_P \langle \exp(-iP_{R'}) \rangle_P \rangle_k$ means the ensemble average $\langle\ \rangle$ over all the kinks.

We shall consider the ith vertical segment of R_o and a segment of R which can be produced by adding p kink pairs to it as in (II). The relevant part of the phase factor is given by (II-11), in which the first and last factors are due to IK's and the others to KP's.

The ensemble averages of the phase factor for R and R' over KP's are given by using the notation of (II) as follows:

$$\begin{aligned} \langle \exp(iP_R) \rangle_P = \ldots \exp[iG(n, m)] \prod_{j=1}^{p} f_g(y_j) \\ \times \exp[-iG(n+X, m+y)] \ldots, \end{aligned} \tag{15a}$$

$$\begin{aligned} \langle \exp(-iP_{R'}) \rangle_P = \ldots \exp[-iG(n', m')] \prod_{j=1}^{p'} f_g^*(y_j') \\ \times \exp[iG(n'+X', m'+y')] \ldots. \end{aligned} \tag{15b}$$

With the approximation (8), relations (II-13) and the fact that $f_o(z) = f_o^*(-z)$ and $f_g(z) = f_g^*(z)$, and using the same notation as in (II-15), the phase correlations relevant to IK are given by

$$\begin{aligned} &\langle \exp[iG(n, m)] \exp[-iG(n', m')] \rangle \\ &\quad = f_o(-\bar{x}_- - x'_- + x_-) f_g(-\bar{y}), \end{aligned} \tag{16a}$$

$$\begin{aligned} &\langle \exp[-iG(n+X, m+y)] \exp[iG(n'+X', m'+y')] \rangle \\ &\quad = f_o^*(-\bar{x}_+) f_g^*(-\bar{y} - y' + y). \end{aligned} \tag{16b}$$

The horizontal segments introduce the factors

$$\prod_{j=1}^{q} f_o^*(x_j) \prod_{j=1}^{q'} f_o(x_j'). \tag{17}$$

Thus, one can write the ensemble average of the phase factor in the form

$$\begin{aligned} &\langle \exp[i(P_R - P_{R'})] \rangle = \ldots \\ &\quad \times f_g(-\bar{y}) \prod_{j=1}^{p} f_g(y_j) \prod_{j=1}^{p'} f_g^*(y_j') f_g^*(-\bar{y} - \textstyle\sum y_j' + \sum y_j) \\ &\quad \times f_o^*(-\bar{x}) \prod_{j=1}^{q} f_o^*(x_j) \prod_{j=1}^{q'} f_o(x_j') f_o(-\bar{x} - \textstyle\sum x_j' + \sum x_j) \\ &\quad \times \ldots. \end{aligned} \tag{18}$$

The relation (18) is an extension of (9).

For the first and last segments of d_o and d_g, special care must be taken. The factor $f(\bar{y})$ is unity for the first vertical segments of d_o and d_g because $\bar{x}_o = \bar{y}_o = 0$ for d_o and d_g. In the last $(r+1)$th vertical segment of d_o, $f_g^*(-y - \sum y_j' + \sum y_j)$ is unity because $\bar{y}_r = 0$ for d_o. Similarly, in the last $(r+1)$th horizontal segment of d_g, $f_o(-\bar{x} - \sum x_j' + \sum x_j)$ is unity because $\bar{x}_{r+1} = 0$ for d_g.

The amplitudes of R and R' are given by equations (II-17), and the summations can be carried out over R', R and then R_o in the same way as in (II).

Thus, one can obtain the averaged intensity as shown in (II-18) with equations (II-19) and (II-20). The function $F(p, p')$ and $F(q, q')$ are defined by

$$\begin{aligned} F(p, p') = S_{\bar{y}} \sum_{y_1} \sum_{y_2} \ldots \sum_{y_p} \sum_{y_1'} \sum_{y_2'} \ldots \sum_{y_{p'}'} \\ \times f_g(y_1) f_g(y_2) \ldots f_g(y_p) \\ \times f_g^*(y_1') f_g^*(y_2') \ldots f_g^*(y_{p'}') \\ \times f_g(-\bar{y}) f_g^*(-\bar{y} - \textstyle\sum y_j' + \sum y_j), \end{aligned} \tag{19a}$$

* The symbol $\tilde{l}$ is used instead of l of II. See equation (II-20).

