

## Study of Perfection of Crystals Using Polarized X-rays

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A new method of assessing the perfection of crystals by using polarized X-rays was tested in detail and the measurements for a number of crystals are reported. The polarization ratio (ratio of the integrated intensities for the two orthogonal states of polarization) was found to lie in all cases within the limits set by theory.

The absolute intensity and the width of reflections were also measured and a comparison was made of the different methods of studying the perfection of crystals. It was found that the measurements were simpler by the new method. The limitations and the optimum conditions for measurements are discussed.

### 1. Introduction

The criteria usually adopted for assessing the perfection of crystals are the absolute integrated intensity and the width of X-ray reflection, both of which are minimum for ideally perfect crystals and increase with increasing degree of imperfection. A new method using polarized X-rays was suggested by Ramaseshan & Ramachandran (1954) which is based on the fact that the ratio of the integrated intensities of a reflection for the two orthogonal states of polarization varies with the degree of perfection of the crystal.

The present paper\* summarizes the results of a detailed study made with various crystals to test the new method. The absolute intensity and line width were also measured and a comparison was made of the different methods of assessing the perfection of crystals.

### 2. Theory of the method

The relevant theory has already been discussed (Hirsch & Ramachandran, 1950; Ramaseshan & Ramachandran, 1954) and here we shall cite only some of the formulae relevant to this paper.

When a beam of plane polarized X-rays is reflected from the surface of a crystal, let  $\varrho(0)$  and  $\varrho(\varphi)$  be the integrated intensities for azimuths  $0^\circ$  and  $\varphi^\circ$  of the plane of incidence. Then, we define

$$r(\varphi) = \varrho(\varphi) / \varrho(0). \quad (1)$$

We can express  $r(\varphi)$  as

$$r(\varphi) = \cos^2 \varphi + \alpha \sin^2 \varphi \quad (2)$$

which follows from the orthogonality of the polarized states. Here  $\alpha$ , which we shall call the polarization ratio, is the ratio of the integrated reflections for azimuths  $90^\circ$  and  $0^\circ$ . The value of this ratio for a mosaic crystal ( $\alpha_M$ ) is  $\cos^2 2\theta$ , while for a perfect crystal of

negligible absorption ( $\alpha_{PN}$ ) it is  $|\cos 2\theta|$ . If absorption is appreciable, the polarization ratio ( $\alpha_{PA}$ ) would be less than  $|\cos 2\theta|$ . Therefore, in all actual crystals, the polarization ratio would lie between the two limits  $\alpha_{PA}$  and  $\alpha_M$ . The upper limit,  $\alpha_{PA}$ , cannot be obtained from theory in terms of an explicit formula, but it can be worked out by numerical integration (Hirsch & Ramachandran, 1950). The influence of absorption in lowering the value of  $\alpha$  below  $|\cos 2\theta|$  was verified in a typical case (Chandrasekaran, 1955a) by studying two orders of reflection from the surface of a freshly cleaved perfect sample of calcite. It was found that there was good agreement between the values of the polarization ratio as calculated from the theory and determined by experiment.

It is possible to define a parameter  $\Delta$ , representing the 'degree of perfection' in terms of the measured value of the polarization ratio for a particular crystal specimen. We define this quantity as

$$\Delta = (\alpha - \alpha_M) / (\alpha_{PA} - \alpha_M). \quad (3)$$

The denominator is the maximum range of variation of the polarization ratio while the numerator represents the actual departure of this ratio from its mosaic crystal value and therefore  $\Delta$  will take the values 0 and 100% respectively for an ideally mosaic and a perfect crystal.

