now lies in the new plane of diffraction for every reflecting angle θ of the sample and hence is further attenuated by a factor $\cos^2 2\theta$. Moreover, when the second reflecting angle θ happens to be 45°, Brewster's law is again invoked resulting in complete extinction of the reflected rays at this angle. Thus an error curve similar to those shown in Fig. 2 would tend towards infinity as θ_m approaches 45° for this special case. For all other angles in θ, however, there would be no error incurred in assuming the monochromator to be ideally mosaic even though it might, in fact, be ideally perfect, as indeed would be the case for the $\rho = 0°$ geometry.

Although in the above discussion on Brewster's law we have talked mainly in terms of the state of perfection of the monochromator, it will be evident from (4) that the conclusions drawn there are also applicable to the polarization ratio ($K = 0$ when $\theta_m = 45°$).

In conclusion, it should be clear from the foregoing analyses that if a monochromator is to be used for precise work such as electron density studies, the need to determine the polarization ratio K in order to eliminate a possible source of systematic errors becomes of prime importance. To this end, Fig. 3 may be used as a guide to assessing the severity of these errors for the particular case in hand. We emphasize that, since the errors rise non-linearly to a maximum at $\theta = 45°$ and are symmetrical about this point (Fig. 1), the determination of structural parameters, notably scale and thermal parameters, from high-angle data (typically in this region) with least-squares procedures may well be in error if no correction is made.

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On the Polarization Factor for Crystal-Monochromated X-radiation. II. A Method for Determining the Polarization Ratio for Crystal Monochromators

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Abstract

An experimental method for determining the polarization ratio K for crystal monochromators is described. Apart from a diffractometer, no additional equipment is required to perform the experiment other than a single crystal. The choice of a suitable crystal is discussed in terms of the theory of the method and from a practical point of view. It is shown that, in the absence of extinction and under certain easily attainable conditions, the crystal can be irregular in shape, of unknown dimensions and highly absorbing. The method has been tested on modelled data and applied in the determination of K for three wavelengths of radiation. The method may be adapted to powder diffractometry. A seemingly simpler method of determining K by least-squares refinement techniques gave unsatisfactory results.

1. Introduction

In a previous paper (Vincent & Flack, 1980, hereafter referred to as VFI), we have assessed the systematic errors that may be incurred in X-ray data through

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failure to consider the *effective* polarization state of the X-ray beam reflected off a crystal monochromator. Methods of experimentally determining correction terms to the polarization factor (the quantity affected) have been proposed by Miyake, Togawa & Hosoya (1964) and by the International Union of Crystallography (1978); the latter has a modification proposed by Le Page, Gabe & Calvert (1979). The method of Miyake, Togawa & Hosoya (1964) involves the determination of a parameter c [see VFI equation (2)] which describes the degree of perfection of the monochromator, whereas that of the IUCr involves the determination of the polarization ratio K [VFI equation (1)], *i.e.* the ratio of power in the incident monochromated beam for the two mutually perpendicular directions of polarization σ and π. The results of Jennings (1968) and Le Page, Gabe & Calvert (1979) would suggest that c is not always appropriate since values of K which lie outside the range defined for c have been found. However, VFI have shown the relation between c and K [VFI equations (3), (4) and (5)] and that the two expressions for the polarization factor [VFI equations (1) and (2)] can be equivalenced by relaxing the constraints on c.

In this paper we describe an alternative method for experimentally determining K for single-crystal diffractometers: it requires no additional equipment for its measurement other than a single-crystal sample. Although we are principally interested in single-crystal diffractometers and hence the theory propounded in the following sections is directly related to this case, analogous expressions can be derived for powder diffractometers which, under certain conditions, will lead to essentially the same method.

2. Basis

The integrated intensity J of a reflection from a single, ideally mosaic crystal may be defined as

$$J = \frac{E_s\,\omega}{I_0} = \frac{N^2\lambda^3}{\sin 2\theta} F^2 B \left(\frac{e^2}{mc^2}\right)^2 AVP, \tag{1}$$

where E_s is the total energy reflected as the crystal rotates with angular velocity ω through the reflecting position, I_0 is the incident beam energy per unit area and unit time, N is the reciprocal of the volume of the unit cell, θ is the Bragg angle, λ is the X-ray wavelength, F is the absolute thermal-vibrational-free structure factor, B is the square of the temperature factor, (e^2/mc^2) is the classical scattering amplitude of an electron, A is the absorption transmission factor, V is the volume of the crystal and P is the appropriate polarization factor [given by VFI equation (1)].

