formed on the basis of particle diameters estimated by screening. This method could be rather good for quasi-isometric particles but for the layer-like graphite particles a fourfold longer diameter is to be expected by comparison with the mean particle diameter defined by (7). Therefore, at high graphite concentrations, when layer-like particles become predominant, curves (a) and (b) on Fig. 5 should be $0\cdot2-0\cdot3$ units lower on the $\log(I_1/I_1^0 C_1)$ scale, and then would show a better fit to the experimental points. This demonstrates how the diffracted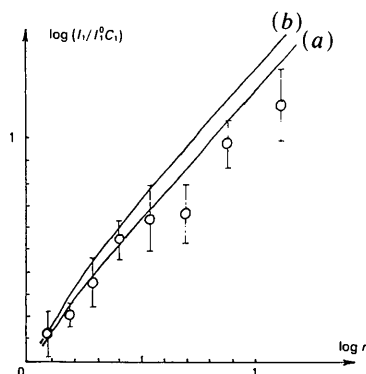 intensities are not only affected by the particle sizes but also by their shapes, and how the theory reflects their influence too.

According to the experimental results for graphite, the model is qualitatively and also quantitatively consistent within certain limits. Also, as was demonstrated in the derivation of the theoretical formulae, this model has as limiting cases the ideal case of Alexander & Klug (1948) and the empirical expressions of Cooper (1965) and Weiss (1966).

For these reasons we estimate that the stated model adequately describes the granularity effects in their most general form.

Fig. 5. Diffracted intensities for quartz, computed from the model for (a) quartz (30 μm)–graphite and (b) quartz (51·5 μm)–graphite. Open circles denote experimental points.

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Use of the Polychromatic Laue Method for Short-Exposure X-ray Diffraction Data Acquisition

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Abstract

The polychromatic Laue method was developed for application in flash X-ray diffraction studies; it can also serve as a valuable tool for fast data acquisition with conventional X-ray and synchrotron sources. The present method was developed with a sealed X-ray tube (Mo anode, 45 kV, 20 mA) and a crystal of known structure for calibration of the source spectrum. The resulting experimental energy distribution of the source has been successfully approximated in the range 0·45–1·9 Å by an analytical expression based on a theoretical curve for white radiation. The problem of coincidence of several harmonics in a single diffraction spot has been partially solved by the multiple-film technique. The efficiency of the method was tested on a crystal of (2-*tert*-butyloxycarbonyl)-9-oxo-6-oxa-1-azabicyclo[5.2.0]nonane, which was also investigated by means of a conventional four-circle X-ray diffractometer. The comparison of about 500 structure factors derived by the two methods yielded an R factor of 0·065. Data acquisition by the Laue method is about two orders of magnitude faster.

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Introduction

The work presented here is part of a comprehensive feasibility study of direct X-ray diffraction analysis of structural changes in single crystals (Lourie, 1983; Green & Rabinovich, 1984). The development of methods for the investigation of fast phenomena in single crystals, by analogy with conventional X-ray diffraction analysis of static crystalline structures, is still in the initial stages, and only a little preliminary work has been done in this direction (*e.g.* Bordas, Glazer & Hauser, 1975; Fujimoto, 1982). A relatively new and very promising technique for time-resolved exploration of transient effects in crystals is the flash X-ray diffraction technique (Johnson, Mitchell & Evans, 1971; Mitchell, Johnson & Evans, 1973; Jamet & Thomer, 1976; Green, 1977; Germer, 1979). In this technique very short X-ray pulses are used, thus ruling out diffraction methods based on moving-crystal principles.

In flash X-ray experiments usually a very small number of flashes are available. This restriction suggests the polychromatic Laue diffraction method as one of the most suitable tools for such experiments. The method is an application of the old and renowned Laue technique, which incorporates polychromatic radiation with a stationary crystal. In this arrangement many crystal planes reflect simultaneously, each one selecting its appropriate wavelength according to its orientation and spacing, and thus a large fraction of all the data can be obtained in one flash. The Laue method can also find use with conventional X-ray and synchrotron radiation sources, when short exposures are relevant, *e.g.* in the study of radiation-sensitive systems. The mechanical simplicity of the technique makes it an outstanding one for studies of fast events in single crystals and allows one to carry out conveniently and simultaneously many other types of experiments. Good summaries of the Laue method are given by Henry, Lipson & Wooster (1951) and by Amoros, Buerger & de Amoros (1975).