It would take intermediate values when the crystal is neither ideally mosaic nor ideally perfect, and  $\Delta$  may therefore be used to represent the degree of perfection. It is to be assumed that if  $\Delta$  is either 0 or 100% for one reflection, it would be so for all the reflections on the same set of planes. However, it is not clear that, when  $\Delta$  does not take either of the limiting values, it would be the same for all the reflections, even on the same set of planes. One of the main purposes of this study was to test this point experimentally. The results seem to indicate that  $\Delta$  is approximately the same for different orders of reflection from the surface of a crystal. The theoretical position in this respect is

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very difficult to work out for a general case. However, it is possible to do so for the cases of small primary and/or secondary extinction. This will be reported in detail in a later paper. It is found that the structure factor  $|F|$  and the polarization factor  $K (= 1 \text{ or } |\cos 2\theta|)$  for the two orthogonal states of polarization go hand in hand, so that a measurement of the polarization ratio should give a valuable indication of the way in which the intensity varies with the structure amplitude—the two limits being proportional to  $|F|^2$  for a mosaic and  $|F|$  for a perfect crystal with negligible absorption.

The advantage of the new method for assessing perfection over the earlier methods is the fact that the polarization ratio can be measured accurately, since it is only the ratio of two quantities of comparable magnitude measured under similar conditions, while the absolute intensity and width are much more difficult to measure. However, an important limitation of the new method is that reflections with Bragg angles too close to  $45^\circ$  would not reveal the texture, since the polarization ratios  $|\cos 2\theta|$  and  $\cos^2 2\theta$  for the perfect or mosaic crystal, respectively, would be nearly the same.

In the present experiments, surface reflections occurring in the range of  $\theta = 25^\circ$  to  $70^\circ$  were studied on a number of crystals. The degree of perfection and the absolute integrated intensity\* were measured in every case. The width of the reflection was also recorded, by a photographic method, for the first order of reflection from the surface of the crystal. The choice of the crystals and reflections for study can be understood by reference to Table 1, where some of the parameters used in the calculation are listed. It is seen that there is a wide range of values for the Bragg angle, absorption, and structure factor of the reflection. Thus for Cu  $K\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) used in

the experiments, the linear absorption coefficient is as low as  $29.8 \text{ cm.}^{-1}$  for lithium fluoride while it is as high as  $307 \text{ cm.}^{-1}$  for fluorite, the other crystals quartz, rock salt and calcite covering the intermediate range. The effect of a large absorption coefficient (Hirsch & Ramachandran, 1950) would be to reduce  $\alpha_{PA}$  from  $|\cos 2\theta|$  towards the mosaic value of  $\cos^2 2\theta$  and thus make the range of variation of the polarization ratio much smaller. This may be seen in the data for the 222 reflection of fluorite where  $|\cos 2\theta|$  is 0.519,  $\alpha_{PA} = 0.306$  and  $\cos^2 \theta = 0.269$ . It is also seen from the data of Table 1 that the choice led to a good range of the absolute intensity values.

### 3. Experimental details

The Geiger counter spectrometer used in these experiments has been described already (Chandrasekaran, 1955*b*). The polarization of the X-ray beam was obtained by reflection from a single crystal of copper, set for the 311 reflection ( $\theta = 45^\circ 6'$ ) and it was verified (Chandrasekaran, 1956) that the polarization was extremely good, the unpolarized component being only 0.2% of the total intensity. An additional feature in the present work was a monitor for the intensity of the polarized X-ray beam.

The method adopted for monitoring was to keep a thin aluminium foil in the path of the polarized beam and to record the 222 powder reflection from the foil, by a separate Geiger Counter ( $M$ ), set for this reflection ( $\theta = 41^\circ$ ) while a Geiger Counter ( $G$ ) recorded the integrated intensity of reflection from the crystal under study. A powder reflection was chosen in preference to a single crystal reflection for the purpose of monitoring, because the setting of the foil with respect to the X-ray beam is not so critical, as that of a single crystal. The loss in intensity due to the absorption by the foil was found to be about 32%; this did not prevent the recording of even the weak reflections listed in Table 1.

\* In this paper, all integrated intensity values are for an X-ray beam polarized with its electric vector in the plane of incidence.

