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Thermal Diffuse Scattering Corrections for Single-Crystal Integrated Intensity Measurements

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A computer program has been developed for calculating one- and two-phonon thermal diffuse scattering corrections for integrated X-ray intensity measurements. The correction includes the anisotropy in the diffuse-scattering intensity distribution and the geometry of the scan for crystals of any symmetry type. The calculated two-phonon correction is not negligible and may be as large as the one-phonon correction for high-order reflections. The effects of slit size, scan range, crystal orientation, crystal misalignment, and neglect of phonon dispersion on the calculated corrections are investigated.

Introduction

The attainment of accurate structure factors from X-ray intensity measurements requires in many cases a correction for the thermal diffuse scattering (TDS) included in intensity scans. The difficulty of the calculations has prevented the routine application of TDS corrections in X-ray crystallography. The general approach to calculating TDS corrections and some of the approximate methods that have been used are described by Cochran (1969).

Until recently, most approximate methods have involved the assumption of a spherical TDS distribution about the Bragg reflection. Rouse & Cooper (1969) have developed a program to calculate the one-phonon correction which correctly includes the anisotropic TDS intensity distribution for crystals of any symmetry. Walker & Chipman (1970) have written two programs for calculating the one-phonon TDS correction which are restricted to cubic crystals. The first program (Walker & Chipman, 1970, 1971*a*) includes the primary-beam divergence, wavelength distribution, and anisotropy of the scattering. The second program (Walker & Chipman, 1970, 1971*b*) neglects the primary-beam divergence, but includes a simplification in the calculation which makes the program fast enough to be used routinely with intensity measurements.

In this paper a TDS correction program for $\theta:2\theta$ scans is described which is similar to the faster program of Walker & Chipman but is not restricted to cubic crystals. In addition, an approximate correction for two-phonon TDS intensity is included. The calculation of the two-phonon correction has also been simplified and requires little additional effort. The program has been used to investigate the effects of scan range, slit size, and crystal orientation and misalignment on the corrections.

Theory

For acoustic phonons, neglecting dispersion, primary-beam divergence, and mosaic spread, the ratio of one-phonon-included TDS intensity to the Bragg intensity for a scan is given by

$$\alpha_1=\frac{I_1}{I_B}=\frac{k_BT}{v}\sum_i w_i\int J_1(\mathbf{q})\mathrm{d}^3q \tag{1}$$

where the integration is over the volume in reciprocal space swept out by the scan and

$$J_1(\mathbf{q})=\frac{1}{q^2}\sum_{j=1}\frac{[\mathbf{H}\,.\,\mathbf{e}_j(\mathbf{q})]^2}{\varrho V_j{}^2(\mathbf{q})}\,. \tag{2}$$

Here $\mathbf{H}$ is the scattering vector, $q=|\mathbf{q}|$, k_B is Boltzman's constant, T is the temperature, ϱ is the density of the crystal, v is the unit-cell volume, and $V_j(\mathbf{q})$ is the velocity of the acoustic lattice wave $\mathbf{q}$. The $\mathbf{e}_j(\mathbf{q})$ $(j=1,2,3)$ are unit vectors in the directions of polarization of the lattice wave.

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The wavelength distribution for a 2θ scan is included by calculating the TDS correction for each peak of the $K\alpha_1, K\alpha_2$ doublet. The contribution of each wavelength component λ_i is weighted by the normalized intensity w_i.

The $J_1(\mathbf{q})$ term can be evaluated if the elastic constants are known. If one defines a matrix $\mathbf{A}$

$$\mathbf{A}_{ij} = \sum_{m,n=1}^{3} c_{ijmn} q_m q_n \tag{3}$$

where the c_{ijmn} are the elastic constants and the q_i are the direction cosines of the wave vector $\mathbf{q}$, then (Wooster, 1962)

$$J_1(\mathbf{q}) = \frac{H^2}{q^2} \sum_{i,j=1}^{3} h_i h_j (\mathbf{A}^{-1})_{ij} \tag{4}$$

where the h_i are the direction cosines of $\mathbf{H}$.