J is related to the measured (net) intensity I of the reflection by

$$I = kJ, \tag{2}$$

where k is a scale factor.

For a particular crystal we can set

$$G = N^2(e^2/mc^2)^2\,V$$

since it is a constant provided that the sample is completely bathed by the incident X-ray beam. Thus, for a reflection measured with one type of X-ray wavelength, we may rewrite (1) after substitution into (2) as

$$I_{11} = \frac{k_{10}\,\lambda_{10}^3}{\sin 2\theta_{11}} F_{11}^2\,B_{01}\,A_{11}\,P_{11}\,G, \tag{3}$$

where the first subscript indicates that the value is a function of wavelength (F therefore includes anomalous dispersion effects if present) and the second subscript is the reflection identifier. (A subscript becomes 0 if one or other is not applicable.)

Accordingly, we have for a second reflection measured under the same conditions as the first

$$I_{12} = \frac{k_{10}\,\lambda_{10}^3}{\sin 2\theta_{12}} F_{12}^2\,B_{02}\,A_{12}\,P_{12}\,G. \tag{4}$$

Dividing (3) by (4) we obtain

$$\frac{I_{11}}{I_{12}} = \frac{\sin 2\theta_{12}}{\sin 2\theta_{11}}\,\frac{F_{11}^2}{F_{12}^2}\,\frac{B_{01}}{B_{02}}\,\frac{A_{11}}{A_{12}}\,\frac{P_{11}}{P_{12}}, \tag{5}$$

which is an expression independent of G and the scale factor k.

Suppose that the two reflections defined by (3) and (4) were measured with the crystal monochromator in place. If we now remeasure the same reflections without the monochromator but with the same wavelength of radiation (effectively monochromatized by β-filter or balanced-filter techniques), then (3) and (4) would become respectively

$$I'_{11} = \frac{k'_{10}\,\lambda_{10}^3}{\sin 2\theta_{11}} F_{11}^2\,B_{01}\,A_{11}\,P'_{11}\,G, \tag{6}$$

$$I'_{12} = \frac{k'_{10}\,\lambda_{10}^3}{\sin 2\theta_{12}} F_{12}^2\,B_{02}\,A_{12}\,P'_{12}\,G, \tag{7}$$

where the primes indicate a relative change in value between equivalent quantities for the two methods of monochromatization, and the polarization factor P' for filtered radiation is defined as

$$P' = (1 + \cos^2 2\theta)/2. \tag{8}$$

Dividing (6) by (7) we obtain a similar expression to (5) *viz*

$$\frac{I'_{11}}{I'_{12}} = \frac{\sin 2\theta_{12}}{\sin 2\theta_{11}}\,\frac{F_{11}^2}{F_{12}^2}\,\frac{B_{01}}{B_{02}}\,\frac{A_{11}}{A_{12}}\,\frac{P'_{11}}{P'_{12}}. \tag{9}$$

Finally, division of (5) by (9) gives

$$\frac{I_{11}}{I_{12}}\,\frac{I'_{12}}{I'_{11}} = \frac{P_{11}}{P_{12}}\,\frac{P'_{12}}{P'_{11}}. \tag{10}$$

Equation (10) forms the basis of the method we propose for experimentally determining the polarization ratio K.

3. Conditions for the validity of (10)

In principle, (10) is only valid for the two sets of measurements if

(*a*) the temperature of the experiment is kept constant (resulting in the cancellation of B's),

(*b*) the orientation of the reciprocal-cell axes of the crystal with respect to the diffractometer axes remains unchanged (resulting in the cancellation of A's),

(*c*) the intensity of the incident beam is stable during the course of the experiment (resulting in cancellation of k's),

(*d*) the effects of other factors such as thermal diffuse scattering (TDS) and extinction can be excluded.

