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# X-RAY STUDIES ON THE TEXTURE OF CRYSTALS

## A New Method Using Internal Reflections and Its Applications to Lithium Fluoride


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SUMMARY

The paper describes a new method of studying crystalline texture, employing internal reflections. It consists in obtaining internal reflection from a wedge-shaped crystal whose thickness varies from top to bottom and determining the variation of integrated reflection with thickness which was shown theoretically by Ramachandran to be different for perfect and mosaic crystals. Experiments were performed with ground, etched and chilled crystals of lithium fluoride and observations were found to be in accordance with the theoretical predictions. Crystals of lithium fluoride, grown from melt, were thus found to be nearly perfect in structure.


### 1. INTRODUCTION

In spite of all the careful attention that has been given to the subject of crystalline texture, there is still no adequate classification of texture types nor any method of stating or measuring quantitatively the features which define a given crystal texture. In their attempts to study the performance of a concentrating X-ray monochromator, Evans, Hirsch and Kellar (1948) investigated the variation of intensity of reflected beam with the surface treatment. Guinier and Tennevin (1949) were able to assess the degree of perfection of certain crystals by studying the reflections from a family of crystal planes, using divergent white X-radiation. Wooster and Macdonald (1948) investigated the absolute integrated intensity of X-ray reflection for more than one wavelength in calcite and other crystals. They observed that such studies give some indication of the extent to which the texture departs from that of a perfect crystal. However, their studies were not conclusive as they themselves indicated. In recent years, the effect of absorption on the intensities of X-rays reflected by crystals has been studied both theoretically and experimentally. Bragg reflections (X-rays reflected from a crystal surface) have been discussed by Hirsch and Ramachandran (1950). For Laue reflections (X-rays reflected through a crystal slab), the experiments of Borrmann (1948) have shown that the absorption coefficient is greatly reduced for X-rays incident at the Bragg angle. This fact can be explained theoretically on the basis of the dynamical theory of X-ray reflections has been shown by Laue (1950), Ramachandran and Kartha (1952), Hirsch (1952) and Zachariasen (1952). Ramachandran (1952 *b*, unpublished) has also worked out the integrated values for the reflected and transmitted beams for perfect and mosaic crystals for an internal reflection. These developments suggest a new method of investigating the texture of a crystal. In all the previous studies, which were made on reflection from the surface planes and not from the interior, the emphasis has invariably been on the measurement of the absolute integrated reflection, as this is known, from theory to be much larger for a mosaic crystal than for a perfect crystal. Absolute measurements are invariably difficult and it would be preferable to have a method whereby measurements made on a single photograph could be used for obtaining the necessary information. For instance, the angular breadth of the Bragg reflections could be used as an indication of the degree of perfection or mosaicity of the crystal (*e.g.*, Ehrenberg, Ewald and Mark, 1928; Ramachandran, 1944). Here again the technique is rather complicated. The present investigation is based on the following consideration. As has been shown by Ramachandran (1952 *b*), theory predicts that in the case of an internal reflection, the *variation* of the integrated reflection with *thickness* of the crystal would be different for mosaic and perfect crystals. Consequently, by experimentally determining this variation one could judge the texture of the crystal. In actual practice, the intensity variation is photographically, recorded in a single photograph by making use of a wedge-shaped crystal plate, so that the thickness varies from top to bottom. The full details are given in Section 2. Lithium fluoride was chosen for the study as it had a conveniently low linear absorption coefficient ($\mu = 34$ cm.$^{-1}$) for Cu K$\alpha$ radiation.

## 2. EXPERIMENTAL DETAILS

A Shearer tube with Cu target was used as the source of X-rays. Fig. 1 gives a horizontal section of the experimental arrangement. S is a slit (0·15×3 mm.) kept close to the window of the X-ray tube which could be