The ratio α_1 can be determined by a numerical integration over the scan volume. The boundaries of the scan volume are defined by the detector slits and the length of the scan. Walker & Chipman (1970, 1971*b*) simplified the numerical integration to a two-dimensional integration over the surface of the scan volume using the $1/q^2$ dependence of $J_1(\mathbf{q})$. Since $J_1(\mathbf{q}) \propto 1/q^2$ and $\mathrm{d}a \propto q^2$, then $J_1(\mathbf{q})\mathrm{d}a$ is a constant, and

$$\begin{aligned}\alpha_1 &= \frac{k_BT}{v} \sum_i w_i \iint J_1(\mathbf{q})\mathrm{d}a \cos \xi \mathrm{d}q \\ &= \frac{k_BT}{v} \sum_i w_i \int_S J_1(\mathbf{g}) g \mathrm{d}A \cos \xi \\ &= \frac{k_BT}{v} \sum_i w_i \sum_{k=1}^{6} g_k \int_{S_k} J_1(\mathbf{g})\mathrm{d}A \end{aligned} \tag{5}$$

where $\mathbf{g}$ is the distance to the surface S_k, ξ is the angle between $\mathbf{g}$ and the vector normal to $\mathrm{d}a$, $g_k = g \cos \xi$, and the summation k is over the six surfaces of the scan volume. A significantly shorter computation results from a reduction to a two-dimensional from a three-dimensional numerical integration.

The ratio of the two-phonon TDS intensity to the Bragg intensity is given by

$$\alpha_2 = \frac{I_2}{I_B} = \frac{k_B{}^2T^2}{v^2} \sum_i w_i \int J_2(\mathbf{q})\mathrm{d}^3q \tag{6}$$

where

$$J_2(\mathbf{q}) = \sum_{j,k=1}^{3} \int \frac{1}{\mathbf{q}_1^2} \frac{1}{(\mathbf{q}-\mathbf{q}_1)^2} \times \frac{[\mathbf{H}\,.\,\mathbf{e}_k(\mathbf{q}_1)]^2[\mathbf{H}\,.\,\mathbf{e}_j(\mathbf{q}-\mathbf{q}_1)]^2}{\varrho^2 V_k^2(\mathbf{q}_1) V_j^2(\mathbf{q}-\mathbf{q}_1)} \mathrm{d}^3\mathbf{q}_1 \,. \tag{7}$$

This term can be approximated (Ramachandran & Wooster, 1951) by

$$J_2(\mathbf{q}) \simeq \frac{1}{q} \frac{\pi^3}{2v^*} \sum_{j=1}^{3} \frac{[\mathbf{H}\,.\,\mathbf{e}_j(\mathbf{q})]^4}{\varrho^2 V_j^4(\mathbf{q})} \,. \tag{8}$$

The numerical integration of $J_2(\mathbf{q})$ can also be reduced to an integration over the surface of the scan by multiplying by $1/q$. Let $J'_2(\mathbf{q}) = (1/q)J_2(\mathbf{q})$ so that $J'_2(\mathbf{q}) \propto 1/q^2$, then

$$\alpha_2 = \frac{k_B{}^2T^2}{v^2} \sum_i w_i \iint qJ'_2(\mathbf{q})\mathrm{d}a \cos \xi \mathrm{d}q \,. \tag{9}$$

Since $J'_2(q)\mathrm{d}a$ is a constant,

$$\alpha_2 = \frac{k_B{}^2T^2}{v^2} \sum_i w_i \int_S \tfrac{1}{2} g^2 J'_2(\mathbf{g})\mathrm{d}A \cos \xi$$

$$\alpha_2 = \frac{k_BT^2}{v^2} \sum_i w_i \sum_{k=1}^{6} \tfrac{1}{2} g_k \int_{S_k} gJ'_2(\mathbf{g})\mathrm{d}A \,. \tag{10}$$