Table 1. *Summary of parameters used in calculation*

Crystal	$hkl$	$ F ^*$	$\theta$	$ \cos 2\theta $	$\alpha_{PA}$	$\cos^2 2\theta$	$\sin 2\theta$	$q_{PA}\dagger$	$q_M\dagger$
1. Calcite $\mu = 190 \text{ cm.}^{-1}$	422	18.9	$30^\circ 30'$	0.485	0.374	0.235	0.875	7.45	20.4
	633	22.9	$49^\circ 39'$	0.159	0.070	0.026	0.987	8.42	28.3
2. Rock salt $\mu = 162 \text{ cm.}^{-1}$	400	50.80	$33^\circ 13'$	0.400	0.329	0.160	0.917	15.53	78.61
	600	30.68	$55^\circ 17'$	0.351	0.249	0.123	0.936	8.44	28.05
3. Lithium fluoride $\mu = 29.8 \text{ cm.}^{-1}$	400	15.2	$50^\circ 27'$	0.189	0.170	0.036	0.982	12.45	261.5
	—	—	—	—	—	—	—	—	—
4. Fluorite $\mu = 307 \text{ cm.}^{-1}$	222	7.92	$29^\circ 22'$	0.519	0.306	0.269	0.855	1.09	1.33
	333	34.0	$47^\circ 21'$	0.082	0.016	0.007	0.997	8.68	21.4
5. Quartz <i>m</i> face $\mu = 92 \text{ cm.}^{-1}$	30.0	9.39	$33^\circ 0'$	0.407	0.297	0.166	0.914	3.70	11.1
	40.0	15.25	$46^\circ 32'$	0.054	0.012	0.003	0.998	6.37	27.6
6. Quartz <i>r</i> face $\mu = 92 \text{ cm.}^{-1}$	20.2	20.04	$27^\circ 28'$	0.575	0.529	0.331	0.818	10.64	58.95
	30.3	3.72	$43^\circ 53'$	0.039	0.003	0.002	0.999	1.03	1.72
	40.4	5.44	$68^\circ 0'$	0.719	0.621	0.517	0.695	2.50	5.11

\*  $|F|$  values for rock salt were taken from Renninger's data (1952) for the crystal at room temperature; for the other crystals, they were calculated using the data of Wyckoff (1948) for the parameters and James-Brindley scattering factors.

† Integrated intensity values, in microradians, for X-rays polarized in the plane of incidence.

Table 2. *Intensity measurements with fluorite 222 reflection*

	Azimuth settings				Scaling
	$\varphi=0^\circ$ (- - - - -)	$\varphi=90^\circ$ (one side)	$\varphi=0^\circ$ (repeat)	$\varphi=90^\circ$ (other side)	
Total counts during four runs	82.3	27.1	81.9	27.6	128
Background for the same period*	16.2	10.8	17.1	9.9	128
Net integrated intensity counts ( $G$ )	66.1	16.3	64.8	17.7	128
Monitor counts during same period	911	901	884	910	8
Background of monitor†	144	144	144	144	8
Net monitor counts ( $M$ )	767	757	740	766	8
Integrated intensity, $G/M$ : (arbitrary units)	1.38	0.345	1.40	0.369	—

\* Background of the counter, taken as an average of the background at either end of the range of integration.

† Background of the monitor which was practically constant.

Table 3. *Summary of measurements on the spectrometer*

(The intensity values are in microradians)

