

## INVESTIGATION OF THE DEGREE OF PERFECTION OF A CRYSTAL BY MEANS OF POLARIZED X-RAYS

BY S. RAMASESHAN AND G. N. RAMACHANDRAN, F.A.Sc.\*

(Department of Physics, Indian Institute of Science, Bangalore 3)

Received November 21, 1953

### 1. INTRODUCTION

It is well known that the state of polarization of X-rays has an influence on the intensity of Bragg reflection from a crystal. It arises essentially because of the fact that the scattering by a single electron is not isotropic. When unpolarized X-rays are incident on an electron, the scattered amplitudes with the vibration directions parallel ( $\pi$ ) and perpendicular ( $\sigma$ ) to the plane of scattering are in the ratio of  $\cos \psi : 1$ , where  $\psi$  is the angle of scattering. For a Bragg reflection, the angle of scattering,  $\psi = 2\theta$ , where  $\theta$  is the Bragg angle. Consequently, in the so-called kinematical theory of X-ray reflection, where each unit cell is supposed to scatter under the action of the incident wave alone and no dynamic interaction is assumed to exist between the incident and scattered waves, the intensities of the two polarized components of the finally emergent beam will be in the ratio of  $\cos^2 2\theta : 1$ , which is the same as the value for a free electron. This theory holds in the case of an ideally mosaic crystal, in which the individual crystallites are so small that no appreciable scattered wave builds up in a single crystallite.

The situation is however different in a perfect crystal. One has to take into account the multiple interactions between the incident and reflected beams and work out a dynamical theory of X-ray reflection, as was first put forward by Darwin (1914) and Ewald (1918, 1924). A good account of the theory is given by Zachariasen (1945) and James (1948). It leads to the result that, in the case of a surface reflection from a perfect non-absorbing crystal, the ratio of the integrated reflections of the two polarized components is only  $|\cos 2\theta| : 1$ . Consequently, if we use completely polarized X-rays and vary the azimuth of polarization keeping all other conditions the same, then the integrated reflection would vary from a maximum to a minimum, the ratio of the two being  $1 : \cos^2 2\theta$  if the crystal is mosaic and  $1 : |\cos 2\theta|$  if it is perfect.

Although this result is implicit in the formulæ which have been known for a long time, no attempt appears to have been made to verify the theoretical

\* Now Professor of Physics, Madras University, Madras 25.

prediction. In fact, it is usually assumed that the so-called 'polarization factor', for which a correction is applied in deducing  $F$  values from measured intensities of Bragg reflections, has the mosaic value  $\frac{1}{2}(1 + \cos^2 2\theta)$ , irrespective of the degree of perfection of the crystal. The present paper describes some experiments which have been made to verify whether there is any difference between the behaviours of a perfect and a mosaic crystal, as would be expected from the above considerations. The experiments clearly indicate that the ratio of the maximum to the minimum (as the azimuth of polarisation is varied) is much higher for a mosaic crystal than for a perfect crystal of the same substance. However, the actual data fit the results of the above simple theory reasonably well only in the mosaic case; they differ appreciably from theory in the case of a perfect crystal (Ramaseshan and Ramachandran, 1953). The deviation has been explained as being due to the inadequacy of the theory when referred to an actual *absorbing* crystal, since it is valid only for a non-absorbing perfect crystal. The theory for an absorbing crystal has been given by Prins (1930) and Kohler (1933) following the Darwin and Ewald methods respectively. They are however not in a form suitable for comparison with experiment. The two theories have been combined and further worked out by Hirsch and Ramachandran (1950). Using their results, it is found that one can measure the degree of perfection of a crystal from the type of experiment mentioned above. This aspect is described in Sections 5 and 6.