An evaluation of the polychromatic Laue method for quantitative structure analysis of micro-samples and structural kinetics has recently been made at Daresbury Laboratory, utilizing a synchrotron-radiation X-ray source in the range 0·1–4 Å (Helliwell, 1985; Helliwell *et al.*, 1986).

Although the polychromatic Laue method was the vehicle for the discovery of X-ray diffraction by crystals, it proved to be inconvenient for crystal structure studies. One of the main complications arises from the coincidence of several harmonics in a single diffraction spot. Another intrinsic limitation of the method is the difficulty of calibration of the source intensity. Therefore, the method has usually been modified when applied in structural studies; for example, a modified Laue method has been utilized in neutron diffraction studies (Hohlwein, 1977) where a quasi-monochromatic beam was used.

In the present work a conventional Laue camera for X-ray diffraction was utilized. The X-ray source spectrum was derived from intensity data of a crystal of known structure, 4,4'-dimethylchalcone (DMC) (Rabinovich & Shakked, 1974). The reliability of the method was checked by independent experiments for a second orientation of this crystal. The quality of the intensity data and the rate of their acquisition were established by comparing data collected on a crystal of 2-(*tert*-butyloxycarbonyl)-9-oxo-6-oxa-1-azabicyclo[5.2.0]nonane (OOABCN) by this method with those obtained by standard four-circle diffractometry.

Experimental

A single crystal of DMC ($a = 15·25$, $b = 5·91$, $c = 14·63$ Å, space group $P2_12_12_1$, 0·03 mm³) was irradiated by unfiltered Mo X-rays (45 kV, 20 mA) at two orientations: a and c axes coincident with the incident X-ray beam (referred to as [100] and [001] directions, respectively).

Diffraction patterns were recorded on six films (Ilford Industrial G) packed together (the films of a pack are referred to as the first, second *etc.* film). For each of the two crystal orientations six experiments were performed with exposure times of 2, 4, 8, 16, 32 and 64 min. The films (72 in total) were then developed, fixed and washed in the usual manner. The optical densities of the reflection spots on the films were measured by means of an Optronics P-1000 microdensitometer (100 × 100 μm raster, OD range 0–2) and recorded digitally on magnetic tape.

The experiment with the OOABCN single crystal was carried out in the same manner. The crystal ($C_{12}H_{19}NO_4$) is monoclinic ($a = 10·98$, $b = 9·59$, $c = 13·54$ Å, $\beta = 110·5°$, space group $P2_1/n$, 0·02 mm³). Four crystal orientations were used, [100], [001], [203] and [101]. The experiments were carried out at two exposure times: 1 and 5 min.

Data processing

Special computer programs were written in order to calculate the locations of diffraction spots on films (Appendix *A*) and the Lorentz and polarization factors for each reflection (Appendix *B*). Several types of reflections were excluded from the overall list at this stage:

(*a*) reflections located too closely to be resolved;

(*b*) reflections outside the wavelength range; low- and high-wavelength cutoffs were set at 0·3 and 1·9 Å, respectively;

(*c*) reflections calculated to be too weak to be observed (in DMC only, where the calculated structure factors were known).

After indexing, the reflected intensities were processed by a special program. This first finds the centroid of a reflection spot and surrounds it with a reasonably large frame comprising about 300 squares of 0.01 mm^2 each. The integrated intensity is then calculated by either of two options:

(a) The intensity is obtained by summing the optical-density values of all squares within the frame. From this total intensity an estimated background was subtracted, derived as the mean intensity of the frame boundary squares multiplied by the number of squares within the frame.

(b) A Gaussian distribution of the reflection intensity and a planar distribution of the background are assumed. The intensity, $I(x, y)$, at a grid point (x, y) within a frame is thus calculated as

$$I(x, y) = I_g(x, y) + I_b(x, y), \qquad (1)$$

where

$$I_g(x, y) = p_1 \exp\left[-p_2(x - x_0)^2 - p_3(y - y_0)^2 - p_4(x - x_0)(y - y_0)\right]$$

is the Gaussian intensity distribution and

$$I_b(x, y) = p_5 + p_6 x + p_7 y$$

is the background intensity.