Specimen	Reflection	Measured intensity			$\Delta$	Calculated intensity*	
		$\varrho(0^\circ)$	$\varrho(90^\circ)$	$\alpha$		$\varrho_{PA}(0^\circ)$	$\varrho_M(0^\circ)$
Rock salt ( $A$ ), synthetic untouched	400	55.7	12.81	0.228	40	15.5	78.6
	600	22.3	3.92	0.176	35	8.4	28.1
Rock salt ( $B$ ), natural	400	60.3	13.87	0.226	40	15.5	78.6
	600	26.8	4.56	0.170	40	8.4	28.1
Rock salt ( $C$ ), synthetic ground with carborundum	400	56.6	12.0	0.212	30	15.5	78.6
	600	26.2	4.19	0.160	30	8.4	28.1
Rock salt ( $D$ ), above sample lightly etched	400	77.0	13.86	0.179	10	15.5	78.6
	600	29.4	4.12	0.138	10	8.4	28.1
Lithium fluoride, front face	400	26.2	4.6	0.175	100	12.45	261.5
Lithium fluoride, back face	400	81.2	6.5	0.060	35		
Quartz, $m$ plate	30.0	10.2	1.75	0.175	10	3.7	11.1
	40.0	18.6	weak	—	—	6.4	27.6
Quartz $r$ plate, front surface	20.2	14.4	7.2	0.50	100	10.6	59.0
	30.3	1.1	weak	—	—	1.0	1.7
	40.4	5.4	3.29	0.61	70	2.5	5.1
Quartz, $r$ plate above, back surface	20.2	15.6	8.11	0.52	100	10.6	59.0
	30.3	1.0	weak	—	—	1.0	1.7
	40.4	5.9	3.66	0.62	70	2.5	5.1
Fluorite	222	2.76	0.72	0.26	0	1.1	1.3 (2.3)
	333	21.6	0.18	0.008	10	8.7	21.4
Calcite etched with HCl	422	12.3	4.3	0.35	80	7.5	20.4
	633	14.1	0.9	0.06	80	8.4	28.3
Calcite, ground	422	16.1	4.7	0.277	30	7.5	20.4
	633	14.9	0.75	0.05	50	8.4	28.3

\* The calculated values are from Table 1.

The pulses from the counters  $G$  and  $M$  were recorded on two separate scaling units of ratios 128 and 8 respectively. All intensity values were expressed as the ratio of the total number of counts in the two channels during the period of integration, with suitable corrections for the background. The exact procedure adopted is explained in Table 2 for the 222 reflection of fluorite, which is very weak. It will be noticed that the actual number of counts was about 17,000

for azimuth  $0^\circ$ , 4,500 for  $90^\circ$  and 12,000 for the monitor. Thus the accuracy of the measurement was good, particularly for the  $0^\circ$  azimuth readings, which were used for the absolute intensity.

This system of monitoring corrects only for slow changes in the X-ray beam intensity. For sudden fluctuation in the tube output, the ratio of the measured integrated intensity ( $G$ ) to the monitor counts ( $M$ ) would depend on the exact time of the integration

period at which the change occurred. Thus a slight change of the X-ray tube intensity would affect this ratio much more if it occurred at the peak of a reflection than at the beginning or end of the reflecting range. In actual practice, each intensity was determined as an average of four runs and the measurements are estimated to be accurate to 5%.

The measured integrated intensity (as in Table 2) was in arbitrary units and this was converted to microradians by comparison with a standard crystal. For this purpose, a rock salt sample was lightly ground and the 400 and 600 reflections were measured. The average of several measurements gave 38.0 and 13.7 units for these reflections, in the same units as in Table 2. The ratio of the 400 to 600 intensity was thus 2.715 as against the theoretical value of 2.802 for a mosaic crystal (Table 1). This gave an estimate of the secondary extinction coefficient as 325 cm.<sup>-1</sup>. With this value, the 400 reflection, corrected for extinction, was 39.9 units. With the absolute integrated intensity of 78.61 microradians, from Table 1, a conversion factor of 1.97 microradians per unit was thus obtained, which was later used in expressing all intensity measurements in absolute units.

#### 4. Results

A summary of the measurements is given in Table 3. The same procedure as indicated in Table 2 was adopted in all cases; but for convenience only the final results are stated. The degree of perfection was rounded off to the nearest multiple of 5%. The results of width measurements are given in section 5.

