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A 'Parallel-Beam' Concentrating Monochromator for X-Rays

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The performance of a concentrating X-ray monochromator, proposed by Fankuchen (1937), in which the beam is monochromatized by reflexion from a crystal surface inclined at an angle ϕ to the Bragg reflecting planes, has been studied experimentally by investigating the variation of the intensity of the reflected beam as a function of ϕ and, for $\phi=0$, of the surface treatment of the crystal. It is found that the ratio of the reflected to the incident intensity reaches a maximum for a certain value of ϕ, and that this maximum is always less than twice the ratio for $\phi=0$. An explanation in terms of surface inhomogeneities is suggested, and the formulae derived on these assumptions are found to fit the experimental curves well. The reflected intensity varies widely with the surface treatment applied to the crystal. With calcite the reflexion is enhanced by rubbing the surface with the wooden end of a pencil or by grinding very lightly on the finest sandpaper, but the use of any coarser abrasive decreases the intensity of reflexion. The practical application of this kind of monochromator is discussed, and a method of providing a very narrow beam of monochromatic radiation is suggested.

Introduction

There are many problems in X-ray analysis in which monochromatic X-rays in the form of a 'parallel' beam are required, and for which the focusing monochromator, owing to the wide angular range of the beam, is unsuitable; examples of these problems are some low-angle scattering studies and certain aspects of the microbeam technique. In such cases where a parallel-beam monochromator must be used, it may be desirable to take advantage of the enhanced intensity of the reflected beam arising from the foreshortening effect produced by reflexion from a crystal surface inclined to the Bragg reflecting planes. Such an arrangement, shown diagrammatically in Fig. 1, was proposed by Fankuchen (1937) and has been discussed by Bozorth & Haworth (1938) and by Fankuchen (1938). Its performance does not, however, seem to have been the subject of any systematic experimental investigation, and it is the purpose of the work here described to determine the conditions under which such a monochromator may be used to best advantage.

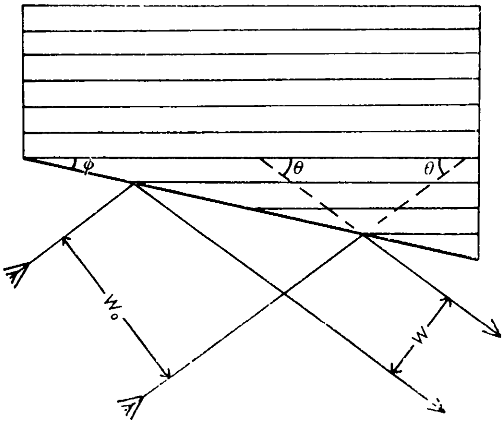

Fig. 1. Diagrammatic representation of condensing monochromator.

Notation

θ	Bragg angle;
ω	angle between the reflecting planes and the crystal surface;
ϕ	angle between the reflecting planes and the trace of the crystal surface in the plane of the incident and reflected beams;
I_0	intensity (rate of flow of energy per unit cross-section) in incident beam;
I	intensity in reflected beam;
W_0	width of incident beam;
W	width of reflected beam;
R	concentrating ratio (W/W_0);
ψ	angle of rotation of crystal about normal to reflecting planes measured from position of unit concentration;
K	reflecting power per unit volume of mosaic crystal;
ρ	integrated reflexion;
t	thickness of 'surface layer'.