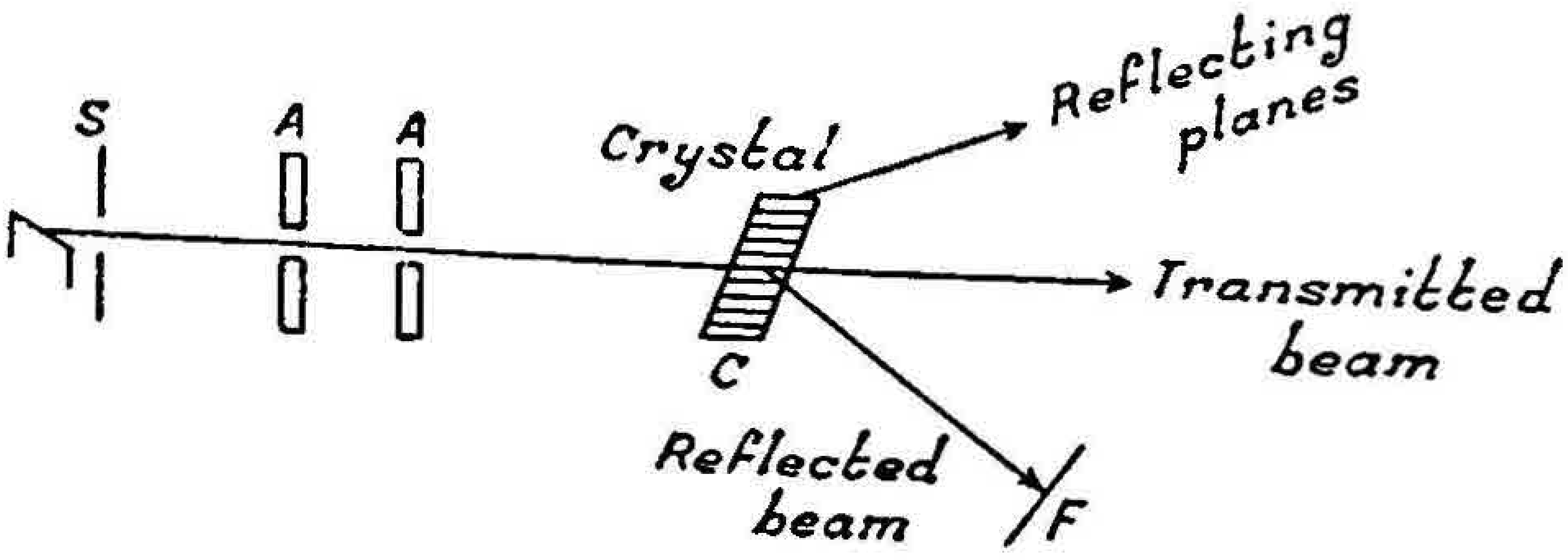


FIG. 1

made either vertical or horizontal. After passing through a series of apertures A A, the X-ray beam fell on the crystal C, the distance between the slit and the crystal being 13·0 cm.

The crystal used was a cleavage plate (010) of LiF and the (100) planes used for obtaining the reflections were normal to the surface and vertical. One face of the crystal was ground at an angle so that the wedge tapered from bottom to top, the thickness varying from about 2 to 0·3 mm. The crystal was mounted on a goniometer rotating about a vertical axis and the angle through which the crystal was rotated could be read with the help of a graduated disc. In all the experiments carried out, symmetrical internal reflections were obtained from the 200 planes as shown in Fig. 1. The distance of the film from the crystal was 4·0 cm. and the film was always kept normal to the reflected beam. Photographs were taken first with the slit vertical and they showed some interesting effects (Fig. 2 on Plate I) which are discussed in the next section. The outline of the Bragg reflection was a tapering triangle, in all cases, although peculiar intensity variations were found inside it according to the texture of the crystal. These photographs were not suitable for the measurement of intensity variations because of (*a*) the vertical spread and the consequent overlap of the effect from regions of varying thickness and (*b*) that one had to find the integrated intensity of a slice of the triangle parallel to the base in order to obtain the intensity corresponding to a particular thickness. For studying the intensity variations with thickness, the slit was made horizontal. The Bragg reflections were obtained in the form of slightly tapering strips (Fig. 2 *e*) and if the slit was long enough, as in the present case, the intensity at any point along the centre of the strip would actually represent the integrated reflection for the corresponding thickness of the crystal. The photographs thus obtained could be conveniently subjected to a microphotometric study. The specimen used for the study was a plate which was first ground into a wedge. Both surfaces were ground on fine emery powder and photographs were obtained as described above using both vertical and horizontal slits. The specimen was then partially etched and then fully etched and the experiment was repeated in each case. The photographs obtained with the fully etched specimen showed that the crystal was nearly perfect (*see* next Section). The crystal was subsequently dipped in liquid air (so as to render it mosaic by sudden cooling) and photographs were taken with this specimen also.

