Short Communications

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Polarization of crystal monochromated X-rays.

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The polarization ratio in a bent crystal monochromated X-ray beam has been measured by examining the scattering at 90° in two orthogonal planes. The value was found only not to be far removed from the value expected on the basis of an ideally mosaic monochromator, but not even to lie between this value and that expected on the basis of an ideally perfect monochromator. This result has the implication that the polarization factor lies outside the range usually assumed possible. An explanation of this result in terms of large secondary extinction is proposed.

In connection with the *Powder Intensity Project* (1967) of the International Union of Crystallography, we have been making a critical study of the various parameters which relate structure factors to measured integrated intensities. One such parameter is the polarization of the crystal monochromated X-ray beam incident on the sample. We have measured this polarization in a typical case and find that the value is outside the limits which are usually tacitly assumed. This leads to polarization factors which may differ by 15% from the generally accepted values. The purpose of this communication is to report these results, to give a physical explanation of their plausibility, and to make a few remarks on their implications.

We made use of a singly bent LiF monochromating crystal diffracting Cu $K\alpha$ X-rays from a line focus source at a scattering angle $2\theta_M=45°$. This monochromatic beam is then used as the incident beam in a standard powder diffractometer whose plane of diffraction is parallel to that of the LiF reflection. In this case, the polarization factor entering into the interpretation of the powder intensities is

$$(1+k\cos^2 2\theta)/(1+k)\,,$$

where 2θ is the scattering angle from the powder sample. The quantity k is the ratio of power in the incident monochromatic beam with polarization in the diffraction plane (π polarization) to that with the other polarization (σ polarization). Miyake, Togawa & Hosoya (1964) have called attention to the importance of using the correct value of k and have suggested a technique for measuring it. This technique is to compare relative integrated intensities obtained with filtered, unpolarized radiation to those obtained with the monochromatic radiation of unknown polarization. This information is sufficient, in principle, to determine the polarization ratio, k. However, the method suffers from the necessity of making accurate integrated intensity measurements with filtered radiation; the result can be no more accurate than these measurements, limiting the advantages of the use of monochromatic radiation. Because of this question of the accuracy of their method, we have instead measured the integrated intensity of Ge (333) from a large perfect crystal face, sweeping first through the vertical divergence, then through the horizontal divergence. Since 2θ is virtually 90° for this reflection, the ratio of these two measurements is k. Actually, it is necessary to make corrections of the order of tenths of one per cent for the fact that the α_1 and α_2 components have different scattering angles and for the fact that the peaking of the thermal diffuse scattering is different in the two measurements. This latter correction requires some rather extensive subsidiary measurements, but does not cause fundamental problems.

Before we give our result, it is fruitful to consider what one might expect for the value of k. If the source of X-rays, as viewed from a point on the monochromating crystal, intercepts an angle larger than the width of the rocking curve for this crystal, then the power reflected from the crystal is proportional to the integrated intensity. Since this statement is true for each state of polarization, k would be given by the ratio, α, of the integrated intensities for each polarization. If the crystal behaves as an ideal mosaic, it is easy to see that $k=\alpha_m\equiv\cos^2 2\theta_M$ ($=0{\cdot}50$ for the present case), regardless of geometrical considerations. When extinction is important, k would be determined by geometry as well as by the value of α, but these two quantities would be equal to the approximation mentioned. In the limit that the crystal is ideally perfect, we shall for convenience consider that the source is surely larger than the rocking curve, and that absorption is negligible, so that $k=\alpha_p\equiv\cos 2\theta_M$ ($=0{\cdot}707$ for the present case). Many workers have assumed that, for a bent and ground monochromator, the value k_m was appropriate. Miyake *et al.* (1964), making use of a common tacit assumption, allowed values of k between k_p and k_m. In fact they found, using their method in their geometry, a value about half-way between k_p and k_m.

For our apparatus we have measured an experimental k value $k_e=0{\cdot}722$. This value is not only far removed from that expected for a mosaic monochromator, but it does not even fall in between the values for a mosaic and a perfect crystal. At $2\theta=90°$, the polarization factor using k_e would differ by 15% from that obtained using the traditional value, k_m.

A plausible physical explanation of this behavior is easily given. Consider a crystal with negligible primary extinction or particle size broadening, and small absorption coefficient, μ. We assume a Gaussian distribution of mosaic blocks with an angular width parameter η. For large η, there is no secondary extinction, and the integrated intensity is given by $Q/2\mu$. In this case, we have $\alpha=\alpha_m=Q_\pi/Q_\sigma=\cos^2 2\theta_M$. For small mosaic spreads, however, the crystal becomes almost completely reflecting throughout the range of its mosaic distribution and thus the integrated intensity becomes almost *independent* of Q. This is the case of extreme secondary extinction and it leads to values of α approaching *unity*.