Experimental details

The experiments consisted in the measurement of the ratio I/I_0 as a function of ϕ and of the character and history of the crystal surface. To study the variation of this ratio with ϕ it was not necessary to prepare a new surface for every value of ϕ required; instead it sufficed to prepare a crystal with the surface inclined to the reflecting planes at a convenient angle ω, and to mount this crystal so that it could be rotated about the normal to the reflecting planes in the manner represented in the stereographic projection (Fig. 2). Here N_p is the pole of the reflecting planes, X_i that of the incident beam, and X_r that of the reflected beam. As the crystal rotates about N_p, the pole N_s of the normal to the surface describes the arc $N_s'N_s''$ of a small circle of radius ω; when $\psi = 90°$, N_s is at N_s'; when $\psi = 0$, N_s is at N_s''. The angle ϕ is then the angle EN_p between the reflecting planes and the trace of the crystal surface in the plane of projection. It follows at once that

$$\tan\phi = \sin\psi \tan\omega, \qquad (1)$$

so that ϕ can be varied at will between the limits $\pm\omega$. This method of achieving a range of values of ϕ with one crystal not only economized effort in the preparation of specimens but also had the advantage of ensuring that the observations at different values of ϕ were all made on the same specimen; as explained below, it was found that the value of the ratio I/I_0 was not only a function of ϕ but was also profoundly dependent on the character and history of the crystal surface.

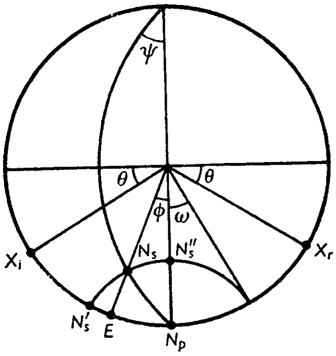

Fig. 2. Stereographic representation of the experimental arrangement. X_i, incident beam; X_r, reflected beam; N_p, normal to reflecting planes; N_s, normal to crystal surface.

The apparatus used is shown diagrammatically in Fig. 3. A collimated beam of X-rays fell on the first crystal, which was ground at such an angle that the reflected monochromatic beam was increased in width relative to the incident beam. The most uniform part of this emergent beam was then selected by means of a beam-defining slit and fell on the second crystal, the specimen under test.

For each setting of ψ the crystal was set in the best Bragg reflecting position by means of a Geiger-Müller counter and counting-rate meter, this precaution being found necessary because the reflexions were in some cases very sharp and the rotation axis was not in practice exactly normal to the Bragg planes. The beam reflected from the crystal and that incident on it were then recorded photographically, both records being made on the same film in order that processing conditions should be identical. During the exposure the output of the X-ray tube was kept constant.

The ratio I/I_0 was determined photometrically from the film, and the values of W and W_0, and hence of R, were also measured directly on the film. From the value of R thus found ϕ was computed by means of the relation

$$R = W/W_0 = \sin(\theta - \phi)/\sin(\theta + \phi), \qquad (2)$$

which follows directly from the geometry of Fig. 1. This method of deducing ϕ was preferred to that of calculating it from the setting angle ψ by means of equation (1), although good agreement was found between the two methods, because it did not demand an accurate knowledge of ψ or ω.

Radiation from a copper target was used throughout and, except in the case of crystal A and the measurements recorded in Table 3, the first crystal was fluorite, the radiation being monochromatized by reflexion from the 111 planes. Fluorite has the advantage that the structure factor of the 222 reflexions is very small, so that the second harmonic of the characteristic radiation was of negligible intensity; while higher harmonics were avoided by operating the X-ray tube at a peak potential below 24 kV. In the case of crystal A and the measurements recorded in Table 2 the radiation was monochromatized by reflexion from the $20\bar{2}2$ planes of calcite.

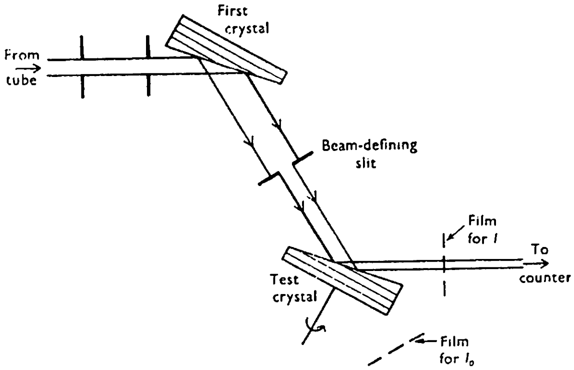

Fig. 3. The experimental arrangement.

