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On the Polarization Factor for Crystal-Monochromated X-radiation.
I. Assessment of Errors

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Abstract

The relation between the parameter c describing the degree of perfection of a crystal monochromator and the polarization ratio K is established. The influence of the incorrect assumption that a monochromator is always ideally mosaic on the polarization factor is discussed in terms of the systematic errors that may be introduced into X-ray data from the neglect to consider it as otherwise. Emphasis is given to a comparison of the errors for the two most common spectrometer geometries which provides some illuminating results.

Introduction

With the mounting interest in accurate electron density studies has come a parallel need to obtain intensities not only of the highest possible quality, but also free from systematic errors. While the former is fairly easy to achieve nowadays, the latter still poses some grave problems in assessment and elimination. A particular facet of these errors takes form in the question of which is the best method of obtaining a set of intensities from a characteristic wavelength of X-radiation (usually $K\alpha$) having the least number of (identifiable) systematic errors associated with it. Many experimenters in the field of electron density studies now prefer to use β-filtered radiation, primarily because of the advent of more sophisticated techniques of determining net intensities (Lehmann & Larson, 1974; Blessing, Coppens & Becker, 1974; Nelmes, 1975) which suffer from, it is believed, fewer systematic errors than other methods. However, the most widely used method of obtaining characteristic wavelength intensities, being also the most efficient and convenient, is with crystal monochromators, yet their very use may well introduce systematic errors into the data of a type which would otherwise be absent in the other methods using filters. A lesser-known form in which these errors can manifest themselves has been the subject of a recent paper by Flack & Vincent (1979). Our interest, however, lies with a better-known form, that of the correct representation of the polarization factor, which has already been the subject of previous articles.

Azároff (1955) derived a general expression for the polarization factor of a twice-diffracted beam applicable to an ideally mosaic crystal monochromator and sample. The validity of the apparently generally accepted assumption that a monochromator always behaves as ideally mosaic has, however, been sufficiently thrown into doubt. Miyake, Togawa & Hosoya (1964) and Hope (1971) have shown experimentally that two of the most commonly used crystal monochromators (LiF and graphite) can exhibit characters which may be described as lying somewhere between ideally mosaic and ideally perfect. For a monochromator which is intermediate between these two cases, Miyake, Togawa & Hosoya (1964) have suggested that the form of the polarization factor, P, for a twice diffracted beam should be expressed as $P = cP_d + (1 - c)P_k$. The fractions c and $(1 - c)$ determine the proportions of the monochromator which behave as ideally perfect (polarization factor P_d) and ideally mosaic (polarization factor P_k) respectively. From an experimental method developed by Miyake, Togawa & Hosoya (1964), these authors and Hope (1971) have determined values for c of $\sim 0{\cdot}6$, indicating that the major parts of their monochromators behave as if they were ideally perfect. Kerr & Ashmore (1974) have examined the differences between the polarization corrections for the extreme cases of ideally mosaic and ideally perfect monochromators of LiF, graphite and quartz for Cu and Mo $K\alpha$ radiations. They conclude that large systematic errors can arise through failure to consider the state of perfection of the monochromator.

Unfortunately, the problem does not just rest with determining the state of perfection of a monochromator lying within the bounds of ideally mosaic and ideally perfect. Jennings (1968), rather than determining the parameter c, focused his attention on determining the polarization ratio K, that is the ratio of power in the incident monochromated beam with polarization in the

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diffraction plane (σ polarization*) to that normal to it (π polarization). Under the direction of Jennings, the IUCr Commission on Crystallographic Apparatus (International Union of Crystallography, 1978) has set up a survey with the aim of obtaining a range of experimentally determined values of K for crystal-monochromated X-ray beams. It has suggested a method for measuring K which requires a certain amount of adaptation of existing instruments with ancillary equipment for the measurements. Le Page, Gabe & Calvert (1979) have used a modified version of the method proposed by the IUCr to determine values of K for their monochromators. Their results and those of Jennings (1968) indicate that values of K may not only be far removed from those expected for an ideally mosaic monochromator, but also may not even fall in between the values for an ideally mosaic and ideally perfect crystal. Possible physical explanations of this behaviour have been given by these authors.