Use of the approximation for $J_2(\mathbf{q})$,

$$J'_2(\mathbf{q}) \simeq \frac{\pi^3}{2v^*} q^2 [J_1(\mathbf{q})]^2,$$

gives

$$\alpha_2 \simeq \frac{\pi^3}{4} \frac{k_B{}^2T^2}{v} \sum_i w_i \sum_{k=1}^{6} g_k \int_{S_k} g^3 [J_1(\mathbf{g})]^2 \mathrm{d}A \,. \tag{11}$$

The amount of one-phonon TDS subtracted by the background measurement expressed as a function of the Bragg reflection intensity is given by

$$\alpha'_1 = \frac{I'_1}{I_B} = \frac{k_BT}{v} \sum_i w_i \left[\tfrac{1}{2} \sum_{k=1}^{2} \int_{S_k} J_1(\mathbf{g})\mathrm{d}A\right](H_2 - H_1) \tag{12}$$

where the integration is over the surfaces at the end of the scan and $(H_2 - H_1)$ is the length of the scan.

The two-phonon scattering removed by the background measurement is given by

$$\alpha'_2 = \frac{k_B{}^2T^2}{v^2} \sum_i w_i \left[\tfrac{1}{2} \sum_{k=1}^{2} \int_{S_k} J_2(\mathbf{g})\mathrm{d}A\right](H_2 - H_1) \,. \tag{13}$$

Using the approximation for $J_2(\mathbf{q})$,

$$\alpha'_2 \simeq \frac{\pi^3}{2} \frac{k_B{}^2T^2}{v} \sum_i w_i \left[\tfrac{1}{2} \sum_{k=1}^{2} \int_{S_k} g^3 [J_1(\mathbf{g})^2 \mathrm{d}A\right](H_2 - H_1) \,. \tag{14}$$

Calculations

A Fortran computer program, *TDS*2, has been written to evaluate the first and second-order TDS corrections for $\theta{:}2\theta$ scans using equations (4) and (5) for α_1 and equations (4) and (11) for α_2. Background corrections are calculated using equation (12) for α'_1 and equation (14) for α'_2. The program neglects primary-beam divergence, dispersion, and crystal dimensions and mosaic spread. It is assumed that the detector slits are rectangular and that the average of the background at both ends has been subtracted from the intensity. The program includes the elastic anisotropy of the crystal and is not limited to cubic crystals or symmetrical scans. The wavelength distribution is included approximately by calculating the correction for each wavelength and using an intensity weighted average. Some of the details of the calculation are described in the Appendix.

The program *TDS*2 has been used to calculate TDS corrections for X-ray intensity measurements of hexamethylenetetramine (HMT), a cubic crystal with three elastic constants, and ammonium tetroxalate (ATO), a triclinic crystal with 21 elastic constants. The elastic constants of HMT have been measured by Haussühl (1958) and those of ATO by Küppers & Siegert (1970). The corrections were calculated with a precision of 0·1 % in approximately 1·5 s per reflection on a Burroughs B6700 computer and 0·05 s per reflection on a CDC 7600 computer. With a square detector slit of 1·0° and a scan of about 2°, it was necessary to perform the numerical integration at only about 1000 points per reflection.

A number of calculations were undertaken to determine the effects of the slit size, scan range, and crystal misalignment on the calculated TDS corrections. A reflection of HMT at a 2θ of 100° with Mo $K\alpha$ radiation was chosen because of the high calculated value of 30 % for the TDS correction.

The calculated TDS corrections are plotted in Fig. 1 as a function of the height of the detector slit. The one-phonon TDS correction increases rapidly both with increasing height and width of the detector slits. Since the slits must be wide enough to accept the Bragg peak, the one-phonon TDS contribution cannot be easily reduced. However, the two-phonon TDS correction increases more slowly and can be significantly reduced if the slits are only as large as required by the Bragg reflection.

The TDS corrections were calculated as a function of scan length. The one-phonon correction also increases rapidly with the length of the scan. As with the detector slits, the size of the Bragg peak and the splitting of the $K\alpha_1, K\alpha_2$ doublet prevents significantly reducing α_1 or α_2 by reducing the length of the scan. In these calculations the scan was begun at $[2\theta(K\alpha_1)-t]$ and ended at $[2\theta(K\alpha_2)+t]$.