The film obtained with the horizontal slit were run through a microphotometer and the curve so obtained was converted into a true intensity scale by making use of standard intensity marks obtained on another film (from the same packet) by giving varying exposures for the surface reflection from the same crystal. The results are plotted in Fig. 3.

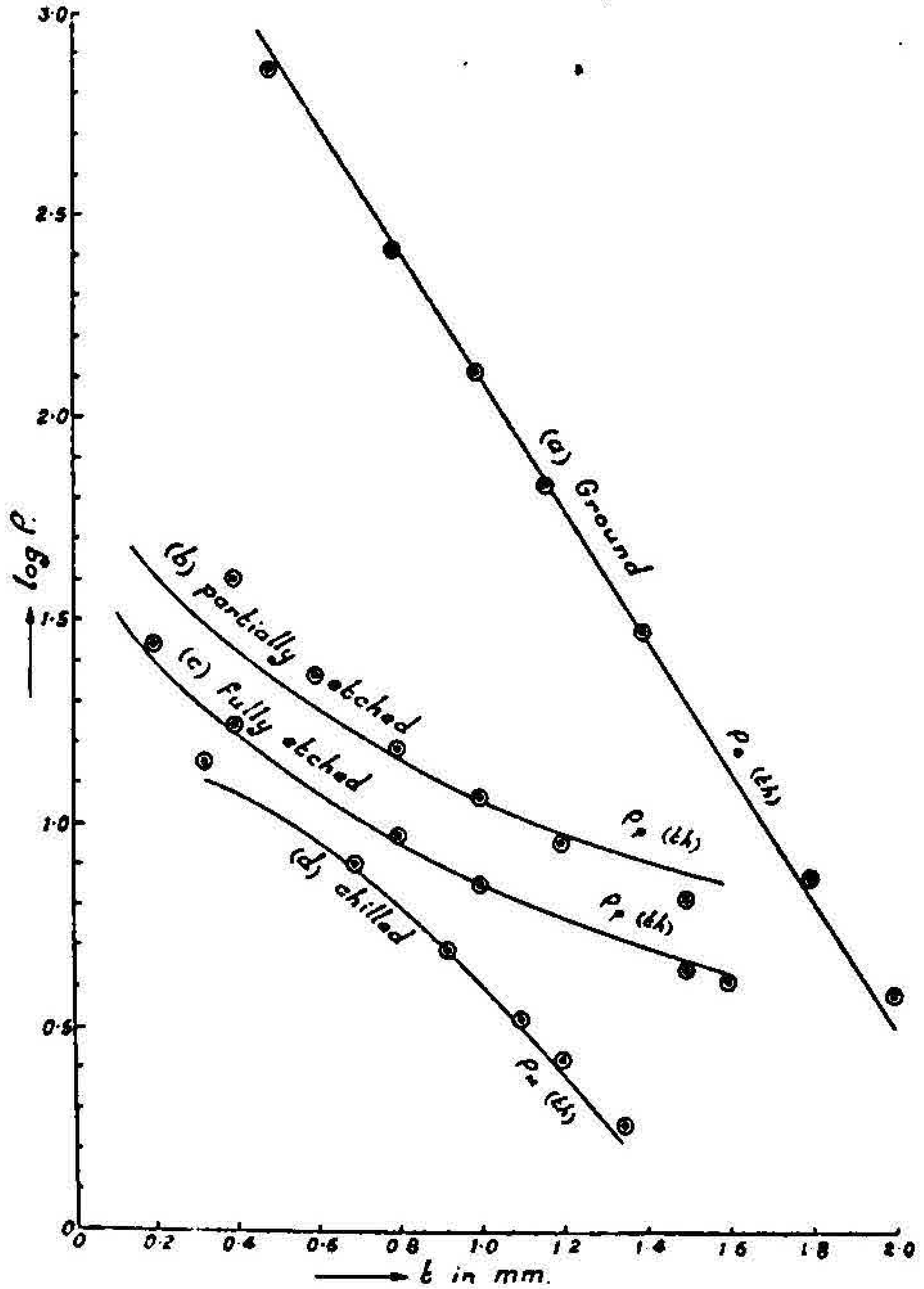


FIG. 3. Log $\rho - t$ curves. Continuous lines are drawn from theory, circles with central dot represent the experimental points.

