liquid crystalline (Bernal & Crowfoot, 1933; see also Chandrasekhar, 1966). Optical, X-ray and infrared studies (Krishnamurti, Krishnamurthy & Shashidhar, 1969) have established that a mixture of methyl stearate and methyl palmitate forms an *ordered* smectic phase over a composition range of 20–75% by weight of stearate. There is effective hexagonal packing in the smectic layers due to the rotation of the lath shaped molecules about their long axes (Bernal & Crowfoot, 1933; Herrmann, 1935).

Cholesteryl oleate is smectic at room temperature (Friedel, 1922). Fig. 3 shows the patterns from a homogeneous drop in which the long axes of the molecules are parallel to the direction of observation. A new feature seen here is the waviness of the fringes, which is due to the presence of hills and craters on the surface. Similar patterns were obtained with cholesteryl palmitate, which is also smectic.

Cholesteryl 2-propyn-1-yl carbonate is optically uniaxial negative at 75 °C and displays bright colours characteristic of the cholesteric mesophase. An open droplet of the liquid crystal invariably consisted of randomly oriented birefringent regions that could be seen in transmitted light between crossed polars. The surface of such a droplet gave smooth fringe contours resembling those from a liquid drop except that the fringes had a grainy appearance probably due to the slight variations of the reflecting power of the birefringent regions. When the droplet was squeezed and made to spread by pressing the cover slip, interesting surface features developed. These are illustrated in Fig. 4 for a region of the droplet that has flowed from the bottom to the top of the photograph. The area of contact between the cover slip and the liquid crystal is not shown. The broad fringes on the right hand top corner are from the glass surface of the microscope slide. The wavy pattern corresponds to the topography of the region of liquid crystal that has flowed upwards without coming into contact with the cover slip. The unevenness of the surface caused by flow was also visible in transmitted light. The wavy pattern disappeared when the substance was heated to the liquid phase.

Nematic liquid crystals gave fringe contours similar to those of the isotropic liquid.

We have carried out some preliminary experiments using multiple-beam interferometry. The upper surface of the microscope slide and the lower surface of the cover slip were semi-silvered. Fig. 5 gives the patterns with oriented droplets of cholesteric oleate in the smectic phase. Comparison with Fig. 3 shows the marked improvement in the sharpness of the fringe system. A number of hills are present on these droplets, but hardly any craters.

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The dependence of X-ray beam homogeneity on absorption by the target.

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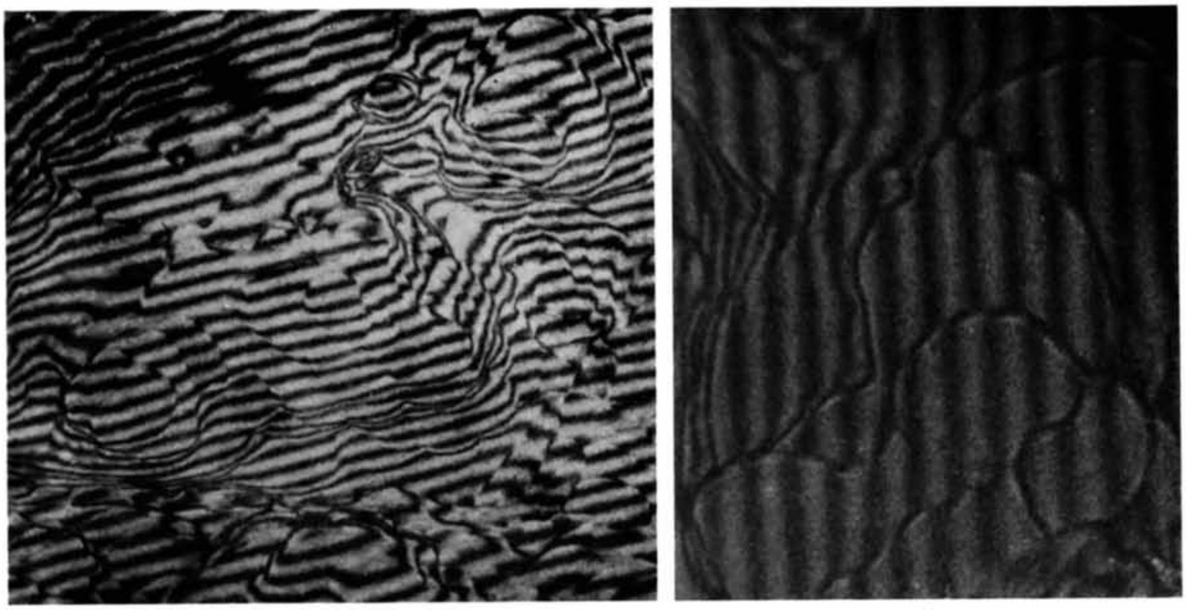
It is found that absorption of X-rays by the target material can result in beam inhomogeneities of more than 30% at low take-off angles.