The nine parameters $p_i(i = 1, 2, \ldots, 7)$, x_0 and y_0 are refined by an iterative least-squares procedure, minimizing the function $D = \sum [I_0(x, y) - I(x, y)]^2$, where $I_0(x, y)$ is the measured optical density at (x, y), and the summation is over all grid points (x, y) within the frame. The integration of the intensity with the use of the Gaussian parameters p_1 to p_4 is straightforward:

$$\int\!\!\!\int_{-\infty}^{\infty} I_g(x, y) \, dx \, dy = \pi p_1/[p_2 p_3 - (p_4/2)^2]^{1/2}.$$

The Gaussian approximation, which eventually justified itself, was chosen on the following grounds: (a) the diffraction spots on the Laue transmission photographs are elliptical in shape; (b) it was found that the intensity profiles of the central cross sections of the spot could be approximated fairly well by a Gaussian curve. Fig. 1 shows the observed and calculated (Gaussian) intensity distributions of one of the diffraction spots of a DMC photograph.
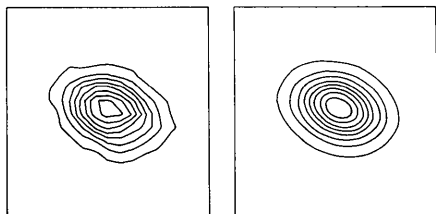

Fig. 1. Observed intensity distribution of a diffraction spot (left); the Gaussian approximation of the distribution (right).

Because of the Laue symmetry of DMC there are generally four symmetry-related spots on each photograph of the [001] and [100] directions. The integrated intensities of these related spots, after processing by each of the alternative methods, were averaged for each film of every film pack of the [001] orientation. The Gaussian approximation yielded significantly better results than the summation method as judged by the R_{sym} agreement factors: 0.031 and 0.055, respectively. Consequently, only the Gaussian approximation was used in all further work. The mean intensities were scaled in accordance with the several exposure times and film absorption factors (Appendix C), taking into account the film-blackening dependence on wavelength and on the angle of incidence.

Calibration of the spectral distribution of the source

The energy distribution of the source was first evaluated from the averaged intensity data of the [001]-direction photographs of DMC. For this purpose reflections consisting of only one harmonic were utilized (about 100 reflections for which R_{sym} was 0.031).

The source intensity, $I_s(\lambda)$, as a function of the wavelength λ, is derived from the relation (Appendix B)

$$I_0(hkl) = I_s(\lambda) Q(\lambda, \theta)|F_c(hkl)|^2, \qquad (2)$$

where $I_0(hkl)$ is the observed integrated intensity of the reflection hkl; $Q(\lambda, \theta)$ is a factor which includes the Lorentz–polarization corrections (Appendix B); and $F_c(hkl)$ is the calculated structure factor based on the known structure.

The derived spectrum $I_s(\lambda)$ was further checked against the independent intensity data of the [100] direction of DMC. In this case the structure factors F_0 for 96 single-harmonic reflections were calculated (R_{sym} for these intensity data was 0.056). The calculation was straightforward, with F_c replaced by F_0 in (2). These observed structure factors F_0 were compared with the calculated values, giving

$$R = \sum ||F_c| - |F_0||/\sum |F_0| = 0.045.$$

This result was obtained by matching observed and calculated structure factors without parameter adjustments; the overall scale factor ($\sum F_0/\sum |F_c|$) was 0.9995.

A major simplification in the experimental and computational procedures has been achieved by approximating the experimental spectral distribution of the source by an analytical expression,

$$I(\lambda) = A \exp[-d\mu(\lambda)](1/\lambda_0 - 1/\lambda)/\lambda^2 \qquad (3)$$

where d is an effective path length representing reabsorption in the target material and, perhaps, in the very thin film of evaporated Mo deposited on the Be windows of the tube; $\mu(\lambda)$ is the linear absorption

coefficient of Mo, which is a function of the wavelength; λ_0 is the short-wavelength cutoff ($\lambda_0 = 12\,398/V$, where V is the tube voltage); and A is a proportionality factor. This expression is based on the theoretical equation given by Compton & Allison (1935), modified by an absorption term.