##### (a) Rock salt

Referring to the data of the rock salt samples *A*, *B* and *D*, it will be seen that in general a low degree of perfection is associated with an intensity value close to the mosaic value  $\rho_m$ . Also, the higher the perfection, the lower is the intensity. This is in fact to be expected. However, this correlation did not hold for sample *C*, which was heavily ground. Here the intensity was small but the perfection was also comparatively low. The small intensity in such a case is probably due to the formation of an amorphous layer on the surface, while grinding. This layer would absorb but not contribute to the reflection and such a situation has been known to happen with abraded crystals (Evans, Hirsch & Kellar, 1948). In such instances, the degree of perfection gives a better picture of the texture than the absolute intensity, because the absorbing layer affects the measurements for the two states of polarization equally.

##### (b) Lithium fluoride

Here, only the second order reflection 400 lay in the range of the instrument. The specimen had a clear front face, while the other surface had a number of scratches on it; both surfaces were examined.

From Table 3, it is seen that the front surface gave almost a perfect crystal value for the polarization ratio. In fact, it was observed that the value was often larger than  $\alpha_{PA}=0.170$ . This may be due to simultaneous reflections but this possibility was not critically tested as an arrangement for continuously rotating the crystal in its own plane could not be easily incorporated. However, a number of measurements, with the crystal reset each time in its own plane, gave values in the range 0.175 to 0.185, all greater than the theoretical value (the minimum value is given in Table 3). This suggests that the explanation for the deviation has to be sought for elsewhere, probably in the exact value of the absorption coefficient. The back surface had a  $\Delta$  value of 35% and the intensity of reflection was nearly thrice that for the other surface.

##### (c) Quartz

Two faces of quartz were studied, both of which were cut plates. One of them parallel to the *m* face (10 $\bar{1}$ 0) was ground, while the other, parallel to *r* (10 $\bar{1}$ 1) was not ground. The specimens were from different pieces of quartz. Two orders 30.0 and 40.0 were measured with the *m* plate while three reflections 20.2, 30.3 and 40.4 could be recorded with the *r* plate. With the *r* plate, both the surfaces of the crystal were studied, but the results were not materially different. The data are given in Table 3.

Referring to the data of the *m* plate, it is seen that the degree of perfection is quite low, about 10% with the 30.0 reflection. With the 40.0 ( $\theta=46^\circ 32'$ ), the measurements are very inaccurate since  $2\theta$  is nearly  $90^\circ$  and consequently the limits of variation of the polarization ratio (see Table 1) are very close. However, the absolute intensities both for 30.0 and 40.0 are close to the mosaic values, in agreement with the degree of perfection obtained with the 30.0 data.

With the *r* plate, both surfaces were nearly perfect, the degree of perfection lying in the range of 70 to 100%. The intensity of 30.3 reflection at  $0^\circ$  azimuth was only about one microradian and  $\theta$  being  $43.53'$ , the intensity at  $90^\circ$  azimuth could not be recorded. Also, the absolute intensity values of 20.2 indicated nearly perfection, while there was a definite divergence in 40.4. However, for such a high order reflection the  $|F|$  value would be very sensitive to slight changes in the assumed parameters for Si and O (Wyckoff, 1948) and also in the exact values of the atomic scattering factors which were used in the calculations. In the case of 30.3, the variation of the integrated intensity with perfection is quite small and therefore not useful for assessing the degree of perfection. In spite of this, the measured values (1.0, 1.1 microradians) agree closely with the perfect crystal value (1.0).