Variation of I/I_0 with ϕ

The crystals tested are listed in Table 1 and the results obtained are shown graphically in Figs. 4–6.

Table 1. *Specimens used to investigate variation of* I/I_0 *with* ϕ

Specimen	Material	Surface treatment
A	Calcite	Ground on coarse carborundum ('220 grit') and polished
B	Calcite	Ground on coarse carborundum ('220 grit')
C	Quartz	Ground on coarse carborundum ('220 grit')
D	Fluorite	Ground on coarse carborundum ('220 grit')

Discussion. A formula derived by Debye & Menke (1931) has been applied by Bozorth & Haworth (1938) to the variation of I/I_0 with ϕ, and a similar expression was derived by Renninger (1937). For a mosaic crystal these expressions can be written in the form

$$I/I_0 = K/\mu\,(1+R), \tag{3}$$

so that according to this relation I/I_0 can range from $K/2\mu$ at $\phi=0$ to K/μ at $\phi=\theta$. Thus the maximum reflected intensity obtainable with a condensing monochromator cannot be expected to exceed twice that obtainable at $\phi=0$. A curve representing equation (3) is shown in Figs. 4–6, scaled in each case to fit the observed value of I/I_0 at $\phi=0$.

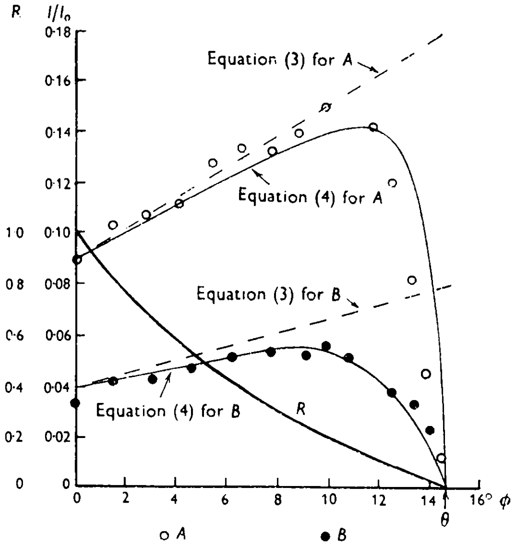

Fig. 4. Variation of I/I_0 with ϕ for $20\bar{2}2$ reflexion from calcite (crystals A and B). Radiation: Cu $K\alpha$ for crystal B; Cu $K\alpha$ with second harmonic for crystal A. $\theta = 14°\ 43'$. The interrupted lines represent equation (3), the full lines equation (4) with $\mu t = 0{\cdot}01$ ($\mu = 230$ cm.$^{-1}$). The curve of R calculated as a function of ϕ is also shown.

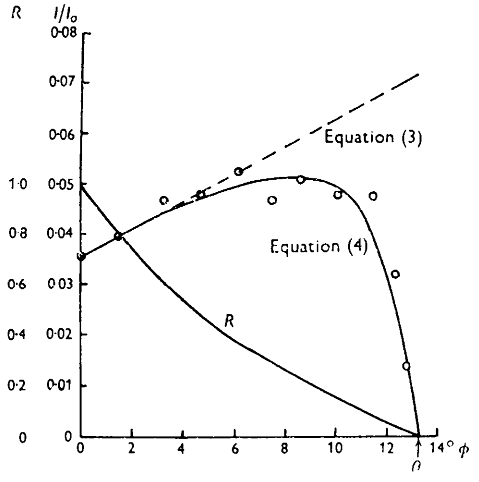

Fig. 5. Variation of I/I_0 with ϕ for $10\bar{1}1$ reflexion from quartz (crystal C). Radiation: Cu $K\alpha$. $\theta = 13°\ 20'$. The interrupted line represents equation (3), the full line equation (4) with $\mu t = 0{\cdot}02$ ($\mu = 91$ cm.$^{-1}$). The curve of R calculated as a function of ϕ is also shown.

