

# An experimental study of diffuse X-ray reflexion by single crystals

By K. LONSDALE AND H. SMITH

*Royal Institution*

(Received 4 March 1941)

[Plates 1-28]

A historical introduction outlines the development of experimental and theoretical interest in the diffuse diffraction of X-rays by single crystals. The present experimental study, illustrated by numerous photographs, has consisted in taking Laue, oscillation and rotation photographs, in many different orientations, of inorganic and organic crystals belonging to various systems, using Cu, Mo and Ag radiations, unfiltered, filtered or monochromatized. Rules are laid down for the indexing of diffuse spots and for the determination of the conditions under which such spots appear. Attention is drawn to the presence of non-radial streaks and to the difference in origin of these and of the more usual radial streaks. The relations of the intensity, shape, size, position and persistence of the diffuse spots to the nature, structure, perfection, orientation and temperature of the crystal examined, to the radiation used and to the conditions of photography, are considered in some detail. The use of diffuse spot patterns as a subsidiary method of crystal structure determination is emphasized. It is pointed out that in reciprocal space each reflecting lattice point is surrounded by a region of diffuse scattering, whose physical significance is open to various theoretical interpretations. These diffusely reflecting regions are not, in general, spherical, but are extended along reciprocal lattice planes and axes.

## INTRODUCTION

Well-exposed X-ray photographs of stationary single crystals frequently show, in addition to the usual clearly defined Laue spots,\* a fainter background pattern of diffuse streaks and spots. When the applied voltage is below that required to excite the X-radiation characteristic of the anti-cathode used, the incident X-ray beam is composed either wholly or in considerable part of continuous radiation. The diffuse pattern then consists mainly of radial streaks running through the strongest Laue spots. Such an effect was first observed by Friedrich (1913). If, however, the incident beam contains a high proportion of characteristic X-radiation, the diffuse

\* In the following discussion the term 'Laue' reflexion will be reserved for the selective reflexion of X-rays of a wave-length not characteristic of the anti-cathode used, the 'Bragg' reflexion being the selective reflexion of characteristic X-rays.



## *Study of diffuse X-ray reflexion by single crystals* 9

pattern may show non-radial streaks and spots which do not apparently correspond in position to the Bragg reflexions from any planes of the stationary crystal. Such diffuse spots have frequently been observed, but it is only in the last two or three years that any serious attempt has been made to study them.

Using tungsten radiation, Wadlund (1938) observed a diffuse background pattern of streaks and spots on Laue photographs of rocksalt and sylvine, but failed to obtain it with mica, fluorite, gypsum or calcite. Preston (1939) made a more precise investigation showing that (1) the diffuse spot pattern persisted when monochromatized (Ag) radiation was used, although the Laue spots of course disappeared and (2) that the intensity of the diffuse spots was greatly enhanced by raising the temperature of the crystals used (Al, NaCl, MgO, each in several different settings). Preston could find no diffuse spots on Laue photographs of diamond, using Ag radiation, though the background scattering gave the impression of not being of uniform intensity, and at 500° C four faint diffuse streaks were visible on a photograph taken with the incident beam parallel to [110].

Independently, and in advance of Preston's investigation, a comprehensive and fundamental experimental study of the diffusion of X-rays by crystals, using ionization spectrometer methods, was carried out by Jean Laval (1938, 1939*a, b*; Mauguin and Laval 1939). Laval's memoir appears to have been almost completely overlooked, so a short résumé may not be out of place. As he pointed out, the Debye theory (1914) indicates that the diffusing power of a crystal should be independent of its orientation. Brillouin (1922), taking into account the longitudinal vibrations due to thermal agitation in a crystal, came to a somewhat different conclusion. He summarized the total X-ray scattering by a single crystal as follows:

- (1) Bragg spots.
- (2) Intense scattering around the central spot.
- (3) Diffuse scattering around each Bragg spot.
- (4) Light general scattering in every direction.

Faxén (1923) and, more completely, Waller (1923, 1925) worked out a theory of diffuse scattering which took into account not only longitudinal, but transverse, thermal vibrations and in which the diffuse scattering in any direction depended not only upon the orientation of the crystal but upon its various elastic constants. Faxén referred to the streaks observed by Friedrich and suggested that an attempt should be made to correlate these streaks with the temperature of the crystal.

A number of experimenters attempted to test the validity of these



various theories and concluded that Debye's theory was correct (Coven 1932; Jauncey and Pennell 1933; Harvey, Williams and Jauncey 1934; and other papers). Laval (1939*b*), in a critical examination of their methods, showed that their experimental conditions were too restricted for a proper conclusion to be reached, and undertook a more complete experimental research using monochromatized Cu and Mo radiations, with single crystals of sylvine, rocksalt, aluminium, calcite and diamond, and a powdered specimen of silver. He varied the orientation of the single crystals and measured their absolute 'diffusing power' in various directions, over a wide range, and also measured the variation of 'diffusing power' with change of temperature from 289° to 665° A. [The 'diffusing power' of a crystal element, mass  $dm$ , is defined by  $P = \frac{1}{\bar{\omega}} \frac{di}{I dm d\omega}$ , where  $\bar{\omega}$  is the diffusing power of a free electron placed in the same beam,  $I$  the intensity of the incident beam,  $di$  the intensity of radiation diffused in a solid angle  $d\omega$  in the given direction.] Laval found that, as Brillouin, Faxén and Waller had predicted, each Bragg reflexion is surrounded by a region of strong diffusion, within which the intensity decreases rapidly as the direction of diffusion departs from that of selective reflexion. There is also a feeble general scattering in every direction. He measured the shape and extent of the regions of strong diffusion and the variations of intensity within those regions, for various Bragg reflexions, expressing his results in terms of the reciprocal lattice. He found that, of all the diffuse regions studied, that surrounding the diamond (111) reflexion was the smallest in extent, while the difference in intensity between the strong diffusion accompanying the Bragg reflexion and the weak background diffusion was also less for diamond than for any of the other crystals studied, considering only planes of equal structure factor. It was, of course, impossible for him to study the diffuse scattering within those regions where selective reflexion occurred, but subject to this limitation he came to the conclusion that the maxima of diffuse reflexion decreased more slowly with increasing order of reflexion than those of the corresponding Bragg reflexions. On the other hand, he found no appreciable difference between the strong diffusion of Mo  $K\alpha$  and of Cu  $K\alpha$  radiations. Temperature experiments were carried out using Mo  $K\alpha$  radiation and a single crystal of sylvine; the maximum diffusing power and the extent of the region of strong diffusion were both found to increase markedly with rise of temperature, more especially for low order reflexions, while the weak general diffusion also increased in absolute intensity as the temperature rose. Laval finally concludes: 'La diffusion forte a son origine surtout dans l'agitation ther-



mique des atomes. Ses domaines s'accroissent lorsque la température s'élève; ils sont beaucoup plus étendus pour la sylvine où l'agitation thermique est forte, que pour la diamant où l'agitation thermique est faible. On peut espérer que la topographie des domaines de la diffusion forte apportera des renseignements précis sur la distribution de l'énergie entre les diverses ondes élastiques qui constituent l'agitation thermique.'

It has been pointed out by Zachariasen (1940), in the course of a new derivation of the intensity expression for the coherent scattering of X-rays by a small crystal, that although the diffuse scattering maxima will coincide with the Bragg maxima when monochromatic radiation is used, there are conditions in which the maxima will be separated. These conditions, which are frequently fulfilled in the taking of a normal Laue photograph, are that the incident beam used should contain both characteristic and continuous or 'white' radiation, and that the stationary single crystal should only be near to, and not actually in, the Bragg reflecting position appropriate to the characteristic wave-length and to the plane under consideration. A preliminary experimental study of such 'separated maxima' has been carried out by Siegel and Zachariasen (1940) who, using a rock-salt crystal and  $\text{Cu } K\alpha$  radiation (filtered but not monochromatized), have studied the peak intensities and half-widths of the diffuse maxima for various degrees of separation, by means of photometered recordings of photographic plates.

More recently, Sir C. V. Raman and his collaborators have published Laue photographs of diamond,  $\text{NaNO}_3$ ,  $\text{NaCl}$  and  $\text{CaCO}_3$  showing a number of these diffuse maxima, together with tables showing the relation between angles of incidence and of scattering for selected maxima (Raman and Nilakantan 1940 *a, b, c*; Raman and Nath 1940 *a, b*). Raman and Nilakantan consider that the 'modified' (diffuse) reflexions are due to pulsations in the crystal lattice having the characteristic infra-red frequencies, which are excited by the incident X-ray beam and which in turn cause periodic variations in the structure-amplitude of the crystal spacings and therefore result in reflexions of the X-rays with change of frequency. They conclude therefore that 'the modified reflection is a quantum effect and is not primarily a thermal phenomenon, though for low lattice frequencies or at high temperatures it may be thermally influenced'. They included among their experiments a temperature study of  $\text{NaNO}_3$ , the X-ray beam being perpendicular to one cleavage face and temperature varied between  $25^\circ$  and  $275^\circ$  C. They found, as Preston had already observed for  $\text{Al}$ ,  $\text{NaCl}$  and  $\text{MgO}$ , that the intensity of the diffuse spots is very greatly increased, while the Laue spots are much fainter in the high temperature photographs than in



those taken at room temperatures. Kracek, Posnjak and Hendricks (1931) had found that, above 180° C, the rise of temperature affects very unequally the intensity of the Bragg (powder) reflexions due to different planes, some being practically wiped out at 250° C. Raman and Nilakantan observed that, for just those planes, a room temperature photograph showed intense Laue spots unaccompanied by any diffuse satellites, while a photograph taken at 275° C showed a great diminution in intensity of the Laue spots (which in fact had practically disappeared) and the appearance of strong diffuse spots in their immediate neighbourhood.

Raman and Nilakantan also pointed out the resemblance between the diffuse pattern observed for an oblique setting of the NaCl crystal and the layer-line diagram of an oscillating or rotating crystal.

During the course of an investigation of the age-hardening of alloys, Guinier (1938) and Preston (1938) independently found well-marked diffuse streaks and spots on Laue photographs, which could clearly be interpreted as 'cross-grating' effects due to the segregation of one metal into thin sheets within the alloy. [See also Calvet, Jacquet and Guinier 1938, 1939; Preston 1940; Barrett and Geisler 1940; Ewald 1940.] Sir William Bragg has suggested that the diffuse spot patterns of sylvine and other crystals may be due to simple three-dimensional diffraction by very small groups of atoms, orientated alike but scattering independently (Bragg 1940); such X-ray diffraction would not, of course, be subject to the usual Bragg condition  $n\lambda = 2d \sin \theta$ .

It is not proposed in the following paper to make any comparison between the various theories put forward, but rather to supply or to emphasize those detailed experimental facts without which no theory can be properly considered.

#### AIMS OF PRESENT RESEARCH

During the course of X-ray investigations covering the past eighteen years, many isolated instances of weak diffuse spots have been observed on Laue photographs taken by various workers (Knaggs, Lonsdale, Müller and Ubbelohde 1940) in this laboratory; but they were usually regarded as evidence of crystal imperfection, since they could not be given any direct interpretation from a structural point of view. More recently, however, Laue photographs of benzil were found to possess such a beautiful and intricate background pattern (plate 3*a*), even with a relatively moderate exposure, that a more extensive investigation was undertaken in order to determine:



(1) Exactly what conditions are needed for the production of diffuse spots on Laue photographs; why, for instance, some substances show them while others do not; why some wave-lengths seem more favourable for their production than others; why they are more easily obtained in some crystal orientations than in others; whether they are in any way related to the imperfection or surface conditions of the crystals.

(2) Under what conditions the spots are accompanied by streaks, radial or non-radial.

(3) How the positions, size, shape and intensity of the diffuse spots are related to the structure and orientation of the crystal for any particular wave-length of incident X-rays.

(4) Whether the study of diffuse patterns can be used as a subsidiary method of crystal structure determination, and what is their relation to the various physical properties of the crystal, including its temperature.

#### EXPERIMENTAL DETAILS

The following experiments, of which a preliminary account has already been published (Lonsdale, Knaggs and Smith 1940), were mainly carried out on the medium (5 kW.) X-ray tube (Clay 1934) at the Davy-Faraday laboratory, using Cu, Ag and Mo anticathodes; the tube was operated at 34 kV (for the copper anticathode) with an output of 140 mA, and exposures varied from 0.5 to 5 min. for oscillation photographs, from 2 to 15 min. for rotation photographs, from 5 to 30 min. for Laue photographs. Ilfex double-coated blue base X-ray film was used throughout, and given 5 min. development at 18° C. Room temperature varied from 20° to 30° C. A few photographs were also taken on the 50 kW X-ray tube (Muller and Clay 1939) with copper anticathode, and some on a small experimental 0.5 kW tube with Mo anticathode. No methods of intensification were used.

The crystals chosen for investigation were all small single specimens, rather larger than would normally be used for structure determination. It was found that crystals obtained by cleavage were sometimes distorted and gave misshapen Laue spots; every effort was therefore made to grow or to choose crystals of a suitable size, but a certain amount of distortion due to cleavage, bending or fracture could not always be avoided. Except for the low temperature experiments, the crystals were mounted on fine glass fibres on arcs, and as far as possible were so placed that the incident X-rays did not strike either adhesive or glass fibre; this meant, of course, that the crystal could not, in general, be wholly bathed in the incident



beam, which was cylindrical and slightly divergent. The arcs carrying the crystal were used with a Müller spectrometer, the film being contained in a plate-holder placed, usually, at right angles to the incident X-ray beam (though a few photographs were taken with the plate-holder parallel to a main crystal face, and not perpendicular to the beam). The crystal to film distance was varied from 3 to 8 cm., but was usually 3.5 or 4 cm., as experiment showed that for the substances examined, these were the distances at which most diffuse spots were recorded on the films. No attempt was made to calibrate the spectrometer and to measure these distances exactly, because the crystals used were all substances whose unit cell dimensions were well known and for purposes of accurate measurement it would therefore be preferable in any particular case to obtain the crystal to film distance from the evidence of the Laue spots themselves.

#### COMPARISON OF LAUE AND OSCILLATION PHOTOGRAPHS

It had been noticed that, using a copper anticathode, diffuse spot patterns were more readily obtained with organic than with inorganic compounds. A quick survey was made of those organic crystals whose structures had either been determined or were undergoing investigation in the laboratory, and detailed preliminary studies were made of  $\alpha$ -resorcinol, an orthorhombic crystal whose structure has been determined by Robertson (1936), of benzil, a hexagonal crystal studied by Knaggs and Lonsdale (1939), and of sorbic acid, a monoclinic crystal whose structure has been investigated by Lonsdale, Robertson and Woodward (1941).

##### *$\alpha$ -Resorcinol. ortho-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>*

The crystals, which were selected from among those used by Robertson, grow in the form of stout needles parallel to the *c* crystallographic axis. The structure is fairly dense, since the hydrogen bonds draw the molecules closer together than the normal van der Waals distance, and it is relatively isotropic. There is no definite cleavage and the crystals are not easily distorted; they give excellent Laue photographs in any orientation. The crystal was first set with the needle axis vertical and the X-ray beam (unfiltered Cu radiation) parallel to the (100) plane. Laue photographs were taken in this position and at 10° intervals of rotation about the [001] axis, until the incident beam was parallel to the (010) plane. Over a limited range photographs were also taken at 1° intervals. Plates 1*a* and 2*b* show two typical photographs. The most noticeable features of the diffuse scattering are the dense halo surrounding the central spot, to which further

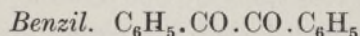


reference will be made later, and the well-marked 'layer lines' of diffuse spots. So striking was the arrangement of the diffuse spots in layer lines similar to those occurring on oscillation photographs that it seemed natural to take and compare an oscillation photograph having the 'Laue' position as the centre of the oscillation. It was found that, in fact, a short-exposure oscillation photograph (plate 1*b*) taken with the crystal oscillating through  $7\frac{1}{2}^\circ$  on each side of the 'Laue' position, gave Bragg spots many of which were practically coincident in position with many of the diffuse spots observed in the corresponding Laue photograph (plate 1*a*). A third photograph, in which the oscillation photograph was superimposed on the Laue photograph (plate 2*a*), shows how closely the positions of Bragg and diffuse spots agree.

This indicates that the diffuse spots may be considered as due to the reflexion of the incident beam by 'planes' which are within a few degrees of the reflecting positions characteristic of ordinary crystal planes and whose spacings are equal, or nearly equal, to those of the normal crystal planes.

Laue photographs are particularly sensitive to mis-setting, and change rapidly in appearance for slight changes of crystal orientation, but the diffuse spot pattern changes much more slowly in successive photographs at slightly different angles. This is easily comprehensible when the similarity of the diffuse spot pattern to the oscillation pattern is taken into account, since the  $15^\circ$  oscillation photograph taken, for instance, with the incident beam at  $20^\circ$  to  $[010]$ , will differ very little from that taken, say, at  $17^\circ$  or  $23^\circ$  to  $[010]$ .

A further point of resemblance is that the shape of the diffuse spots is, in general, similar to that of the oscillation spots and quite unlike that of the Laue spots.



Benzil forms good undistorted crystals in the form of hexagonal prisms bounded by  $\{10\bar{1}0\}$  planes, which give excellent Laue photographs with Cu or Mo radiation. The structure of benzil has not been fully determined, but it is known that the crystals are built up of skew molecules grouped round a hexagonal alternating axis in such a way that the benzene rings are more nearly parallel than perpendicular to the axis.

The hexagonal pattern obtained when a well-exposed Laue photograph is taken with the incident Cu radiation parallel to the  $[0001]$  axis (plate 3*a*) is strongly reminiscent of a benzene ring, and suggests that there may be some connexion between these diffuse patterns and those observed by



Charlesby, Finch and Williams (1939) on electron diffraction photographs of aromatic substances. An analogy would only be possible, however, if the benzene rings of the benzil molecule were normal or nearly normal to the [0001] axis, which they certainly are not. [A better compound on which to compare X-ray and electron diffraction diffuse patterns would have been anthracene, but the Laue photographs of anthracene all revealed so much distortion of the crystals that this compound was felt to be unsuitable for present study.] Photographs taken in directions more nearly normal to the benzene rings (plates 9 and 10 *a* and *b*) showed no trace of trigonal or hexagonal symmetry.