$$F^*(q,q') = S_{\bar{x}} \sum_{x_1} \sum_{x_2} \dots \sum_{x_q} \sum_{x_1'} \sum_{x_2'} \dots \sum_{x_{q'}'} \times f_o^*(x_1) f_o^*(x_2) \dots f_o^*(x_q) \times f_o(x_1') f_o(x_2') \dots f_o(x_{q'}') \times f_o^*(-\bar{x}) f_o(-\bar{x} - \sum x_j' + \sum x_j), \quad (19b)$$

where the summations $\sum$ run from 0 to Δ_0 for $F(q,q')$ and from 0 to Δ_g for $F(p,p')$, and the summations S from $-\Delta_o$ to Δ_o for $F(q,q')$ and from $-\Delta_g$ to Δ_g for $F(p,p')$ except when it applies to the first and the last segments. The quantities p and q denote the numbers of KP's in the vertical and horizontal segments, respectively.

To carry out a kind of conditional summation in (19), we shall use the approximation

$$f_o(-\bar{x} - \sum x_j' + \sum x_j) = f_o(-\bar{x}) \prod_{j=1}^{q} f_o(x_j) \prod_{j=1}^{q'} f_o(-x_j'), \quad (20a)$$

$$f_g^*(-\bar{y} - \sum y_j' + \sum y_j) = f_g^*(-\bar{y}) \prod_{j=1}^{p} f_g^*(y_j) \prod_{j=1}^{p'} f_g^*(-y_j'). \quad (20b)$$

The justification for this follows the same lines as Appendix II-*B*. Under this approximation, one can regard $\bar{y}$, $\{y_j\}$, $\bar{x}$ and $\{x_j\}$ as independent variables. Further, we assume that

$$\tau_2^0 \simeq a \sum_{z=0}^{\infty} |f_o(z)|^2, \qquad \tau_2^g \simeq a \sum_{z=0}^{\infty} |f_g(z)|^2. \quad (21)$$

Then we obtain

$$F(p,p') \simeq (1/a)^{p+p'+1} (\tau_2^g)^{p+p'} (2\tau_2^g), \quad (22a)$$

$$F^*(q,q') \simeq (1/a)^{q+q'+1} (\tau_2^o)^{q+q'} (2\tau_2^o). \quad (22b)$$

For the first vertical segment for d_o and d_g ($\bar{x} = \bar{y} = 0$),

$$F_1(p,p') \simeq (1/a)^{p+p'} (\tau_2^g)^{p+p'}. \quad (22c)$$

For the last vertical segment for d_o ($\bar{y} = 0$),

$$F_{r+1}(p,p') \simeq (1/a)^{p+p'} (\tau_2^g)^{p+p'}. \quad (22d)$$

For the last horizontal segment for d_g ($\bar{x} = 0$),

$$F_{r+1}^*(q,q') \simeq (1/a)^{q+q'} (\tau_2^o)^{q+q'}. \quad (22e)$$

Substituting the relations (II-20) and (22) into (II-19), we have

(first vertical segment)

$$= \exp\{-\tau_2^g[(\kappa_g \kappa_{-g}) l_{0,1} + (\kappa_g^* \kappa_{-g}^*) l_{o,1}']\}, \quad (23a)$$

(*i*th vertical segment)

$$= \exp\{-\tau_2^g[(\kappa_g \kappa_{-g}) l_{o,i} + (\kappa_g^* \kappa_{-g}^*) l_{o,i}'] 2\tau_2^g / a\}, \quad (23b)$$

(*i*th horizontal segment)

$$= \exp\{-\tau_2^0[(\kappa_g \kappa_{-g}) l_{g,i} + (\kappa_g^* \kappa_{-g}^*) l_{g,i}'] 2\tau_2^o / a\}, \quad (23c)$$

[$(r+1)$th vertical segment for d_o]

$$= \exp\{-\tau_2^g[(\kappa_g \kappa_{-g}) l_{o,r+1} + (\kappa_g^* \kappa_{-g}^*) l_{o,r+1}']\}, \quad (23d)$$

[$(r+1)$th horizontal segment for d_g]

$$= \exp\{-\tau_2^o[(\kappa_g \kappa_{-g}) l_{o,r+1} + (\kappa_g^* \kappa_{-g}^*) l_{o,r+1}']\}. \quad (23e)$$