In a practical situation, points (*a*) and (*b*) can be easily achieved. The latter requires that, once mounted on the instrument, the crystal is never touched during the course of the experiment, or, if removed, it can be remounted in the same orientation, a possibility which exists on most instruments. (*c*) requires that the operational voltage and current of the X-ray tube is maintained throughout the measurement of the individual sets of data, but may be changed from one set to the other. Fluctuations can be monitored by measuring standard reflections and, if necessary, eliminated by correcting the sets of raw data by pre-scaling in the usual way.

The important and interesting inference that can be drawn from (*a*), (*b*) and (*c*) in conjunction with (10) is that, in theory, the crystal used for the measurements can be irregular in shape, of unknown dimensions, highly absorbing and of unknown structure and composition. However, in practice one would need to know the structure in order to use the method to its fullest extent. This does not detract from the validity of the other points as long as extinction effects are absent in the crystal.

The major objection to allowing the data to be affected by extinction is that the effect varies with the polarization state of the incident X-rays and hence the correction terms derived from the formalism (see for example Becker & Coppens, 1974, 1975) will, in general, differ for the two sets of measurements for corresponding reflections and will not, therefore, cancel in pairs as the other quantities do. Thus a crystal will have to be chosen where the absence of extinction effects has previously been established or such effects have been eliminated.

Unlike extinction, corrections for TDS, if present, will in principle cancel in pairs provided that the following precautions are taken. Apart from (*a*) above, the requirements are that the region of reciprocal space scanned (scan width) for the measurements of intensities and the relative peak positions within the scan range remain identical for corresponding reflections (Stevens, 1974). Again, these conditions are not difficult to achieve in practice if (*b*) is maintained. Moreover, experience has shown that small discrepancies between the relative peak positions for corresponding reflections within the scan can be tolerated without loss of accuracy for compounds with low TDS corrections. Finally, corrections to the intensities for multiple-reflection effects (if present) will also cancel in pairs if, again, (*b*) is maintained throughout the experiment.

4. Method and strategy

Substituting in the general expression for P [VFI equation (1)] and rearranging in terms of K, we may rewrite (10) in the more general form for the ith and jth reflections as

$$\begin{aligned} K_{ij} = [(\cos^2\rho + \sin^2\rho\cos^2 2\theta_i) - \gamma_{ij}(\cos^2\rho \\ + \sin^2\rho\cos^2 2\theta_j)]/[\gamma_{ij}(\sin^2\rho + \cos^2\rho\cos^2 2\theta_j) \\ - (\sin^2\rho + \cos^2\rho\cos^2 2\theta_i)], \qquad (11) \end{aligned}$$

where

$$\gamma_{ij} = \frac{I_i}{I_j}\,\frac{I'_j}{I'_i}\,\frac{P'_i}{P'_j},$$

the subscripts for the wavelength-dependent terms now being dropped. The P' are given by (8). For $\rho = 0$ and $\rho = 90°$, (11) simplifies to

$$K^0_{ij} = \frac{1-\gamma_{ij}}{\gamma_{ij}\cos^2 2\theta_j - \cos^2 2\theta_i}, \qquad (12a)$$

$$K^{90}_{ij} = \frac{\cos^2 2\theta_i - \gamma_{ij}\cos^2 2\theta_j}{\gamma_{ij} - 1} = \frac{1}{K^0_{ij}}. \qquad (12b)$$

As (11) implies, the principle of the method is to collect the same set of data in two different modes, one with the monochromator in place and the other either with β-filter or balanced-filter techniques. From the two sets of measurements the ratios of net intensities of corresponding pairs of reflections are determined in the manner indicated by (10). Hence from the series of intensity ratios, a series of values for K can be derived from (11).

The optimum conditions for determining K are, in general, those where the error τ discussed in VFI attains maximum values. Consequently, the points outlined there are useful for making the choice of a suitable crystal for the experiment. From VFI Fig. 1 we see that the maximum errors occur at $\theta = 45°$. Hence the reflections that give the most valuable information on the value of K are those which lie in a region on either side of this point. However, since the method of calculating K is based on taking ratios of quantities, it is also necessary to consider the relative errors incurred in the polarization factors for the individual reflections used to form these ratios. It will be seen, therefore, that very little information on K is gained by taking ratios of reflections with similar θ values. On the other hand, maximum information is gained from ratios formed with reflections lying in the low-τ region (minimal errors, VFI Fig. 1) with those in the high-τ region, since the difference between the relative magnitudes of the individual errors in these two regions is greatest. It is useful here to consider the variation of τ with wavelength of radiation for not only does it give an insight into how large these differences can be, but also provides information on how large the θ ranges should be to define the low- and high-τ regions. These factors become important when the results of Le Page, Gabe & Calvert (1979) are taken into consideration. These authors found that the parameter c, to which K is related [VFI equations (4) and (5)], also varied with wavelength of radiation. Hence it will be necessary to determine K for each X-ray wavelength to be used for data collection.