A Laue photograph taken with the X-ray beam at about  $7^\circ$  to the [0001] axis, and the [11 $\bar{2}$ 0] axis only approximately vertical (plate 3*b*), had lost all hexagonal symmetry as far as the Laue spots were concerned. The diffuse pattern, however, still showed approximate hexagonal alternating symmetry. A photograph taken with the crystal oscillating through  $7\frac{1}{2}^\circ$  on each side of this Laue position (plate 4*a*) showed Bragg spots corresponding in position with many of the diffuse spots of the Laue photograph. This oscillation photograph had only a one-minute exposure to Cu radiation filtered through 0.0008 in. Ni foil; an otherwise identical photograph given ten times this exposure (plate 4*b*) shows a strong diffuse background similar to that found on the Laue photograph but accompanied by much stronger radial streaks.

It is clear, from Laval's experiments and from the present study, that every type of X-ray photograph, Laue, oscillation, rotation, powder, etc., may if *sufficiently exposed* show a diffuse background picture, characteristic of the crystal in its particular setting. If Bragg reflexions are possible, the diffuse scattering will occur as a background to the Bragg reflexions (whether spots as in rotation photographs, lines or rings as in powder photographs). If Bragg reflexions are not possible, the diffuse background spots will still occur provided that the planes giving the corresponding Bragg reflexions are only a few degrees mis-set. In Laue photographs the *indices* of the plane corresponding to any particular diffuse spot can be determined, with reasonable certainty, by treating the diffuse spot pattern as though it were an oscillation photograph covering some  $10^\circ$  or  $15^\circ$  on each side of the stationary position of the crystal (the oscillations must, of course, be considered as taking place in every direction, and not only about a vertical axis); the *true position* of the plane having those indices can then be determined by reference to its Laue reflexion.

In this way the Laue photograph of benzil shown in plate 3*a* has been interpreted, and the indices of all spots, both Laue and diffuse, are given







vector, but this does not always seem to be true, and exceptions will be indicated later.

*Sorbic acid.*  $\text{CH}_3.\text{CH}:\text{CH}.\text{CH}:\text{CH}.\text{COOH}$

Sorbic acid forms monoclinic crystals in the form of prisms elongated on the  $b$  axis. The structure will be described later in some detail. Laue photographs have been taken with filtered Cu radiation at  $10^\circ$  intervals with the  $[010]$  axis vertical and the grouping of the diffuse spots into layer lines is most striking (plates 5*a*, 11, 12, 23*a*). A  $[010]$  rotation photograph is shown for comparison (plate 5*b*). In this case the vertical crystallographic axis is short (4.03 Å) and there is well-marked separation of the layer lines. Photographs taken with the long  $c$  axis (15.83 Å) vertical show, on a suitably orientated Laue photograph, well-marked *rows* of diffuse spots corresponding to outstanding reflexions in the  $[001]$  rotation photograph, the layer lines being in this case closer together and therefore less obviously defined (plate 6*a* and *b*).

*Other compounds*

In order to make sure that the relation between the diffuse spot pattern and that of the corresponding oscillation diagram is a perfectly general one, applying to X-radiation of any wave-length and to crystals of any kind, organic or inorganic, photographs have been taken of

(1) Several other organic compounds, using Cu radiation, filtered and unfiltered.

(2) Benzil, using Mo radiation (by Dr I. E. Knaggs).

(3) Sylvine, KCl; complete sets of Laue and oscillation photographs with cube axis vertical, using Mo radiation (by Dr I. E. Knaggs).

(4) Sylvine; complete sets of Laue and rotation photographs with cube axis and  $[011]$  axis vertical, using Ag radiation.

(5) Rocksalt, NaCl; complete sets of Laue and rotation photographs with cube axis vertical, using Ag radiation.

(6)  $\text{NaNO}_3$ ,  $\text{CaCO}_3$ , quartz in various orientations, using Ag, Mo and Cu radiations.

(7) Diamond; Laue and rotation photographs in various orientations, using Cu and Mo radiations.

Further reference will be made later to many of these experiments, but the following deductions have been made from a preliminary survey of the results:

I. The relation between the diffuse spot pattern on a Laue photograph and the oscillation photograph taken with the Laue position as centre of



the oscillation is quite general; it applies both to organic and to inorganic compounds; to crystals of any system and to all the different kinds of X-radiation used (Cu, Mo, Ag;  $K\alpha$  and  $K\beta$ ).

II. The same conditions, to a certain extent, govern the appearance of a diffuse spot diagram as govern the appearance of the corresponding oscillation photograph. If the wave-length of the radiation used is such that very few spots would appear on an oscillation photograph, then a Laue photograph taken with the crystal stationary at the centre of the oscillation range would also show very few diffuse spots, though it might show radial streaks corresponding to the diffuse scattering of general radiation of other wave-lengths. Since Cu radiation is, in general, most suitable for the examination of organic crystals, together with a crystal to film distance of about 3.5–4 cm., Laue photographs of organic crystals will show most diffuse spots when taken with Cu radiation at that distance. The strongest Bragg reflexions from organic crystals are nearly always those of spacing greater than 2 Å, and with Cu radiation these are well placed on the film; the lower symmetry of the crystals also ensures that, whatever the crystal orientation, some planes will nearly always be near to a reflecting position. On the other hand, simple inorganic compounds such as KCl, NaCl,  $\text{NaNO}_3$ ,  $\text{CaCO}_3$ ,  $\text{SiO}_2$ , crystallizing in the cubic or hexagonal system, have relatively few planes which reflect Cu radiation with appreciable intensity within the range of a quarter-plate size film (3 cm. being the nearest possible distance of approach to a crystal set on arcs), and a shorter wave-length is much more suitable both for rotation or oscillation photographs and for the production of diffuse spot patterns.

This, perhaps, can best be illustrated by examples.

TABLE 1

crystal to film distance (cm.)	3	3.5	4	5	6
$\sin \theta$ (min.)	0.05	0.04	0.04	0.03	0.02
$\sin \theta$ (max.)	0.54	0.51	0.48	0.44	0.40

In table 1 are given the limiting observable values of  $\lambda/2d$  ( $\sin \theta$ , where  $2\theta$  is the angle of deflexion) for quarter-plate size films at various crystal to film distances. Table 2 shows the indices of the principal Bragg reflexions from NaCl, together with their intensities (Brill, Grimm, Hermann and Peters 1939) including all reflexions above 1 % of the maximum observed, and the observable values of  $\lambda/2d$  corresponding to Cr, Cu, Mo and Ag  $K\alpha$  radiations. Table 3 gives the corresponding data for  $\alpha$ -resorcinol, except



that in this case only ( $hkl$ ) reflexions are included, since otherwise the list would be much too long. Table 4 gives similar data for diamond.

TABLE 2. NaCl

$hkl$	intensity	$\sin \theta$			
		Cr	Cu	Mo	Ag
111	5.5	0.35	0.23	0.11	0.08
200	100	0.41	0.27	0.12	0.10
220	44	0.57	0.38	0.18	0.13
222	28	—	0.47	0.22	0.17
400	18	—	0.54	0.25	0.20
420	11	—	0.61	0.28	0.22
422	9	—	—	0.30	0.23
440	4.5	—	—	0.35	0.28
442	3.5	—	—	0.38	0.30
600	3.5	—	—	0.38	0.30
620	3	—	—	0.40	0.31
622	3	—	—	0.42	0.33
444	2	—	—	0.43	0.34
640	1.5	—	—	0.45	0.36
642	1.5	—	—	0.47	0.37
800	1	—	—	0.50	0.40

It will be seen that for NaCl, which is typical of many inorganic crystals, either Mo or Ag radiation gives values of  $\sin \theta$  which would be readily observable on a film set at 3–5 cm. from the crystal, although either Cu or, worse still, Cr radiation would give only a few spots towards the outside of the picture.

On the other hand, for  $\alpha$ -resorcinol Cu is the most suitable radiation with which to obtain an even distribution of spots. With either Mo or Ag radiation the strongest spots would be very close to the central spot and there would be no spots observable towards the outside of the film. The number of diffuse spots observable in the case of  $\alpha$ -resorcinol will also clearly be much larger than that from NaCl; in fact, all those reflexions whose indices are given in table 3 will occur only on the zero layer line in '[001] axis vertical' photographs.

Diamond is rather an interesting case; it is clear from table 4 that Mo or Ag radiation should give a great many more characteristic reflexions than Cu. In fact, Cu radiation will only give the  $\{111\}$  reflexions, as can readily be proved by rotation photographs. Yet all successful experiments so far reported for diamond have been made using Cu radiation, while previous attempts to obtain diffuse spots with Ag radiation have been unsuccessful. This is due to the fact that only symmetrical settings of



TABLE 3.  $\alpha$ -RESORCINOL: ( $hk0$ )

$hk0$	intensity	$\sin \theta$			
		Cr	Cu	Mo	Ag
110	1	0.16	0.11	0.05	0.04
200	7	0.21	0.14	0.07	0.05
020	1	0.24	0.16	0.07	0.06
210	100	0.24	0.16	0.07	0.06
120	52	0.26	0.17	0.08	0.06
220	79	0.32	0.22	0.10	0.08
130	2	0.38	0.25	0.12	0.09
320	3	0.40	0.27	0.12	0.10
230	1.5	0.42	0.28	0.13	0.10
400	5	0.43	0.29	0.13	0.10
410	8	0.45	0.30	0.14	0.11
040	5	0.48	0.32	0.15	0.12
330	12	0.48	0.32	0.15	0.12
140	1	0.49	0.33	0.15	0.12
420	7	0.50	0.33	0.15	0.12
240	2.5	0.52	0.35	0.16	0.13
510	2	—	0.37	0.17	0.13
430	1.5	—	0.38	0.18	0.14
440	3	—	0.43	0.20	0.16
600	2	—	0.44	0.20	0.16
610	8	—	0.44	0.21	0.16
620	1.5	—	0.46	0.21	0.17
060	1.5	—	0.48	0.22	0.17
540	1	—	0.49	0.23	0.18
160	1	—	0.49	0.23	0.18
710	3	—	0.52	0.24	0.19
640	1	—	—	0.25	0.20
170	2.5	—	—	0.26	0.20
800	1.5	—	—	0.27	0.21
470	1.5	—	—	0.29	0.23
660	3	—	—	0.30	0.24
580	1	—	—	0.34	0.27
390	1.5	—	—	0.35	0.27

TABLE 4. DIAMOND

$hkl$	intensity	$\sin \theta$			
		Cr	Cu	Mo	Ag
111	100	0.55	0.37	0.17	0.13
022	46	—	0.61	0.28	0.22
311	17	—	—	0.33	0.26
400	21.5	—	—	0.40	0.31
133	9.5	—	—	0.43	0.34
422	11	—	—	0.49	0.38
333	5.5	—	—	0.52	0.41
511	5.5	—	—	0.52	0.41
044	9	—	—	—	0.44



diamond have been investigated. It so happens that when the incident beam is normal to a (111) plane, three other {111} planes are nearly in a reflecting position for Cu radiation, and these give diffuse spots on a Laue photograph taken in that setting. Such a Laue photograph taken with Mo or Ag radiation would show no diffuse spots, only perhaps white radiation streaks through the {111} Laue spots. In order to obtain diffuse spots the crystal must be turned into those particular orientations in which the planes indicated in table 4 are either in or near the position of selective reflexion of Mo or Ag reflexion. This has been confirmed experimentally.

It seems almost certain that every crystal will give diffuse spots when both conditions are fulfilled, namely, that the radiation chosen gives values of  $\sin \theta$ , for Bragg reflexions of appreciable intensity, within the observable range on the film, and that the crystal setting should be such that planes giving those Bragg reflexions should be at or near to the correct angle of incidence for selective reflexion. In any particular case the best conditions can be determined either by trial, or for crystals of known structure, by calculation. It may safely be said that if, with a given radiation and crystal to film distance, a good rotation picture is obtained, then there will be crystal orientations which will give a good diffuse spot picture.

It should be added, however, that an exposure time sufficient to give a good Laue picture is not usually sufficient to show the diffuse spots as well; the exposures must be greatly increased for the production of good diffuse spot patterns. Only the fact that extremely powerful sources of X-radiation were being used accounts for the short exposure times given in this paper. In general, therefore, choice of radiation and crystal setting should be made first by calculation, if possible.

#### MONOCHROMATIC PHOTOGRAPHS

In the above discussion it has been tacitly assumed, in comparing diffuse with Bragg reflexions, that the diffuse spots are due to scattering of the *characteristic* radiation. This was, of course, proved both by Laval and by Preston, for the inorganic compounds and elements they investigated. It is also indicated, as Raman and Nilakantan have pointed out, by the fact that pairs of diffuse spots, obviously due to  $K\alpha$  and  $K\beta$  components, are frequently observed, the  $K\beta$  spots being removable by the use of a suitable filter. Our experiments with different radiations also show that the positions of the diffuse spots shift in accordance with what would be



expected for characteristic reflexion when the X-radiation used is changed from Cu to Mo or from Mo to Ag (plate 7*a* and *b*). The most satisfactory test, however, is provided by using monochromatized radiation; this has been carried out for benzil, sorbic acid and diamond using Cu  $K\alpha$  radiation, and for sylvine using Ag  $K\alpha$  radiation. A further advantage of using monochromatized radiation is that it has been possible to find out whether the diffuse streaks and the diffuse halo surrounding the central spot are due to white or to characteristic radiation.

In order to obtain a good Laue photograph continuous radiation covering as large as possible a range of wave-lengths is usually employed. [It was very noticeable, for instance, that the 50 kW tube, for which hexa-phase rectification was employed, gave far fewer Laue spots than the 5 kW tube, which had bi-phase rectification, since it followed that the latter was running at less than the critical voltage for characteristic emission for a considerable part of the exposure time, while the former maintained a constant applied voltage to within a few per cent.] When the incident beam contains a high proportion of characteristic radiation, it may happen that some crystal planes will be in a position to reflect it and these will then give exceptionally strong spots on a Laue photograph, but they will be relatively few. A Laue photograph taken with strictly monochromatized radiation will usually, therefore, show few or no spots due to selective reflexion. If there are any, they will be easily recognizable because of the sharpness of their definition.

The method of obtaining monochromatic Laue photographs was, first, to set the crystal in position using an unfiltered beam, and then to monochromatize the beam by reflexion from the cleavage plane of a large crystal of urea nitrate (Lonsdale 1941). Considerable difficulties were experienced owing to the fact that after monochromatization the direction of the incident beam relative to the crystal had frequently changed slightly, so that the crystal setting was no longer perfect. The presence of a few Laue spots on the photograph was therefore an advantage, as it enabled any such imperfection of setting to be detected at once. Fortunately, however, our previous experiments showed that the diffuse picture would not be affected by slight mis-setting, but it was naturally avoided as much as possible.

*Benzil.* Plate 8*a* shows the appearance of the Laue photograph of benzil taken with ordinary Cu radiation, when the incident beam is along the  $[0001]$  axis, and  $\{10\bar{1}0\}$  faces are vertical; the corresponding monochromatic (Cu  $K\alpha$ ) photograph, plate 8*b*, was given 2 hr. exposure as compared with 10 min. for the ordinary photograph. It shows a few sharp Laue spots,



not quite symmetrically placed. It also shows a beautifully symmetrical pattern of diffuse spots and streaks. The most remarkable features of this pattern are:

(1) That no *radial* streaks are present (except traces towards the outside of the film).

(2) That the diffuse spots are partly joined by *non-radial* streaks of considerable intensity which follow the direction of the main  $[11\bar{2}0]$  'layer lines'. Through the strongest spots there are traces of layer line streaks corresponding to the  $[40\bar{4}0]$  periodicity.

(3) The innermost of these streaks are very fine and at their points of intersection there are very small, but still diffuse, spots.

(4) No diffuse halo appears around the central spot, although the background intensity does not appear to be absolutely uniform.

The diffuse pattern is thus clearly proved to be due to characteristic radiation, as far as spots and non-radial streaks are concerned. The same diffuse pattern is of course visible in the background of plate 8a.

In plates 9a and b, 10a and b, are seen ordinary and monochromatic Laue photographs of benzil with the X-rays normal to the  $[0001]$  axis. It was thought possible that in these photographs traces of diffuse circles might occur, corresponding to the strong hyperbolic streaks on the photographs taken with the beam along  $[0001]$ , but nothing of the kind was found. The streaks are much more fragmentary than before and there are roughly triangular patches of diffuse scattering, some accompanied and others unaccompanied by clearly defined diffuse spots.

*Sorbic acid.* The photographs of sorbic acid (plate 11 a and b) also show incipient streaks. The diffuse spot corresponding to the strong  $(40\bar{2})$  Bragg reflexion, in particular, is accompanied by diagonal streaks giving it the appearance of a cross. The ordinary photograph shows an intense diffuse halo around the central spot, but in the monochromatic photograph this has almost completely disappeared.

*Diamond.* This disappearance of the diffuse halo is also characteristic of the monochromatic photographs of diamond which, in fact, are singularly blank, since they show nothing but the  $\{111\}$  diffuse spots and (in suitable orientations) their accompanying non-radial streamers. The statement of Raman and Nilakantan, that the most intense region of the halo owes its origin to the monochromatic  $K\alpha$  and  $K\beta$  radiations of the copper anticathode, is therefore not confirmed.

*Sylvine.* Monochromatic photographs of sylvine taken with  $\text{Ag } K\alpha$  radiation show that there are weak non-radial streaks connecting the diffuse spots. Similar streaks also occur on Preston's monochromatic



*Study of diffuse X-ray reflexion by single crystals* 25

photographs of aluminium, and on photographs of sylvine taken with ordinary radiation (plate 7*b*).

*Origin of radial streaks*

The disappearance of the majority of radial streaks from monochromatic photographs shows that they are almost always due to white radiation. There is no reason, of course, why some radial streaks due to characteristic radiation should not occur in special circumstances; indeed, traces of such streaks do occur towards the outside of the benzil [0001] monochromatic photograph (plate 8*b*), apparently emanating from alternate ( $3\bar{3}02$ ) diffuse spots (compare figure 1). In most of the monochromatic photographs, however, radial streaks are conspicuous only by their absence.

On ordinary Laue photographs of undistorted crystals, the radial streaks are due to *diffuse* reflexion of white radiation; on oscillation or rotation photographs (and on Laue photographs of distorted crystals) the radial streaks are due to *selective* reflexion of white radiation, with, of course, the appropriate diffuse background. They are only straight lines in the neighbourhood of the central spot; extended, they trace out the ' $\alpha$  constant curves' (Bernal 1926) often seen on rotation photographs taken with a beam containing a good deal of white radiation (plates 5*b*, 6*b* and 20*b*).