Since the crystal may often be slightly misaligned with respect to the scan volume during the data collection, the effects of misalignment on the TDS corrections have been investigated. The dependence of α_1 and α_2 on misalignment of length (2θ), height (χ), and width (ω) of the scan was calculated. The values of α_1 and α_2 are found to be nearly independent of small errors in crystal orientation. The TDS corrections are plotted in Fig. 2 as a function of misalignment in height.

The calculated TDS corrections for HMT do not vary significantly with crystal orientation because HMT is nearly elastically isotropic. However, with ATO the correction varies with crystal orientation. The variation of the first and second-order TDS corrections with rotation around the diffraction vector is plotted in Fig. 3. for an ATO reflection at a 2θ of 125° with Mo $K\alpha$ radiation. For elastically anisotropic crystals the variation of the TDS with orientation will contribute to disagreement between the intensities of symmetry-equivalent reflections.

A model calculation was performed to obtain a quantitative estimate of the effect of neglecting phonon dispersion. An isotropic model was used for the idealized one and two-phonon scattering distributions

$$I_1(\mathbf{q}) = \frac{C_1}{q^2}$$

$$I_2(\mathbf{q}) = \frac{C_2}{q}$$

where C_1 and C_2 are constants for a particular reflection. The distributions including dispersion are given by

$$I_{1D}(\mathbf{q}) = \frac{C_1}{q^2}\left[\frac{1}{D(q)}\right]^2$$

$$I_{2D}(\mathbf{q}) \simeq \frac{C_2}{q}\left[\frac{1}{D(q)}\right]^{*}$$

where $D(\mathbf{q})$ describes the functional form of the dispersion curve.

Assuming linear chain dispersion for the model gives

$$D(\mathbf{q}) = \frac{\sin\left(\frac{\pi}{2}\frac{q}{q_m}\right)}{\frac{\pi}{2}\frac{q}{q_m}}$$

where q_m is the distance to the Brillouin zone boundary. The scan volume is taken to be a sphere of radius g and the Brillouin zone by a sphere of radius q_m.

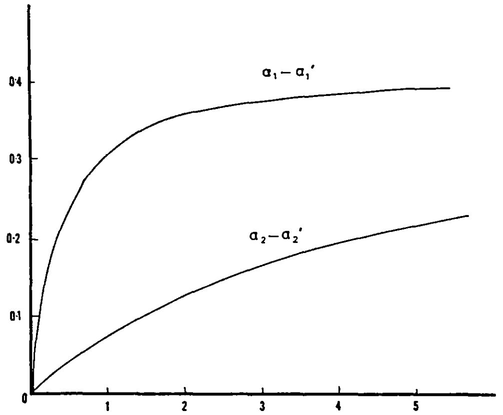

Fig. 1. Calculated one and two-phonon TDS corrections for a reflection of HMT as a function of the height in degrees of the detector slit. The detector slit width is 1·0° and the scan range 2·2°.

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* The two-phonon expression should include an integration over all wave vectors

$$I_{2D}(\mathbf{q}) = C_2' \int \frac{1}{|\mathbf{q}_1|^2}\left[\frac{1}{D(\mathbf{q}_1)}\right]^2 \frac{1}{|\mathbf{q}-\mathbf{q}_1|^2}\left[\frac{1}{D(\mathbf{q}-\mathbf{q}_1)}\right]^2 \mathrm{d}^3q_1\,.$$

For this application, an approximation similar to equation (8) is used.

The calculated corrections including background corrections are given by

$$\alpha_1-\alpha_1'=\int_0^g I_1(\mathbf{q})\mathrm{d}^3q-\frac{4\pi}{3}g^3I_1(g)=\frac{8\pi}{3}gC_1$$

$$\alpha_2-\alpha_2'=\int_0^g I_2(\mathbf{q})d^3q-\frac{4\pi}{3}g^3I_2(g)=\frac{2\pi}{3}g^2C_2$$

$$\alpha_{1D}-\alpha_{1D}'=\int_0^g I_{1D}(\mathbf{q})\mathrm{d}^3q-\frac{4\pi}{3}g^3I_{1D}(g)$$

$$\alpha_{2D}-\alpha_{1D}'=\int_0^g I_{2D}(\mathbf{q})\mathrm{d}^3q-\frac{4\pi}{3}g^3I_{2D}(g)\,.$$