## 3. DISCUSSION OF RESULTS

(i) *Photographs with Slit Vertical.*—Fig. 2 on Plate I is a typical reproduction (positive) of the internal reflection of the four different cases:

(*a*) ground, (*b*) partially etched, (*c*) fully etched and (*d*) chilled crystal. It is interesting to note that in the case of the ground crystal (*a*) only the edges appear in the reflection without much intensity at the centre. The obvious reason for this is that the grinding has made the two surfaces highly mosaic, so that most of the reflection occurs in a very narrow region of thickness close to the two surfaces. If this were so, then the separation between the two lines in the reflection can readily be shown to be $2t \sin \theta$ corresponding to a thickness $t$. This was in fact verified to be true.

The existence of the relatively weak reflection at the centre suggests that the bulk of the crystal is nearly perfect. That this is really the case is also shown by Figs. 2 (*b*) and (*c*). In both of these, the central region is recorded. While the edge appears with slightly larger intensity than the interior in the partially etched crystal [Fig. 2 (*b*)], the edge is not at all noticeable in the fully etched crystal [Fig. 2 (*c*)]. In this case the entire triangle is of fairly uniform intensity, except for local irregularities.

Finally Fig. 2 (*d*) which is obtained with the fully etched crystal dipped in liquid air, is not appreciably different from Fig. 2 (*c*) obtained before the chilling treatment. However, it was found that after chilling the absolute intensity increased showing that a certain degree of mosaicity was introduced. The surfaces of the chilled crystal was again ground and a photograph was taken (not reproduced). It was observed that the edges appeared with more intensity than the interior indicating that the liquid air treatment did not make lithium fluoride crystal ideally mosaic but only introduced a small amount of disorientation.

(ii) *Photographs with Slit Horizontal.*—The thickness intensity curves obtained for the four cases are shown in Fig. 3. The curves have been displaced vertically so that they do not overlap. Each curve represents only the relative measurements made with a single specimen and no attempt has been made to measure the absolute intensity. Consequently, it does not follow that a curve higher up corresponds to a case which had larger absolute intensity. The same symbols (*a*), (*b*), (*c*), (*d*), as in the previous paragraph have been used to indicate the four cases. Before proceeding to discuss the experimental results, the theory of these cases has been considered.

The formulæ for the variation of the integrated reflection ($\rho$) with thickness for an ideally mosaic and perfect crystal are (Ramachandran, 1952)

$$\rho_M \alpha \, Pe^{-P} \qquad \text{(mosaic)}$$

$$\rho_P \alpha \; e^{-P} \{I_0 (kP/G) - 1 + \int_0^{P/G} J_0 (x) \, dx\}, \qquad \text{(perfect)}$$

where

$$P = \mu t/\gamma,\ k = \chi_{hi}/\chi_{hr},\ G = \chi_{0i}/C\chi_{hr}.$$

Here $\mu$ is the absorption coefficient, $\gamma = \cos\theta$, $\chi_{0r}$, $\chi_{0i}$ are the real and imaginary parts of the Fourier component of index zero of $4\pi$ times the polarisability, $\chi_{hr}$, $\chi_{hi}$ the coefficients corresponding to the (200) reflection and C polarisation factor. For large values of P/G, as are met with in the present study $\int_0^{P.G} J_0(x)\,dx \rightarrow 1$ so that the formula for the perfect crystal reduces to

$$\rho_P \alpha e^{-P} I_0(jP),\ \text{where } j = C\chi_{hi}/\chi_{0i}.$$

Making use of similar considerations we may work out the intensity variation with thickness for a ground crystal. As was deduced in the previous section, most of the intensity is contributed only by two narrow strips close to the two surfaces. Assuming that the strips are of uniform thickness throughout the crystal, and that the intensity is entirely due to the X-rays reflected from them, it is clear that the only parameter affecting the reflected intensity, which varies with thickness, is the path $t/\gamma$ through the crystal. This leads to a factor $(P = \mu t/\gamma)$ due to absorption, so that the integrated reflection in the case is