*Change of crystal to film distance*

It has been mentioned previously that photographs taken at a crystal to film distance of 3.5 or 4 cm. usually give the best diffuse pictures within a reasonable exposure time. In order to find out whether the sizes of the diffuse spots change with distance in the same proportion as those of the Laue spots, Laue photographs have been taken at different distances with the same setting of various crystals. Two of these are shown in plates 12*a* and *b*; the 6 cm. photograph was given four times the exposure of the 3 cm. photograph. It will be seen that, owing to the divergence of the incident beam, both Laue and diffuse spots have increased in size on the film taken at the greater distance. There is no measurable difference in the rate of increase with distance for the two types of spot. This result was common to all such photographs taken.

*Effect of condition of crystal surface*

In order to determine whether the condition of the crystal surface affected the diffuse pattern, successive Laue photographs were taken of a crystal of  $\alpha$ -resorcinol (water soluble), first dry and then sprayed gently



with water until at last it was almost completely dissolved. For some of the photographs the crystal surface was actually covered with a drop of water. No change in the diffuse pattern could be detected, it became neither weaker nor stronger, and the crystal continued to give an excellent Laue photograph even when it was practically eaten away.

Nor was there any noticeable change in the diffuse pattern when a freshly cleaved surface was used, although such cleaved specimens were frequently found to be rather distorted, giving bad Laue spots. Occasionally the diffuse spots from cleaved or fractured crystals were found to have an intense and rather sharply defined core, not usually at the centre of the spot, even when the Laue pattern appeared to be undistorted. This effect may be seen on plates 12*b* and 18*a*, and was observed by Wadlund (1938) on his photographs of NaCl and KCl. That this core is also due to characteristic radiation is proved by the fact that it persists when the incident beam is monochromatized.

#### INTENSITY OF THE DIFFUSE SPOTS

No attempt has been made at this stage to obtain a quantitative estimate of the diffuse spot intensities, particularly as these are known to be affected by several different factors. The two principal factors at room temperature are:

(1) That the intensity of a diffuse spot is related to the absolute intensity of the corresponding Bragg reflexion (in particular there are no diffuse spots corresponding to Bragg reflexions either far from the observable region of the sphere of reflexion, or 'forbidden' by the space-group).

(2) That it is dependent on the degree of misorientation involved, that is, on the angular separation between the diffuse spot and its corresponding Laue spot, or alternately, on the angle through which the crystal must be turned in order to obtain the selective Bragg reflexion corresponding to the diffuse spot in question (subsequently referred to as the 'angle of mis-setting').

Factor (1) may be observed in a number of different ways. For instance, plate 6*a* and *b* show that the diffuse spots correspond to the *strongest* of the reflexions seen on the rotation photograph. In Laue photographs showing diffuse spots corresponding to different orders of the same plane (plate 2*b*) the relative intensities of the diffuse spots approximate roughly to the known relative intensities of the Bragg reflexions, *as long as the diffuse spots compared are equidistant from the corresponding Laue reflexion*. Laval states that a comparison of five even orders of reflexion from the



sylvine cube face shows that whereas the Bragg reflecting power falls off in the ratio 100:20:7:3:1, the maxima of the diffuse scattering curves corresponding to a mis-setting of  $2^{\circ}5$  decrease more slowly, in the ratio 42:21:14:9:6. Any rigorous comparison, however, must involve integrated intensity measurements, with monochromatized radiation if possible, for a *complete range* of crystal mis-setting. Even then, the results would be incomplete, since for the angle of selective reflexion and for a small range of angles about this value the diffuse scattering simply forms a background to the Bragg reflexion and is therefore included in any measurements that are made of intensity of the latter.

The fact that many spots are accompanied by monochromatic streaks must also make intensity measurements difficult and uncertain in those cases. Experiments show that this includes not only such an interesting case as the diffuse reflexions of Cu radiation corresponding to the {111} planes of diamond, but also those from KCl, Al and various organic compounds.

The absolute maximum peak intensity of diffuse scattering cannot be measured, as it coincides with that of the Bragg reflexion; the maximum peak intensity for any particular angle of mis-setting greater than that included under the Bragg reflexion could be measured by ionization or photometer methods. This has been done by Laval (1939 *a, b*) and by Siegel and Zachariasen (1940), both of whom find that there is a rapid falling off of intensity as the angle of mis-setting increases. Plates 13 and 14 show this in rather a striking way. The diffuse spot is that corresponding to the (002) cleavage plane of urea nitrate. In the first strip the X-rays are parallel to the cleavage plane; a diffuse spot may be seen on each side of the central spot. Then as the angle of incidence increases, the (00*l*) Laue spot moves outwards towards the position of the diffuse spot and the intensity of the latter increases until the diffuse and Laue spots coincide, after which the diffuse spot intensity decreases as the Laue spot moves away towards the edge of the film. The actual series of photographs includes several for which the Laue spot has gone beyond the edge of the film and the diffuse spot is still just visible, though not reproducible. The range of angles of incidence is from  $0^{\circ}$  to over  $30^{\circ}$  in this series; the Bragg angle is  $14^{\circ}1$ . On the opposite side of the central spot in the films corresponding to orientations of  $17^{\circ}7$ ,  $18^{\circ}7$  and  $19^{\circ}6$  may be seen a very small diffuse spot, evidently corresponding to a much less intense Bragg reflexion. This diffuse spot fades out very quickly, and is a good contrast to the persistent, intense (002) spot.

As Raman and Nilakantan have pointed out, it frequently happens that



the  $K\beta$  diffuse spot is actually more intense than the  $K\alpha$ , because it is nearer to the corresponding Laue reflexion; its angle of mis-setting is less. This may be seen in plates 2*b*, 7*b* and 24*a*. Except in the case of diamond (plate 24*a*) and sylvine (plates 7*b*, 26, etc.), the observed  $K\beta$  diffuse spots are always much *smaller* than the  $K\alpha$  (plates 1*a*, 2*b*, 6*a*, 20*a* and 21*d*).

#### LOW-TEMPERATURE EXPERIMENTS

Laval, Preston, and Raman and Nilakantan found a great enhancement of the intensity of many of the diffuse spots when the crystal temperature was raised. Organic crystals, in general, melt at relatively low temperatures; a test experiment showed that even a rise of temperature of 50° C was sufficient to give a marked increase of intensity in the case of the diffuse spots of benzil (m.p. 95° C). The next step was to try the effect of lowering the temperature. The experimental technique, which was very simple, was similar to that described by us (Lonsdale and Smith 1939) for the investigation of crystal structure at liquid air temperatures.

The crystal was set with cellulose solution on a glass or metal rod, and enclosed in a thin cellophane tube, the whole being set on a pair of arcs with cellulose solution, and adjusted to the orientation required. A photograph having been taken at room temperature, a fine stream of liquid air was allowed to impinge directly on the cellophane-covered crystal all the time a second photograph was being taken. No ice formed on the crystal during the experiment, and although no attempt was made to measure the temperature attained, it seems probable that this was at least as low as that of liquid air. When the crystal had warmed up again, a third photograph was taken at room temperature. Sometimes a fourth and a fifth photograph were taken at liquid air and room temperatures again. The exposures were made as nearly as possible the same, but a further check was sometimes made by taking a room temperature photograph at considerably less than the exposure given to the corresponding low temperature photograph (see plate 17*a* and *b*). Photographs were also taken of the cellophane tube alone (plate 15*a*), of cellophane + liquid air stream (plate 15*b*) and of liquid air stream alone. All the photographs taken at low temperatures showed rings due to the cellophane and liquid air stream; these were of varying intensity, because sometimes the cellophane tube was vertical and the liquid air streamed over it continuously; at other times the cellophane tube was inclined and the liquid air stream impinged on it and was sprayed off in such a way as to give no clear reflecting jet.



*Study of diffuse X-ray reflexion by single crystals* 29

The substances photographed in this way were  $\alpha$ -resorcinol,\* benzil (plate 16 *a* and *b*), sorbic acid (plate 17 *a* and *b*), KCl, NaNO<sub>3</sub> (plate 18 *a* and *b*) and diamond (plate 19 *a* and *b*). In all cases except diamond the diffuse spot pattern is practically non-existent at liquid air temperatures. The Laue pattern, on the other hand, shows many more spots and has a much clearer background. *In every case the changes are completely reversible* and can be repeated as often as desired. The Laue spots remain consistently sharp at all temperatures. The few diffuse spots which do not completely disappear are much sharper at low than at room temperatures (plates 16 *b* and 18 *b*).

The {111} diffuse spots of diamond (all orientations) show only a slight diminution of intensity at low temperatures, but it should be noted that the lowering of temperature involved (some 200°) is relatively small compared with the characteristic temperature of diamond (2340°).

## SHAPE AND SIZE OF THE DIFFUSE SPOTS

No intensity measurements giving only peak values can be considered satisfactory, since the size and shape of individual spots vary enormously. Sometimes the diffuse spots are approximately circular, in which case estimates of the size given by 'half-maximum-intensity' or 'half-width' measurements would have some meaning; but more often they are not circular. Frequently, as has been mentioned in the discussion on  $\alpha$ -resorcinol, the diffuse spots are quite different in shape from the Laue spots; a close examination of the diffuse spot group seen in plate 20 *a* shows this clearly. The crystal used was a small lath of urea oxalate obtained by cleavage and set with the long axis vertical. The cleavage plane (20 $\bar{1}$ ), to which corresponds the prominent diffuse spot on the film (seen accompanied by a smaller  $K\beta$  component), is parallel to the thin faces of the lath; the main faces are {010} planes. The rotation photograph (plate 20 *b*) shows, as might be expected, Bragg spots whose length is parallel to the 'row lines'; the diffuse spots are similar in shape to the Bragg spots although different in size; by contrast, many of the Laue spots slope sharply; in the original film the (20 $\bar{1}$ ) Laue spot can be seen sloping between the  $K\alpha$  and  $K\beta$  diffuse spots.

The (220) and (330) diffuse spots of  $\alpha$ -resorcinol (plate 2 *b*) appear to be slightly concave towards the (*h**h*0) Laue spot accompanying them, and definitely appear to increase in size as the angle of mis-setting increases.

\* Note: photographs reproduced in *Nature* 1941, 147, 469.



In three photographs of sorbic acid (plate 16 *a*, *b* and *c*) taken at  $5^\circ$  intervals it will also be seen that the diffuse spots on the outer films are longer than the corresponding diffuse spot on the central film, for which the crystal was more nearly in the position for Bragg reflexion. On the other hand, the size of the urea nitrate (002) diffuse spot (plates 13 and 14) does not appreciably change with change of crystal orientation. It sometimes appears that spots occurring at larger angles of deviation are larger than those occurring at smaller angles, but this is by no means a general rule. For instance, the (002) diffuse spot of hexamethylbenzene (plate 21*e*) is smaller than the (001) diffuse spot (plate 21*d*). Moreover, as Laval's measurements and Preston's photographs show very clearly, at elevated temperatures the inner spots increase remarkably in size, whereas the outer spots are comparatively unchanged in this respect and are much smaller.

#### *Relation of shape and size to crystal structure*

Many experiments agree in showing that both shape and size of the diffuse spots are closely related to the crystal structure. *Layer structures* always give Laue photographs showing, for suitable orientations, one outstanding oval diffuse spot which corresponds to the layer plane (Lonsdale 1941). Plate 21*d* shows such a Laue photograph of hexamethylbenzene, a triclinic crystal in which all the atoms lie practically in the (001) planes (Lonsdale 1929; Brockway and Robertson 1939). Laue photographs taken with the (001) plane inclined at various angles to the vertical show that the maximum length of the diffuse spot is always parallel to the layers of atoms. Urea nitrate (plates 13, 14 and 22*a*), monoclinic, with all the atoms in or very near to the (002) plane, and urea oxalate (plate 20*a*), with all the atoms in or near to the (20 $\bar{1}$ ) plane, each show the same prominent type of spot; large, oval, intense and persistent over a wide range of angles of incidence.

*Chain structures* give diffuse spots of a completely different type. They are fine, needle-like, with only a small intense core in orientations not far from the correct setting for Bragg reflexion. The length of the spot is roughly perpendicular to the length of the chains. Such diffuse spots have been observed on Laue photographs of single crystals of long chain compounds, where they are so sharp as to be barely distinguishable from genuine Laue spots. They are most clearly seen, however, on certain Laue photographs of sorbic acid (Lonsdale, Robertson and Woodward 1941).

*Sorbic acid* is a monoclinic crystal, the unit cell of which contains eight  $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{COOH}$  molecules, linked in pairs by hydrogen



bonds about the symmetry centres of the crystal. The long chain axes of the molecules lie in or near to the (010) plane and are inclined at a small angle to the  $a$  axis in the obtuse angle  $\beta$ . The molecules are plane (lath-shaped) and the atoms lie in or near to the  $\{11\bar{3}\}$  crystal planes. The results, which are given by the usual X-ray, optical and magnetic methods, are most interesting when considered in relation to the diffuse spot patterns. It is found that the diffuse spots observed may be divided into two main classes (except for a few spots which are intermediate in shape), one set corresponding to the 'layer' type, the other to the 'chain' type (plates 5*a*, 11, 12, 21 *a*, *b* and *c* and 23 *a* and *b*). In the Laue photograph taken with the incident beam along [010] (plate 23*b*) the shapes of the diffuse spots in various positions directly indicate the direction of the molecule length in that particular projection. The correspondence between spot and structure is shown in figure 2.

It is clear that in the case of compounds whose crystals, though perhaps composed of complicated molecules, possess a well-defined chain or layer structure (or both, as in sorbic acid), the study of diffuse spot pictures can supply a most useful secondary method of structure determination. It is particularly useful as a quick method of detecting layer structures, even when a rotation photograph reveals nothing outstanding (compare plate 21 *a* and *b*). A *very well exposed* rotation (Weissenberg, etc.) photograph of a layer structure, however, always shows that the Bragg spot corresponding to the layer plane has an intense diffuse background.

#### *Shape of diffuse spots from diamond*

When Cu radiation is used, the diffuse spots from the  $\{111\}$  planes of diamond are particularly interesting as regards shape. The crystal used (kindly given by Professor Gordon) was a perfect octahedron, edge lengths about 1 mm. With an incident beam normal, or nearly normal, to a (111) face, photographs similar to those already published by Raman and Nilakantan (1940*b*) have been obtained. That is to say, the  $K\alpha$  and  $K\beta$  diffuse spots are small, nearly circular, and accompanied when near to the (111) Laue spot by fine streaks directed away from the Laue spot, and either towards or away from the other two  $\{111\}$  diffuse spots (plate 24*a*). When, however, the crystal is set with a [110] axis vertical and the vertical  $\{111\}$  planes making angles of nearly  $-21^\circ.9$  and  $+48^\circ.6$  respectively with the incident beam, so that, in effect, diffuse scattering takes place from the *other side* of the (111) plane ( $21^\circ.9$  being the Bragg angle), then the diffuse spot is of an entirely different shape (Jahn and Lonsdale 1941). For various angles of mis-setting it consists of three small spots grouped tri-



angularly about a more diffuse centre. The radial apex of the triangle always points away from the Laue spot and as the angle of mis-setting increases the three spots separate without increasing individually in size (plates 24*b* and 25*b*). One rather extraordinary result of this (easily

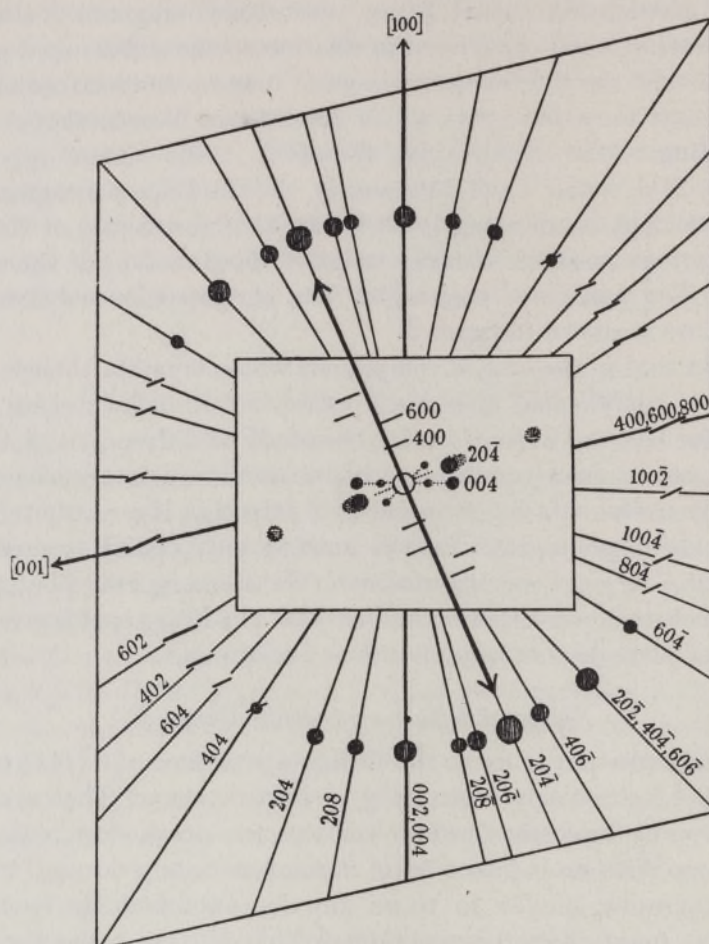


FIGURE 2. Sorbic acid: [010] projection, showing direction of length of molecular chain relative to planes giving broad —●— and fine —/— diffuse spots. Inset is actual appearance of diffuse spots on the corresponding Laue photograph (plate 23*b*).

observed, but not reproducible) is that for angles of scattering less than twice the angle of incidence the  $K\beta$  group of spots is larger than the  $K\alpha$  group. When the crystal is properly set for selective  $\text{Cu } K\alpha$  reflexion, the  $K\alpha$  diffuse spot forms an apparently circular background to the Bragg spot, while the  $K\beta$  diffuse spot forms a weak triangular group nearer, of course, to the undeviated beam (plate 25*a*).



## Study of diffuse X-ray reflexion by single crystals 33

In other positions of the (111) plane, as for instance when one edge is horizontal, the diffuse spot is asymmetric in shape.

Monochromatic photographs prove that the compound diffuse spot and the circular spot with streamers are both due entirely to scattering of the Cu  $K\alpha$  radiation.