The following conclusions can be drawn from the observations recorded in Figs. 4–6.

(a) The experimental points follow the curve of equation (3) only for small values of ϕ.

(b) The ratio I/I_0 reaches a maximum at a certain value ϕ_b of ϕ, and this maximum is always less than twice the value at $\phi=0$.

(c) The ratio I/I_0 for a given ϕ varies widely with surface treatment for the two calcite crystals A and B, being considerably greater for reflexion from a ground and subsequently polished surface than from a coarsely ground surface.

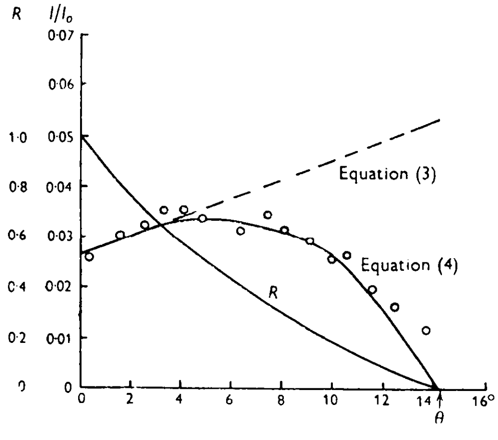

Fig. 6. Variation of I/I_0 with ϕ for 111 reflexion from fluorite (crystal D). Radiation: Cu $K\alpha$. $\theta = 14°\ 9'$. The interrupted line represents equation (3), the full line equation (4) with $\mu t = 0{\cdot}08$ ($\mu = 307$ cm.$^{-1}$). The curve of R calculated as a function of ϕ is also shown.

Equation (3) above applies only when both the reflecting power per unit volume and the absorption coefficient of the crystal are uniform from the surface inwards. We have found it possible to account for the observed variation of I/I_0 by assuming inhomogeneities in the surface regions of the crystal; and by considering the idealized case in which the surface is treated as being covered by a uniform layer of absorbing material of zero reflexion coefficient and of thickness t we have derived the expression

$$\frac{I}{I_0} = \frac{K}{\mu(1+R)}\{1-\exp[-\mu W_0(1+R)/\sin 2\theta]\} \times \exp[-\mu t\{\operatorname{cosec}(\theta+\phi)+\operatorname{cosec}(\theta-\phi)\}]. \tag{4}$$

For suitable values of μt this expression gives curves which fit the experimental observations remarkably well, as can be seen from Figs. 4–6. It is intended, at a later date, to present a more detailed discussion of the derivation of expressions of this type and to review the conclusions about surface texture to which they give rise.

The rapid decrease in the intensity of the reflected beam as ϕ approaches θ, due to the long path of this beam in the non-reflecting and absorbing layer, leads to the idea of using a 'cut-off' crystal, as shown for calcite in Fig. 7, when a very fine beam of maximum intensity is required. With such an arrangement the reflected beam emerges from the face AB of the crystal without traversing any great path in the non-reflecting layer, and very nearly the full twofold improvement in intensity would be expected to result. Calcite is particularly favourable for this purpose, for it is possible first to grind the surface BC at the desired angle ϕ and then subsequently, by taking advantage of the excellent cleavage, to prepare a fresh face AB with the minimum of disturbance to the surface in the region traversed by the emergent beam.

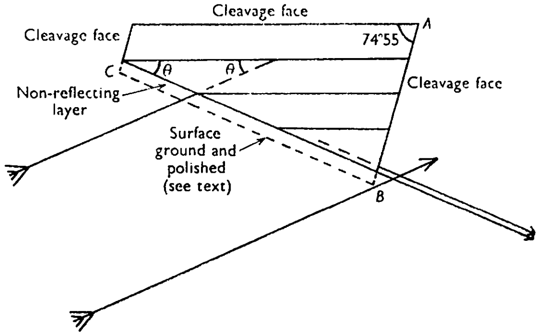

Fig. 7. 'Cut-off' concentrating monochromator of calcite.