Since

$$\sum_{i=1}^{r+1} l_{o,i} = \sum_{i=1}^{r+1} l_{o,i}' = s_o \quad \text{and} \quad \sum_{i=1}^{r} l_{g,i} = \sum_{i=1}^{r} l_{g,i}' = s_g$$

for d_o, and

$$\sum_{i=1}^{r+1} l_{o,i} = \sum_{i=1}^{r+1} l_{o,i}' = s_o \quad \text{and} \quad \sum_{i=1}^{r+1} l_{g,i} = \sum_{i=1}^{r+1} l_{g,i}' = s_g$$

for d_g, one obtains from (II-18) that

$$\langle I_o \rangle = |A|^2 \exp[-(\kappa_g \kappa_{-g} + \kappa_g^* \kappa_{-g}^*) \times (\tau_2^g \sum_{i=1}^{r+1} l_{oi} + \tau_2^o \sum_{i=1}^{r} l_{g,i})] \times \sum_{R_o} |\kappa_g \kappa_{-g}|^{2r} a^{4r-2} \left(1 \frac{2\tau_2^o}{a}\right) \left(\frac{2\tau_2^g}{a} \frac{2\tau_2^o}{a}\right)^{r-1} \quad (1)$$

$$= |A|^2 \exp[-2\,\mathrm{Re}\,(\kappa_g \kappa_{-g})(\tau_2^g s_o + \tau_2^o s_g)] \times \sum_{R_o} |\kappa_g \kappa_{-g}|^{2r} a^{4r-2} (2\tau_2^o/a)^r (2\tau_2^g/a)^{r-1} \quad (24a)$$

for the o beam, and

$$\langle I_g \rangle = |A|^2 |\kappa_g|^2 \exp\left[-(\kappa_g \kappa_{-g} + \kappa_g^* \kappa_{-g}^*) \times \left(\tau_2^g \sum_{i=1}^{r+1} l_{o,i} + \tau_2^o \sum_{i=1}^{r+1} l_{g,i}\right)\right] \times \sum_{R_o} |\kappa_g \kappa_{-g}|^{2r} a^{4r} \left(1 \frac{2\tau_2^o}{a}\right) \left(\frac{2\tau_2^g}{a} \frac{2\tau_2^o}{a}\right)^{r-1} \left(\frac{2\tau_2^g}{a} 1\right)$$

$$= |A|^2 |\kappa_g|^2 \exp[-2\,\mathrm{Re}\,(\kappa_g \kappa_{-g})(\tau_2^g s_o + \tau_2^o S_g)] \times \sum_{R_o} |\kappa_g \kappa_{-g}|^{2r} a^{4r} (2\tau_2^o/a)^r (2\tau_2^g/a)^r \quad (24b)$$

for the g beam. The segments corresponding to the factors in the above equations are shown in Fig. 1. As in the case of (11) and (14), $\sum_{R_o}$ can be replaced by $\sum_{r=1}^{\infty} \alpha_r$ so that we have finally

$$\langle I_o \rangle = |A|^2 \exp[-2\,\mathrm{Re}\,(\kappa_g \kappa_{-g})(\tau_2^g s_o + \tau_2^o s_g)] \times |\kappa_g \kappa_{-g}| \left(\frac{\tau_2^o s_o}{\tau_2^g s_g}\right)^{1/2} I_1[4|\kappa_g \kappa_{-g}|(\tau_2^o \tau_2^g s_o s_g)^{1/2}] \quad (25a)$$

for the o beam, and

$$\langle I_g \rangle = |A|^2 \exp[-2\,\mathrm{Re}\,(\kappa_g \kappa_{-g})(\tau_2^g s_o + \tau_2^o s_g)] \times |\kappa_g|^2 I_0[4|\kappa_g \kappa_{-g}|(\tau_2^o \tau_2^g s_o s_g)^{1/2}] \quad (25b)$$

for the g beam.

In deriving these results, the essential approximation adopted, which is the same as in (II), is to

represent the correlation of the lattice phases by the product of the second-order correlation function defined by (5). This approximation can be justified when the number of KP's along all vertical segments, $\bar{p}$, that of KP's along all horizontal segments, $\bar{q}$, and that of IK's of type (a) defined in (I), $\bar{r}$, satisfy the condition

$$\bar{p}+\bar{r}<s_o/\Delta_o a<s_o/\tau_2^o, \tag{26a}$$

$$\bar{q}+\bar{r}<s_g/\Delta_g a<s_g/\tau_a^g. \tag{26b}$$

Accordingly, if the higher-order terms in the power-series expansions of the factors in (25) are negligibly small, as mentioned in (II), the above approximation would not harm the final results (25). These conditions are obviously