$$\rho_G \alpha e^{-P}.$$

In Fig. 3, the continuous curves are drawn from theory, while the experimental data are indicated by points. The data are plotted on a semi-logarithmic scale, *viz.*, $\log\rho$ *vs.* $t$. Taking first the ground crystal (*a*), theory predicts that the points should lie on a straight line of slope $-\mu/\gamma$. It is found that the points lie close to the theoretical straight line whose slope, calculated from the data for $\mu$ and $\gamma$ is 16·1. Thus the explanation mentioned earlier for the origin of the edges being bright in Fig. 2 (*a*) is confirmed. The data for both partially and fully etched crystal approximate to the curve for $\rho_p$. The value of the constant $j$ was obtained from experiment as follows. If $\rho_1$ and $\rho_2$ are the intensities corresponding to $P_1$ and $P_2$, then $\rho_2/\rho_1 = e^{-(P_2-P_1)} I_0(jP_2)/I_0(jP_1)$ from which $j$ can be obtained since all the other quantities are known. Actually the $\log\rho$ values for $t = 0{\cdot}04$ and $0{\cdot}12$ cm. for the fully etched crystal were used, which gave $I_0(jP_2)/I_0(jP_1) = 5{\cdot}47$ for $jP_2/jP_1 = 3$. Using a table of Bessel functions $I_0(x)$, this reduces to finding the value of $x$ for which $I_0(3x)/I_0(x) = 5{\cdot}47$. The value of $j$ comes out to be 0·88. The theoretical curves have been drawn for both (*b*) and (*c*) using the calculated value of $j = 0{\cdot}85$ (see below). It will be noticed that the experimental results with the fully etched crystal (*c*) fall very close to the theoretical curve indicating that the crystal is nearly perfect in structure. Those with the partially etched crystal (*b*) deviate from theory. This is to be expected.

As has been pointed out by Ramachandran (1952), the study of the integrated reflection of a perfect crystal using internal reflections gives one an idea of the imaginary component ($\chi_{h_i}$) of the structure factor. In our case we have found $j = 0 \cdot 88$ from experiment. It is interesting to compare this with what is to be expected from the theory of Hönl (1933) regarding the anomalous dispersion of X-rays. Writing $f$ to be total atomic scattering factor for frequency $\omega_i$, then $f = f_0 + \Delta f' + i \Delta f''$, where $f_0$ is the atomic scattering factor for frequencies high in comparison with any atomic absorption frequency and is independent of incident frequency, while $\Delta f'$ and $\Delta f''$ are the real and imaginary parts of $f$ that depend on frequency. Considering $\Delta f''$ in which we are primarily concerned the contribution to this by all the other elctrons except the *k*-electrons is negligible at the frequencies usually used for crystal analysis. Also, for small $\sin \theta/\lambda$, the contribution of the *k*-electrons is not likely to vary appreciably. Consequently $\Delta f''$ is practically a constant independent of $(\sin \theta/\lambda)$. Further in LiF, both the structure amplitudes $F_{000}$ and $F_{200}$ are equal to $4f_{Li} + 4f_F$ so that one thus obtains $\chi_{h_i} = \chi_{0_i}$ for the 200 reflection of LiF. Hence $j = C\chi_{h_i}/\chi_{0_i} = C$. The polarisation factor is equal to 1 for perpendicular component and $0 \cdot 71$ ($\cos 2\theta$) for the parallel component, so that the mean value for $j$ is $0 \cdot 85$. This agrees well with the experimentally deduced value of $0 \cdot 88$, thus verifying the correctness of the theoretical deductions made from the dynamical theory of Ewald by Ramachandran.

Considering lastly the chilled crystal, the points do not lie close to the theoretical curve. This again agrees with what was deduced from the photographs obtained with a vertical slit, namely that the crystal is partially mosaic.

## 4. Concluding Remarks

The present investigation thus offers a new method of determining the perfection or otherwise of a crystal. Unlike the various methods suggested earlier, the bulk of the reflection in this method occurs in the interior of the crystal so that it gives an idea of the degree of perfection of the crystal as a whole and not of the surface layers alone. Another great advantage is that the measurements need be made only on relative intensities on a single photograph and no absolute measurements are necessary. It would be worthwhile to extend these studies to other crystals and attempts are being made in this direction.