As VFI Fig. 3 shows, τ diminishes fairly rapidly with diminishing wavelength for a particular monochromator. To take an example, for the worst case ($\theta = 45°$) with Ag $K\alpha$ radiation, the relative difference between τ for an ideally mosaic graphite (or quartz) monochromator and an ideally perfect one is only ~0·7% ($\rho = 0$ and 90°). This value may be compared to the equivalent one for Cu $K\alpha$ radiation which is an order of magnitude greater (~5–6%). It will be clear therefore that the relative differences between the errors in the low- and high-τ regions for the shorter wavelengths are substantially smaller than their equivalents for the longer wavelengths. Thus it becomes more critical to define the low- and high-τ regions near to $\theta \simeq 0$ and $\theta \simeq 45°$ respectively for the shorter wavelengths than it is for the longer wavelengths* to obtain the maximum benefit from the relative differences in errors of reflections lying in these regions. A crystal should therefore be chosen with these points in mind, noting that one with a large unit cell may suffice.

The greatest restriction on the choice of a suitable crystal, besides the problem of extinction, is that the reflections to be used in the determination of K must be intense enough so that statistical and/or other errors (*e.g.* in the methods of reducing raw intensities to net intensities) influencing the accuracy of the data can be deemed negligible. While this is not necessarily a problem with low-τ reflections, it can be so for high-τ ones, particularly when measurements are made with the shorter wavelengths of radiation.

One further point concerns the accuracy of the measurements as judged by the ratio $I/\sigma(I)$. The intensity measurements enter into (10) as the product of two ratios, I_{11}/I_{12} and I'_{12}/I'_{11}. The variance of a ratio ($r = y/x$) may be calculated from the approximation, given by Hamilton (1964),

$$(\sigma(r)/r)^2 \simeq (\sigma(x)/x)^2 + (\sigma(y)/y)^2.$$

However, as Hamilton (1964) points out, for this approximation to be valid there must be virtually no probability that either x or y is near to zero. To ensure that this is the case it is necessary to use only those intensity measurements for which $I/\sigma(I)$ is reasonably large. Experience has shown that reflections with $I/\sigma(I)$ of 20 or more give good results and therefore the experiment should be tailored to meet this criterion.

The number of reflections to be measured is very much dependent on the above criteria and on the convenience of the measuring techniques adopted. However, if M low-τ and N high-τ reflections are measured, then a possible $M \times N$ ratios can be formed, giving $M \times N$ values of K. In this respect it is useful to note that a crystal of cubic symmetry will give the greatest number of reflections for particular values of θ, a point worth considering when measuring K for the shorter wavelengths of radiation where a sufficient number of intense reflections are sought after.

The best value of K is estimated by taking the weighted mean of the $M \times N$ individual values K_{ij}. A weighting scheme which we have found satisfactory is described in a following paper (Flack & Vincent, 1980).

5. Experimental

All intensities were measured with a sphere of Mg_2Si (space group $Fm3m$, $a = 6{\cdot}352$ Å) radius 63(1) μm. Three types of radiation were used, Cu $K\alpha$, Mo $K\alpha$ and Ag $K\alpha$, and, for each, measurements were made successively with our pyrolytic-graphite monochromator and the relevant β filter. A Philips PW1100 four-circle diffractometer was employed which has the $\rho = 90°$ geometry. A resumé of the data-collection conditions is contained in Table 1. $\frac{1}{16}$ of the volume of reciprocal space was measured initially. However, for the Ag $K\alpha$ radiation this yielded an insufficient number of accurately measured data. Thus the following forms of reflections, chosen for their intensity and value of θ, were measured more accurately; in the low-τ region {111}, {200}, {220}, {311}, {222}, {400} and {331}; in the high-τ region, {10,10,4}, {12,6,6} and {12,8,0}. Data were measured in the step-scan mode and were treated according to the algorithm of Lehmann &

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* For the longer wavelengths of radiation such as Cu $K\alpha$, it may be possible to measure reflections with θ values approaching 90°. A low-τ region may also be defined about this point as can be seen from VFI Fig. 1.