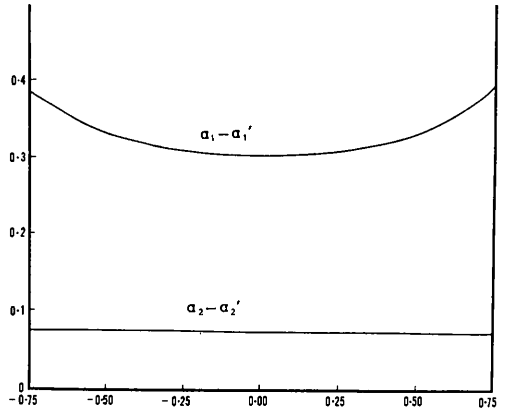

Fig. 2. Calculated one and two-phonon TDS corrections as a function of misalignment in degrees of the height of the scan. The dimensions of the detector slits are 1·0° and the scan range is 2·2°.

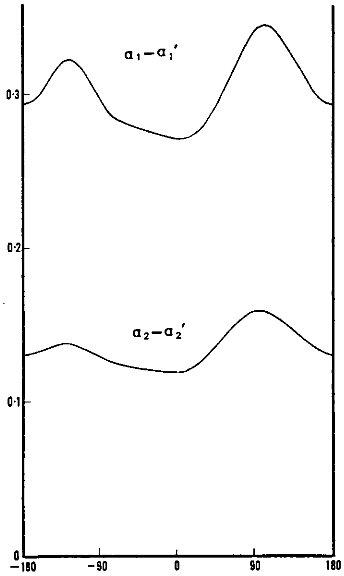

Fig. 3. Calculated one and two-phonon TDS corrections for a reflection of ATO as a function of rotation (in degrees) about the diffraction vector. The dimensions of the detector slits are 1·0° and the scan range is 2·4°.

The evaluations of α_{1D} and α_{2D} require numerical integrations. In Fig. 4, the ratios $R_1=(\alpha_{1D}-\alpha_{1D}')/(\alpha_1-\alpha_1')$ and $R_2=(\alpha_{2D}-\alpha_{2D}')/(\alpha_2-\alpha_2')$ are plotted as a function of g/q_m.

Discussion

The computer program *TDS*2 is a generalization of Walker & Chipman's (1970, 1971*b*) approach for calculating the correction thermal diffuse scattering included in intensity measurements. The program is applicable to crystals of any symmetry type and includes both one and two-phonon scattering. The corrections are calculated rapidly at a level of approximation which appears to be reasonable for most real experiments.

Since most of the included TDS occurs close to the Bragg reflection, *i.e.* at small values of $\mathbf{q}$, the neglect of primary-beam divergence, wavelength distribution, and dimensions and mosaic spread of the crystal are expected to be good approximations when the boundaries of the scan volume are not too close to the Bragg peak.

Walker & Chipman (1970) found that the neglect of primary-beam divergence results in an average change in the correction of about 3 % or less for one-phonon scattering. Neglect of the $K\alpha_1,K\alpha_2$ doublet results in a larger overcorrection which increases with scattering angle. A more detailed study of the effects of experimental resolution by Scheringer (1973) using an isotropic model for the TDS distribution and spherical scan range indicates that the one-phonon correction may be as much as 20 % too large, but in most cases will be about 5 % too large.