Preliminary calculations indicate that it is possible to explain the different shapes of these diamond (111) diffuse spots by means of an extension of Waller's theory, taking particular values of the elastic constants (Jahn and Lonsdale 1941).

Photographs taken using Mo radiation and appropriate crystal settings show diffuse spots corresponding to the (111) (022) (311) (400) planes. None of these have either streaks or structure similar to those obtained for (111) with Cu radiation. They are small, circular, and fade out more rapidly as the angle of mis-setting increases than those of any other crystal examined. It will be shown in a later section that if the positions of the diffuse spots and streaks are plotted on a reciprocal lattice net, the reason for the difference in behaviour with Cu and Mo radiation becomes apparent.

### POSITION OF THE DIFFUSE SPOTS

#### *Relation between angles of incidence and of deflexion*

It has been made clear by the similarity between diffuse spot and oscillation photographs that the positions of the diffuse spots are nearly those of the corresponding Bragg spots. The words 'nearly' and 'approximately' have been used deliberately, because the correspondence is not always exact. It is exact when the orientation of the crystal is such that selective reflexion takes place. The diffuse spot then forms a background to the Bragg spot. In this position  $\theta$ , the angle of incidence;  $\theta + \phi$ , the total angle of deflexion; and  $\theta_B$ , the Bragg angle, are related as follows:  $2\theta = \theta + \phi = 2\theta_B$ . As has been seen (plates 13 and 14) the angle  $\theta + \phi$  changes very little even when  $\theta$  varies by over  $30^\circ$ , and  $\theta + \phi$  is always *nearly* equal to  $2\theta_B$ ; but the small differences involved depend on the nature of the crystal and its orientation and are therefore very important.

Faxén deduced that a formula of the type  $a(\sin \theta + \tan \phi \cos \theta) = \lambda$  would give the relation between the incident and diffusely scattered beams in the simplest case of a cubic crystal, lattice constant  $a$ , for which spherical symmetry of the elastic constants is assumed. Zachariasen (1940) deduced the same formula, in the form  $[1 + \lambda \tau_{\min.}] k_m = B_H + k_0$  (the original paper should be consulted for the meanings of these terms), which for small values of  $(\theta - \theta_B)$  reduces to  $\theta + \phi \approx 2\theta_B + 2(\theta - \theta_B) \sin^2 \theta_B$ ; and Raman and



Nilakantan found empirically that the same formula (expressed in the form  $d \sin (\theta + \phi) = \lambda \cos \phi$ ) holds approximately for diamond, when the incident Cu radiation is nearly normal to a (111) face (cf. plate 24*a*) and three {111} diffuse spots are observed for various angles of incidence within a range of about  $4^\circ$ . More recently still, Jauncey (1941) has deduced the same formula, in yet another form, for angles of incidence not far from the Bragg angle, on the assumption (Bragg 1940) that the diffuse spots are due to simple diffraction by very small groups of atoms.

For  $\text{NaNO}_3$ ,  $\text{CaCO}_3$  and  $\text{NaCl}$ , Raman and Nilakantan state that a symmetrical formula  $2d \sin \frac{1}{2}(\theta + \phi) = \lambda$  (which implies that  $\theta + \phi$  is independent of crystal orientation) suits the results of diffuse spot measurements better than the Faxén formula. In fact, however, neither the symmetrical nor the unsymmetrical formula is really satisfactory for any of the crystals examined, and Raman and Nath (1940*b*) have recently suggested a more general formula,  $2d \sin \psi \cdot \sin (I + \epsilon) = n\lambda \sin I$ , where  $I$ , in terms of their theory, is the inclination of the 'phase-waves of the lattice vibration' to the static crystal planes under consideration,  $2\psi$  is the angle of deflexion (that is,  $\theta + \phi$  in the previous notation), and  $\epsilon$  is the inclination of the 'static' to the 'dynamic stratifications'. If the plane of incidence (plane containing the incident beam and the normal to the undisturbed crystal plane) contains also the diffusely reflected beam, then  $\epsilon = \frac{1}{2}(\phi - \theta)$  and the equation becomes

$$2d \sin \frac{1}{2}(\phi + \theta) \sin (I + \frac{1}{2}(\phi - \theta)) = n\lambda \sin I.$$

Taking  $I = \frac{1}{2}\pi - \phi$ , this formula reduces to Faxén's original formula  $d \sin (\phi + \theta) = n\lambda \cos \phi$ ;  $I = \frac{1}{2}\pi - \frac{1}{4}(\phi - \theta)$  gives the symmetrical formula  $2d \sin \frac{1}{2}(\phi + \theta) = n\lambda$ . Raman and Nilakantan (1941) suggest that for rock-salt  $I = \frac{1}{2}\pi$  and for diamond  $I = 55 \pm 1^\circ$  (half the tetrahedral angle). These results will be examined more critically in a later section.

Measurements of the photographs taken in the course of the present study are too numerous to be given in detail. Certain general results may however be mentioned. One of the most noticeable features of diffuse spot photographs of organic crystals is that the diffuse spot tends to be displaced from the Bragg position *towards* the Laue spot corresponding to it. In other words,  $\theta + \phi \gtrless 2\theta_B$  according as  $\theta \gtrless \theta_B$ . This may be seen on the three photographs of sorbic acid (plate 21 *a*, *b* and *c*) showing the displacements of the (604) Laue and diffuse spots as the crystal is rotated by  $5^\circ$  at a time. The diffuse spot positions in this case agree well with Faxén's formula. The photograph of benzil in plate 3*b*, where the crystal is set so that the incident beam makes an angle of about  $7^\circ$  with the hexagonal



axis, shows that the layer line diffuse streaks, with the spots lying on them, are also displaced in the same sense. That the relationship between  $\theta$  and  $\phi$  cannot always be expressed in terms of a single formula over a wide range of values of  $\theta$ , is shown by measurements on the set of diffuse spots illustrated in plates 13 and 14. In table 5 is given the value of the (002)

TABLE 5

$\theta$	$\theta + \phi$	$\phi$	$\theta - \phi$	calculated (002) spacing			
				(1)	(2)	(3)	(4)
0°	27° 38'	27° 38'	-27° 38'	3.32	2.94	3.22 <sub>5</sub>	3.13
4° 0'	27° 51'	23° 51'	-19° 51'	3.25	3.01 <sub>5</sub>	3.20	3.15
5° 0'	27° 51'	22° 51'	-17° 51'	3.24	3.04	3.20	3.16
5° 56'	27° 51'	21° 55'	-15° 59'	3.23	3.05 <sub>5</sub>	3.20	3.16 <sub>5</sub>
7° 7'	27° 45'	20° 38'	-13° 31'	3.23	3.09	3.21	3.18 <sub>5</sub>
8° 2'	28° 5'	20° 3'	-12° 1'	3.18 <sub>5</sub>	3.07	3.17	3.15 <sub>5</sub>
8° 55'	27° 58'	19° 3'	-10° 8'	3.19 <sub>5</sub>	3.10	3.18	3.17
9° 58'	28° 5'	18° 7'	-8° 9'	3.18	3.10 <sub>5</sub>	3.17	3.16
11° 2'	28° 5'	17° 3'	-6° 1'	3.17 <sub>5</sub>	3.13	3.17	3.16 <sub>5</sub>
12° 7'	28° 5'	15° 58'	-3° 51'	3.17 <sub>5</sub>	3.14	3.17	3.17
13° 7'	28° 12'	15° 5'	-1° 58'	3.16	3.15	3.16	3.16
14° 6'	28° 12'	14° 6'	0°	3.16	3.16	3.16	3.16
14° 32'	28° 12'	13° 40'	0° 52'	3.16	3.17	3.16	3.16
15° 35'	28° 25'	12° 50'	2° 45'	3.13 <sub>5</sub>	3.15 <sub>5</sub>	3.13 <sub>5</sub>	3.13 <sub>5</sub>
16° 39'	28° 25'	11° 46'	4° 53'	3.14	3.16 <sub>5</sub>	3.13 <sub>5</sub>	3.13 <sub>5</sub>
17° 41'	28° 32'	10° 51'	6° 50'	3.13	3.16	3.12 <sub>5</sub>	3.12
18° 40'	28° 38'	9° 58'	8° 42'	3.12 <sub>5</sub>	3.16 <sub>5</sub>	3.11 <sub>5</sub>	3.10 <sub>5</sub>
19° 36'	28° 38'	9° 2'	10° 34'	3.13	3.17	3.11 <sub>5</sub>	3.10
20° 36'	28° 38'	8° 2'	12° 34'	3.13 <sub>5</sub>	3.18	3.11 <sub>5</sub>	3.09 <sub>5</sub>
21° 28'	28° 46'	7° 18'	14° 10'	3.12 <sub>5</sub>	3.17 <sub>5</sub>	3.10	3.07 <sub>5</sub>
22° 39'	28° 51'	6° 12'	16° 27'	3.12	3.17	3.09	3.06
24° 30'	29° 4'	4° 34'	19° 56'	3.11 <sub>5</sub>	3.16	3.07	3.02
26° 23'	29° 18'	2° 55'	23° 28'	3.10 <sub>5</sub>	3.14	3.04	2.98
28° 27'	29° 25'	0° 58'	27° 29'	3.12	3.13 <sub>5</sub>	3.03	2.94
30° 25'	29° 30'	-0° 55'	31° 20'	3.14 <sub>5</sub>	3.13	3.03	2.92

spacing of urea nitrate (to which this set of diffuse spots corresponds) deduced from various modifications of the general formula, as follows:

$$\begin{aligned}
 (1) \quad I &= \frac{1}{2}\pi. & d &= \frac{\lambda}{2 \sin \frac{1}{2}(\theta + \phi) \cdot \cos \frac{1}{2}(\theta - \phi)}. \\
 (2) \quad I &= \frac{1}{2}\pi - \phi. & d &= \frac{\lambda \cos \phi}{\sin (\theta + \phi)} \quad (\text{Faxén's formula}). \\
 (3) \quad I &= \frac{1}{2}\pi - \frac{1}{4}(\phi - \theta). & d &= \frac{\lambda}{2 \sin \frac{1}{2}(\theta + \phi)} \\
 & & & (\text{Raman's symmetrical formula}). \\
 (4) \quad I &= \frac{1}{2}\pi - \frac{1}{2}(\phi - \theta). & d &= \frac{\lambda \cos \frac{1}{2}(\theta - \phi)}{2 \sin \frac{1}{2}(\theta + \phi)}.
 \end{aligned}$$



Other values of  $I$  have been tested, but these are sufficient to show the general trend of the results.

It will be seen that for values of  $\theta$  from about  $0^\circ \rightarrow 15^\circ$ , (4) gives the best agreement, whereas for values of  $\theta$  from  $15^\circ \rightarrow 30^\circ$ , (2) agrees best. No constant value of  $I$  can be found which gives good agreement over the whole range of  $\theta$ . For a small range of angles near to the Bragg angle,  $14^\circ 6'$ , there is little to choose between all the values tested.

One factor that makes measurements a little uncertain is the difficulty of determining the exact position of the origin on oblique Laue photographs, since the undeflected beam cannot usually be allowed to mark the film for fear of fogging. This point will be referred to later.

#### *Direction of diffuse scattering relative to plane of incidence*

In some previous work it has been assumed or asserted that the diffusely scattered beam lies in the plane of incidence; in other words, that the incident beam, the diffusely scattered characteristic beam and the corresponding selectively reflected 'white' beam are coplanar. This is not always the case, but as deviations are only observable when the Laue and diffuse spots are well separated, measurements are most difficult to make.

On plate 28 *a* and *b* it is quite clear that the streak extending from the central spot to the ( $h00$ ) Laue spot is a curved one, and that the diffuse spots corresponding to the 2nd, 4th, 6th and 8th order reflexions lie on this curve, and not on the straight line joining the Laue spot to the trace of the undeviated incident beam. This curve apparently corresponds to the direction along which the Laue spot moves as the crystal is rotated about a  $[\bar{1}10]$  vertical axis, as may clearly be seen on successive photographs taken at  $5^\circ$  intervals (plates 26, 27 and 28 give a selection of these). It appears to be, in fact, one of the ' $\alpha$  constant curves, given in Chart III of Bernal's paper (1926) on 'The interpretation of X-ray, single crystal, rotation photographs', which may be seen traced out by the white radiation streaks on rotation photographs taken with an X-ray beam containing a considerable amount of continuous radiation (cf. plates 5*b*, 6*b* and 20*b*).

When the X-rays are normal to a (001) face,  $[\bar{1}10]$  axis vertical (as in plate 26*a*) the ( $h00$ ) planes are parallel to the incident beam and the corresponding plane of incidence (plane containing the incident beam and the  $[100]$  axis) is inclined at  $45^\circ$  to the vertical. The diffuse spots corresponding to the (200) (400) Bragg reflexions then lie exactly along  $45^\circ$  diagonals on



the X-ray film. As the crystal rotates through an angle  $\omega$ , the inclination of the plane of incidence to the vertical decreases to  $\psi'$ , where

$$\sin(45^\circ - \psi') = \sin^2 \frac{1}{2} \omega / \sqrt{1 - \frac{1}{2} \sin^2 \omega}.$$

This change of inclination is very slow at first ( $\omega = 30^\circ$  gives  $45^\circ - \psi' = 4^\circ.1$ ;  $\omega = 35^\circ$  gives  $5^\circ.7$ ). The angle of incidence  $\theta$  after a rotation  $\omega$  is given by

$$\sin \theta = \frac{1}{\sqrt{2}} \sin \omega \text{ and hence the positions of the } (h00) \text{ Laue spot and the}$$

corresponding value or values of  $\lambda$  may be calculated for any value of  $\omega$ , by means of the relations  $r = D \tan 2\theta$ ,  $\psi = \psi'$ ,  $n\lambda = 2d \sin \theta$ , where  $r$ ,  $\psi$  are the angular co-ordinates of the Laue spot on a plane film at distance  $D$  from the crystal, relative to the central spot and vertical axis. The fact that the values of  $\psi$  corresponding to the diffuse spots for any particular value of  $\omega$  are not the same as that of the Laue spot, but lie between  $\psi'$  and  $45^\circ$  must mean that, as the crystal rotates, the diffuse spot moves nearly in the small arc of a circle, since the total angle of scattering ( $\theta + \phi$ ) remains approximately constant. This small circular movement is, however, less than it would be if the diffuse reflexion remained always in the plane of incidence.

The movement is very apparent in the case of the diffuse spots corresponding to  $(\bar{1}10)$ , the horizontal plane. When  $\omega = 0$  or  $90^\circ$ , these diffuse reflexions lie just above and below the central disk in the vertical plane of incidence. As  $\omega$  increases from  $0^\circ$  to  $45^\circ$ , the diffuse spots move out of the vertical plane, the displacement being clearly seen in plates 27 and 28. A similar displacement is seen on plate 7 in the case of the  $(200)$  and  $(400)$  diffuse spots corresponding to the  $(100)$  horizontal plane. In neither case, however, is there any question of a tilting of the plane of incidence, which remains always vertical.

That the diffuse spots do not always lie on the ' $\alpha$  constant' curves is at once apparent from a consideration of such Laue spots as  $(\bar{2}21)$  and the corresponding  $(\bar{4}42)$  diffuse spot. The  $(\bar{2}21)$  plane of incidence is initially vertical, but as  $\omega$  increases, its inclination  $\psi$  to the vertical increases from  $0^\circ$  to a maximum value of  $19^\circ.5$ . For very small values of  $\omega$ , however,  $\psi$  is also small and the  $\alpha$  constant curve is nearly horizontal. The  $(\bar{4}42)$  diffuse spot is initially in the plane of incidence,  $(\theta + \phi)$  being considerably less than  $2\theta$ , and it appears to move with and remain in the plane of incidence as the Laue spot traverses the  $\alpha$  constant curve. When  $\omega = 60^\circ$  it is still just observable,  $(\theta + \phi) \gg 2\theta$ . In this case the values of  $\psi$  are apparently the same for both Laue and corresponding diffuse spots. That discrepancies in  $\psi$  do frequently occur (even when exact measurements



would be very difficult to make) is apparent from the fact that early attempts to locate the true centre of the Laue photograph by finding the point of intersection of straight lines drawn through corresponding Laue and diffuse spots seemed, in many cases of oblique setting, to be almost impossible, because such lines had no common point of intersection.

Future measurements on any series of diffuse spots should give not only  $r$  but also  $\psi$ , preferably for various initial orientations of the plane of incidence, as well as for different angles of mis-setting. The fact that the ( $\bar{2}20$ ) diffuse spots, for instance, move out of the vertical plane of incidence as the crystal setting (plates 27 and 28) becomes more oblique, indicates that the 'modified plane' responsible for these diffuse spots *moves with the crystal*, that is, that its direction bears a fairly definite relation to the crystal framework. This important result would be entirely overlooked in measurements giving only the angles of incidence and total deflexion.

#### REPRESENTATION OF RESULTS IN RECIPROCAL SPACE

Most of the workers in this field have expressed their results, whether experimental or theoretical, in terms of reciprocal space. The convenience of this must be apparent when the similarity of diffuse spot and oscillation photographs is considered, since the interpretation of oscillation and rotation photographs is greatly facilitated by the use of reciprocal lattice methods (Bernal 1926). According to the usual theory, selective (Bragg) reflexion takes place, during the oscillation or rotation of the crystal, just as each reciprocal lattice point  $P$  coincides with the sphere of reflexion (figure 3). The Bragg condition  $\lambda = 2d \sin \theta_B$  is then fulfilled.

When the positions of the diffuse reflexions are plotted in reciprocal space, it is found that the strongest of these reflexions correspond to points which are not far from strongly reflecting reciprocal lattice points. As the angle of mis-setting ( $\theta - \theta_B$ ) increases, the point of diffuse reflexion moves away from its corresponding reciprocal lattice point, and the reflexion decreases in intensity.