The main object of this series of papers is to describe an alternative method of measuring K without the necessity of adapting existing instruments. This part deals with the relation between c and K and its physical reasonableness, and examines in greater detail the systematic errors that may be incurred by the use of an inappropriate expression for the polarization factor. Emphasis is given to a comparison of the errors for the two most common spectrometer geometries.

The relation between *c* and *K*

The general expression for the polarization factor of a twice-diffracted beam (Azároff, 1955) may be defined as

$$P = [(\cos^2\rho + K\sin^2\rho) + (\sin^2\rho + K\cos^2\rho) \times \cos^2 2\theta]/(1+K), \quad (1)$$

where K is the polarization ratio, equal to $\cos^2 2\theta_m$ for an ideally mosaic monochromator, θ_m being the Bragg angle at which the monochromator is set to reflect a particular wavelength of X-radiation; θ is the Bragg angle of a reflection from the sample and ρ is the angle between the two planes of diffraction, *i.e.* the planes containing the incident and reflected rays of the monochromator and sample. For the two most common spectrometer geometries, ρ takes a value of either 0 or 90°.

For an ideally mosaic monochromator,

$$P_k = P \quad \text{with } K = K_k = \cos^2 2\theta_m \text{ in (1).}$$

Similarly, for an ideally perfect monochromator

$$P_d = P \quad \text{with } K = K_d = |\cos 2\theta_m|.$$

According to Miyake, Togawa & Hosoya (1964) a general expression for the polarization factor may be defined as

$$P_i = (1-c)P_k + cP_d, \quad (2)$$

where c is the fractional part of the monochromator considered to be perfect. It can be shown on expanding (2) with a certain amount of rearrangement that

$$P_i = [(\cos^2\rho + K_i\sin^2\rho) + (\sin^2\rho + K_i\cos^2\rho) \times \cos^2 2\theta]/(1+K_i), \quad (3)$$

where

$$K_i = \frac{(1-c)(1+K_d)K_k + c(1+K_k)K_d}{(1-c)(1+K_d) + c\,(1+K_k)}. \quad (4)$$

It will be seen, therefore, that (3) is equivalent to (1) on setting $K = K_i$, a result which confirms the physical reasonableness of (2). From (4), c can be expressed in terms of K_i *viz*

$$c = \frac{(K_i - K_k)(K_d + 1)}{(K_d - K_k)(K_i + 1)}. \quad (5)$$

Assessment of errors

It is useful to define the polarization factors for the cases of ideally mosaic and perfect monochromators for $\rho = 0$ and $\rho = 90°$. From an appropriate use of (1) we find

$$P_k^0 = (1 + K_k\cos^2 2\theta)/(1+K_k), \quad (6a)$$

$$P_k^{90} = (K_k + \cos^2 2\theta)/(1+K_k), \quad (6b)$$

$$P_d^0 = (1 + K_d\cos^2 2\theta)/(1+K_d) \quad (6c)$$

$$P_d^{90} = (K_d + \cos^2 2\theta)/(1+K_d), \quad (6d)$$

where the superscript on P defines the value of ρ.

To find the maximum and minimum values of the polarization factor P, we need to determine at which values of θ $\mathrm{d}P/\mathrm{d}\theta = 0$. It is easily shown that for general values of θ_m the condition to be met is the same for all of (1), (2), (3) and (6), *i.e.* $\sin 4\theta = 0$. Hence, the maximum values of P occur at $\theta = 0$ and 90° and the minimum at $\theta = 45°$ ($0 \le \theta \le 90°$). Thus, the largest polarization correction occurs at $\theta = 45°$.

A more useful quantity here is the relative error τ incurred by assuming the monochromator to be ideally mosaic. This error may be defined as

$$\tau = |P - P_k|/P_k. \quad (7)$$

It should be noted that K in (1) is not constrained to lie between the limits K_k and K_d whereas c in (2), in principle, is. Therefore, error analyses should ideally be based on (1). However, (2) has properties which are more amenable to analysis and reveal characteristics

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* Notation of Azároff (1955).

which might otherwise be hidden in (1). For these reasons we prefer to use (2) in the assessment of errors. This is not unreasonable since we have established the relation between c and K which may be interconverted by (4) and (5). The only requirement to equivalence the two definitions of P is to relax the constraints on c.