Dependence of the reflecting power of calcite on surface treatment

A series of measurements were made on the apparatus described above, using calcite crystals with surfaces parallel to the reflecting planes $20\bar{2}2$ (i.e. with $\phi = 0$), to investigate the variation of reflecting power with surface treatment.

The values of I/I_0 obtained photographically depend not only on the reflecting power of the crystal but also on the angular range of the incident beam. Thus the values of I/I_0 obtained for different crystals, such as quartz and fluorite shown in Figs. 5 and 6, are not necessarily in accord with the respective reflecting powers. We have found, however, that if this range is sufficiently wide it is possible, by making comparison measurements on an ionization spectrometer, to derive a conversion factor by means of which the photographically observed values of I/I_0 may be transformed into values of the integrated reflexion, ρ. These comparison measurements were made for us by Dr W. A. Wooster and Mr G. L. Macdonald, and it was found that the value of the conversion factor varied little as between different crystals subjected to different surface treatments, even when the value of the integrated reflexion varied widely. This is shown by the figures in Table 2 in which the values of ρ measured on the ionization spectrometer for three different specimens are compared with those deduced from the photographic records using the mean value of the conversion factor derived from these same three crystals. The agreement will be seen to lie well within the limits of experimental error.

Table 2. *Comparison measurements of integrated reflexions of* Cu $K\alpha$ *radiation from calcite surfaces parallel to the reflecting planes* $20\bar{2}2$

Surface treatment	ρ in microradians	
	Photographic	Ionization spectrometer
Natural cleavage (history uncertain)	104	104
Ground on coarse carborundum ('220 grit')	56·7	58·5
Ground on coarse carborundum ('200 grit') and polished	96·5	94·4

Table 3 records values of the integrated reflexion observed from a number of crystals of calcite subjected to different surface treatments. Each section of the table refers to a separate specimen subjected successively to the treatments indicated. The reflexions were all recorded photographically and transformed into values of the integrated reflexion by the use of the above-mentioned conversion factor.

Table 3. *Integrated reflexions of* Cu $K\alpha$ *radiation from calcite surfaces parallel to the reflecting planes* $20\bar{2}2$ *after various surface treatments*

Etching was in every case for 7 sec. in 0·7 N-HCl (Manning, 1934).

'*Pencilling*' means rubbing the surface with the wooden end of an ordinary unsharpened pencil, applying considerable force.

Surface treatment	ρ in microradians
Untouched cleavage	76·5
Ground on coarse carborundum ('220 grit')	43·6
Polished	79·6
Etched	56·6
Untouched cleavage	75
Ground on finest sandpaper ('flour')	75
Ground on coarser sandpaper (F 2)	72
Ground on coarser sandpaper (S 2)	50
Ground on F 2 sandpaper again	67·5
Ground on 'flour' sandpaper again, very lightly	126
Polished	84
Etched	74
Untouched cleavage	76·5
Dipped in liquid air	73
Etched	59
Untouched cleavage	71·5
Polished	72·5
Etched	71
Untouched cleavage	66·5
Ground on 'flour' sandpaper, very lightly	116·5
Ground on 'flour' sandpaper, with more force	85·6
Ground on 'flour' sandpaper with full force of arm	74
Untouched cleavage	76
Rubbed with finger	86
'Pencilled'	131
Etched	76·5
Untouched cleavage	73·2
'Pencilled'	136
Etched	69

Discussion. Several remarkable facts emerge from the data in Table 3.

(*a*) The $20\bar{2}2$ reflexion from calcite does not, as does the $10\bar{1}1$ from quartz (Sakisaka, 1927), increase with increasing coarseness of abrasive; indeed, it is not difficult with coarse carborundum to reduce the reflecting power considerably. It is possible to bring about a substantial increase in reflecting power by grinding only if the finest abrasive is most gently used.