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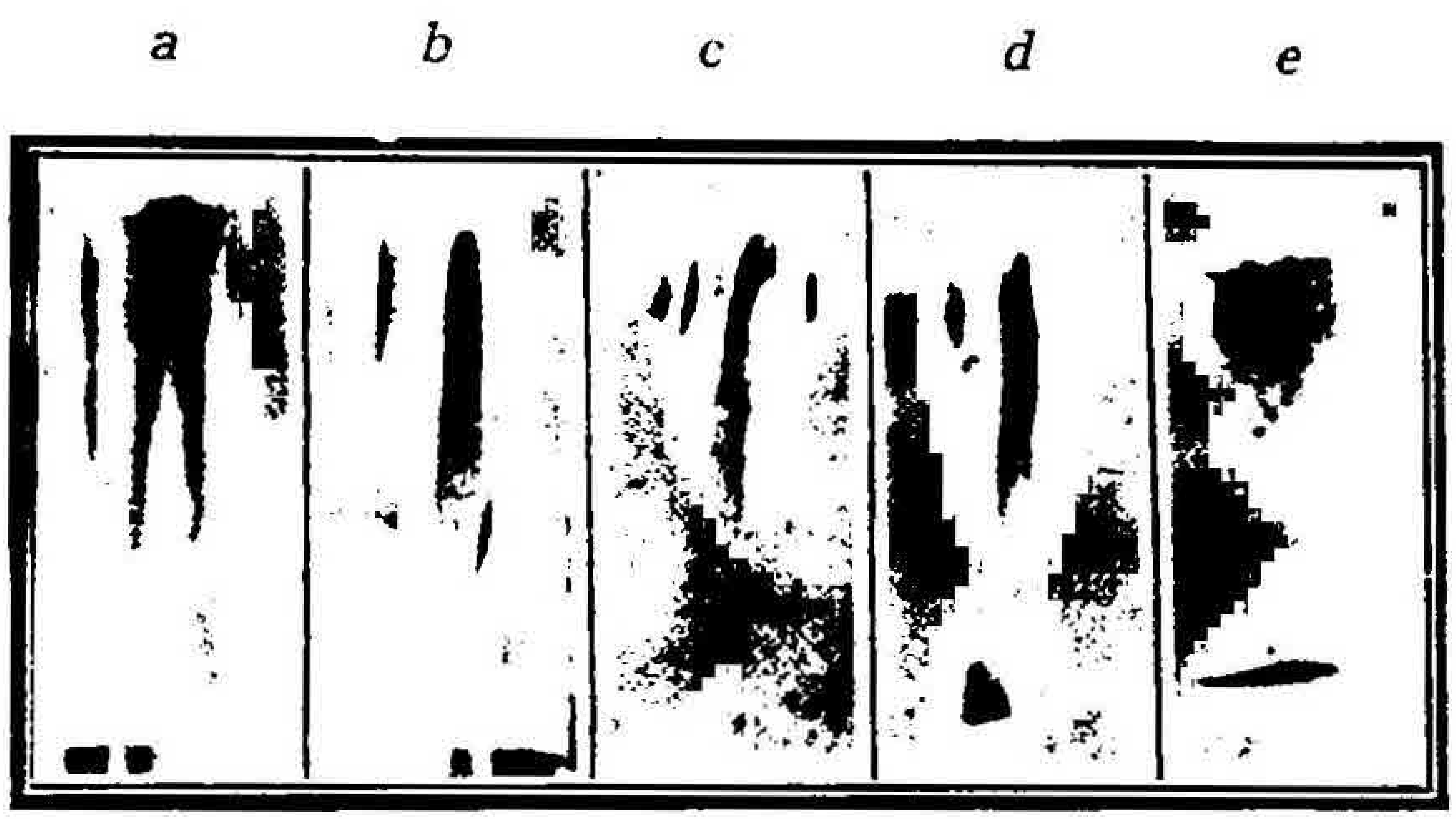


F.G. 2

Internal reflection in the case of

(*a*) ground crystal, with slit vertical
(*b*) partially etched crystal, ,, ,, ,,
(*c*) fully etched crystal, ,, ,, ,,
(*d*) chilled crystal, ,, ,, ,,
(*e*) partially etched crystal with slit horizontal.