The formulae describing this effect, making the above assumptions, have been given by Zachariasen (1945) and evaluated by Bacon & Lowde (1948), but not in such a way as to emphasize the α values. We have therefore evaluated α for various values of η for $2\theta_M=45°$. Rather than plotting these directly, it is more instructive to evaluate also S, the integrated intensity (in units of $Q_\sigma/2\mu$) for the σ polarization for each η. Thus in Fig. 1 we plot as the solid curve the calculated values of α *versus* S. It should be clearly understood that, for a given reflection, the parameter being varied to produce this curve is η (*i.e.* the extinction), and that all values of η large enough to produce a situation free of extinction are represented by the single point labeled α_m. One may notice that the curve starts from α_m on the right and approaches unity on the left, conforming to the physical reasoning given above. In particular, $\alpha>\alpha_p$ for all values of $S<0{\cdot}33$.

The calculations leading to the solid curve in Fig. 1 are exact within the assumptions. The actual sample will deviate from these assumptions and may also give values of k somewhat different from α because of geometrical considerations. To assess roughly the significance of these deviations, we measured the integrated intensity of our monochromating crystal. Thus we may plot on Fig. 1 our experimental value, k_e, at its measured value of S. Although the former is known to high precision, the latter varied from point to point on the crystal, and this range is indicated on the Figure. This result is taken to indicate general confirmation of the ideas outlined above.

In actual crystals, as one decreases η, it is not possible to maintain negligible primary extinction and yet have particle size broadening small compared to η. In terms of the parameters of Fig. 1, this situation must arise as S approaches the perfect crystal value, S_p. To illustrate this result, we have plotted the point α_p at the value of S_p appropriate to our LiF case. We have also indicated, with the dashed line, a possible dependence of k on S. It is interesting to note that k is greater than k_p over a range of a factor of 10 in S, whereas it lies between k_p and k_m only over a factor of 3 in S.

The appearance that Fig. 1 would take for other materials and other wavelengths may readily be indicated. The calculated curve depends only on $2\theta_M$. It may adequately be characterized by noting that $\alpha=\alpha_m\equiv\cos^2 2\theta_M$ at $S=1$, and by giving the critical value of S $(=S_c)$ for which $\alpha=\alpha_p\equiv\cos 2\theta_M$. The values of S_c are shown in the insert to Fig. 1 and they show that S_c is not strongly dependent on angle over the range likely to be used for monochromatization. Near $2\theta_M=90°$, $S_c=\cos 2\theta_M$. The other important consideration is how far to the left of the Figure is S_p. This is determined by the enhancement factor (Chipman & Batterman, 1963), which is given closely, in practical cases, by $S_m/S_p=(3\pi r_eF\lambda)/(16\mu V)$. From these results one can see, for example, that a given crystal at Mo $K\alpha$ would be more likely to have $k>k_p$ than at Cu $K\alpha$. This is the case because both S_c and the enhancement factor are greater for Mo $K\alpha$. The serious implications of this result to the value of k are, however, mitigated by the fact that the entire possible range $k_m<k<l$ is less for the Mo $K\alpha$.