The general formula which was given by Raman and Nath (putting  $n = 1$  for simplicity),

$$2d \sin \psi \sin (I + \epsilon) = \lambda \sin I, \quad (\text{i})$$

is readily deduced from a reciprocal lattice diagram,  $\psi$ ,  $I$  and  $\epsilon$  being definite angles in reciprocal space (figure 4).  $O$  is the reciprocal lattice origin,  $P$  a reciprocal lattice point (corresponding to an infinite set of



crystal planes of spacing  $d$ ),  $CO$  the direction of the incident beam,  $CD$  that of the diffusely reflected beam ( $CO = CD = 1/\lambda$ ),  $D$  being the point of diffuse reflexion.  $D$ , which lies on the sphere of reflexion, is not necessarily in the plane  $COP$ . If  $CN$  is the perpendicular from  $C$  to  $OP$ , the angle  $OCN$  is  $\theta$ , the angle of incidence. The angle  $OCD$  is  $2\psi$ , the angle of total deflexion. Then in the triangle  $OCD$ ,

$$OD = \frac{2 \sin \psi}{\lambda}.$$

In the triangle  $OPD$ , 
$$OD = \frac{\frac{1}{d} \sin I}{\sin (\pi - (I + \epsilon))}.$$

Hence 
$$\frac{2}{\lambda} \sin \psi = \frac{\sin I}{d \sin (I + \epsilon)},$$

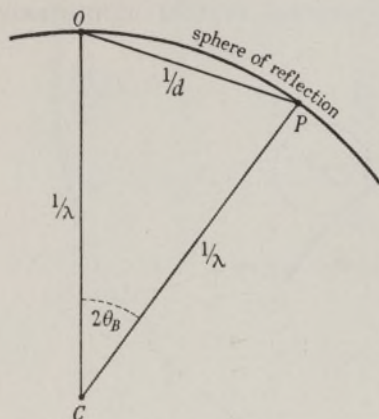


FIGURE 3

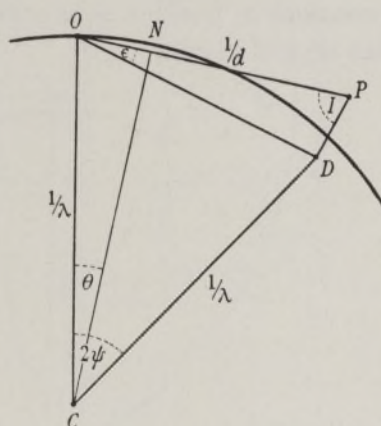


FIGURE 4

where  $I$  is defined as the angle  $OPD$ , and  $\epsilon$  as the angle  $POD$ . These two angles are sufficient to determine  $D$  uniquely. It may easily be proved also that

$$\cos \epsilon = \sin \theta \sin \psi + \cos \theta \cos \psi \cos \delta, \quad (\text{ii})$$

where  $\delta$  is the (measurable) angle between the plane of incidence  $COP$  and the plane of diffuse reflexion  $COD$ . If  $\delta = 0$ ,

$$\epsilon = \psi - \theta = \frac{1}{2}(\phi - \theta).$$

It should be clearly recognized that the general formula (i), proved above, is a purely geometrical relationship in reciprocal space, connecting



$O$ ,  $C$ ,  $P$  and  $D$ . It involves no other assumptions than that  $P$  is a point distant  $1/d$  from  $O$ , and that  $O$  and  $D$  lie on the sphere, radius  $1/\lambda$ , whose centre is  $C$ . It is quite independent of the particular physical interpretation given to the point  $D$ , or to the angles  $\psi$ ,  $I$  or  $\epsilon$ . Any theory which involves the existence of a cloud of diffusely reflecting points around each or any reciprocal lattice point will give the diffuse spot positions in terms of this general formula. Such diffusely reflecting points may result from the existence of harmonic vibrations in the crystal (either due to thermal motions as in the Faxén-Waller theory, or to quantum excitation as in the Raman theory), or from the limiting of the crystal size so that the sets of crystal planes are not of infinite extent (Laue and Riewe 1936; Preston 1939; Ewald 1940; Bragg 1940; Jauncey 1941). It seems probable that measurements of diffuse spot positions alone will not give material for a decisive choice to be made between the different theories put forward, unless one theory can be shown to account, correctly and uniquely, for the variations in position over a wide range of substances, crystal orientations and crystal planes.

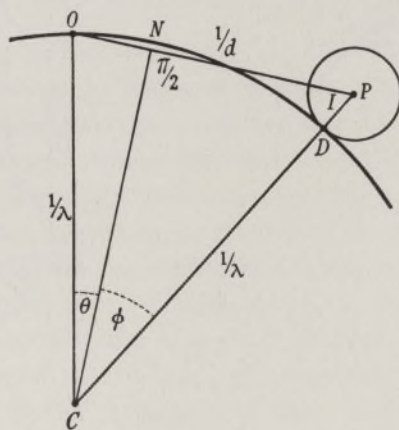


FIGURE 5

It would be simplest to assume, as Preston does, that there is a *spherical* distribution of the diffusely reflecting points around each reciprocal lattice point  $P$ , and that diffuse reflexion reaches its maximum intensity when  $D$  lies on the straight line  $CP$  (cf. Zachariasen 1940), or in other words, when  $CO$  and  $CDP$  are coplanar and  $I = \frac{1}{2}\pi - \phi$  (figure 5). In that case

$$d \sin (\theta + \phi) = \lambda \cos \phi.$$

The experimental results, however, show that although this formula applies in certain cases, yet in general, and over a wide range of values of  $\theta$ , it



does not apply. In particular, it does not hold for KCl, which may reasonably be taken as a simple cubic crystal. On the other hand, even preliminary measurements can usefully indicate the general distribution of diffuse scattering power in reciprocal space.

In figures 6 and 7 are shown the observed diffuse reflexions from KCl of Mo and Ag radiations respectively, plotted on reciprocal lattice nets, the

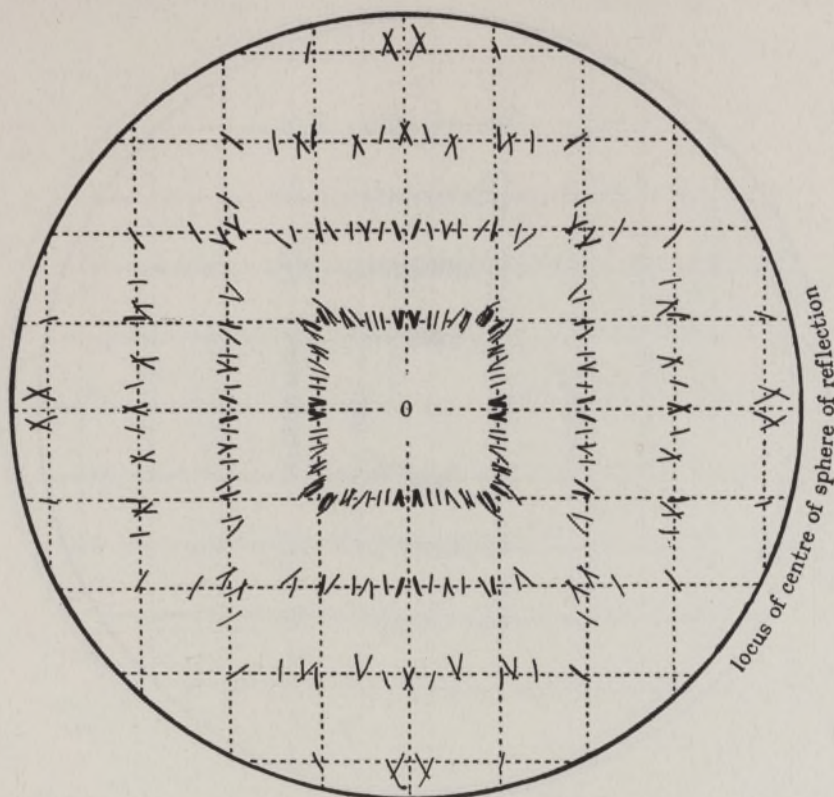


FIGURE 6. KCl; Mo  $K\alpha$ ; reciprocal net showing positions of diffuse spots on central layer line of Laue photographs taken with cube axis of crystal vertical. Each spot is shown as an arc of the appropriate sphere of reflection.

data being obtained from the zero layer lines of Laue photographs taken with a  $[001]$  axis vertical, for which the angle of incidence to a cube face was varied by small angular intervals over the whole range of  $360^\circ$ . Allowance being made for inaccuracies of measurement (due chiefly to uncertainty as to the exact position of the origin on successive photographs), it is clear that the points of diffuse reflexion tend to congregate in the neighbourhood of reciprocal lattice axes, being most dense near to reciprocal lattice points. Only certain axes are favoured, however; no diffuse



reflexion takes place at points in reciprocal space which would correspond to a considerable variation in *spacing* of real crystal planes.

These results are confirmed by a study of diffuse reflexions not in the zero layer line and also of those on Laue photographs taken with the  $[110]$  axis vertical (figure 8). In particular, the movements of the plane of deflexion relative to the plane of incidence are significant, in that the

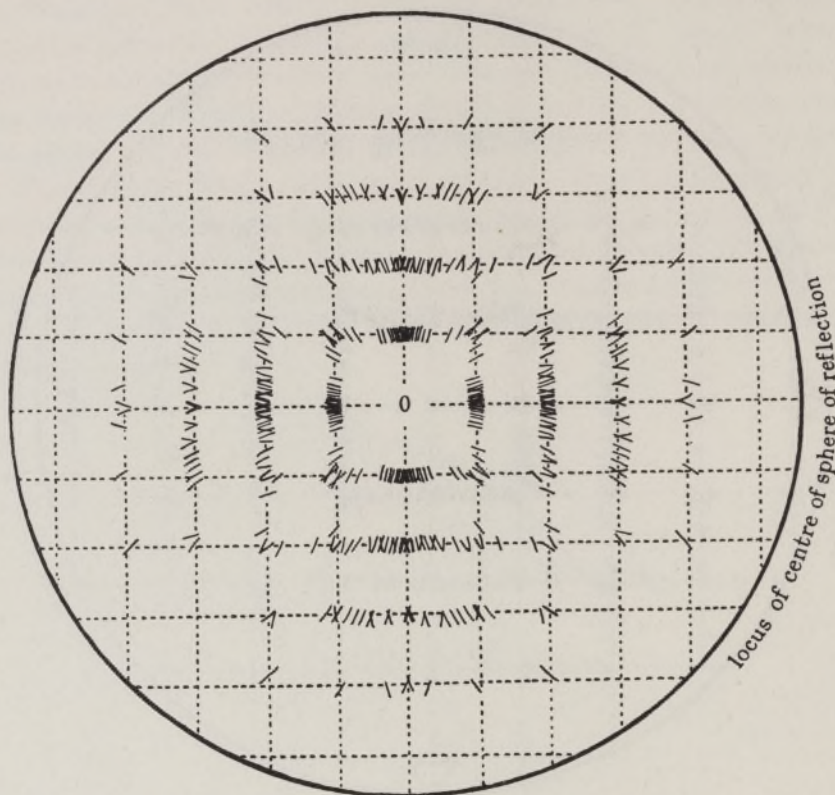


FIGURE 7. KCl; Ag  $K\alpha$ ; reciprocal net showing positions of diffuse spots on central layer line of Laue photographs taken with cube axis of crystal vertical.

effect in reciprocal space of non-coincidence of these planes is always such as to bring the point of diffuse reflexion nearer to a reciprocal lattice axis. The existence of the faint diffuse streaks connecting strong diffuse spots is also interesting in this connexion, because such streaks, plotted in reciprocal space, are found always to correspond to reflexion along or near to reciprocal lattice axes. Diffuse *radial* streaks would correspond to reciprocal lattice axes passing through the origin  $O$ , that is, to large variations of crystal spacing in real space. As our monochromatic photographs



showed, such streaks do not, in general, occur. Indeed, even the marked preference of the diffusely reflecting points for the neighbourhood of reciprocal lattice axes appears to be modified by a tendency to avoid much variation of crystal spacing.

This is also apparent in Raman and Nilakantan's measurements on rocksalt. These workers have suggested that  $I = \frac{1}{2}\pi$  gives quite good

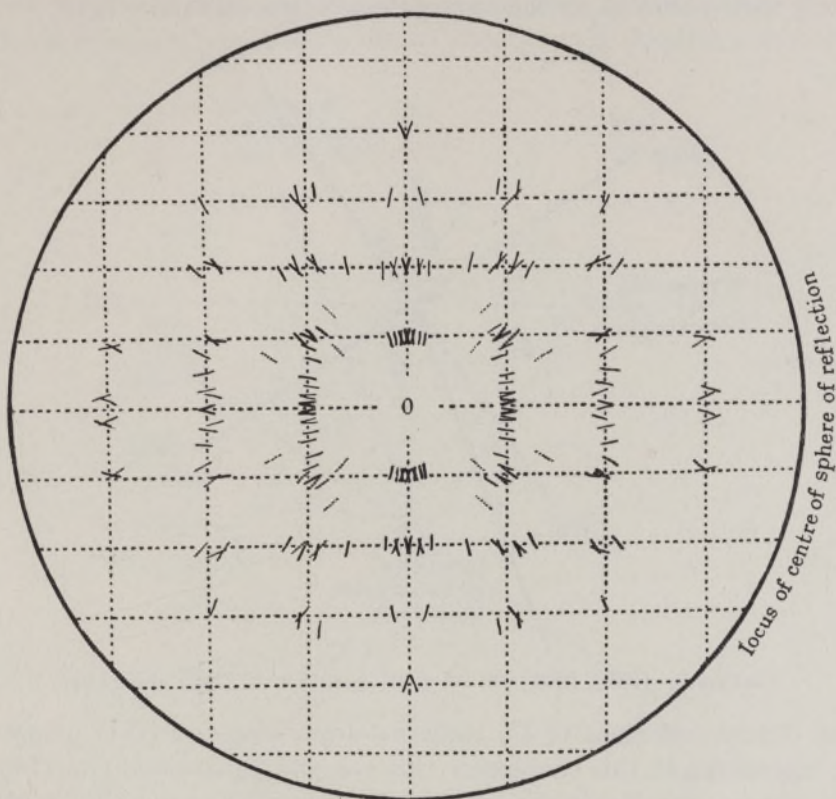


FIGURE 8. KCl; Ag  $K\alpha$ ; reciprocal net showing positions of diffuse spots on central layer line of Laue photographs taken with  $[110]$  axis of crystal vertical.

agreement with their data. This is approximately the case, at least for diffuse spots corresponding to the (400) plane, but in fact  $I = \frac{1}{2}\pi - \epsilon$  gives much better agreement with their data for (200) and (220), while  $I = \frac{1}{2}\pi - \frac{1}{2}\epsilon$  gives the best agreement for (400). In each case the effect is to reduce the change of spacing that would otherwise be involved.\*

The fact that the diffuse streaks in the (0001) Laue photographs of benzil are in the positions of layer lines in rotation photographs, that is,

\* There is, in general, however, a *small* change of spacing, as is shown both by their own data, and by the more recent investigation of Jauncey and Baltzer (1940).



that they correspond to the main crystal *periodicities*, means that in reciprocal space these streaks are given by unusually strong diffuse reflexion from reciprocal lattice planes or axes which happen to be roughly tangential to the sphere of reflexion in that particular crystal orientation. Similar considerations apply to the fragmentary streaks and patches of diffuse scattering found in other orientations. This is easily verified by plotting their positions on the appropriate reciprocal lattice nets.

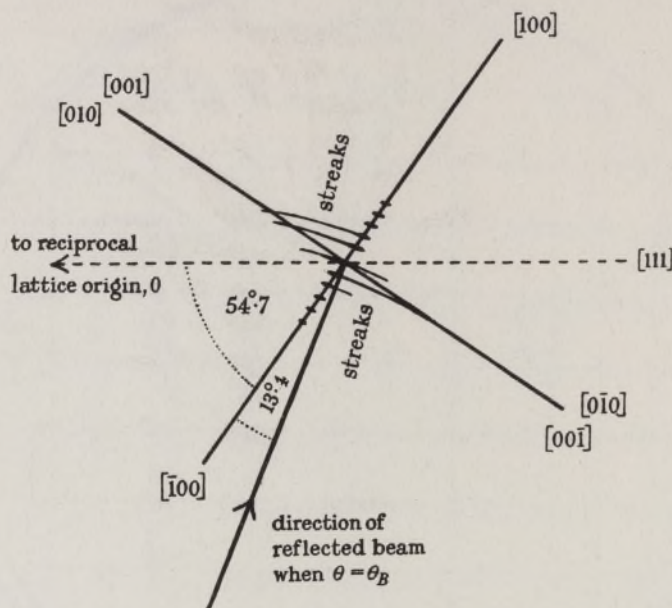


FIGURE 9.  $[010]$ ,  $[001]$  are at  $\pm 45^\circ$  to plane of  $[100]$  and  $[111]$ .

The diffuse reflexions of Cu radiation from diamond  $\{111\}$  planes are most interesting in this connexion. Raman and Nilakantan (1941) found that although the Faxén formula fitted their measurements (on diffuse spots similar to those shown in plate 24*a*) fairly well, an even better agreement resulted from the substitution of  $I = 54^\circ\cdot 7$  in the general formula. This result, which agrees with our own measurements on spots of this type, shows that for diamond also the points of diffuse reflexion lie mainly along reciprocal lattice axes, in this case along  $[100]$  directions. The same result is obtained very quickly by plotting the experimental data on a reciprocal lattice net. It is found, moreover, that the diffuse streaks observed on Laue photographs where the  $(111)$  diffuse spot is very near to its Laue spot, correspond to diffuse reflexion along  $[010]$  and  $[001]$  directions in reciprocal space which are nearly tangential to the sphere of reflexion (figure 9).



# Study of diffuse X-ray reflexion by single crystals 45

When, however, the direction of the incident beam is such that the diffusely reflected beam is almost equally inclined to the  $[100]$ ,  $[010]$  and  $[001]$  directions in reciprocal space (figure 10), a triangular group of three diffuse spots results (plate 24*b* and 25*a* and *b*). Two of the spots in each group form striking examples of non-coincidence of the planes of incidence and deflexion. The maximum observed value of  $\delta$  was  $11^\circ.8$ . All three spots in each group are relatively sharp (showing that the diffusely reflecting regions in reciprocal space are confined closely to the neighbourhood of the

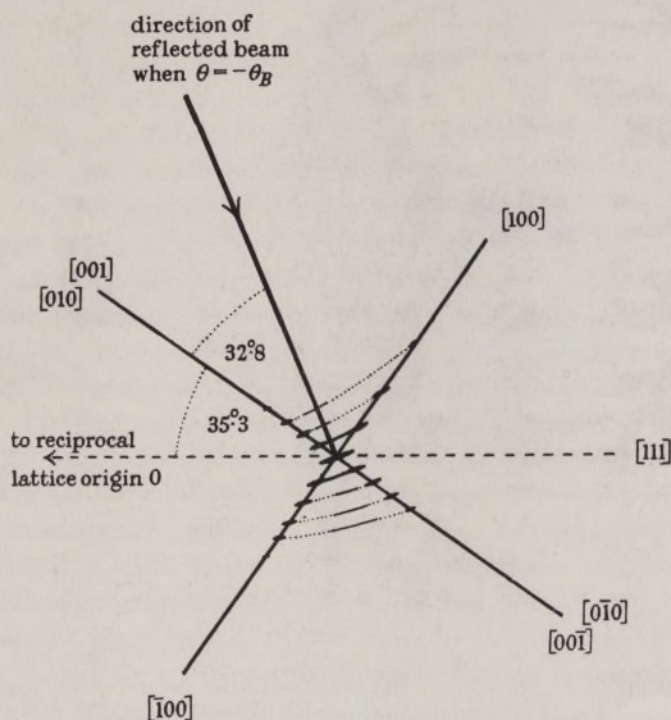


FIGURE 10.  $[010]$ ,  $[001]$  are at  $45^\circ$  to plane of  $[100]$  and  $[111]$ .