The two parameters A and d were adjusted by a least-squares procedure utilizing 152 observed intensities of single-harmonic reflections of both the [100] and [001] orientations of DMC (the characteristic wavelength range, 0·70–0·72 Å, was excluded). Overall agreement factor $R(I) = \sum |I_o - I_c| / \sum I_c$ was 0.084 (typical value of d is 0.4 μm). The observed and analytically calculated energy distributions of the Mo X-ray source in the wavelength range 0·3–1·9 Å are plotted in Fig. 2. The analytical function is an excellent match down to 0·45 Å but poor in the 0·3–0·45 Å region. However, there are few reflections in this region and therefore it was not used in further work.

Resolution of higher harmonic reflections

The multiple-film technique allows a resolution of diffraction spots consisting of several harmonics. This technique takes advantage of the difference in the film absorption factor for different wavelengths recorded on the same spot (Appendix C). The structure factors $F_j(hkl) = F_o(jh, jk, jl)$ were fitted to the spot intensities $I_i(hkl)$ represented by

$$I_i(hkl) = \sum_{j=1}^{n} C_i(\lambda_j) I_s(\lambda_j) Q(\lambda_j, \theta) |F_j(hkl)|^2 \quad (4)$$

where $C_i(\lambda_j)$ is the absorption correction for the ith film, and the summation is over n harmonics of a reflection.

The system of equations (4) is, as a rule, overdetermined. The number of equations equals the number of films in the film pack, and the number of unknowns is the number of harmonics recorded in a spot. In order to test the method the set of equations was solved only for a small number of reflections consisting of two harmonics. The comparison of 18 observed

and calculated structure factors (nine spots) yielded $R = 0·07$. We have had no success in resolving reflections containing higher (three or more) harmonics.

Data acquisition by the Laue method

Taking advantage of the simplicity and convenience introduced by the analytical calibration curve, we established the quality of a data set and its rate of acquisition by using Laue diffraction data collected from a crystal of OOABCN. Multiple-film diffraction photographs of this crystal were recorded for four different orientations of the crystal in 1 and 5 min exposures. Structure factors were calculated from 754 single- and 271 double-harmonic spots. The rate of data collection was about 1000 reflections in 24 min, *i.e.* almost one reflection per second. Another set of structure factors for the same indices was obtained on a four-circle X-ray diffractometer (CAD-4) with Mo $K\alpha$ and counting times of 40 s per reflection. Comparison of these two sets yielded an agreement factor of 0·065 for about 500 common unique reflections.

Concluding remarks

Our results on the polychromatic Laue method indicate its feasibility as a means for data acquisition. It has been shown that the problem of higher harmonics can, at least partially, be solved by the multiple-film technique. The utilization of a crystal of known structure allowed successful calibration of the conventional Mo X-ray source. This tedious calibration task is, however, not necessary after establishing the adequacy of the analytical expression (3). A fair agreement factor, $R = 0·065$, between the Laue and Bragg methods obtained in OOABCN appears quite impressive, taking into account the long pathway leading from the spot intensities on the films through the spectral calibration and the various corrections applied.

It must be noted that we had no success in the resolution of three or more harmonics. This might be achievable, however, either by a more precise intensity measurement or by an increase of the number of films in the film pack or by interleaving the films with absorbing metal foils. In any case the work becomes rather complicated and, in general, not very useful; the number of spots consisting of three or more harmonics is usually small (about 10% in the case of OOABCN).

One of the advantages of the Laue method lies in the possibility of obtaining a large volume of information during relatively short exposures. For a comparable number of reflections the Laue method allows the use of exposure times more than ten times shorter than conventional diffractometry. Thus, the Laue method is the most useful one for flash X-ray experi-
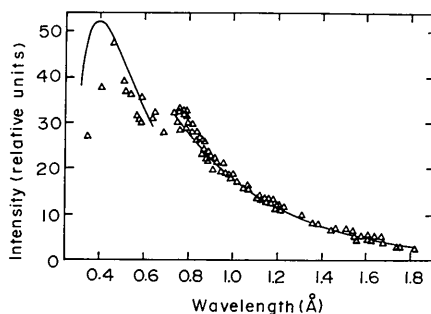
Fig. 2. Observed ($\triangle$) and calculated energy distribution of Mo X-ray source.

ments. It can also find uses with conventional X-ray sources in the study of radiation-sensitive systems; for example, the data acquisition rate in the experiment with OOABCN was close to one reflection per second. Although the Laue method was developed here for the transmission diffraction geometry, it can easily be applied in back-reflection experiments.