Table 1. *Data-collection parameters for polarization-ratio measurements*

Radiation (Å)		μ (mm^{-1})	μR	$2\theta_M$ (°)	Filter absorption edge (Å)		$(\sin\theta/\lambda)_{\max}$ (Å^{-1})
Cu $K\alpha$	1·5418	9·69	0·606	26·56	Ni	1·488	0·63
Mo $K\alpha$	0·71069	0·955	0·060	12·16	Nb	0·6529	1·15
Ag $K\alpha$	0·5608	0·479	0·030	9·59	Pd	0·509	1·46

Larson (1974) and Lehman (1975). The removal of the white-radiation background for the β-filtered data was performed by the method of Nelmes (1975) and it is for this reason that the β-filter material indicated in Table 1 was selected. The performance of the Lehmann–Larson algorithm may be judged by plotting out the estimated peak width as a function of θ with reflections split into five classes based on their intensity, *viz* class (i) contains reflections with intensities in the range $n_i \le I/\sigma(I) < n_{i+1}$, with $n_1 = 0$, $n_2 = 4$, $n_3 = 8$, $n_4 = 16$, $n_5 = 32$ and $n_6 = \infty$. For the β-filtered data the results showed a clear, approximately linear, increase of estimated peak width with θ and there was little, if any, dependence on the class of the reflection. However, for the data measured with the monochromator, there was a much larger dispersion of estimated peak widths at any value of θ and a clear tendency for the stronger reflections to have a greater estimated peak width. This behaviour of the Lehmann–Larson (1974) algorithm is due to the exceedingly low number of background counts when using a monochromator. We have very briefly experimented with the auto-correlation technique of Rigoult (1979) and find that it suffers from the same shortcoming. As the estimated peak widths for the monochromator and β-filtered data were thus not comparable, all data, unless otherwise mentioned, were corrected for the effect of first- and second-order thermal diffuse scattering by the method of Stevens (1974). The elastic constants of Mg_2Si were taken from Whitten, Chung & Danielson (1965).

6. A refinement procedure for determining *K*

Before describing the application of our experimental data to the method outlined in §§ 2, 3 and 4 above, we will report the results of a seemingly simpler method of determining K but which unfortunately proved not to work for the short wavelengths of Mo $K\alpha$ and Ag $K\alpha$ when used with a graphite monochromator.

For each data collection an absorption correction for a sphere was applied with the table of values of Dwiggins (1975). The intensities were then corrected for Lorentz–polarization effects based on some value of K, and reduced to $|F|$ values. Least-squares refinement of the structural parameters of Mg_2Si was carried out based on nine variables, *viz* one scale factor, six anisotropic extinction parameters with a Lorentzian distribution and the model of Becker & Coppens (1974, 1975) as modified by Thornley & Nelmes (1974) and two isotropic temperature factors (both Mg and Si are in special positions in Mg_2Si and there are no variable positional parameters and harmonic vibrations are restricted to be isotropic). It was known from previous measurements that anisotropic extinction was significant in this crystal (Vincent, Yvon & Levinson, 1980). A weighting scheme $1/\sigma^2(F_o)$ was applied and reflections with $I > 3\sigma(I)$ were used in the least-squares refinement. We attempted to find a minimum from the converged refinements of the goodness of fit parameter,

$$g = \left[\sum_i W_i(|F_o|_i - |F_c|_i)^2/(N_{\text{obs}} - N_{\text{var}})\right]^{1/2},$$

as a function of the postulated value of K (W_i is the weight assigned to the ith observation, N_{obs} is the number of observed reflections and N_{var} is the number of variable parameters). This method was also tested with simulated data based on a model value of K with pseudo-random Gaussian errors added having approximately the same relative error as the observed data. The real and the simulated data showed the same behaviour. The results for each radiation are as follows.