## 2. EXPERIMENTAL DETAILS

The polarizer-monochromator was a large crystal of KCl (M of Fig. 1), with a *ground* face parallel to the (110) planes. The 440 reflection has a Bragg angle of  $43^\circ 58'$ , so that  $2\theta$  is approximately  $88^\circ$  and the Bragg-reflected beam would be almost completely polarized. The fraction of unpolarized X-rays is less than one per cent. and the maximum error arising from this cause in the measurements is much less than the other experimental errors. The KCl crystal was mounted on a horizontal axis, fixed to the window of the X-ray tube, which could be rotated by means of a tangent screw (T). The monochromator was surrounded by a brass box (B) lined with lead, having an aperture at the position where the reflected beam occurred. The monochromatic beam thus passed down the aperture in a vertical direction.

The crystal under study (in this particular case a crystal of sodium nitrate) was mounted on a goniometer head (G) fixed to a vertical axis of rotation on the spectrometer. The collimator (CC) consisted of a tube 1 mm. in diameter and 4 cm. long fixed so as to coincide exactly with the axis of the spectrometer. The spectrometer itself was aligned to admit the maximum

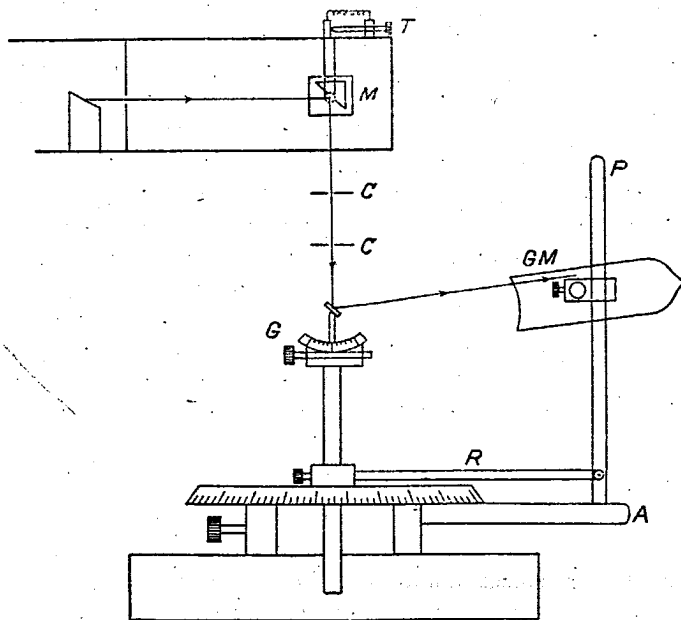


Fig. 1. Schematic diagram of the experimental set up

intensity of the monochromatized X-ray beam and thus to be exactly in line with it.

In order to detect the Bragg-reflected beam from the crystal under study, a Geiger Müller counter tube (GM) was used. The G.M. tube was mounted on a pillar (P) fixed to a movable arm (A) which rotated about the same axis as the crystal. There was provision whereby both the height of the G.M. tube as well as its inclination to the horizontal could be adjusted. In this way, the G.M. tube could be aligned so as to catch the reflected beam for any Bragg angle  $\theta$ . Having once adjusted the crystal and G.M. tube so as to be in alignment, the two could be coupled by means of a rod (R) which could be attached to the axis of rotation of the crystal and the pillar on the counter arm. Both the crystal and the counter could thereafter be rotated together and thus the angle between the plane of reflection and the plane of vibration of the polarized X-rays (denoted as the azimuth  $\phi$  of polarization) could be varied. The azimuth could also be read from a graduated circle by means of a mark made on the counter arm.

At each azimuth, the integrated reflection was obtained as follows: The crystal was first set at the peak of the Bragg reflection. It was then

rotated away from this setting by  $1^\circ$  by means of the tangent screw of the goniometer. The counting rate generally reduced to the background value when the setting was changed by  $1^\circ$ . Thereafter, readings of the reflected intensity were taken at steps of  $0.1^\circ$  ( $0.05^\circ$  close to the peak). These were plotted on a graph paper and the area was taken to be proportional to the integrated intensity. The same experiment was repeated for different azimuths. The voltage and current through the tube (35 KV, 17 ma) were maintained constant by careful manual control. No attempt was made to directly measure the intensity of the monochromatized beam incident on the crystal under study, but it was seen to be constant to within  $\pm 5$  per cent., as verified by the constancy of the twice-reflected Bragg intensity measured on various occasions. The final data are therefore accurate to 5 per cent., as the various other processes involved in their evaluation are more accurate than this.