$$2|\kappa_g\kappa_{-g}|\tau_2^o s_o<\bar{p}, \tag{27a}$$

$$2|\kappa_g\kappa_{-g}|\tau_2^g s_g<\bar{q}, \tag{27b}$$

$$2|\kappa_g\kappa_{-g}|(\tau_2^o\tau_2^g s_o s_g)^{1/2}<\bar{r}, \tag{27c}$$

where $\mathrm{Re}\,(\kappa_g\kappa_{-g})$ and $|\kappa_g\kappa_{-g}|$ are not distinguished. The necessary and sufficient condition for such $\bar{p}$, $\bar{q}$ and $\bar{r}$ is

$$2|\kappa_g\kappa_{-g}|[(\tau_2^o s_o)^{1/2}+(\tau_2^g s_g)^{1/2}]^2<\bar{p}+\bar{q}+2\bar{r}<(s_o/\tau_2^o)+(s_g/\tau_2^g),$$

that is,

$$\begin{aligned}&|\kappa_g\kappa_{-g}|\tau_2^o\tau_2^g\\&\ll\tfrac{1}{2}[(s_o/\tau_2^o)+(s_g/\tau_2^g)\\&\quad\times[(s_o/\tau_2^o)+(s_g/\tau_2^g)+2(s_o s_g/\tau_2^o\tau_2^g)^{1/2}]^{-1}\\&<\tfrac{1}{2}.\end{aligned} \tag{28a}$$

This implies that

$$(\tau_2^o\tau_2^g)^{1/2}\ll\tfrac{1}{2}|\kappa_g\kappa_{-g}|^{-1/2}\sim\Lambda, \tag{28b}$$

where Λ is the *Pendellösung* fringe spacing or primary extinction distance in order of magnitude.

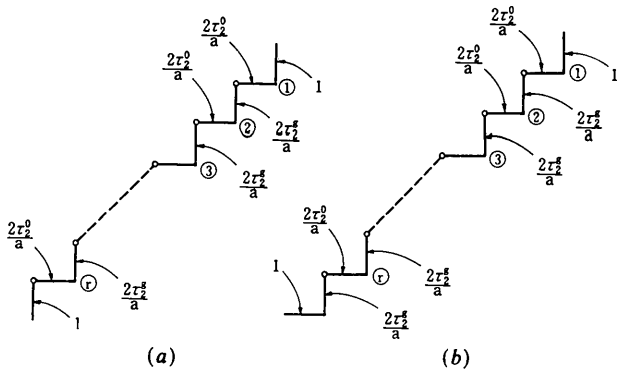

Fig. 1. The difference between the contributions from the vertical and horizontal segments to the o beam (a) and g beam (b) described in equations (24a) and (24b).

Discussion

The formulae (25a,b) are good approximations to $\langle I_o\rangle$ and $\langle I_g\rangle$ under condition (28) and the prescribed boundary conditions (I-12), as in (II). It is a straightforward matter to show that they satisfy the differential equations

$$\partial\langle I_o\rangle/\partial s_o=-2\,\mathrm{Re}\,(\kappa_b\kappa_{-g})\tau_2^g\langle I_o\rangle+2|\kappa_{-g}|^2\tau_2^o\langle I_g\rangle, \tag{29a}$$

$$\partial\langle I_g\rangle/\partial s_g=-2\,\mathrm{Re}\,(\kappa_g\kappa_{\ }\ )\tau_2^o\langle I_g\rangle+2|\kappa_g|^2\tau_2^g\langle I_{\ }\rangle. \tag{29b}$$

These have the same form as (II-30), and are nothing but a set of energy-transfer equations with anisotropic correlation lengths τ_2^o and τ_2^g. Those correlation lengths depend on the character of the assumed statistical ensemble of a distorted crystal, especially on the anisotropy between the o and g directions.

As in (II), it is straightforward to assume a model of a crystal with anisotropic elastic strain, or some other model. Coppens & Hamilton (1970) introduced anisotropy in the angular mosaic distribution in the Zachariasen approximation. Becker & Coppens (1975) also introduced the anisotropy of mosaic spread with both Lorentzian and Gaussian distribution functions of the Coppens–Hamilton (1970) and Thornley–Nelmes (1974) descriptions. The distribution function of the deviation angle from the exact Bragg condition for the misorientation model for a crystal was given by Kato (1982). If the notation introduced by Coppens & Hamilton (1970) is used, the distribution function for the misorientation model of an anisotropic crystal can be written as follows:

$$\Phi_o(\varphi_o,\varphi_g)=\det(\boldsymbol{Z}_o\boldsymbol{Z}_g)^{1/2}\times 2^3\exp[-2\pi(q_o^2\varphi_o^2+q_g^2\varphi_g^2)], \tag{30}$$

where

$$\begin{aligned}q_0^2&=\boldsymbol{D}^t\boldsymbol{Z}_o\boldsymbol{D},\\q_g^2&=\boldsymbol{D}^t\boldsymbol{Z}_g\boldsymbol{D},\end{aligned} \tag{31}$$