(*a*) Cu $K\alpha$. There were 122 reflections, the weakest of which had $I/\sigma(I) \simeq 30$. The refinements proceeded smoothly. For the simulated data, g showed sharp parabolic-shaped minima at the model value of K ($K = 0{\cdot}916$ and $1{\cdot}00$ for the monochromator and β-filter data respectively). The observed data also produced sharp parabolic-shaped minima at $K = 0{\cdot}916\ (9)$ for the monochromator data [$g = 2{\cdot}91$, $R(F) = 0{\cdot}008$] and at $K = 1{\cdot}00\ (2)$ for the β-filter data [$g = 2{\cdot}64$, $R(F) = 0{\cdot}009$].

(*b*) Mo $K\alpha$. There were 580 and 552 reflections for the monochromator and β-filter data respectively. With all reflections included, in either the real or simulated data, the anisotropic extinction parameters went non-positive-definite even when the least-squares refinement was heavily damped. The problem is with the data coverage of the low-angle region of reciprocal space as Vincent, Yvon & Levinson (1980) encountered no trouble in refining comparable data from the same crystal for which a whole sphere of reflections had been measured in the low-angle region. We thus decided to limit the refinement to reflections with $\sin\theta/\lambda \geq 0{\cdot}32$ Å^{-1} thus eliminating 19 reflections. With this restriction, the anisotropic extinction parameters converged to positive-definite values. The simulated data produced sharp minima in g as a function of K close to the model values of K. However, the minimum for the monochromator data was far from having a parabolic shape and was fairly shallow (0·01 in g). The real data for the monochromator produced no minimum of g in the range $0{\cdot}896 < K < 0{\cdot}978$, the smallest value of g being at $K = 0{\cdot}896$ [$g = 1{\cdot}256$, $R(F) = 0{\cdot}013$]. The β-filter data produced a parabolic minimum at $K = 0{\cdot}95\,(4)$ [$g = 1{\cdot}186$, $R(F) = 0{\cdot}018$].

(*c*) Ag $K\alpha$. There were 675 and 361 reflections with $I > 3\sigma(I)$ for the monochromator and filter data respectively. With all reflections or limited to $\sin\theta/\lambda \geq 0{\cdot}32$ Å^{-1}, both the real and simulated monochromator data produced non-positive-definite extinction parameters and were thus unable to converge. The real filter data limited to $\sin\theta/\lambda \geq 0{\cdot}32$ Å^{-1} produced a very shallow minimum of g against K at $K = 1{\cdot}0\,(2)$ [$g = 1{\cdot}205$, $R(F) = 0{\cdot}028$] for data uncorrected for thermal diffuse scattering.

7. Results

We have found it advantageous to check the correctness of our analysis and computer programs by carrying out tests on simulated data. These data are generated from the real measurements with model values of the anisotropic extinction parameters, and the isotropic temperature factors of the crystal of Mg_2Si together with a model value of K. Pseudo-random Gaussian errors were added to the intensity values derived from the model to give $I/\sigma(I)$ values approximately equal to those for the real measurements.

Intensity measurements of reflections are divided into two mutually exclusive sets. (1) Low τ with $0 \leq \theta \leq \theta_l$ or $90 - \theta_l \leq \theta \leq 90°$ and (2) high τ $\theta_h \leq \theta \leq 90 - \theta_h°$. It is possible to change the number of reflections in each set by changing the values of θ_l and θ_h. We also found it convenient to include a test that rejected pairs of intensity measurements (monochromator and β filter) of a reflection if the relative extinction-correction difference was larger than a chosen amount (*ypc*).

Simulations on the data measured with Mo $K\alpha$ and Ag $K\alpha$ immediately showed up problems with an initial simple weighting scheme for deriving the weighted mean of the values of K_{ij}. Weighted mean K was significantly different from the model values of K. The simple weighting scheme was based on a direct application of the propagation of errors ignoring correlations. The weighting scheme we finally adopted is described in Flack & Vincent (1980).

Table 2 shows the results of simulations on the Cu $K\alpha$ data. The largest extinction correction on $|F|$ in this model was for 220 with $y_{\text{ext}} = 0{\cdot}702$ and $0{\cdot}698$ for the monochromator and filter data respectively. It may be seen that although the influence of extinction on the value of K is not great, a value of the relative extinction-correction difference (*ypc*) of 0·0005 brings the determined value of K within one e.s.d. of the model value. The value of $ypc = 0{\cdot}0005$ was thus adopted in treating the real data. We found with $\theta_l = 30°$, $\theta_h = 38{\cdot}5°$, giving 28 low-τ and 31 high-τ measurements, K to be 0·860 (14), for Cu $K\alpha$ radiation.