$[100]$ ,  $[010]$  and  $[001]$  directions, figure 11), *especially* when the angle of incidence differs considerably from the Bragg angle (plate 25*b*). In contrast to this, the diffuse centre of the triangle, which fairly closely obeys Faxén's formula, becomes relatively much weaker and more diffuse as the Laue and diffuse spots separate, that is, as the angle of mis-setting increases.

When Mo radiation is used instead of Cu, the scale of the reciprocal net is considerably reduced relative to the sphere of reflexion. More diffuse reflexions are observed, but any structure that these might possess is

swallowed up within the inevitable size of the spots themselves (due to the width of the X-ray beam and the size of the crystal).

A more detailed account of the measurements of the diamond diffuse spots and of their significance will be given in a subsequent publication.

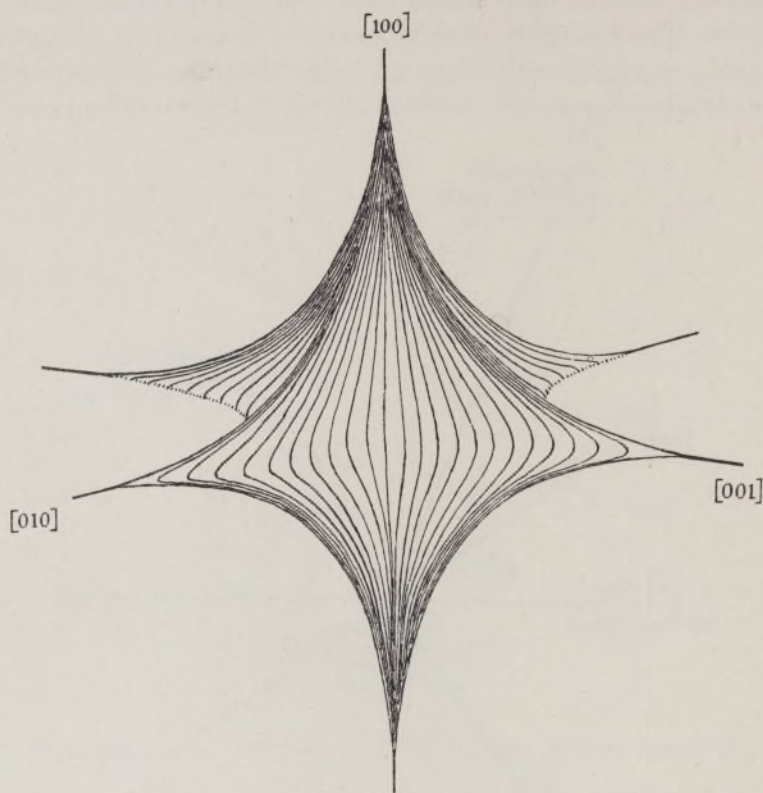


FIGURE 11. Approximate distribution of diffuse reflecting power about (111) reciprocal lattice point of diamond.

It is perhaps worth mentioning, however, that in terms of *any* wave theory, the fact that diffusely reflecting regions in reciprocal space are confined to, or extended along, certain directions implies that in real space the atoms or molecules tend to remain strictly in phase with each other along those directions; whereas in the 'finite crystal' theory the intensity spikes are normal to the boundary planes (Laue and Riewe 1936).



## CONCLUSION

The main facts that emerge from this study may be summed up as follows.

1. The diffuse spots sometimes found on Laue photographs lie very nearly or sometimes exactly in the positions of Bragg reflexions from crystal planes which are not necessarily, however, quite at their proper reflecting angle. The indices of the corresponding Bragg reflexion can be found by treating the diffuse spot picture as though it were an oscillation photograph taken about the Laue position as centre of oscillation. This is a general fact applying to inorganic and organic crystals of any system, and to all wave-lengths of X-radiation used.

2. Conversely, a diffuse spot picture will only be found under conditions in which Bragg spots would be obtained on an oscillation photograph if the crystal, instead of being held stationary, were allowed to oscillate through a small angle about any direction normal to the incident beam. This involves relationships between wave-length, crystal structure and orientation, size and distance of photographic film, which are readily determined.

3. Such diffuse spot patterns may not only be seen on Laue photographs, where the diffuse spot and its corresponding Laue spot are, in general, well separated, but also on oscillation, rotation, Weissenberg and powder photographs, where the diffuse spots form a background to the selective Bragg reflexions. They may also, of course, be observed and measured by ionization spectrometer methods.

4. In general, a much longer exposure is necessary in order to produce the diffuse background picture than to obtain a normally satisfactory Laue or rotation photograph.

5. That the diffuse spots are due to diffraction of *characteristic* X-rays may be proved by using a monochromatized beam (Laval 1939; Preston 1939).

6. The diffuse halo surrounding the central spot on ordinary Laue or rotation photographs does not appear on monochromatic Laue photographs, even when the diffuse spot pattern on the latter is stronger than that on the former, showing the exposure to be more than equivalent.

7. The radial streaks on ordinary Laue photographs are almost always due to diffuse reflexion of *white* radiation. The radial streaks on oscillation or rotation photographs are due to selective reflexion of white radiation, but must also have a diffuse background.

8. Monochromatic Laue photographs sometimes show non-radial diffuse streaks, some well defined and some fragmentary; also triangular patches



of diffuse scattering and other anomalies which have, as yet, received no theoretical attention.

9. The diffuse spot pattern is not apparently affected by the condition of the crystal surface or by crystal imperfection, except that sometimes diffuse spots show an intense and sharply defined core which may be due to distortion, as it is only found for cleaved or fractured crystals.

10. The intensity of a diffuse spot is related to the absolute intensity of the corresponding Bragg reflexion; it depends also very markedly on the angle of incidence  $\theta$  (angle between the incident beam and the set of planes giving the corresponding Bragg reflexion), reaching a maximum when  $\theta = \theta_B$ .

11. A most important factor affecting intensity is the crystal temperature. At elevated temperatures (experiments extend up to 500° C) some diffuse spots increase enormously both in intensity and in size (Laval 1939, and others), and non-radial streaks appear which were not previously visible (Preston 1939). Other diffuse spots, however, are not so strongly affected. Planes which show a big increase in diffuse spot intensity show a corresponding decrease in the Laue or Bragg spot intensity. Conversely, at liquid air temperatures the diffuse spot pattern almost completely disappears, the Laue spots become more profuse and the general background clearer. These effects are reversible.

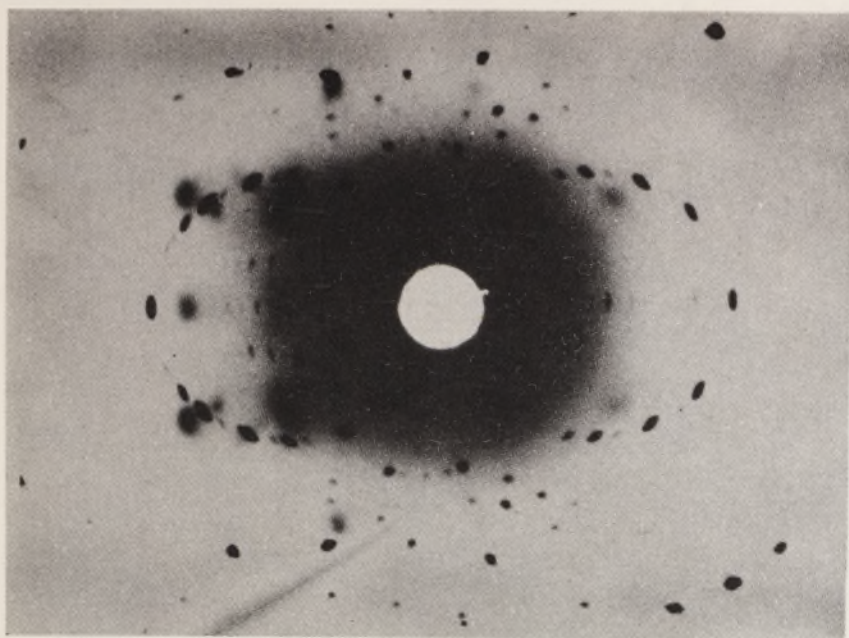
12. The shapes and sizes of the diffuse spots vary considerably. Very frequently they are not circular or even elliptical. They are more closely related to the shape of the corresponding Bragg spots than to those of the Laue spots. They are definitely and obviously related to the structure and nature of the crystal planes to which they correspond. 'Layer' planes and planes perpendicular to 'chain' directions give rise to diffuse spots which are very different in several respects. This indicates that diffuse spot patterns may give valuable subsidiary help in structure determination, and also points to a relation between the physical properties of a set of crystal planes and the character of the corresponding diffuse reflexion.

13. The shapes of the diffuse spots from diamond {111} planes, using Cu radiation, are different from those of any other substance yet examined, and provide valuable data for theoretical investigation.

14. The diffuse spots, although occurring nearly in the positions where the corresponding Bragg spots would be, may deviate from those positions by small amounts. The total angle of deflexion may be slightly more or less than twice the Bragg angle, and the plane of diffuse scattering may be inclined at a small angle to the 'plane of incidence'.

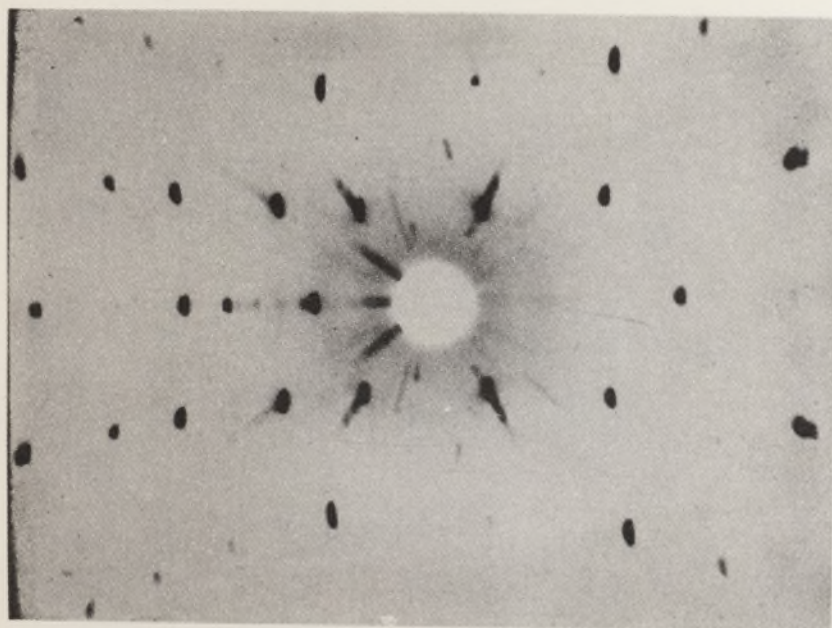
15. These facts may be visualized most easily by considering the rela-





(a)

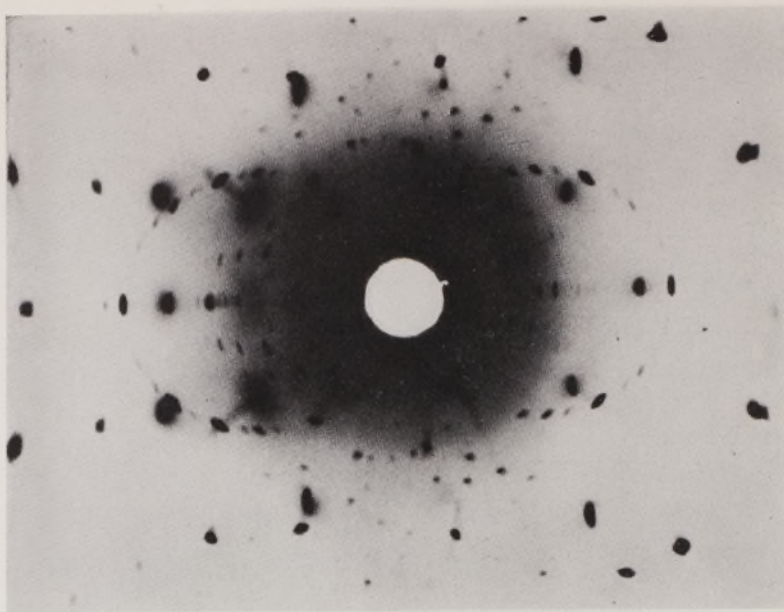
$\alpha$ -Resorcinol: [001] vertical: 4 cm.; unfiltered Cu radiation at  $21^{\circ}3$  to [010].  
Note arrangement of diffuse spots in layer lines, and intense central halo.



(b)

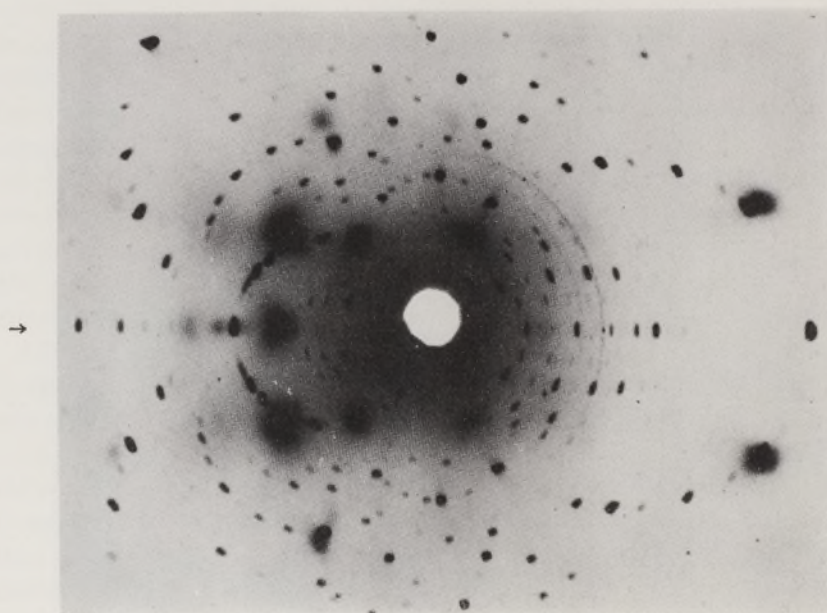
$\alpha$ -Resorcinol: filtered Cu radiation: oscillation  $7^{\circ}5$  each side of Laue position  
given above. 2 min. exposure, cf. 20 min. Laue exposure.

(Facing p. 48)



(a)

$\alpha$ -Resorcinol: filtered Cu radiation; position as in plate 1 *a* and *b*. Oscillation (2 min.) superposed on Laue (20 min.) photograph.

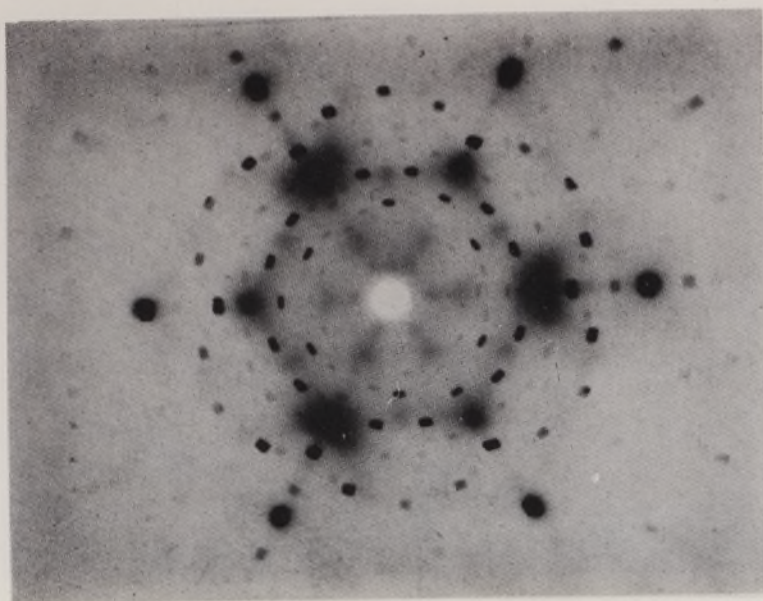


(b)

$\uparrow$   $\uparrow$   $\uparrow$   $\uparrow$   
 $330\alpha$   $\beta$   $Laue$   $220\alpha$

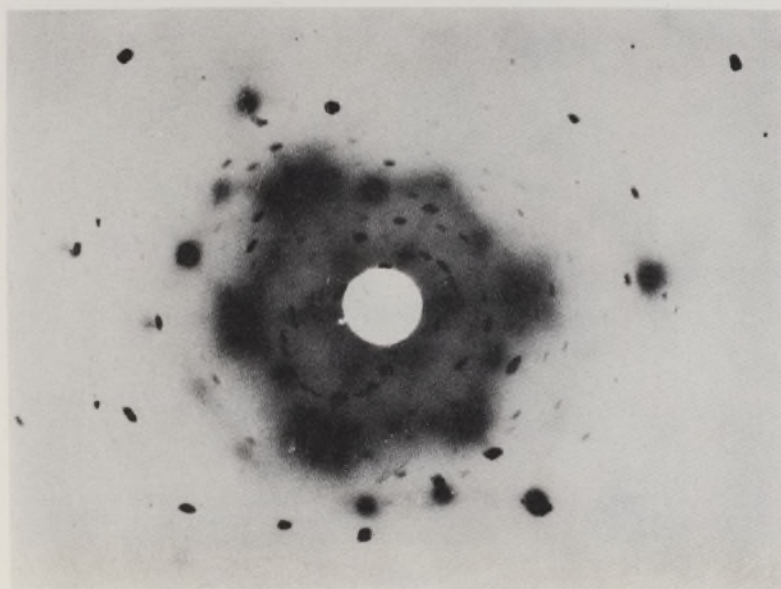
$\alpha$ -Resorcinol: [001] vertical: 4 cm.; unfiltered Cu radiation at  $25^{\circ}9$  to [010]. Note relative intensity, size, shape of  $220\alpha$ ,  $330\alpha$  and  $\beta$  diffuse spots on either side of  $hh0$  Laue spot.