It has often been implied or specifically stated (*e.g.* Furnas, 1957; Alexander & Smith, 1962; Burbank, 1964; Young, 1969) that if all parts of the crystal can 'see' all parts of the focal spot in an X-ray diffraction experiment, then the crystal is effectively bathed in a uniform flux of radiation. Although this may be generally true, the absorption of X-rays at low take-off angles by the target is rather high, and as the measurements of Cole, Chambers & Wood (1962) for example show, the rate of change of flux with take-off angle is considerable.

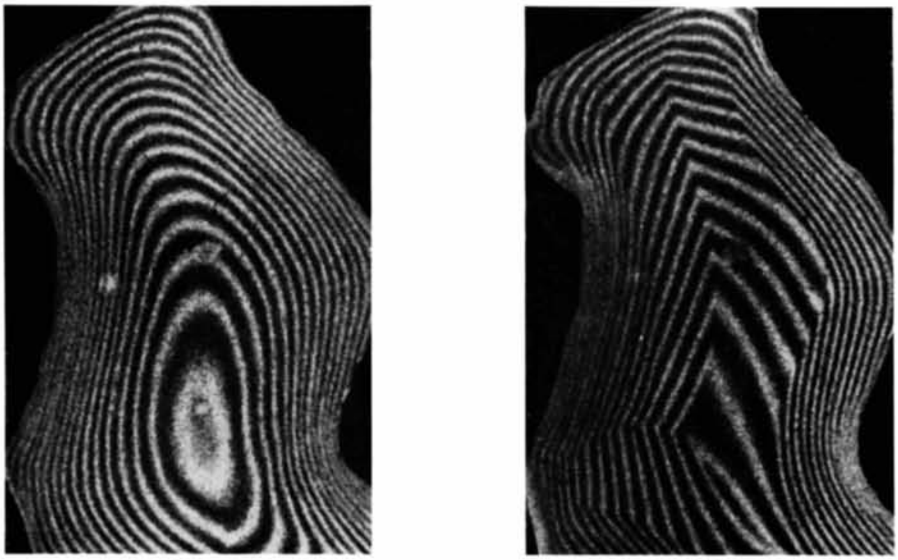
Assessment of the consequent change of flux across the X-ray beam in the region of the crystal was made with a 4-circle diffractometer which has a facility for easy change of tube orientation without disturbing the alignment of the system. A pinhole of diameter 0·0005 inch in lead sheet was mounted on a goniometer head at the centre of all four circles and the counter was set to monitor the resulting direct beam. Movement of the arcs adjustments had little effect on the counting rate, confirming that the aperture size was relatively insensitive to orientation, and a stepwise scan of the counter verified that the scintillation counter had constant sensitivity over the active area. For each of a range of take-off angles the pinhole was used to produce a photograph of the focal spot, and in each case it showed that from the crystal position there was an unimpeded view of all parts of the focus. The pinhole was then made to traverse the beam in the plane of the take-off angle by using the traverse adjustment slide and then in the plane perpendicular to it by rotating the χ-circle through 90·0°. The resulting profiles are shown in Fig. 1.

It is evident that appreciable inhomogeneity exists in the take-off plane for angles less than about 5°, whereas there is none in the plane perpendicular to this, as expected. Such flux variations can result in quite significant systematic errors in accurate intensity measurements especially if the crystal is irregularly shaped or inadequately centred.



(*a*) (*b*)

Fig. 1. (*a*) Fringe pattern from an extended area of solution of potassium oleate in aqueous methyl alcohol in the smectic phase (× 200). (*b*) A stepped drop (goutte à gradins) of the same substance (× 400).