Simulations on the Mo $K\alpha$ data showed that the maximum relative difference between the extinction corrections for the two sets of data to be negligibly small [$ypc = 0{\cdot}0007$ corresponding to $y_{\text{ext}} = 0{\cdot}81544$ (monochromator) and 0·81488 (filter) for the 220 reflection]. Hence, no reflections were rejected by this criterion. However, there was a marked dependence of the value of K on the goodness of the data used as judged by the minimum $I/\sigma(I)$ used. It was found that a minimum $I/\sigma(I)$ of 25 produced values of K within one e.s.d. of the model K. Hence $\theta_l = 25°$, $\theta_h = 35°$ gave 70 low-τ and 55 high-τ reflections with $I/\sigma(I) \geq 25$. These conditions produced a value of $K = 0{\cdot}907$ (11) for the real data.

The intensities of the forms of the reflections mentioned in § 5 above were collected with Ag $K\alpha$ radiation. The experiment was tailored so that $I/\sigma(I) > 25$. The anisotropic extinction parameters (Lorentzian, type I) determined by Vincent, Yvon & Levinson

Table 2. *Simulations on the* Cu $K\alpha$ *data*

All reflections used have $I/\sigma(I) > 28$. The weights were calculated with a damping factor of 0·1 and maximum relative shift on the last cycle of 0·005. The model was based on a value of $K = 0{\cdot}9162$.

θ_l (°) low-τ region definition	θ_h (°) high-τ region definition	*ypc* maximum acceptable relative extinction difference	Number of low-τ reflections	Number of high-τ reflections	K
25	35	1·0	38	50	0·929 (8)
25	35	0·001	32	50	0·930 (9)
25	35	0·0005	32	39	0·927 (10)
30	38·5	0·0005	49	24	0·926 (11)
25	30	0·001	32	64	0·930 (9)

(1980) for the same crystal and radiation were used to derive the relative magnitudes of the extinction corrections for the two sets of data. The reasonableness of using the same extinction tensor can be understood from the fact that the crystal had not been removed from its support between the two experiments; consequently the directions of the normals to the planes of diffraction for corresponding reflections remained unchanged. To obviate the need for making TDS corrections, the peak widths of the monochromator data were adjusted to be identical to their equivalents in the filtered data with peak maxima in identical positions relative to the peak widths. It was felt prudent not to include the $\{111\}$ reflections in the determination of K since the absorption edge of the β filter fell beneath their peaks. No reflections were rejected on the basis of the difference between extinction corrections [maximum value of ypc was 0·0007 corresponding to $y_{\rm ext} = 0{\cdot}8885$ (monochromator) and 0·8891 (filter) for the 220 reflection]. The value of K determined under these conditions was 0·805 (11).

In summary, our experimentally derived K for Cu $K\alpha$ radiation falls between the expected values for an ideally mosaic and perfect graphite monochromator. In contrast, the values we have obtained for Mo $K\alpha$ and Ag $K\alpha$ radiation fall outside this range. Moreover, and contrary to the results of Jennings (1968) and Le Page, Gabe & Calvert (1979), they are smaller than those expected for an ideally mosaic crystal.

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On the Polarization Factor for Crystal-Monochromated X-radiation. III. A Weighting Scheme for Products

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Abstract

The minimum-variance weighting scheme for calculating the weighted mean of a quantity for the following unusual case is analysed. The quantity is derived from the product of two independent quantities for each of which a set of data is available. All the products between the two sets of data are taken into consideration. The application to measurements of the polarization state of X-radiation is outlined.

Introduction

In a previous paper (Vincent & Flack, 1980), a method is described for determining the polarization ratio, K, of X-radiation reflected from a monochromator. This value is estimated by taking the weighted mean of $M \times N$ individual values K_{ij}, *i.e.*

$$\hat{K} = \sum_{i=1}^{M} \sum_{j=1}^{N} a_{ij} K_{ij} \Big/ \sum_{i=1}^{M} \sum_{j=1}^{N} a_{ij}, \qquad (1)$$

where a_{ij} is the weight attributed to K_{ij}.

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