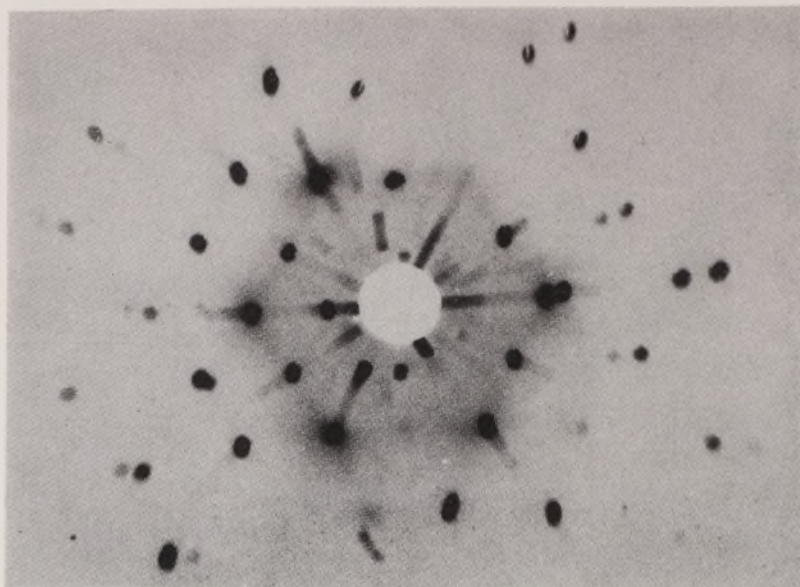
(a)

Benzil:  $[11\bar{2}0]$  vertical: 4 cm.: unfiltered Cu radiation along  $[0001]$ ; 10 min. exposure.  
Note alternating hexagonal symmetry of both Laue and diffuse patterns (cf. figure 1).



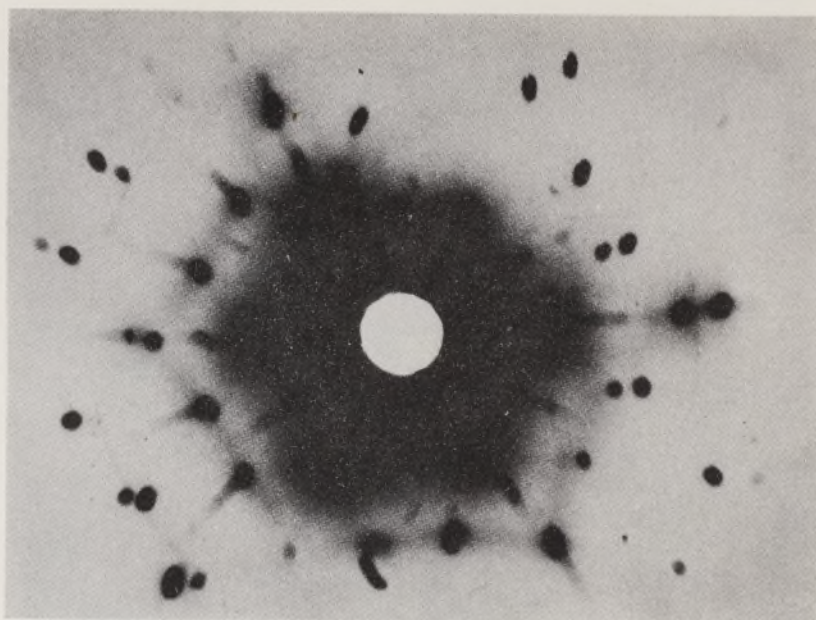
(b)

Benzil: filtered Cu radiation at about  $7^\circ$  from  $[0001]$ . Note loss of symmetry of Laue pattern, although diffuse pattern still shows approximate hexagonal alternating symmetry.



(a)

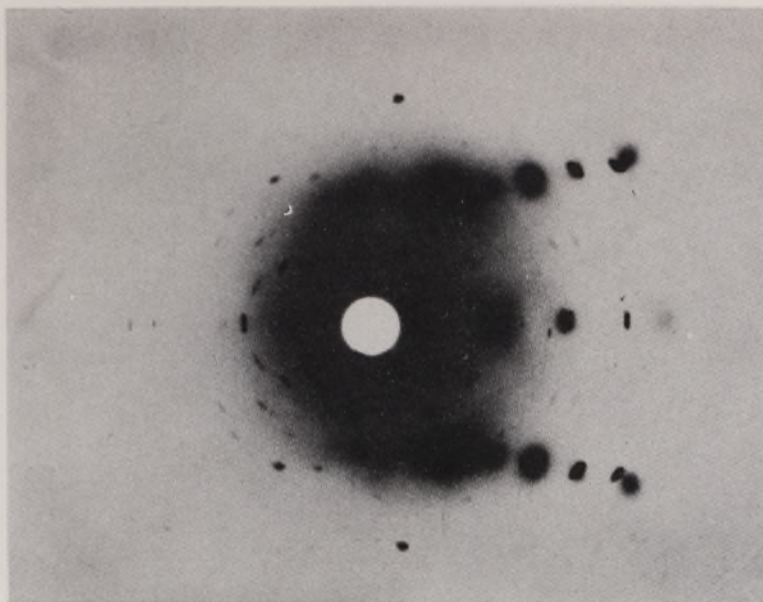
Benzil: 4 cm.; filtered Cu radiation: oscillation  $7^{\circ}5$  on each side of Laue position in plate 3*b*; 1 min. exposure. Note weak background pattern.



(b)

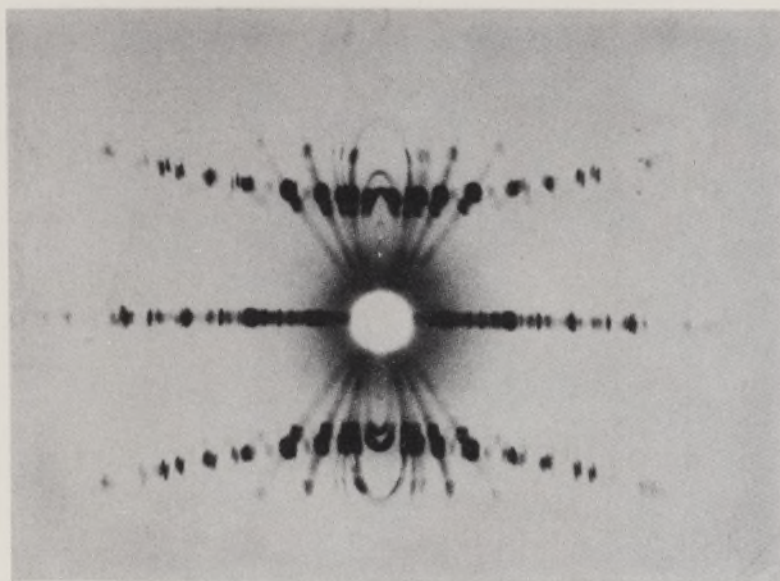
Benzil: same as (a), but exposure 10 min. Note strong background pattern and intense radial streaks.





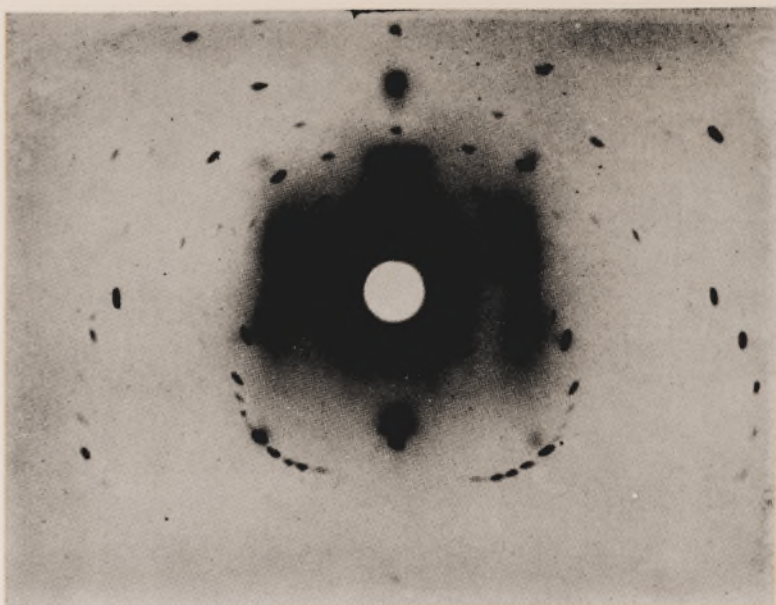
(a)

Sorbic acid: [010] vertical: 4 cm.; filtered Cu radiation at  $70^{\circ} \cdot 6$  to [001] in obtuse  $\beta$ .  
Note arrangement of diffuse spots in layer lines and compare 5b.



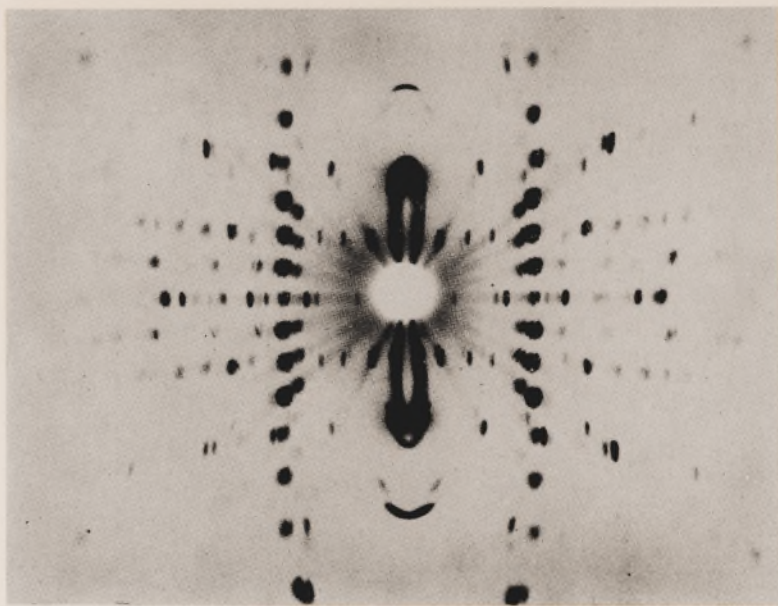
(b)

Sorbic acid: [010] vertical: 4 cm.; rotation using unfiltered Cu radiation. Shows layer lines corresponding to  $4 \cdot 03 \text{ \AA}$  periodicity, and also strong ' $\alpha$  constant' curves due to white radiation.



(a)

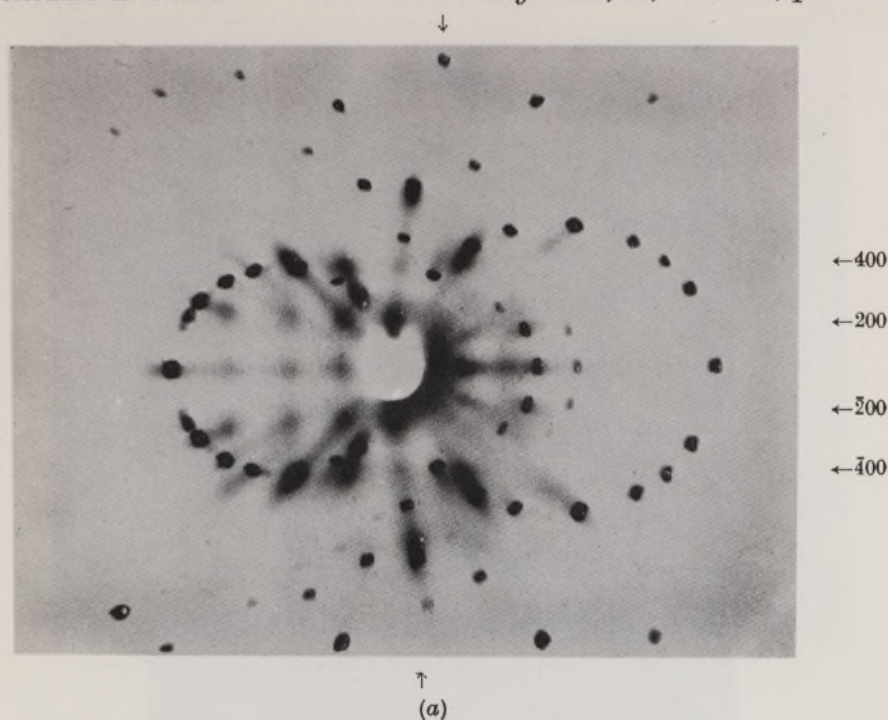
Sorbic acid: [001] vertical: 4 cm.; unfiltered Cu radiation nearly along [110]. Shows strong diffuse spots corresponding with strong spots on rotation photograph below.



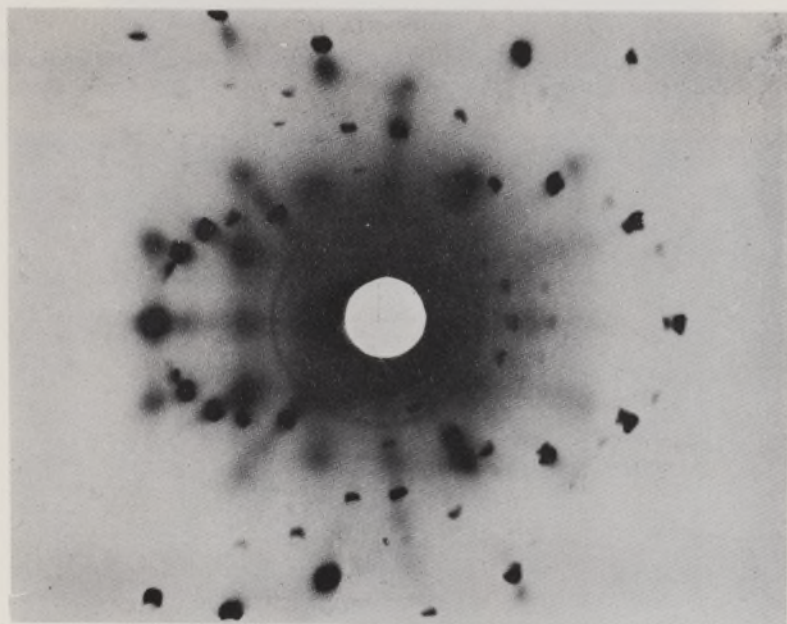
(b)

Sorbic acid: [001] vertical: 4 cm.; rotation using unfiltered Cu radiation: 1 min. exposure. Layer lines close together corresponding to  $15.83\text{\AA}$  periodicity. Note strong spots on (11 $\bar{l}$ ) row line, and compare with 6*a*.

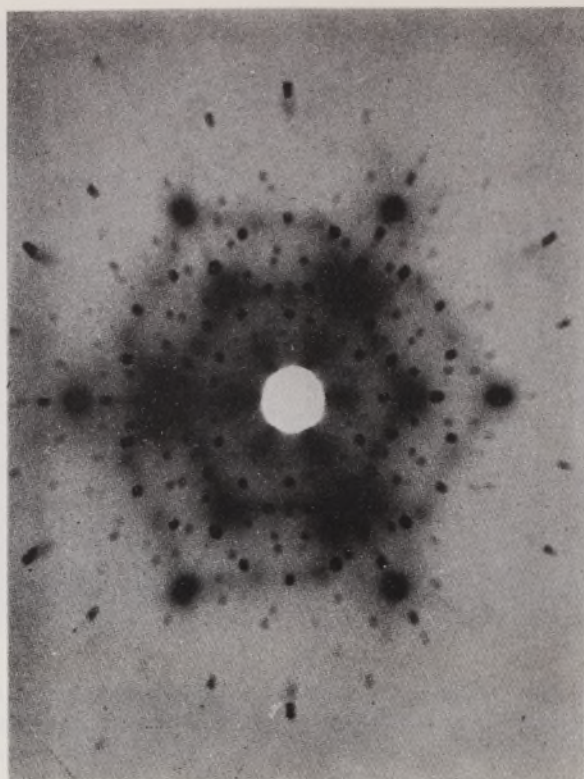




Sylvine: [100] vertical:  $\sim 3.5$  cm.; unfiltered Ag radiation at  $20^\circ$  to [010] axis. Note displacement of diffuse 200, 400 spots out of vertical plane of incidence.

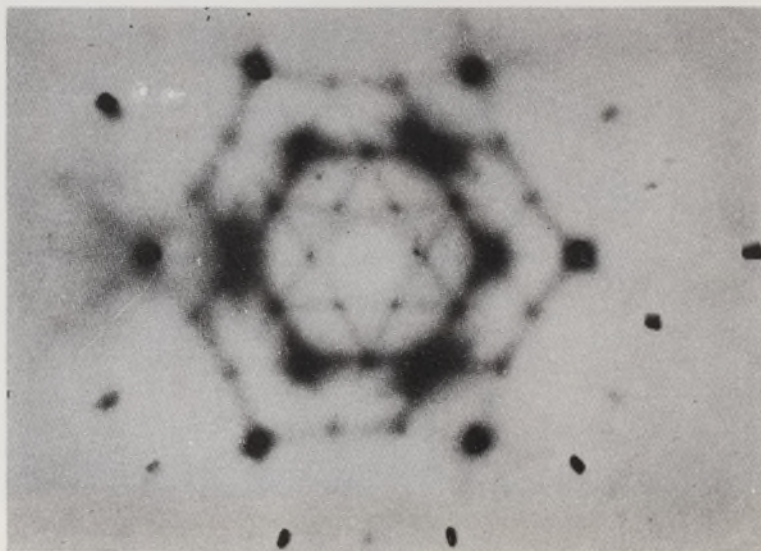


Sylvine: [100] vertical:  $\sim 3.5$  cm.; unfiltered Mo radiation at  $20^\circ$  to [010] axis. Note that while the Laue pattern is relatively unaltered, the diffuse pattern has expanded compared with that due to Ag radiation.