Substitution of (2) into (7) gives

$$\tau = |c(P_d/P_k - 1)|. \tag{8}$$

The modulus signs now cover the whole expression in (8) since $P_d^0/P_k^0 \leq 1$ (the converse is true, however, for $\rho = 90°$).

Figs. 1, 2 and 3 illustrate some of the properties of τ for some commonly used monochromators and X-ray wavelengths. Although we have only considered values of c up to 1·0, it should be clear that c can take any value, positive or negative. One of the useful properties of (8) is that the errors are symmetric about $c = 0$, *i.e.* we can replace c by $|c|$. The properties of τ can be summarized as follows.

(*a*) The maximum errors occur at $\theta = 45°$ for any value of c. Similarly, the minimum errors (*i.e.* no errors) occur at $\theta = 0$ and 90° [but see (*c*) below].

(*b*) For any value of $|c| > 0$, the errors incurred by the $\rho = 0°$ geometry are *smaller* than the errors incurred by the $\rho = 90°$ geometry by a factor

$$\left| - \frac{K_k + \cos^2 2\theta}{1 + K_k \cos^2 2\theta} \right| = \left| - \frac{P_k^{90}}{P_k^0} \right| \tag{9}$$

(*i.e.* the ratio of τ for $\rho = 0°$ to τ for $\rho = 90°$).

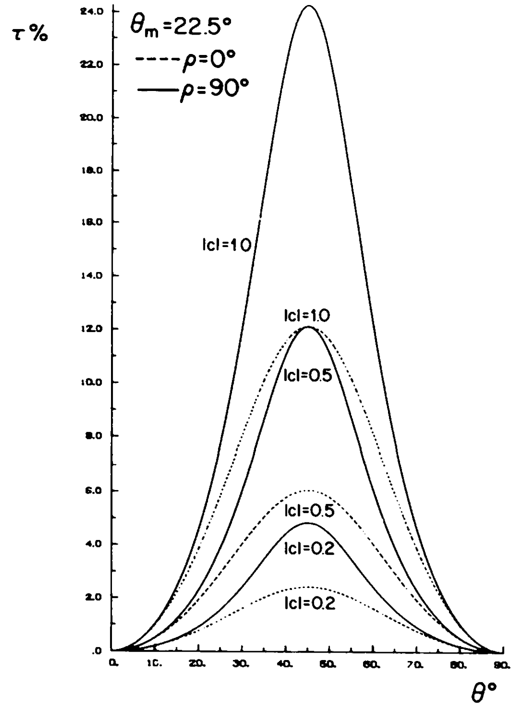


Fig. 1. Graph of $\tau = |c(P_d/P_k - 1)|$ (%) against θ(°) at fixed values of $|c|$ and θ_m for $\rho = 0$ and 90°.

(*c*) For the $\rho = 0°$ geometry, no errors are incurred whatsoever if $\theta_m = 45°$ [$P_d^0/P_k^0 = 1$ in (8) for all values of θ]. This is also true for the $\rho = 90°$ geometry for all θ except at $\theta = 45°$ [$P_d^{90}/P_k^{90} = \cos^2 2\theta/\cos^2 2\theta$ in (8)].

(*d*) In general (the generality being solely determined by the types of crystals currently being used as monochromators), a reduction in θ_m at constant wavelength results in a reduction of the errors. However, as Fig. 2 indicates, the latter statement is not universally true.

(*e*) A decrease in wavelength at constant θ_m will also result in a decrease in the errors.

(*f*) Relatively, a decrease in wavelength at constant θ_m results in a greater reduction in the errors than a decrease in θ_m at constant wavelength.

(*g*) A combination of (*d*) and (*e*) may produce a substantial reduction in the errors.