##### (d) Fluorite

The specimen studied was a cleavage plate (111) of a natural crystal, showing a pale pink colour. Measure-

ments were made for the 222 and 333 reflections. The measured value of the degree of perfection was nearly 0% for the 222, while with 333, the measurement was not accurate,  $2\theta$  being nearly  $90^\circ$ . The intensity of 333 was, however, in good agreement with the value for a mosaic crystal while that for 222 definitely disagreed. The measured value of 2.76 microradians for this reflection was distinctly higher than  $\rho_M$  (1.33  $\mu$ r.). This particular measurement was repeated a number of times and the values were all consistent, being 2.76, 2.70, 2.78 and 2.80 microradians. The discrepancy was then found to be due to the atomic scattering factors. The four calcium and eight fluorine atoms in the unit cell are in opposite phase for this reflection and the  $|F|$  value is the difference in their contributions. The calculated value of  $\rho_M=1.33 \mu$ r. was on the basis  $f_{Ca^{++}}=11.06$ ,  $f_{F^-}=4.54$  for  $\sin \theta/\lambda=0.32$ , giving 7.9 as the  $|F|$  value for the reflection. However, if the values for unionised atoms were taken namely  $f_{Ca}=11.06$ ,  $f_{F}=4.23$  then the  $|F|$  value was 10.4. This resulted in  $\rho_M=2.3$  microradians which was in better agreement with the measured value of 2.76.

It was interesting to note that when this crystal was ground, the intensity decreased from 21.6 to 16.8  $\mu$ r. for 333 and from 2.76 to 1.98  $\mu$ r. for 222. This behaviour was similar to the observation with rock salt where grinding led to a decrease in intensity due to the formation of an amorphous layer on the surface.

#### (e) Calcite

Measurements were made on two specimens of calcite, one a cleavage face lightly ground with fine emery and the other, a face which was first ground and then etched with HCl for a few seconds. These are called the ground and etched faces respectively.

It is seen that the  $\Delta$  value was only about 80% for the etched face, showing that etching, subsequent to grinding did not bring the perfection very close to 100%. Such high perfection in calcite was in fact recorded with the untouched cleavage face of good specimens (Chandrasekaran, 1955*a*). The integrated intensity in the present case was also higher than  $\rho_{PA}$ . The other sample which was ground showed a low perfection but the intensity was not appreciably larger. In fact, further grinding only reduced the intensity.

### 5. Width measurements

The width of a Bragg reflection from a perfect crystal is known to be of the order of a few seconds of arc while for mosaic crystals it may vary from a minute to a degree or even more. The smallest imperfections tend to increase the width. Some measurements were made of the width and the degree of perfection for a few specimens, which were nearly perfect.

The experiment was performed with a Hilger microfocus X-ray unit, making use of a photographic method. The divergent beam from the 40 micron

source of X-rays was allowed to fall on a stationary crystal set at about the Bragg angle and the reflected beam was photographed at various distances from 10 cm. to 100 cm. from the crystal. The crystal itself was kept at 5 cm. from the focal spot of the X-ray tube. The technique adopted was essentially the same as used by Ramachandran (1944) but for the difference that no fine pinhole was required in the present experiments conducted with the microfocus tube. Photographs could be obtained in about 45 minutes at a distance of 100 cm. The width of the reflections were measured on a Hilger non-recording microphotometer.

The angular divergence in this experiment arises from two causes (a) the width of X-ray reflection from the crystal and (b) the inherent wavelength spread of the X-ray line. Let  $w$  be the half width (i.e., full width at half maximum intensity) due to the former and  $l$  be the half width due to the X-ray line breadth. It can be shown that if the distribution of intensity of crystal reflection ( $w$ ) and line spread ( $l$ ) are both Gaussian, then the combined half width ( $W$ ) is given by  $W^2=w^2+l^2$  from which the half width of the crystal reflection  $w$  is obtained, assuming  $l$  to be known.

For the spectral width of the Cu  $K\alpha$  radiation used in these experiments, an average value of  $0.67 \times U$  was taken for the  $\alpha_1$  and  $\alpha_2$  components (Compton & Allison, 1935). If this be denoted by  $\Delta\lambda$ , the corresponding angular width is

$$(\Delta\lambda/\lambda) \tan \theta = 4.36 \times 10^{-3} \tan \theta.$$

Thus for the 211 reflection of calcite,  $\tan \theta=0.27$  and so  $l=1.18 \times 10^{-4}$ .