APPENDIX A
Reflection indexing†

Let a crystal with unit-cell vectors $\mathbf{a}_i$ $(i = 1, 2, 3)$ in direct space,‡ or $\mathbf{a}^j$ in reciprocal space, be oriented in some known manner with respect to the orthogonal basis $\mathbf{q}_i$ of the X-ray device. The corresponding orientation matrix t^{ij} is defined by

$$\mathbf{a}^i = t^{ij}\mathbf{q}_j. \qquad (A1)$$

If the orientation matrix of the crystal as well as the crystal-to-film distance M are known, the film position (X^1, X^2) of a reflection $h_i = (hkl)$ can be calculated as follows (see Fig. 3).

The diffraction vector $\mathbf{r}^*$ is defined by

$$\mathbf{r}^* = h_i\mathbf{a}^i = w^j\mathbf{a}_j \qquad (A2)$$

and has the device Cartesian coordinates q^i. When $\mathbf{r}^*$ lies on the sphere of reflection corresponding to wavelength λ, one obtains the following relations for the unit vectors $\mathbf{s}_0$ and $\mathbf{s}_1$ and for the film coordinates (Fig. 3):

$$\mathbf{s}_1 - \mathbf{s}_0 = \lambda\mathbf{r}^*, \quad X^1 = MBD/OD, \quad X^2 = MAD/OD. \qquad (A3)$$

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† Back reflections may be indexed in an analogous way (Ploc, 1978).
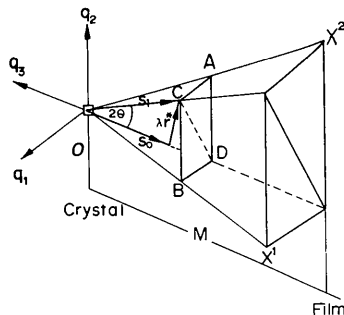‡ In all calculations tensor notation is used.

Fig. 3. Reflection indexing.

In the device coordinate system the components of vectors $\mathbf{r}^*$, $\mathbf{s}_0$ and $\mathbf{s}_1 = \lambda\mathbf{r}^* + \mathbf{s}_0$ are

$$\mathbf{r}^* = (q^1, q^2, q^3), \quad \mathbf{s}_0 = (0, 0, -1),$$

$$\mathbf{s}_1 = (\lambda q^1, \lambda q^2, \lambda q^3 - 1).$$

It follows (Fig. 3) that

$$OD = \mathbf{s}_1.\mathbf{s}_0 = 1 - \lambda q^3, \quad BD = \mathbf{s}_1.(1, 0, 0) = \lambda q^1,$$

$$AD = \mathbf{s}_1.(0, 1, 0) = \lambda q^2.$$

Substituting this in $(A3)$ one obtains

$$X^1 = M\lambda q^1/(1 - \lambda q^3), \quad X^2 = M\lambda q^2/(1 - \lambda q^3). \qquad (A4)$$

To find coordinates q^i one must express the vector $\mathbf{r}^*$ in two different bases:

$$\mathbf{r}^* = h_i\mathbf{a}^i = q^i\mathbf{q}_i. \qquad (A5)$$

From $(A5)$ and $(A1)$ it follows that

$$q^i\mathbf{q}_i = h_it^{ij}\mathbf{q}_j \quad \text{or} \quad q^j = h_it^{ij}. \qquad (A6)$$

Hence the film coordinates are given by

$$X^1 = M\lambda h_it^{i,1}/(1 - \lambda h_it^{i,3}),$$
$$X^2 = M\lambda h_it^{i,2}/(1 - \lambda h_it^{i,3}). \qquad (A7)$$

The cutoff wavelength λ_{min} is given by

$$\lambda_{min} = 12\,398/V \text{ (Å)},$$

V is the voltage of the X-ray tube (in volts) ($V = 45$ kV in our case, and $\lambda_{min} = 0.28$ Å).