To exemplify some of the above points, we see from Fig. 1 that the values of τ for the $\rho = 0°$ curves at $\theta = 45°$ are all half the values of τ for the $\rho = 90°$ curves for corresponding values of c. The factor defined by (9) reduces to $|-K_k|$ for $\theta = 45°$ and since $\theta_m = 22·5°$, this factor becomes 0·5, thus explaining the difference.

It is evident, therefore, that for a monochromator lying outside the bounds of ideally mosaic, a diffraction experiment (intensity measurements) with the $\rho = 0°$ geometry is preferable to an equivalent experiment with the $\rho = 90°$ geometry if no correction to the polarization factor for this state of affairs of the monochromator is to be made. Furthermore, the validity of (2) and (3) from an apt use of (9) would be

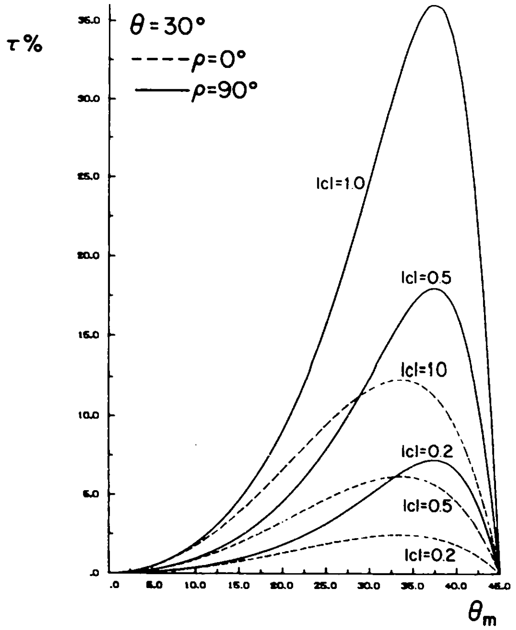
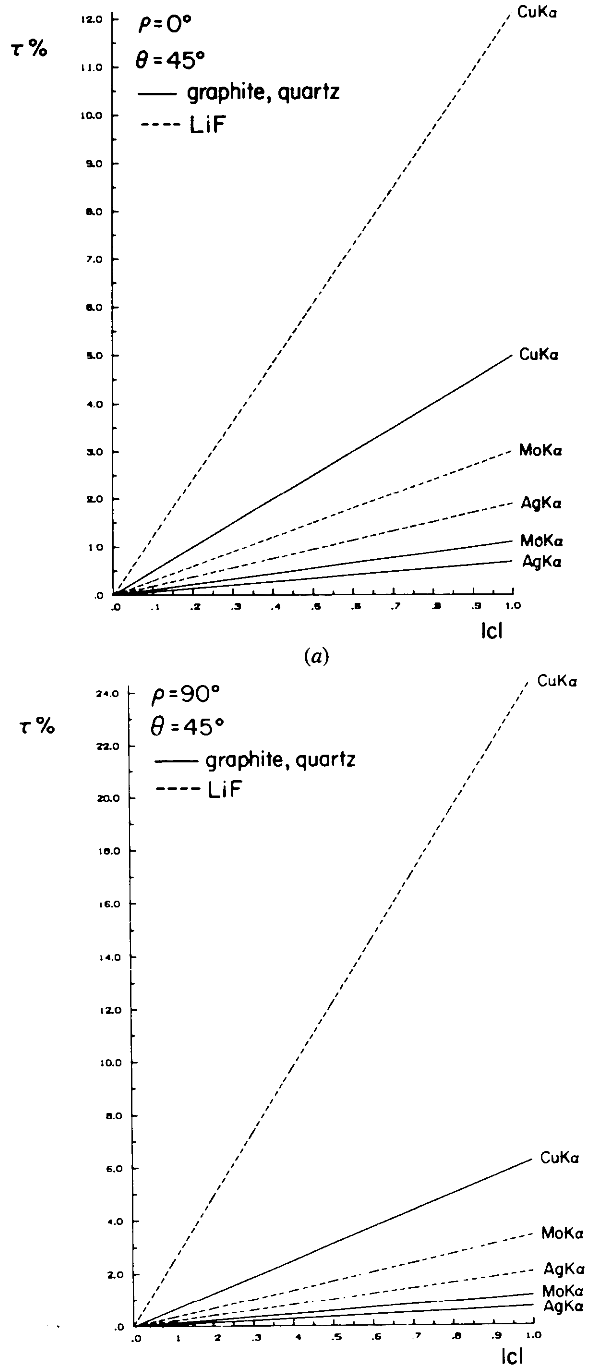


Fig. 2. Graph of τ(%) against θ_m (°) at fixed values of $|c|$ and θ for $\rho = 0$ and 90°.

adequately tested if it was possible to perform appropriate, identical experiments in the two geometries under the most favourable conditions [defined by the magnitude of (9)].