(*b*) The effect of the 'pencilling' treatment is most striking, as is also the appreciable increase in reflecting power produced by rubbing the surface with the finger. It is evident that the 'pencilling' treatment is able to deform the natural cleavage state into a state of much higher reflecting power, while the use of coarse abrasives on the relatively soft material produces much disorder.

It is of interest to observe that the values of ρ for the $20\bar{2}2$ reflexions of calcite with Cu $K\alpha$ radiation, calculated from the 'perfect' and 'mosaic' crystal formulae

$$\rho_{\text{perfect}} = \frac{e^2}{mc^2}\,\frac{\lambda^2}{V}\,\frac{|F|}{\sin 2\theta}\,\frac{1+\cos 2\theta}{2},$$

and $$\rho_{\text{mosaic}} = \left(\frac{e^2}{mc^2}\right)^2 \frac{\lambda^3}{V^2}\,\frac{|F|^2}{\sin 2\theta}\,\frac{1+\cos^2 2\theta}{4\mu},$$

where the symbols have the usual meanings, are 43·5 and 206 microradians respectively. These values may be compared with those recorded in Table 3, but it is important to note that a crystal giving a value of ρ intermediate between these values cannot in fact be assumed to be in a condition intermediate between the 'perfect' and 'mosaic' states. The state to which the calcite crystal is reduced by coarse grinding is a case in point.

The concentrating monochromator in practice

It is clear that for the practical use of the concentrating monochromator ϕ should not exceed the value ϕ_b unless the crystal is used in the 'cut-off' form. Although our experiments have been made only with copper radiation it is thought to be justifiable to calculate values of ϕ_b for other wave-lengths on the assumption that equation (4) represents the state of affairs with sufficient accuracy.

From the maximum of equation (4), regarded as a function of ϕ, it is possible to derive an approximate expression for ϕ_b:

$$\phi_b \fallingdotseq \theta - \sqrt{(\mu t \sin 2\theta)}.$$

Introducing the known values of μ and θ at various wave-lengths and of t for the appropriate crystal, we derive for calcite and quartz the curves shown in Fig. 8, from which ϕ_b for any wave-length may be obtained.

For *calcite* it is recommended that the surface be ground to the appropriate angle on medium sandpaper, polished and finally 'pencilled'. It has been found, however, that crystals vary considerably in reflecting power, and it is advisable to treat several specimens and to select the best.

For *quartz* it is evident from Sakisaka (1927) that grinding on coarse carborundum, such as '220 grit', is the most suitable treatment.

If a crystal is prepared for use in the 'cut-off' form, care must be taken to ensure that ϕ is not less than θ. Unless this is the case, two separate reflected beams will be observed, emerging from the prepared and cleavage surfaces respectively; and these will be appreciably divergent owing to the greater effect of refraction on the beam leaving the prepared surface at a very small glancing angle.

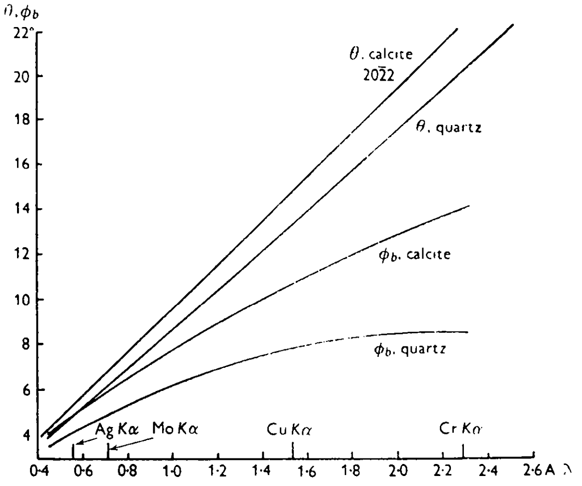

Fig. 8. Bragg angle and optimum grinding angle, ϕ_b, for $20\bar{2}2$ reflexions from calcite and $10\bar{1}1$ reflexions from quartz as a function of wave-length.