On the other hand, the diffraction angle θ is limited by the film radius R_{max}:

$$\theta_{max} = 0.5 \text{ arc tan } (R_{max}/M).$$

This means that only those reflections should be taken into account for which the diffraction vector $\mathbf{r}^*$ satisfies the inequality $|\mathbf{r}| < 2|\sin \theta_{max}|/\lambda_{min}$. To calculate the length of the vector $\mathbf{r}^*$ the metric tensor $\mathbf{g}$ is needed. From $(A2)$ it follows that $|\mathbf{r}^*| = h_iw^i$. Taking into account that $w^i = g^{ij}h_j$ one obtains

$$|\mathbf{r}^*|^2 = h_ig^{ij}h_j.$$

The Fortran program which calculates the locations of the diffraction spots on the films is available at the Feinberg Graduate School of the Weizmann Institute of Science.

APPENDIX B
Lorentz factor for the Laue method

In calculating the Lorentz factor for the polychromatic Laue method we follow the treatment of James (1962).

Consider a series of parallel scattering planes whose spacing is d, and an unpolarized incident beam falling at a glancing angle θ upon these planes. The ratio of the reflected to the incident amplitude, q, is

given by

$$q = e^2 \lambda p^{1/2} d |F(hkl)|/(umc^2 \sin \theta_0), \quad (B1)$$

where e and m are the charge and the mass of the electron, respectively, c is the velocity of light, $p = (1 + \cos^2 2\theta_0)/2$ is the polarization factor, $F(hkl)$ is the structure factor, and u is the volume of the unit cell.

Each plane scatters an amplitude q but there is a phase difference between the amplitudes contributed by successive planes, equal to $4\pi d(\sin \theta)/\lambda$. Let θ_0 and λ_0 be the values of the incident angle and wavelength satisfying Bragg's law. The phase difference in this case is an integral number of times 2π and so effectively zero.

Here we depart from the classical treatment of the Bragg method where the integrated intensity is obtained by rocking the crystal. In the Laue method θ is fixed, the spectrum of the incident beam is continuous, and all waves in the range $\lambda_0 \pm \varepsilon$ (ε being small compared to λ_0) contribute to the integrated reflection in the direction of θ_0.

The phase difference between the amplitudes of successive planes when the wavelength is $\lambda_0 + \varepsilon$ becomes, since ε is small,

$$\delta = 4\pi d \sin \theta_0 [1/\lambda_0 - 1/(\lambda_0 + \varepsilon)] = 2B\varepsilon \quad (B2)$$

where $B = 2\pi d \sin \theta_0/\lambda_0^2$. The resultant amplitude of the reflected beam, A, due to s successive planes is

$$A = A_0 q \{1 + \exp(-i\delta) + \cdots + \exp[-(s-1)i\delta]\}$$

$$= A_0 q [1 - \exp(-is\delta)]/[1 - \exp(-i\delta)] \quad (B3)$$

where A_0 is the amplitude of the incident beam. Since ε is small we assume $A_0(\lambda_0 + \varepsilon)$ to be equal to $A_0(\lambda_0)$.

Let I_0 and I_ε be the corresponding intensities, or energy per square centimetre per second, in the incident and reflected beams, respectively; then $I_\varepsilon = I_0 R(\varepsilon)$. $R(\varepsilon)$ is obtained by multiplying $(B3)$ by its complex conjugate:

$$R(\varepsilon) = q^2 \sin^2(sB\varepsilon)/\sin^2(B\varepsilon). \quad (B4)$$

In order to calculate the integrated reflection we have to evaluate $\int R(\varepsilon) d\varepsilon$ in the region of the intensity maximum. Let a small area S be perpendicular to the reflected beam. The total energy passing through S in t seconds is $E_s = I_0 S t \int R(\varepsilon) d\varepsilon$ and the quantity

$$E_s/tI_0 = S \int R(\varepsilon) d\varepsilon \quad (B5)$$

is equivalent to $E_s \omega/I_0$, the 'integrated reflection', in the Bragg method.