The resultant half width  $W$  can be measured from experiment. The source may be effectively taken to have a linear breadth  $2a'$  over which the intensity is uniform. The effect of the finite width of the slit of the microphotometer used for measurements will be to increase this to an effective value, say  $2a$ . This cannot be calculated exactly, though from the known focal spot size (40 microns) and the width of the image of the microphotometer slit (0.01 mm.), this is expected to be close to  $5 \times 10^{-3}$  cm.

The angular half width of the reflection was determined as follows. The linear width at half maximum ( $2b$ ) was measured at a large distance ( $R=50$  to 100 cm.). This is obviously due to the superposition of the effective slit width ( $2a$ ) and the Gaussian distribution of X-ray intensity of width ( $2c$ ). The relation between  $a$ ,  $b$ , and  $c$  has been theoretically worked out (Ramachandran, 1944) and given in a tabular form by him. This table was used to find  $c$  from the measured values of  $a$  and  $b$ . For  $a$  the effective half width of the slit, the photograph taken at a close distance ( $R=10$  cm.), was used. This distance was sufficiently small for the measured width to be taken as equal to the effective width of the source.

The data are given in Table 4, being the mean values for the Cu  $K\alpha_1$  and  $K\alpha_2$  lines. For all the crys-

Table 4. Summary of width measurements for perfect crystals

Crystal	Reflec- tion	$\Delta$	Width measured in divisions (1 div. = $5 \times 10^{-4}$ cm.)			Distance $R$ in cm.	Angular width $W = 2c/R$ in $10^{-4}$ radians	$l$ in $10^{-4}$ radians	Width of crystal reflection	
			Total measured $2a$	Effective width of slit $2b$	Cor- rected width $2c$				in $10^{-4}$ radians	in seconds
Calcite (near perfect)	211	90%	33	10	32.3	106	1.5	1.2	0.92	19
Calcite (natural face)	211	50	34	12	33	76	2.2	1.2	1.86	38
Calcite (ground)	211	35	30	12	29	56	2.6	1.2	2.33	48
Lithium fluoride (perfect face)	200	100	31	16	29	76	1.9	1.8	0.6	12
Quartz ( $r$ face)	10-1	80	28	12	27	76	1.8	1.05	1.46	30

tals, the lowest order reflection from the surface was studied to keep the width  $l$  a minimum. It will be seen that the measured width at 10 cm. is about 12 divisions (1 division =  $5 \times 10^{-4}$  cm.), which corresponds to  $6 \times 10^{-3}$  cm., close to the estimated value of  $5 \times 10^{-3}$  cm. However, with LiF, this width was appreciably larger (16 divisions =  $8 \times 10^{-3}$  cm.), which is due to the low absorption and consequent deeper penetration of the X-ray beam into the crystal.

The accuracy of the method was such that for small half width of the crystal reflection (say less than  $15''$ ), it was not possible to say anything except that it was small. For example, if the width of the LiF reflection was measured to be 32 divisions instead of 31, then the calculated width  $w$  would be  $15''$  while if it was estimated at 29.5 divisions,  $w$  would become zero. Consequently the values of  $19''$  and  $12''$  obtained for perfect calcite and LiF must be taken to mean that the width was negligibly small, approaching the theoretical values, e.g., for the 211 of calcite it is  $5''$  (Zachariasen, 1945). It is seen from Table 4 that there is a fairly good correlation between the degree of perfection given by the polarization study and the measured width in the case of the calcite samples, the smaller the width, the higher being the perfection.

## 6. Discussion and scope of the present method

The results of the measurements with various crystals showed that in all the cases both the absolute intensity  $\rho$  and the polarization ratio  $\alpha$  lay within the limits set by the theory (Hirsch & Ramachandran, 1950), as would be seen from a comparison of Table 1 and 3. In fact, the values occurred right from one limit to the other with different specimens. Thus fluorite and rock salt carefully ground approached the mosaic end while lithium fluoride and calcite lay near the other end of ideal perfection.