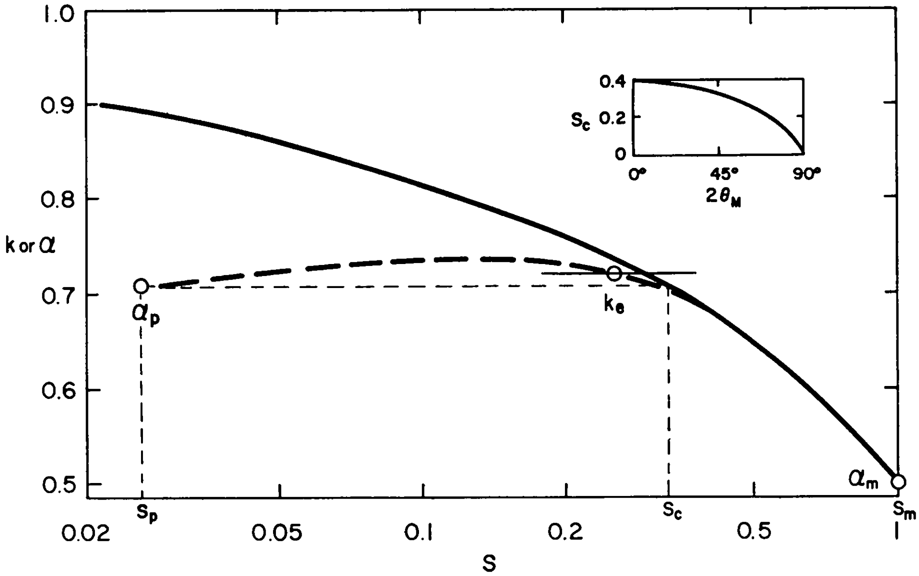

Fig. 1. The variation in polarization ratio with integrated intensity. The ratio of integrated intensity for the two polarization states is denoted by α. The ratio of power in the two polarization states after an unpolarized beam is diffracted by a crystal in a fixed position is denoted by k. It is thus a property of both the crystal and geometry, but it is approximately equal to α. The value of integrated intensity for the σ polarization, expressed in units of $Q_\sigma/2\mu$, is denoted by S. The solid curve gives the calculated dependence of α on S, induced by secondary extinction alone, for the case of $2\theta_M=45°$. The points with the subscripts m and p refer to the mosaic and perfect limits and e to the experimental point. The horizontal line through the latter does not refer to experimental error but to the range of values over the face of the crystal. The dashed curve is a guess as to the course of k or α in an actual crystal. The insert indicates how the solid curve would appear for other values of $2\theta_M$ as discussed in the text.

It is of interest to examine the results of Chandrasekaran (1959) in the light of the present point of view. He measured values of α in a number of cases in the hope that it would be a suitable measure of the perfection of the crystals studied. If α traversed a smooth curve between α_p and α_m, it would indeed be suitable, but the form of the dashed curve in Fig. 1 shows that α is not a good measure of perfection. As a matter of fact, Chandrasekaran gives data which support the general form of the dashed curve. In one case for $S=(0{\cdot}10)S_m$ he found $\alpha=(1{\cdot}06)\alpha_p$, and in another for $S=(0{\cdot}26)S_m$ he found $\alpha=(0{\cdot}98)\alpha_p$. The corresponding enhancement factors were 20 and 6, and these were the two largest enhancement factors which he studied. These cases had different values of $2\theta_M$, but this does not affect the general argument greatly, as was pointed out above.

In conclusion, it should be pointed out that the important consideration is the fact that we have measured the value of the polarization ratio of a monochromated beam for an actual apparatus using an accurate technique. The value obtained not only is not close to that appropriate to a mosaic monochromator, but is not even in the range between such a value and that calculated for a perfect monochromator. Using the mosaic value may lead to an error in the polarization factor of up to 15%. This result has important applications to any study of the angular dependence of monochromatic X-ray scattering, no matter what the form of the sample, for both Bragg and diffuse scattering, and regardless of the position of the monochromator with respect to the sample. In fact, it may be necessary to use these considerations for reflections of unpolarized radiation which suffer appreciable extinction. The validity of the plausibility arguments given to explain the situation do not alter the necessity of accepting the measured value of polarization ratio.

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Comments on a paper by Sabine.

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A recent calculation of the diffraction effects produced by condensed sheets of interstitial atoms is discussed. An error is pointed out; this error vitiates the calculation.

Sabine (1966) has recently published a calculation of the diffraction effects produced by condensed layers of interstitial atoms in face-centered cubic crystals. His calculation predicts peak shifts which, for small values of the fault probability α, are opposite to the shifts previously computed for extrinsic faults by Johnson (1963) (for $0 \le \alpha \le 1$) and by Warren (1963) (for $\alpha \ll 1$). The results given by Johnson and by Warren agree when $\alpha \ll 1$. Sabine notes that in the limit of low fault probability ($\alpha \ll 1$) the diffraction effects produced by condensed interstitial layers should be the same as those produced by extrinsic faults. He does not explain the discrepancy.

I believe that this discrepancy is accounted for by the fact that there is an error in Sabine's calculation. This error is to be found in the difference equation scheme by which Sabine computes the probabilities of the possible stacking sequences. (Since we are particularly interested in case $\alpha \ll 1$, Sabine's parameter $\beta=\alpha/(1+\alpha)$ will be used interchangeably with α).

Suppose that a given layer is A. If this layer is part of the original crystal then the probability that the next layer will be B is $(1-\beta)$. But if this A layer is a *condensed* layer then the probability that the next layer will be B is β. [For suppose that this A layer is the only condensed layer in the crystal (so that $\beta \to 0$); in this case the next layer is *necessarily* C.] This distinction between original and condensed planes is shown in Sabine's 'probability tree'. Unfortunately, Sabine's difference equation scheme does not incorporate this distinction between original and condensed layers. Specifically, the 'additional relation'

$$P_m^A = \beta P_{m-1}^B + (1-\beta) P_{m-1}^C {}^*$$

is true only if the $(m-1)$ layer is part of the original crystal. If the $(m-1)$ layer is a *condensed* layer this relation must be changed to

$$P_m^A = (1-\beta) P_{m-1}^B + \beta P_{m-1}^C \,.$$

This difficulty seems to be insurmountable in the difference equation approach used, and clearly vitiates Sabine's subsequent results for all values of the fault probability.

The inherent difficulty in applying such a difference equation scheme to this problem can be seen as follows. There are, allowing for normalization of the probabilities to unity, two independent probabilities for the stacking of

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* There is a typographical error in this equation in Sabine's paper. The last term should read $(1-\beta)P_{m-2}{}^C$. Sabine's subsequent equations follow only if this correction is made.