It should be noted that the increase in exposure time which results in practice from the use of a monochromatizing crystal such as those discussed here depends on the experimental conditions under which the monochromator is applied, as well as on the reflecting power of the crystal, and cannot, in general, be computed simply from the values of I/I_0 given. These values can, however, be used to compare the reflecting properties of a given crystal for various values of ϕ, or, in the circumstances discussed above, of two or more crystals. A discussion of the properties of monochromatizing crystals which make them applicable in particular cases has been given by Lipson, Nelson & Riley (1945).

The preparation of a surface inclined to the natural faces of a crystal can be conveniently achieved by the use of the grinding jig described by Thomas & Campbell Smith (1913–16).

Our thanks are due to Prof. Sir Lawrence Bragg and to Dr W. H. Taylor, in whose Laboratories the work was carried out, for much help and encouragement. We have enjoyed the collaboration of the Department of Mineralogy and Petrology in the provision and preparation of specimens.

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The Low-Temperature Form of $C_{18}H_{38}$

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The low-temperature form of $C_{18}H_{38}$, which is iso-structural with that of other even paraffins from C_{22} down to C_6, is shown to be triclinic, with one molecule in the unit cell, which has dimensions

$$a = 4{\cdot}28_5\text{ A.},\quad b = 4{\cdot}82_0\text{ A.},\quad c = 23{\cdot}07_0\text{ A.}$$
$$\alpha = 91^\circ\ 6',\quad \beta = 92^\circ\ 4',\quad \gamma = 107^\circ\ 18'.$$

Measurements were made of 118 spacings and 65 angles, by means of Laue, powder, rotation and Weissenberg photographs. The 'X-ray' density is 0·93 g.cm.$^{-3}$ at 21° C., as compared with the liquid density at the melting-point, 27° C., of 0·777 g.cm.$^{-3}$.

Introduction

It is known that $C_{18}H_{38}$, like a number of other hydrocarbons, can give two characteristic powder patterns. One is the 'normal' pattern, in which the chains are believed to be packed in a prismatic cell of rectangular cross-section, their lengths being perpendicular to the base of the cell. The long spacing is about 25·3 A. (Müller, 1930, 1932*a*). This form is observed at temperatures near to the melting-point, 27° C., and also at room temperatures if the octadecane contains more than about 2·2 % of the C_{16} or C_{20} paraffins (Ubbelohde, 1938). The long spacing in this form lies on a straight line (spacing versus number of carbon atoms) which extends from C_{11} upwards, including both odd- and even-numbered paraffins. There is, however, a second form of lower symmetry, having a long spacing of about 23 A., which is also typical of even paraffins from C_{22} (or possibly C_{24}) downwards to C_6, and which gives a characteristic pattern in which there are three strong side-spacing lines (at 4·56, 3·79 and 3·58 A. in $C_{20}H_{42}$ at room temperatures). It is the object of the present paper to describe this second modification, as found for pure octadecane at room temperatures. Single crystals were successfully grown from xylene. These were flakes, optically positive, with the acute bisectrix emerging at a small angle to the flake face normal.

Experimental

Laue photographs were first taken with the X-ray beam normal to the flake face; these photographs (which provide the most searching test of crystal perfection) showed that the flakes were somewhat distorted and possibly not single, but they also gave the directions of some important zone axes, about which rotation and Weissenberg photographs were subsequently taken. One very small and relatively undistorted crystal gave good photographs about axes which were chosen as the [100] and [010] zone axes, but it was twinned by reflexion on the (001) flake face. The crystals were proved to be triclinic, first of all from their optical properties, and then from photographs of a second crystal which was not twinned. This crystal, however, was bent, and although it gave Weissenberg photographs about the

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* Deceased. This work was begun by Dr Müller in 1940, and continued by K. Lonsdale during his absence through illness in the winter of 1940–1. It was written up after his death in 1947.

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