Cu  $K\alpha$  radiations were used throughout the investigation and the reflections studied were the 422 and 633 of  $\text{NaNO}_3$ , obtained from a natural (211) face of the crystal. The crystals were obtained by slowly growing them from solution and the specimens studied had faces with an area of about  $1 \text{ cm.}^2$  and a thickness of about 2 mm. The integrated reflections for different azimuths varying from  $0^\circ$  to  $90^\circ$  were first measured with the natural face and later after lightly grinding the surface on emery.

### 3. INTERPRETATION OF THE EXPERIMENTAL RESULTS

The data obtained are shown in Figs. 2 and 3 in which they are presented as follows. Representing by  $\rho_\phi$  the integrated reflection for an azimuth  $\phi$  ( $\phi=0$  corresponding to the case when the electric vector is perpendicular to the plane of reflection, *i.e.*,  $\sigma$ ), we may define a new quantity

$$r(\phi) = \rho_\phi / \rho_0 \quad (1)$$

Thus,  $r(\phi)$  is the relative integrated reflection with respect to that for azimuth zero. The data in Fig. 2 are the values of  $r(\phi)$  for different azimuths both for the natural and the ground surfaces obtained with the 422 reflection; Fig. 3 gives similar data for 633. It will be noticed that the two sets of values of  $r(\phi)$  progressively deviate as  $\phi$  increases from  $0^\circ$  to  $90^\circ$ , the difference being largest for  $\phi=90^\circ$ . Thus, the state of perfection of a crystal modifies the relative intensity of Bragg reflection for different azimuths of polarization.

The following two formulæ for the integrated reflections of the "surface" reflections from a mosaic crystal ( $\rho_M$ ) and from a perfect non-absorbing crystal

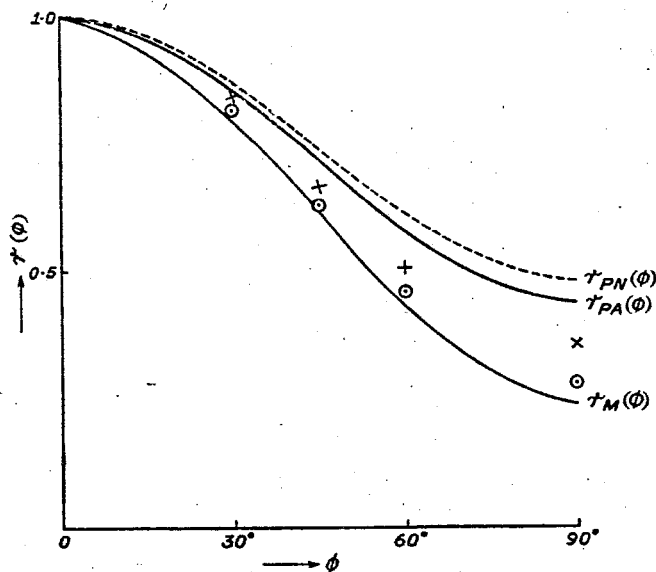


FIG. 2. Variation of  $r(\phi)$  with azimuth  $\phi$  for  $\text{NaNO}_3$ , 422 reflection. The thick lines are the theoretical curves for the limiting cases of a perfect ( $r_{PA}$ ) and a mosaic ( $r_M$ ) crystal. The dotted curve  $r_{PN}$  refers to an idealised perfect crystal having no absorption. The experimental data are indicated by circles for the ground crystal and crosses for the natural crystal. Note that all the experimental data occur between the limits set by theory.