(*a*) (*b*)

Fig. 2. A large drop of the mixture of methyl stearate and methyl palmitate (× 300); (*a*) liquid phase, (*b*) mesomorphic phase (goutte à facettes).

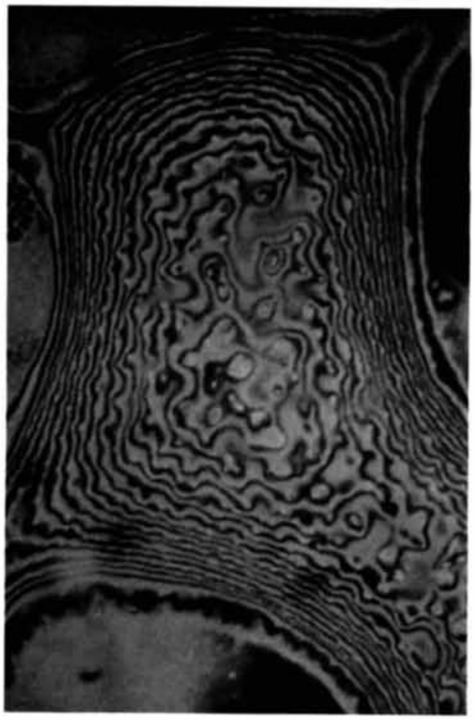


Fig. 3. Cholesteryl oleate in the smectic phase with hills and craters on the surface (× 200).

Fig. 4. Unevenness of surface caused by flow in the cholesteric phase of cholesteryl 2-propyn-1-yl carbonate (× 150).

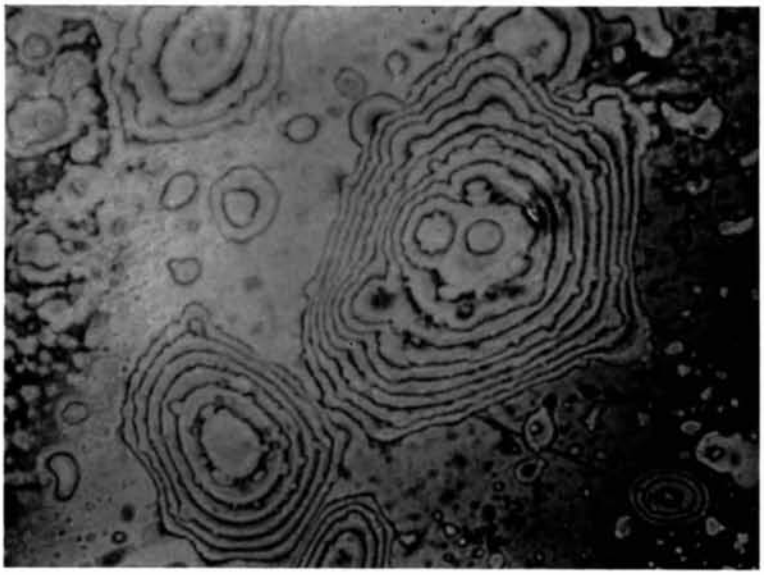


Fig. 5 Cholesteryl oleate in the smectic phase (multiple-beam interferogram, × 200).

The results of Fig. 1 are compared with the work of Cole, Chambers & Wood in Fig. 2. The latter measurements were also made with a Cu target but a tube voltage of 12 kV was used as opposed to 30 kV in the present work. The relation between the apparent power of the source P, the take-off angle α, and the absorption coefficients μ_λ and μ_e of the X-rays and electrons respectively,

$$P \simeq \sin\alpha/(\sin\alpha + \mu_\lambda/\mu_e)\,, \tag{1}$$

which was used in the previous work, holds well for the

Table 1. *The observed and predicted change of flux across an X-ray beam subtending* 16 *minutes of arc at the focus*

Take-off angle (degrees)	Observed at 30 kV (%)	Predicted at 30 kV (%)	Predicted at 12 kV (%)
0·7	34·8	31·4	28·4
1·7	9·0	9·9	8·6
2·7	4·0	5·2	4·2
3·7	2·9	2·9	2·5
4·7	1·0	2·1	1·7
5·7	1·1	1·5	1·2
6·7	0·4	1·1	0·9