The neglect of dispersion will be a good approximation when $\mathbf{q}$ is small with respect to the boundaries of the Brillouin zone. The effects of dispersion will be important if the reciprocal axes are short, since the Brillouin zone will be close in size to the scan volume. At

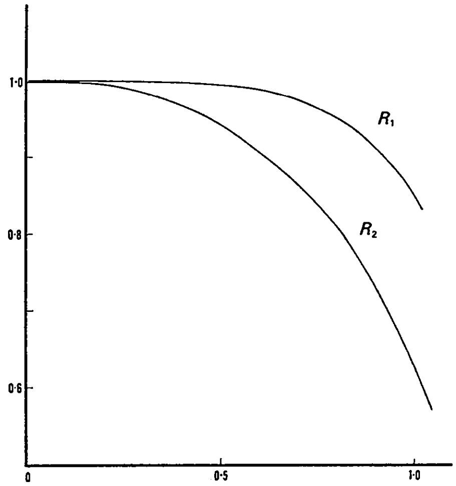

Fig. 4. The R functions for one and two-phonon corrections as a function of g/q_m, the ratio of the size of the scan to the size of the Brillouin zone.

high scattering angles, dispersion may become important because of the long 2θ scan necessary for the $K\alpha_1$, $K\alpha_2$ doublet. Assuming linear-chain dispersion, the results of the model calculation given in Fig. 4 represent an upper limit to the overcorrection error since the scan-range dimensions will not approach the Brillouin zone boundary in all directions in real experiments.

The magnitudes of the first and second-order TDS corrections indicate that the neglect of included TDS is a significant remaining source of systematic error in the determination of structure factors from intensity measurements. The approximate dependence of the first order TDS on H^2 introduces a systematic error in the determination of atomic thermal parameters. The influence of the neglect of second-order TDS has not been studied.

It is difficult to estimate the errors involved in the approximation to the second-order TDS correction since an evaluation using equation (7) is extremely tedious. A calculation of the two-phonon intensity distribution at a few points in the scan volume indicates that, depending on the direction, both over- and underestimates of the scattering can be expected when the approximation given by equation (8) is used. The second-order scattering may be expected to have a more complicated dependence on orientation than the dependence predicted using the approximation.

Cooper (1970) has noted that the neglect of resolution effects will partially compensate for neglect of two-phonon scattering. However, the two-phonon correction is approximately proportional to H^4 and at high angles will be many times larger than the effects of neglecting resolution in calculating the one-phonon correction.

The close relation between the atomic thermal parameters and the apparent electron density distribution requires a careful treatment of the TDS in the experimental determination of electron density distributions. The importance of included TDS in the comparison of X-ray and neutron diffraction results has been discussed by Cooper (1969).

Studies of the effects of slit size and scan length and the effect of neglecting resolution factors suggest some favorable choices of experimental conditions, which have been noted by Scheringer (1973). If no TDS correction is to be applied to X-ray intensity measurements, then the diffuse scattering will be minimized by using the minimum detector-slit dimensions and scan range allowed by the size of the Bragg reflection. If TDS corrections are to be calculated, then somewhat larger detector slits and scan ranges are desirable to avoid large resolution effects.

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APPENDIX

The evaluation of equations (5) and (11) involves numerical integrations over the surface of the scan volume. The boundaries of the scan volume can be easily defined in a coordinate system related to the diffraction geometry (Fig. 5). A point, **X**, in this system can be related to a point, **X**′, in the coordinate system in which the elastic constants are defined by the matrix equation

$$\mathbf{X}=\boldsymbol{\theta}\boldsymbol{\Omega}\mathbf{X}\boldsymbol{\Phi}\mathbf{S}\mathbf{T}\mathbf{X}'$$

where

$$\mathbf{X}=\begin{pmatrix}x\\ y\\ z\end{pmatrix}$$

and **T** is the matrix which relates the coordinate system of the elastic constants to the reciprocal axes, **S** is the crystal orientation matrix which contains the direction cosines of the reciprocal axes in the instrument coordinate system, and **Ω**, **X**, and **Φ** are the rotation matrices corresponding to the ω, χ, and φ motions of a four-circle diffractometer (Busing & Levy, 1967). The matrix **θ** is defined by

$$\boldsymbol{\theta}=\begin{pmatrix}\sin\theta & 0 & 0\\ -\cos\theta & 1 & 0\\ 0 & 0 & 1\end{pmatrix}$$

where 2θ is the Bragg scattering angle.