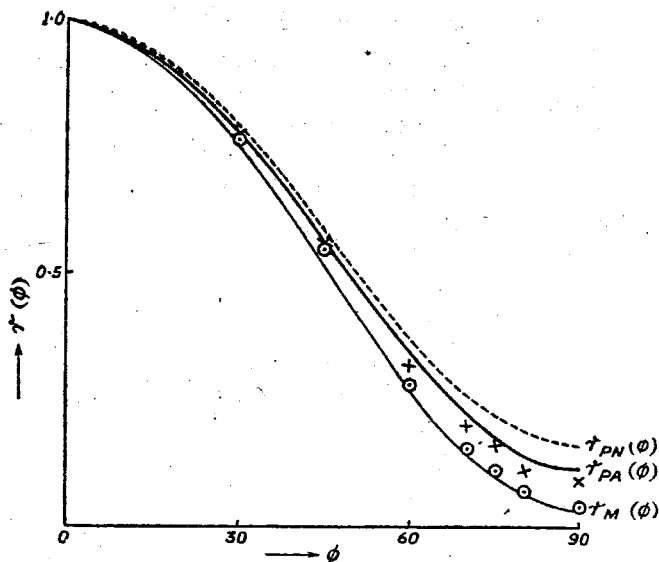


FIG. 3. Variation of  $r(\phi)$  with azimuth  $\phi$  for  $\text{NaNO}_3$ , 633 reflection. The diagram is exactly similar to Fig. 2 and the remarks made in that case also hold here.

( $\rho_{PN}$ ) are well known (*cf.* Internationale Tabellen, 1935, Vol. II, p. 562-64)

$$\rho_M = \frac{1}{2\mu} \frac{e^2}{m^2 c^4} N^2 |F|^2 \frac{\lambda^3}{\sin 2\theta} \frac{(1 + \cos^2 2\theta)}{2} = R_M (1 + \cos^2 2\theta) \quad (2)$$

$$\rho_{PN} = \frac{8}{3\pi} \frac{e}{mc^2} N |F| \frac{\lambda^2}{\sin 2\theta} \frac{(1 + |\cos 2\theta|)}{2} = R_{PN} (1 + |\cos 2\theta|) \quad (3)$$

These formulæ refer to unpolarized incident X-rays. If the incident X-rays are completely polarized at an azimuth  $\phi$ , then the corresponding formulæ are

$$\rho_M(\phi) = R_M (\cos^2 \phi + \sin^2 \phi \cos^2 2\theta) \quad (4)$$

$$\rho_{PN}(\phi) = R_{PN} (\cos^2 \phi + \sin^2 \phi |\cos 2\theta|) \quad (5)$$

Thus, we have

$$r_M(\phi) = \cos^2 \phi + \sin^2 \phi \cos^2 2\theta \quad (6)$$

$$r_{PN}(\phi) = \cos^2 \phi + \sin^2 \phi |\cos 2\theta| \quad (7)$$

The relative integrated reflection, expressed as a function of  $\phi$ , is different in the two cases. Since  $|\cos 2\theta| \leq 1$ ,  $r_M(\phi) \leq r_{PN}(\phi)$ , so that the values of  $r(\phi)$  for a mosaic crystal would in general be smaller than for a perfect crystal. Both start at a value equal to unity for  $\phi = 0$ , but  $r_M(\phi)$  decreases much more rapidly than  $r_{PN}(\phi)$ , and the difference is a maximum at  $\theta = 90^\circ$ .

However, for  $\theta = 0^\circ, 45^\circ$  or  $90^\circ$ ,  $\cos^2 2\theta = |\cos 2\theta|$ , and for these particular Bragg angles, the perfect and mosaic crystals behave similarly. The difference is a maximum for  $\theta = 30^\circ$  and  $60^\circ$ .