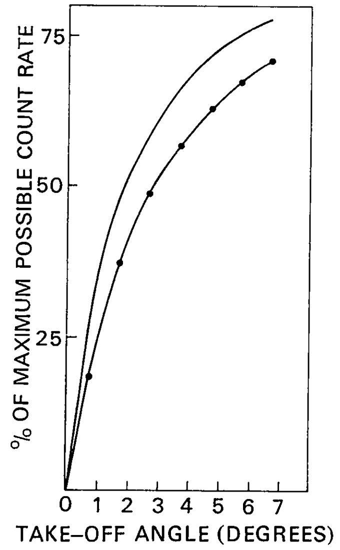


Fig. 2. X-ray flux against take-off angle; continuous curves are Cole, Chambers & Wood's equation.

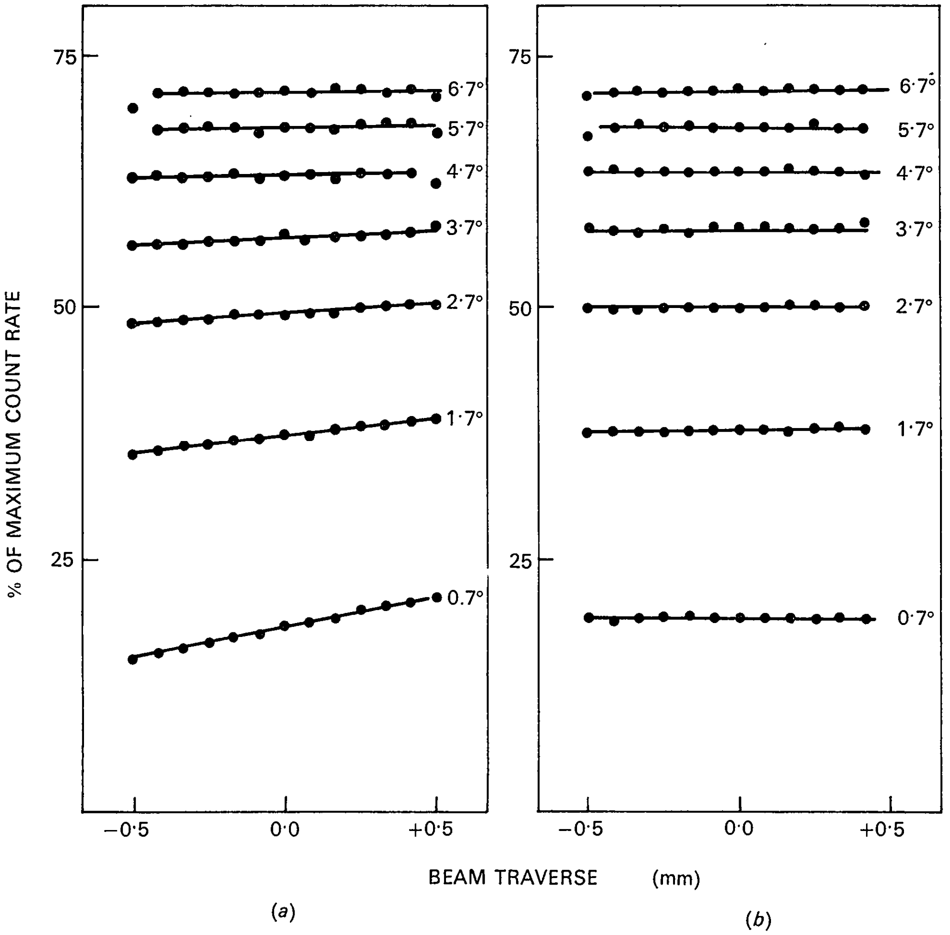


Fig. 1. Horizontal and vertical beam profiles for a range of take-off angles.

present measurements. The ratio μ_λ/μ_e however, was found to rise from 0·033 to 0·048 with the increased accelerating potential and so the beam homogeneity appears to be substantially independent of tube voltage.