To emphasize points (*d*), (*e*), (*f*) and (*g*), we see from Fig. 3(*a*), for example, that the value of τ for the LiF monochromator reflecting Cu $K\alpha$ radiation at $|c| = 1$ is $\sim 12{\cdot}1\%$. If, instead, a graphite or quartz* monochromator is used to reflect the same radiation, τ would be reduced to $\sim 6{\cdot}2\%$, *i.e.* approximately half the error. If, on the other hand, the LiF monochromator is retained but the radiation is changed to Mo $K\alpha$, τ would be $\sim 3\%$ *i.e.* approximately a quarter of the original error. Finally, if we change both the monochromator and radiation to graphite (or quartz) and Mo $K\alpha$ respectively, the error would be reduced to approximately one tenth of its original value ($\tau \simeq 1{\cdot}2\%$). These relative reductions in the error are the same for all values of $|c| > 0$ as, in fact, Fig. 3 implies.



(*b*)

Fig. 3. Graphs of $\tau(\%)$ against $|c|$ at a fixed value of θ for three common wavelengths of X-radiation and crystal monochromators. (*a*) $\rho = 0°$, (*b*) $\rho = 90°$.

Perhaps the most interesting aspect of the present discussion is point (*c*) since it corresponds to the ideal situations of either not having to correct intensities for polarization effects at all ($\rho = 0°$ geometry) or only having to apply a correction equal to $1/\cos^2 2\theta$ ($\rho = 90°$ geometry), being the same correction no matter what the polarization state of the incident monochromated beam happens to be and hence independent of c or K. The reasons for these rather Utopian cases can be simply explained. According to Brewster's law for the polarization of electromagnetic radiation, if the angle between the reflected and refracted rays associated with an unpolarized incident beam is 90°, the reflected rays would be completely plane polarized. Following the notation of Azároff (1955), a beam of unpolarized X-rays, described by the electric vector **E**, incident on an ideally mosaic crystal monochromator, for example, may be resolved into the two components $\mathbf{E}_\sigma$ (the component in the plane of diffraction) and $\mathbf{E}_\pi$ (the component normal to $\mathbf{E}_\sigma$) such that $E_\sigma^2 = E_\pi^2 = \frac{1}{2}E^2 = \frac{1}{2}I$, I being the intensity of the incident beam. Now, since the refractive index for X-rays is less than unity by a few parts per million for most materials (James, 1967), Brewster's law is fulfilled when $2\theta_m = 90°$ to a good approximation. Hence the reflected beam from the monochromator at $\theta_m = 45°$ will be plane polarized with the magnitude of the component $\mathbf{E}_\sigma$ falling to zero at this angle ($E_\sigma^2 = 0$). For the $\rho = 0°$ geometry, the remaining component $\mathbf{E}_\pi$ incident on the crystal sample is always normal to the new plane of diffraction no matter what the value of θ and hence is never further attenuated by polarization. Since the polarization factor defined by (1) has been evaluated in terms of the intensity just before the second reflection, no corrections for polarization effects are therefore necessary for the $\rho = 0°$ geometry.

This is not, however, the case for the $\rho = 90°$ geometry. In this mode the component $\mathbf{E}_\pi$ of the plane-polarized beam arriving at the crystal sample

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* The reflecting planes used for monochromatization for both graphite (002) and quartz ($10\bar{1}1$) have nearly the same d spacings (3·353 and 3·343 Å respectively). It is only with wavelengths longer than Cu $K\alpha$ (*e.g.* Cr $K\alpha$) that their respective error curves become effectively resolved.

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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