In Fig. 2, the values of  $r_M(\phi)$  and  $r_{PN}(\phi)$  are indicated by the respective curves. It will be seen that the former agrees very well with the data for the ground crystal, as is to be expected. However, the data obtained with the natural surface of the crystal lie significantly below the curve for  $r_{PN}(\phi)$ . This might be due to two causes: either (a) the natural surface is far from being near-perfect, or (b) the theoretical curve  $r_{PN}(\phi)$  does not correspond to what one would expect for a perfect crystal. As mentioned in the introduction, the theory is in fact not valid for an absorbing crystal. We shall therefore investigate how the theoretical values are modified when the crystal has a finite absorption coefficient.

#### 4. CALCULATION OF $r(\phi)$ FOR AN ABSORBING PERFECT CRYSTAL

The theoretical formula for the Bragg reflection curve of an absorbing perfect crystal has been given by Prins (1930) and Kohler (1933). For a symmetrical surface reflection, these theories give the following formula for the intensity ( $\bar{I}_R$ ) of the reflected beam in terms of the incident intensity

( $I_0$ ) [see Zachariassen, Eqn. (3.190) and also Hirsch and Ramachandran, Eqn. (19)].

$$I_R/I_0 = L - \sqrt{L^2 - 1} \quad (8 a)$$

where

$$L = \{y^2 + g^2 + \sqrt{[(y^2 - g^2 - 1 - k^2)^2 + 4(gy - k)^2]}/(1+k^2)\} \quad (8 b)$$

Here, the angular deviation ( $\theta' - \theta$ ) from the Bragg setting is given by the parameter  $y$  whose value is

$$y = \frac{Z}{K|F'|} + \frac{\pi mc^2}{e^2 \lambda^2 N} \cdot \frac{(\theta' - \theta) \sin 2\theta}{K|F'|} \quad (9)$$

The other quantities have the values:

$$g = \frac{1}{2K} \cdot \frac{mc^2}{e^2 \lambda^2 N} \cdot \frac{\mu \sqrt{1+k^2}}{|F|} \quad (10)$$

$$k = F''/F' \quad (11)$$

$$K = 1 \text{ for the } \sigma \text{ component, and} \quad (12 a)$$

$$K = |\cos 2\theta| \text{ for the } \pi \text{ component} \quad (12 b)$$

$F'$  and  $F''$  are the real and imaginary components of the structure amplitude  $F$  and  $\mu$  is the linear absorption coefficient. In order to obtain the integrated reflection, we want the quantity  $\rho = \int (I_R/I_0) d\theta'$ , which may be expressed in terms of the integral

$$R_y = \int (I_R/I_0) dy \quad (13)$$

The exact formula is

$$\rho = \frac{K}{\pi} \cdot \frac{e}{mc^2} \cdot N |F| \cdot \frac{\lambda^2}{\sin^2 \theta} \cdot R_y(g, k) \quad (14)$$

No analytical form has been obtained for the function  $R_y(g, k)$ , but its variation with the parameters  $g$ , and  $k$  has been computed by numerical integration and exhibited in a graphical form by Hirsch and Ramachandran (1950). They have also deduced an empirical formula for this variation:

$$R_{yF} = \frac{\pi(1+k^2)}{4 \{ \exp[-(1+k^2)^2(|g|+C)] + |g| \}}, \quad C = \log_e 32/3\pi \quad (15)$$

The same formula (14) can be used for a mosaic crystal, but then  $R_y$  has a different form,  $R_{yM}$ , given by

$$R_{yM} = \pi(1+k^2)/4|g| \quad (16)$$

In either case, therefore, the integrated reflection  $\rho$  is a function of  $K$ , the other quantities being the same, since  $g$  is a function of  $K$ . If  $\rho$  is the function  $Q(K)$  of  $K$ , then clearly

$$r(\phi) = \cos^2 \phi + a \sin^2 \phi \quad (17)$$

where

$$\alpha = Q(|\cos 2\theta|)/Q(1)$$

The problem therefore reduces to finding  $\alpha$ . In the case of a mosaic crystal, we find from the above equations that  $\rho_M = \text{const. } K^2$  and therefore  $\alpha = \cos^2 2\theta$ , in conformity with what is to be expected from Equation (6) above. For a non-absorbing perfect crystal,  $|g| = 0$  and we have from Equation (15),  $R_y = 8/3$ , so that  $\rho_{PN} = \text{const. } K$  and  $\alpha = |\cos 2\theta|$ , again agreeing with Equation (7). For a perfect absorbing crystal, the relation (15) between  $R_y$  and  $K$  is complicated and so no explicit analytical form is possible for  $\alpha$  in this case.