In Table 1 the observed flux changes at 30 kV are compared with those predicted on the basis of (1) for 30 kV and 12 kV for a beam of 1 mm diameter that subtends 16 minutes of arc (0·26°) at the tube focus. The results show that for intensity measurements of 1% accuracy the take-off angle should never be less than about 5° for Cu $K\alpha$ radiation.

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Low temperature X-ray investigation of NH_4Br.*

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The lattice parameters of NH_4Br have been measured as a function of temperature from 5 to 150°K, a range which includes the region of the transition between cubic and tetragonal ordered phases. The low-temperature CsCl-type phase exhibits normal thermal expansion up to ~108°K on warming, while the tetragonal diffraction pattern persists down to ~80°K on cooling. The present data are combined with previous measurements between 150 and 300°K to yield an overall picture of the variations associated with changes in ordering.

Four different structural modifications of NH_4Br are known to exist at low pressures, and a fifth modification of unknown structure has recently been observed above 2000 atm (Garland & Young, 1968). At one atmosphere and high temperatures NH_4Br has a disordered NaCl-type structure, but it undergoes a first-order transition at 410°K to a disordered CsCl-type structure. [Pöyhönen, Mansikka & Heiskanen (1964) have measured the lattice parameters between 297 and 467°K.] This modification undergoes a cooperative λ transition at 234·5°K to an ordered tetragonal structure which is closely related to the CsCl structure (Levy & Peterson, 1953). At lower temperatures there is a sluggish first-order transition to an ordered CsCl-type structure. Associated with this latter phase change is a marked hysteresis: the transition occurs at ~78°K on cooling and at ~108°K on warming (Stephenson & Adams, 1952; Sorai, Suga & Seki, 1965). The order-disorder referred to above involves the relative orientations of adjacent NH_4^+ ions. Below 234·5°K there is a long-range order in these orientations although this ordering will not be the same in the tetragonal and CsCl-type structure.

Hovi, Heiskanen & Varteva (1965) have carried out a detailed X-ray determination of the lattice parameters of NH_4Br as a function of temperature between 150 and 300°K. The object of the present investigation was to confirm the cubic structure of the low-temperature phase, to determine the lattice parameter as a function of temperature, and to investigate by means of X-ray diffraction the region of the order–order transition at ~100°K. To achieve these goals, we have obtained data between 5 and 150°K.

Except for a measurement at 5°K and a reference measurement at 295°K, all data were obtained on a General Electric Model XRD-5 diffractometer using a 'Cryo-tip' temperature regulator with X-ray vacuum shroud. The specimen was a layer of finely ground NH_4Br (Mallinckrodt Analytical Reagent) with a small amount of collodion used as binder and adhesive. Temperatures were measured with a chromel–constantan thermocouple and are accurate to within ±1°K. A Philips diffractometer with liquid helium sample holder was used to obtain data at ~5°K.

Silicon powder (40% by weight) was added to the NH_4Br as an internal standard except for some of the measurements in the ordered cubic phase. A silicon lattice parameter of 5·43097 Å was used at 25°C (Straumanis & Aka, 1952), and values at low temperatures were obtained from the thermal expansion data of Erfling (1942). The instrumental corrections indicated by the Si lines were always quite small: $\Delta(2\theta) \simeq 0{\cdot}17°$ for lines with 2θ values between 70 and 125°. Stronger lines obtained with pure NH_4Br permitted a better determination of the small shifts which occur with temperature below 100°K, and such measurements were also made. Ten high-angle NH_4Br lines – 300+221, 310, 311, 222, 321, 400, 410+322, 411+330, 420, 421 – were used to determine the lattice parameters. The uncertainty in the absolute values of the cubic lattice parameters is ±0·001 Å, and relative values are quite a bit more precise. The errors associated with the a_3 values in the tetragonal phase are greater due to the small separation between the *hhl* and the *hll* components of a line and the presence of Cu $K\alpha_1\alpha_2$ splitting.

Fig. 1 shows the variation in the NH_4Br lattice parameters between 0° and 300°K after a correction has been applied to the data of Hovi *et al.* (1965). At 295°K, we obtained 4·0588±0·0006 Å for the lattice parameter of NH_4Br, whereas Hovi *et al.* give a value of 4·0574±0·0005 Å. Since our value is in good agreement with other recent room-temperature values (see Fig. 1), it is probable that all the

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