By $(B4)$ the last equation becomes

$$E_s/tI_0 = (S/B) \int [q^2 \sin^2(sB\varepsilon)/\sin^2(B\varepsilon)] d(B\varepsilon). \quad (B6)$$

The integrand in $(B6)$ has appreciable values only when ε is very small. We can thus assume q^2 to be

constant during the integration and equal to its value at $\lambda = \lambda_0$, and take $\sin(B\varepsilon) = B\varepsilon$. If we now put $sB\varepsilon = x$, $(B6)$ becomes

$$E_s/tI_0 = (Sq^2 s/B) \int_{-\infty}^{\infty} (\sin^2 x/x^2) dx = Sq^2 \pi s/B.$$

The precise limits of integration are unimportant since the integrand has values appreciably different from zero only near $x = 0$. Inserting the values of q and B from $(B1)$ and $(B2)$ we obtain

$$E_s/tI_0 = (\lambda_0^4/2 \sin^2 \theta_0) p |F(hkl)|^2$$

$$\times (e^2/umc^2)^2 s \, dS/\sin \theta_0. \quad (B7)$$

$s \, dS/\sin \theta_0 = \Delta v$ is the volume of the crystal which contributes reflected radiation to the area S.

We can now finally express the integrated reflection in terms of the Lorentz factor $L = L(\lambda_0, \theta_0)$ for the polychromatic Laue method:

$$E_s/tI_0 = |F(hkl)|^2 (e^2/umc^2)^2 \Delta v L p \quad (B8)$$

where $L = \lambda_0^4/2 \sin^2 \theta_0$.

The same formula was derived by Zachariasen (1945) by a different method.

APPENDIX C
Film-absorption correction factors

The correction factor for the film-blackening dependence upon wavelength and the diffraction angle θ is (Milledge, de Wolff & Parrish, 1968):

$$C_b(2\theta, \lambda) = C(2\theta, \lambda)/C(0, \lambda)$$

where

$$C(2\theta, \lambda) = [1 - \exp(-\mu_1 d_1/\cos 2\theta)]$$

$$\times [1 + \exp(-\mu_1 d_1 - \mu_2 d_2)/\cos 2\theta]$$

and $\mu_i = \mu_i(\lambda)$ is the linear absorption coefficient for the photoemulsion ($i = 1$) or for the base ($i = 2$) of a film; d_i is the thickness of the photoemulsion or of the base.

The absorption correction for different layers of a film pack can be expressed as

$$C_j(2\theta, \lambda) = \exp[(1-j)(2\mu_1 d_1 + \mu_2 d_2)/2 \cos \theta]$$

where j is the layer number.

In our calculations the Victoreen empirical relation (Victoreen, 1948) for the mass-absorption coefficients (μ_i/ρ_i) was utilized:

$$\mu_i/\rho_i = A\lambda^3 + B\lambda^4 + C$$

where ρ_i is the 'atomic' density of the absorbing element. The coefficients A, B and C were taken from Koch, MacGillavry, Milledge, Koopmans, Rieck & Bacon (1968). They were different for different λ ranges in accordance with the edge-absorption limits.

The film (Ilford Industrial G) was assumed to contain $1·45$ mg cm^{-2} of silver bromide and 25 mg cm^{-2} of a base (40%C, 10%N, 40%O and 10%H) (Morimoto & Uyeda, 1963).

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Best Density Maps in Low-Resolution Crystallography with Contrast Variation

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Abstract

A method is presented of merging experimental diffraction data measured at different contrasts and structure factors calculated with models defined (and refined) at some of these contrasts (or at any other) in order to calculate an optimal density map at any contrast. It is based on a probabilistic approach which uses a joint probability distribution, for each $[h, k, l]$, of the measured intensities and the calculated structure factors.

1. Introduction

The technique of low-resolution single-crystal diffraction with contrast variation has been applied in several protein-structure determinations. It is especially useful in cases where, for instance, a part of the molecule is disordered in the crystal, like the

RNA in viruses (Bentley, Lewit-Bentley, Liljas, Skoglund, Roth & Unge, 1987, or the detergent in membrane-protein crystals (Zulauf, Timmins & Garavito, 1986). It has also been used to initiate the structural study of systems where no isomorphous derivative is yet available (Bentley, Lewit-Bentley, Finch, Podjarny & Roth, 1984; Zulauf, Timmins & Garavito, 1986). The technique consists of the collection of several diffraction data sets to a given resolution with crystals of the same molecule soaked in solvents with different scattering-length density. For the case of neutrons, the scattering-length density of the solvent is usually modified by changing its concentration of D_2O/H_2O. For X-rays, the scattering-length density can be modified by changing some salt concentration, for instance (Bragg & Perutz, 1952).

Often, in using this technique, one has to solve the problem of interpolating or extrapolating structure factors from one or a few contrasts for which model densities have been determined to another contrast for which the density has to be determined, using the

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