However, one may make the following general observation. Hirsch and Ramachandran (1950) have shown that, with increasing  $|g|$ ,  $R_y(g, k)$  of a perfect crystal monotonically decreases, ultimately having the same value as the mosaic crystal for very large values of  $|g|$ , which corresponds to a large absorption coefficient, the 'reflecting power' or F-value remaining the same. Thus, the effect of a finite absorption coefficient will be to alter the value of the function  $\alpha$  from  $|\cos 2\theta|$  towards the mosaic value  $\cos^2 2\theta$ . It would be interesting to repeat the investigations with different wave-lengths for which the crystal would have different values for the absorption coefficient.

Numerical calculations may readily be made for the particular cases in which we are interested. The following are the relevant data for  $\text{NaNO}_3$  422 and 633 reflections, obtained or calculated from those available from standard tables.

TABLE I

*Data for the calculation of  $\alpha$  for the 422 and 633 reflections of  $\text{NaNO}_3$*

	422			633		
	$\sigma$	$\tau$	$\pi$	$\sigma$	$\tau$	$\pi$
$\theta$		30° 29'			49° 36'	
F		10.9			16.3	
K	1.000		0.485	1.000		0.160
$g$	0.0242		0.0491	0.0162		0.0995
$R_y$	3.038		2.729	3.148		2.257
$K R_y$	3.038		1.323	3.148		0.360
$\alpha$		0.436			0.115	



The formulae for  $r_{PA}(\phi)$  are thus

$$\text{for 422, } r_{PA}(\phi) = \cos^2 \phi + 0.436 \sin^2 \phi \quad (18)$$

$$\text{and for 633, } r_{PA}(\phi) = \cos^2 \phi + 0.115 \sin^2 \phi \quad (19)$$

The calculated values from (18) and (19) are shown by the thick lines in Figs. 2 and 3.

### 5. CALCULATION OF THE DEGREE OF PERFECTION

As mentioned earlier, the data for  $r(\phi)$  obtained with the ground surface occur very close to the theoretical curve for a mosaic crystal [ $r_M(\phi)$ ]. This is satisfactory. However, it may be noted that in both Fig. 2 and Fig. 3, the experimental data are consistently above the theoretical mosaic crystal curve, particularly in the region near  $\phi = 90^\circ$ , which is the most sensitive region. Thus it appears that the grinding has not made the crystal ideally mosaic. Similarly, the experimental data with the natural crystal surface occur consistently below the theoretical curve for an absorbing perfect crystal [ $r_{PA}(\phi)$ ]. This shows that the natural crystal studied was not ideally perfect.

It is very gratifying to note that the experimental data occur almost completely in between the two theoretical curves [*viz.*,  $r_{PA}(\phi)$  and  $r_M(\phi)$ ]. The actual value of  $r(\phi)$  could therefore be used for assessing the degree of perfection of a crystal. Thus, if  $r(\phi)$  is the experimental value for a crystal, then its degree of perfection ( $\Delta$ ) may be defined as

$$\Delta = \frac{r(\phi) - r_M(\phi)}{r_{PA}(\phi) - r_M(\phi)} \quad (20)$$

It can readily be shown that  $\Delta$  is independent of  $\phi$ , for we have from Equations (6), (7) and (17),

$$\Delta = (\alpha - \cos^2 2\theta) / (|\cos 2\theta| - \cos^2 2\theta)$$

the right-hand side being independent of  $\phi$ .