About the relative merits of the two quantities  $\rho$  and  $\alpha$  for assessing perfection, in general the measurement of  $\alpha$  is simpler, as explained in section 2. Further when crystal samples have been ground with abrasives, the absolute intensity may give a wrong indication of the texture of the crystal, as was observed in the case of some rock salt specimens, due to the formation of an amorphous powder layer on the surface. In such a context the polarization ratio would give a more reliable information on the degree of perfection.

However, the measurements indicated that near the perfect crystal end of the scale, the intensity seemed much more sensitive to small changes in texture than the polarization ratio. This was particularly seen with crystals of low absorption like lithium fluoride, where with a degree of perfection close to 100%, the intensity was nearly twice that expected for a perfect crystal. For intermediate textures, both the quantities appeared equally useful, the main criterion being how much they varied from the mosaic to the perfect state. A strong reflection with the Bragg

angle not too close to  $45^\circ$  is ideal for obtaining information about perfection by the polarization method. This is so because for a strong reflection,  $\alpha_{PA}$  is not reduced much below the value of  $\alpha_{PN}$  by absorption and the full range from  $|\cos 2\theta|$  to  $\cos^2 2\theta$  is available.

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## The Crystal Structures of some Anthracene Derivatives VI. 9-Anthraldehyde

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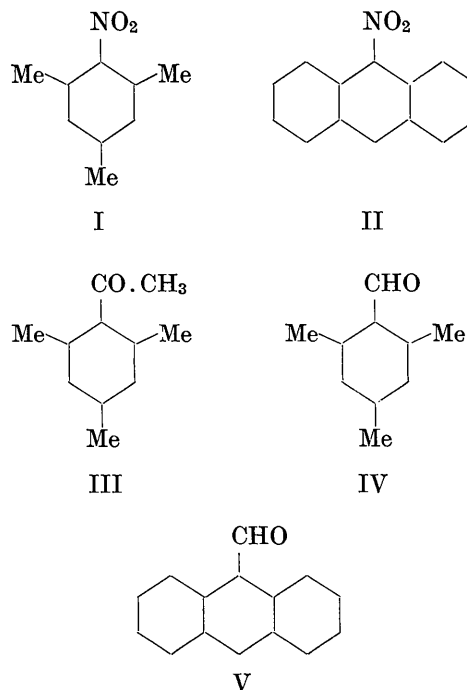
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Crystals of 9-anthraldehyde are orthorhombic, space group  $P2_12_12_1$ , with four molecules in the unit cell. The structure has been determined from the projection along the short  $a$ -axis, and refined by three-dimensional differential syntheses. The anthracene skeleton is completely planar, but not coplanar with the plane of the aldehyde group, the angle between the planes being  $27^\circ$ .

### Introduction

The physical properties of nitromesitylene (I), such as Raman and infrared frequencies, dipole moment and ultraviolet absorption spectrum, indicate that resonance interaction between the nitro group and the aromatic ring is markedly reduced in comparison with nitrobenzene, suggesting that the steric effect of the ortho methyl groups prevents the attainment of a completely coplanar configuration (see, for example, Wheland, 1955). Recently this deviation from planarity has been confirmed and in addition accurately measured by a detailed X-ray analysis of crystals of nitromesitylene (Trotter, 1959*a, b*); the nitro group is rotated about the C-N bond  $66^\circ$  out of the plane of the aromatic ring, and this measured angle can be correlated with the characteristic  $\text{NO}_2$  vibration frequencies (Trotter, 1959*f*). The X-ray investigations have also been extended to 9-nitroanthracene (II) and 9:10-dinitroanthracene (Trotter, 1958, 1959*c, d*), where the environments of the nitro groups are very similar to those in nitromesitylene, and the measured deviations from coplanarity have been correlated with the



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