Each surface is divided into a grid and the coordinates of each point are transformed into the coordinate system of the elastic constants by the inverse transformation

$$\mathbf{X}'=(\boldsymbol{\theta}\boldsymbol{\Omega}\mathbf{X}\boldsymbol{\Phi}\mathbf{S}\mathbf{T})^{-1}\mathbf{X}\,.$$

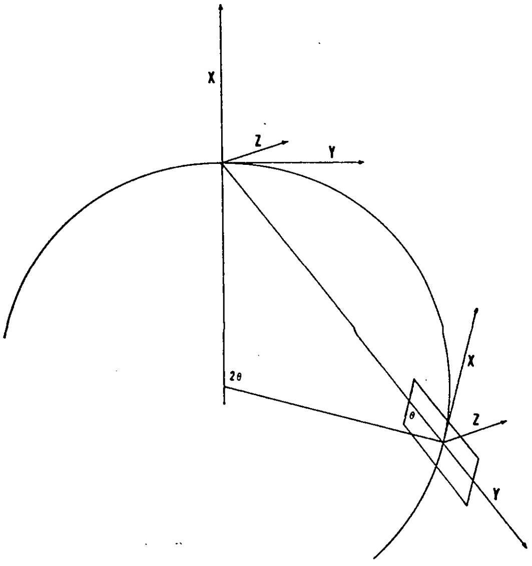

Fig. 5. The coordinate system defined by the diffraction geometry and the scan is shown in the lower right of the Figure. The instrument coordinate system is shown at the top of the Figure.

After the numerical integration has been performed, the number of points along each dimension of the grid is doubled and the calculation is repeated. The final result is obtained by extrapolation to da=0.

The program *TDS*2 is included as a subroutine in our program for applying Lorentz and polarization corrections to intensity measurements. The intensity correction is given by

$$I_{\text{corr}} = I_{\text{obs}}/(1+\alpha_1-\alpha_1'+\alpha_2-\alpha_2') .$$

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On Some Problems Connected with Thermal Motion in Molecular Crystals and a Lattice-Dynamical Interpretation

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Interpretation of thermal motion in molecular crystals is important for obtaining accurate bond lengths. However, even in a simple case, such as a rigid body, serious difficulties may arise. Contrary to what seems to be a widespread feeling, mathematical methods for overcoming these difficulties, such as regression on principal components, may often lead to results without physical meaning, and a good fit to individual B's is not necessarily a proof of a correct procedure. For an accurate bond-length correction, a lattice-dynamical treatment is particularly promising as a practical method of solution: examples of application, which result in a satisfactory interpretation of molecular motion, are given.

Introduction

For some years, it has been good practice for crystallographers to apply libration corrections to bond distances: for these corrections the molecular motion must be interpreted (Cruickshank, 1956*a*, *b*, *c*, 1961; Busing & Levy, 1964). More recently, the Schomaker–Trueblood approach (Schomaker & Trueblood, 1968) has afforded a complete mathematical method for solving this problem for rigid molecules, and extended discussion of this technique is reported (Johnson, 1970*b*; Pawley, 1970). Among the more noteworthy developments are Pawley's proposal of introducing rigid-body constraints directly into least-squares refinement, with a considerable reduction of the number of parameters to be determined (Pawley, 1964, 1971), and Johnson's 'segmented rigid-body' model (Johnson, 1970*a*).

In the Schomaker–Trueblood treatment, apart from indeterminacy of the trace of S, singularity or severe ill-conditioning of the normal-equation matrix may often be encountered; for overcoming some of these difficulties, regression on principal components has been proposed (Johnson, 1970*a*, *b*). We feel that in some cases correct interpretation of thermal motion from diffraction data can be particularly difficult, even for a rigid body, and indiscriminate use of regression on principal components is far from being satisfactory. A detailed discussion about the possibility of obtaining a physically meaningful solution seems to us therefore to be particularly needed.

Regression on principal components

This argument is exhaustively treated in some mathematical and crystallographic works (Golub & Kahan, 1965; Massy, 1965; Kendall & Stuart, 1966; Hanson & Lawson, 1969; Rollett, 1970; Johnson, 1970*b*; Golub & Reinsch, 1970); for our purpose, it is only necessary to keep a few points in mind.

Because of the orthogonality of the latent vectors