This fact, namely, that  $\Delta$ , as defined by (20), is independent of  $\phi$  can readily be checked from the data shown in Figs. 2 and 3. Tables II and III contain the values of  $r_{PA}(\phi)$ ,  $r_M(\phi)$  and  $r(\phi)$  both for the natural and ground surfaces in the two cases, namely 422 and 633. Since the calculation of  $\Delta$  from Equation (20) involves the *differences* of the measured values of  $r(\phi)$ , and the latter are themselves accurate only to about 5 per cent., large differences are to be expected in the calculated values of  $\Delta$ . The values calculated from the data for  $\phi < 60^\circ$  are particularly susceptible to this inaccuracy. However, the trend of the data show clearly that  $\Delta$  is constant within the limits of experimental error.

Taking the mean value of  $\Delta$  from the different measurements, it is seen that the natural surface is about 68 per cent. perfect, while the ground surface has only a degree of perfection of about 20 per cent., showing that it approaches the ideally mosaic case.

TABLE II

Data for calculating the degree of perfection for the 422 reflection ( $\theta = 30^\circ 29'$ )

$\phi$	30°	45°	60°	90°	
$r_{PA}(\phi)$	0.859	0.720	0.577	0.436	
$r_M(\phi)$	0.809	0.617	0.427	0.235	
$r(\phi)$ —natural	0.84	0.67	0.54	0.36	
$r(\phi)$ —ground	0.82	0.63	0.46	0.28	
$\Delta$ —natural	62%	51%	76%	62%	Mean 63%
$\Delta$ —ground	22%	13%	22%	22%	Mean 20%

TABLE III

Data for calculating the degree of perfection for the 633 reflection ( $\theta = 49^\circ 36'$ )

$\phi$	30°	45°	60°	70°	75°	80°	90°	
$r_{PA}(\phi)$	0.779	0.558	0.337	0.228	0.174	0.125	0.115	
$r_M(\phi)$	0.756	0.513	0.269	0.140	0.100	0.055	0.028	
$r(\phi)$ —natural	0.77	0.55	0.32	0.20	0.16	0.11	0.09	
$r(\phi)$ —ground	0.76	0.53	0.28	0.15	0.11	0.07	0.04	
$\Delta$ —natural	63%	84%	75%	68%	80%	78%	72%	Mean 74%
$\Delta$ —ground	17%	40%	16%	12%	13%	20%	15%	Mean 19%

## 6. CONCLUSION

Thus, we have a new method for determining the "degree of perfection" of a crystal. It only requires the measurement of the integrated reflections for various azimuths of polarization, and further only relative intensity data with respect to that for azimuth zero are needed. It would be of great interest to study the relationship between the value of the degree of perfection given by this type of experiment and the sharpness of X-ray reflection, or the absolute value of the integrated reflection, both of which are also highly sensitive to the degree of perfection of a crystal. A study of these aspects have been taken on hand.

Another extension that could be made is to the case of an "internal" reflection. The theory (von Laue, 1949; Ramachandran and Kartha, 1952) indicates that in this case also the behaviours of a perfect and a mosaic crystal are quite different, and it requires experimental verification. The use of the internal reflection has the advantage that it would bring out the texture of the whole volume of the crystal and not merely that of the surface layers, which play the most important part in the experiments described in the present paper.

We wish to thank Mr. V. Radhakrishnan for constructing the electronic equipment with which the measurements of X-ray intensities were made.

#### SUMMARY

The paper describes an investigation of the intensity of Bragg reflection when the incident X-rays are polarized and the azimuth of the electric vector is varied with respect to the plane of reflection. It is observed, using natural and ground (211) faces of  $\text{NaNO}_3$ , that the variation of intensity with azimuth of polarization is different for a mosaic and a perfect crystal. Such a difference is in fact to be expected from theoretical considerations. The actual behaviour of both the ground and the natural faces was found to be intermediate between what is predicted by theory for an ideally perfect and an ideally mosaic crystal. By comparing the observed azimuthal variation of the integrated reflection with the theoretical expectation for the two limiting cases, it is possible to assess the degree of perfection of the crystal.

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