φ_o and φ_g are the deviation angles from the exact Bragg condition measured from the o and g directions, respectively, and $\boldsymbol{Z}$ and $\boldsymbol{D}$ are, respectively, a tensor and a unit vector normal to the diffraction plane which contains the o and g beams. The transposed matrix of $\boldsymbol{D}$ is denoted by $\boldsymbol{D}^t$. Analogous expressions can be written for a Lorentzian distribution. The correlation lengths for some crystal models with anisotropic elastic strain will be reported in a separate work. The formalism for primary extinction in an anisotropic crystal generalized from the formlism developed by Kato (1980a, 1980b) will also be discussed in a following work.

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References

BECKER, P. J. & COPPENS, P. (1973). First Eur. Crystallogr. Meet., Bordeaux, France.
BECKER, P. J. & COPPENS, P. (1974*a*). *Acta Cryst.* A**30**, 129-147.
BECKER, P. J. & COPPENS, P. (1974*b*). *Acta Cryst.* A**30**, 148-153.
BECKER, P. J. & COPPENS, P. (1975). *Acta Cryst.* A**31**, 417-425.
COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71-83.
KATO, N. (1976*a*). *Acta Cryst.* A**32**, 453-457.
KATO, N. (1976*b*). *Acta Cryst.* A**32**, 458-466.
KATO, N. (1980*a*). *Acta Cryst.* A**36**, 763-769.
KATO, N. (1980*b*). *Acta Cryst.* A**36**, 770-778.
KATO, N. (1982). *Z. Naturforsch. Teil A*, **37**, 485-489.
TAKAGI, S. (1962). *Acta Cryst.* **15**, 1311-1312.
TAKAGI, S. (1969). *J. Phys. Soc. Jpn*, **26**, 1239-1253.
THORNLEY, F. R. & NELMES, R. J. (1974). *Acta Cryst.* A**30**, 748-757.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558-564.

Acta Cryst. (1986). A**42**, 469-478

Accurate Measurement of the Si Structure Factor by the *Pendellösung* Method

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Abstract

The X-ray structure factor of Si was measured for 30 net planes from the thickness dependence of the integrated intensity on the λ scale. In ten low-order planes, the accuracy level was estimated to be 0·05% in the probable error. Therefore, the deviation from the standard model of Hartree-Fock isolated atoms under harmonic oscillation could be determined with high precision. In the remaining net planes, the accuracy level was 0·1%. Dawson's rule (that even and higher-order reflections should be normal) was well satisfied for eight net planes higher than 660. Against this background, some F_g values of odd and middle-order planes deviate from the standard model. In the difference Fourier map, not only the bonding charge and the charge deficit in the anti-bonding region but also a slight excess near the atomic position were recognized.

1. Introduction

The accurate structure factor (F_g) in X-ray diffraction gives valuable information on electron distribution in crystals. At present, the highest accuracy on the absolute scale is obtained in Si by the *Pendellösung* method, using the fact that the X-ray intensity field oscillates with either a spatial or an angular period which is proportional to $|F_g|^{-1}$.

Since the first experiment (Hattori, Kuriyama, Katagawa & Kato, 1965), several groups have attempted a more accurate measurement and explored the methodology as well as the underlying theory. The earlier work was reviewed by Kato (1969); at that stage, the accuracy level was about 0·5% in the probable error. Tanemura & Kato (1972) and the extensive work of Aldred & Hart (1973*a*, *b*) advanced the accuracy level to approximately 0·1%. 15 net planes were measured in the latter work. In these experiments, essentially *Pendellösung* fringes in the section topograph were used. Although the experimental set-up was extremely simple, its disadvantage lies in the need for a large well defined wedge of perfect crystal.

Several modifications were proposed to overcome this disadvantage. Takama, Iwasaki & Sato (1980) used the λ dependence of the integrated intensity on the λ scale, and Utemisov, Somenkova, Somenkov & Shil'shtein (1980) and Utemisov, Shil'shtein & Somenkov (1981) used the t dependence of the integrated intensity on the θ scale, where t is the effective thickness and can be continuously changed by rotating the azimuthal angle φ with the Bragg condition fixed. More recently, Teworte & Bonse (1984) used the intensity oscillation in the high-

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