(a)

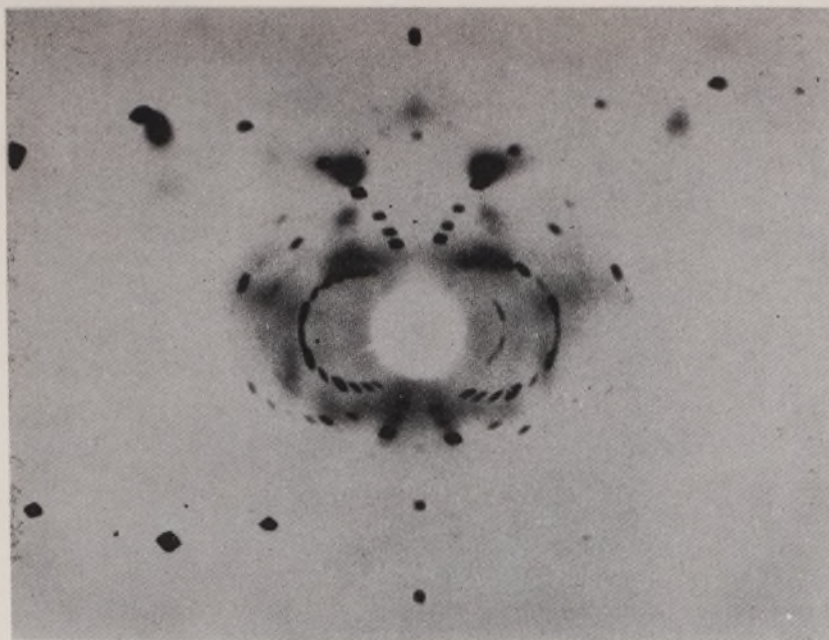
Benzil:  $[11\bar{2}0]$  vertical: 3.5 cm.; unfiltered Cu radiation along  $[0001]$ ; 10 min. exposure. Note background diffuse pattern, especially near central spot.



(b)

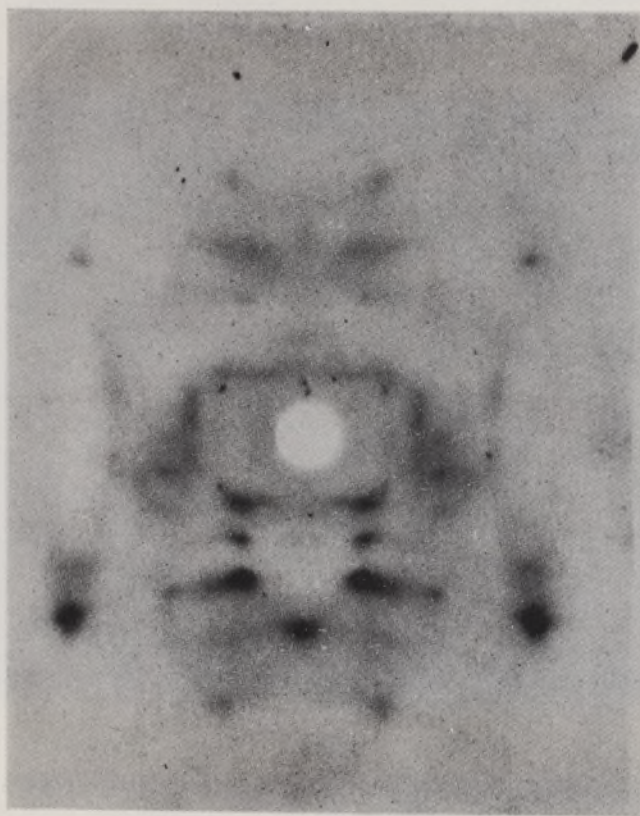
Benzil:  $[11\bar{2}0]$  vertical: 3.5 cm.; monochromatized Cu  $K\alpha$  radiation very nearly along  $[0001]$ ; 2 hr. exposure. Note disappearance of radial streaks near to central spot and general cleanness of background in that region. Non-radial streaks correspond to  $[11\bar{2}0]$  and  $[40\bar{4}0]$  periodicities.





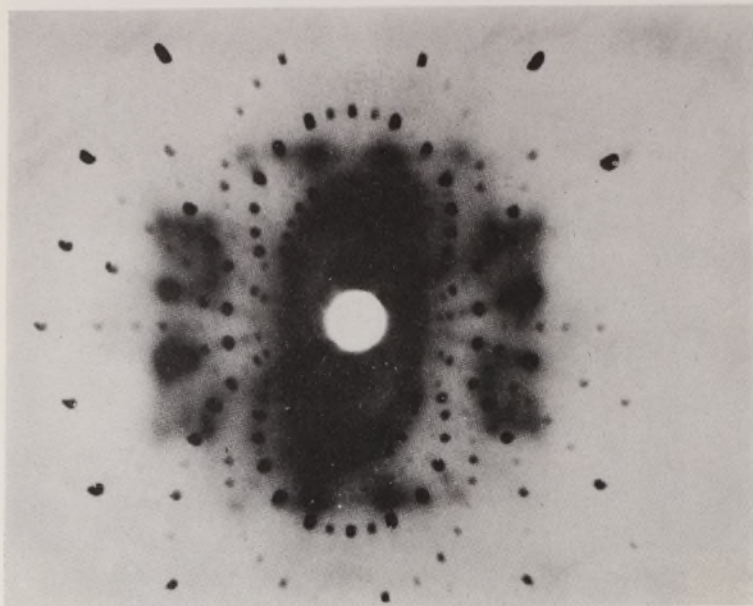
(a)

Benzil: [0001] vertical: 3.5 cm.; filtered Cu radiation along [10 $\bar{1}$ 0]; 10 min. exposure.



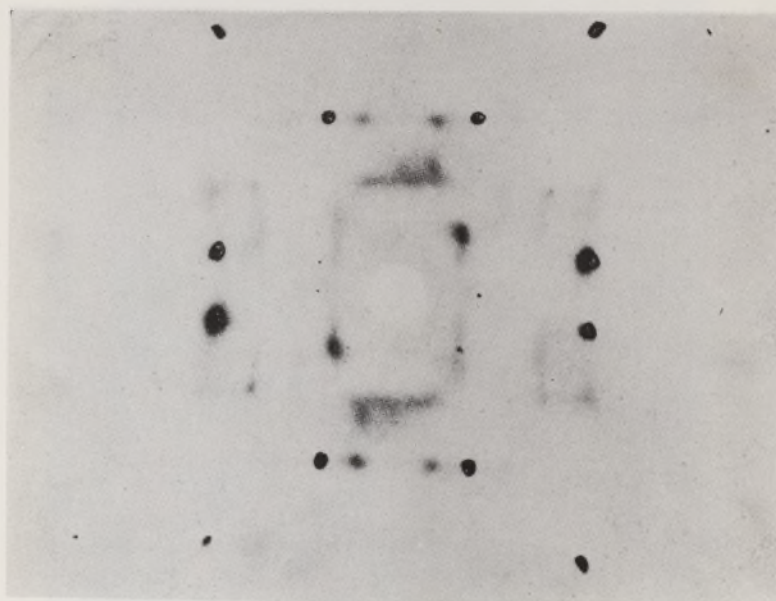
(b)

Benzil: [0001] vertical: 3.5 cm.; monochromatized Cu  $K\alpha$  radiation along [10 $\bar{1}$ 0]: 1 hr. exposure. Note patches of diffuse radiation and partial streaks.



$\tau(a)$

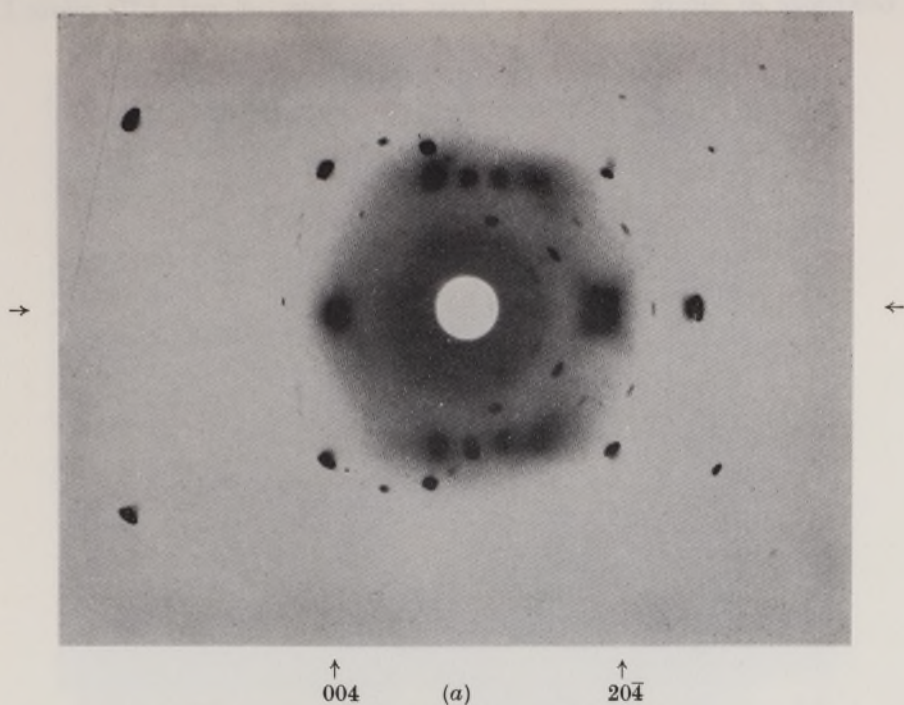
Benzil: [0001] vertical: 3.5 cm.; unfiltered Cu radiation  
along [11 $\bar{2}$ 0]; 10 min. exposure.



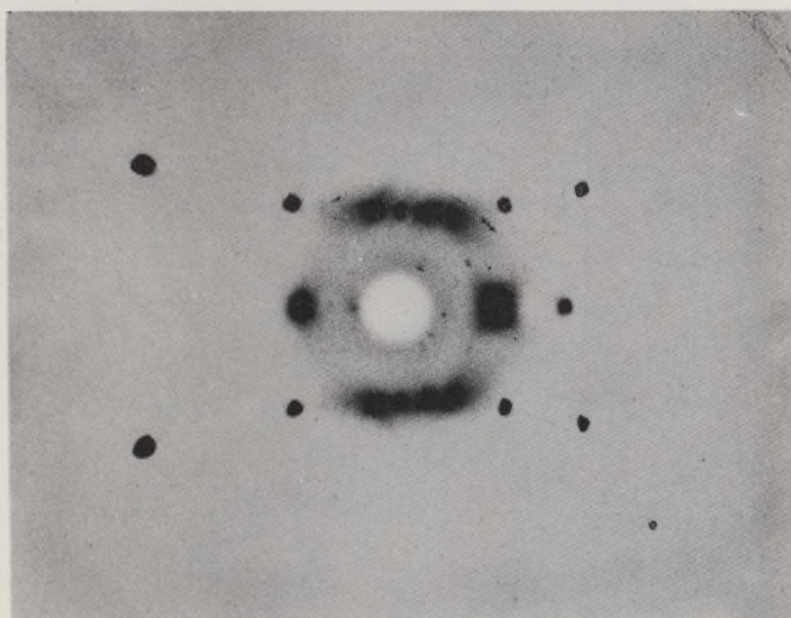
(b)

Benzil: [0001] vertical: 3.5 cm.; monochromatized Cu  $K\alpha$   
radiation along [11 $\bar{2}$ 0]; 1½ hr. exposure.



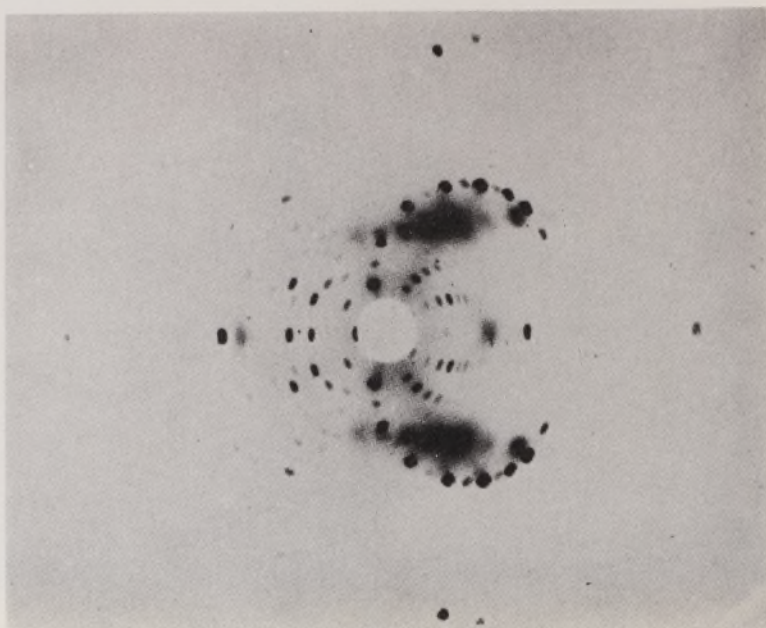


Sorbic acid: [010] vertical: 4 cm.; filtered Cu radiation nearly normal to (100); 10 min. exposure. Note streaks through  $20\bar{4}$  diffuse spot.



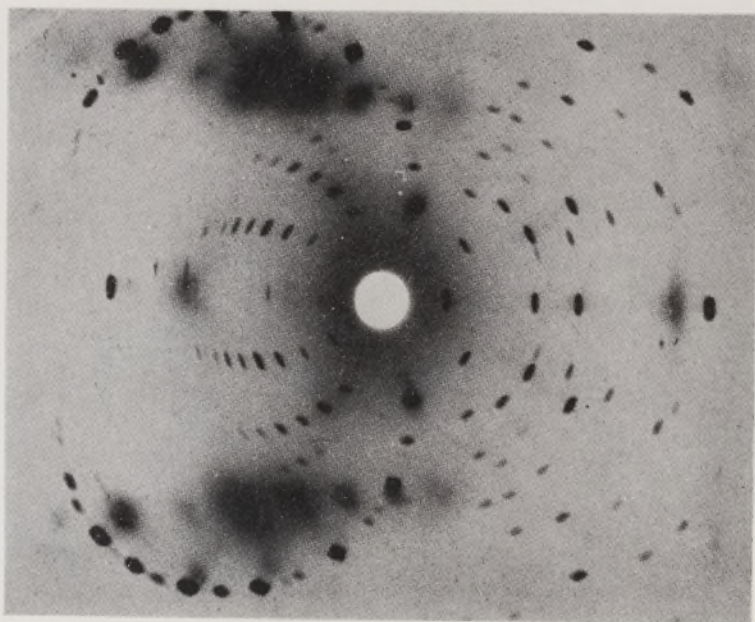
(b)

Sorbic acid: [010] vertical: 3 cm.; monochromatized Cu  $K\alpha$  radiation nearly normal to (100); 2 hr. exposure. Note almost complete disappearance of diffuse scattering in neighbourhood of central spot.



(a)

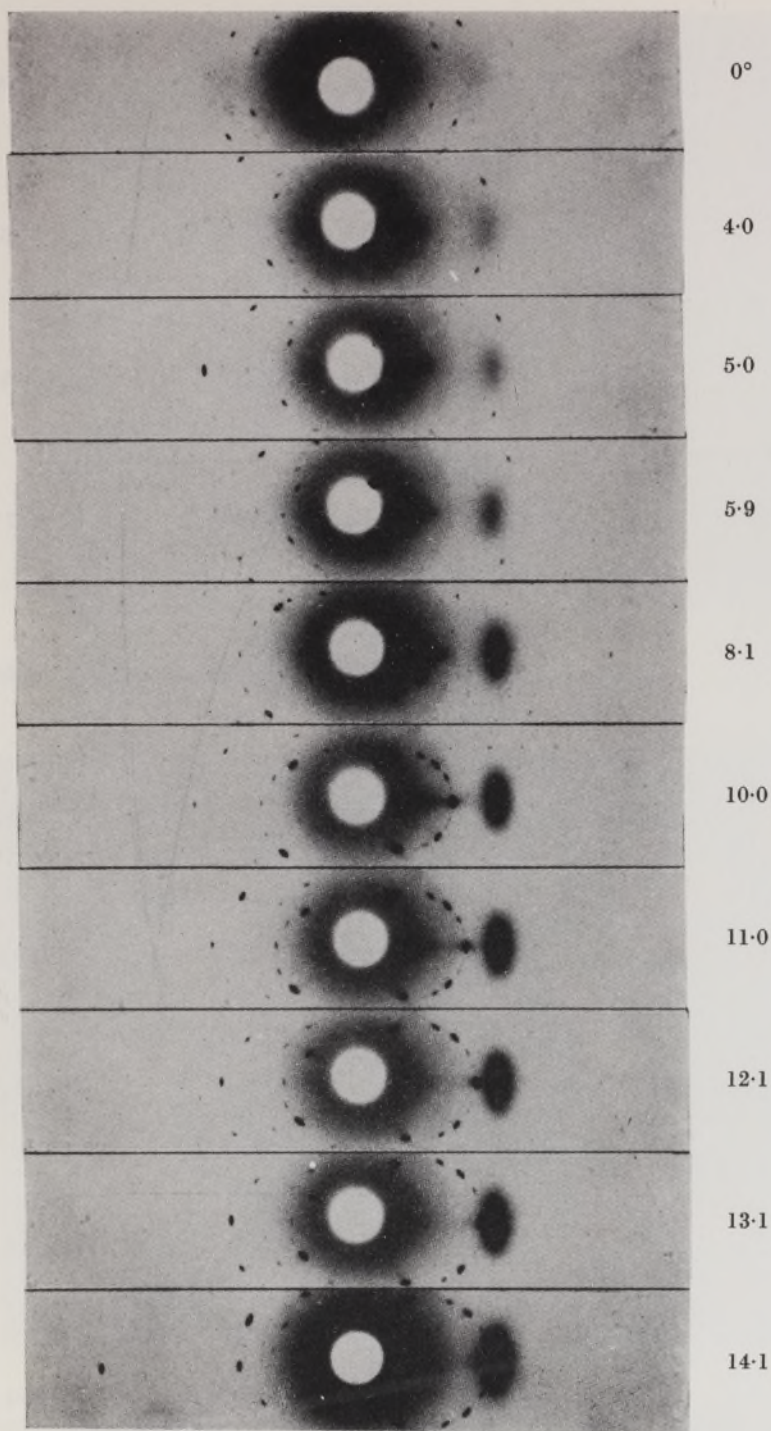
Sorbic acid: filtered Cu radiation: 3 cm.

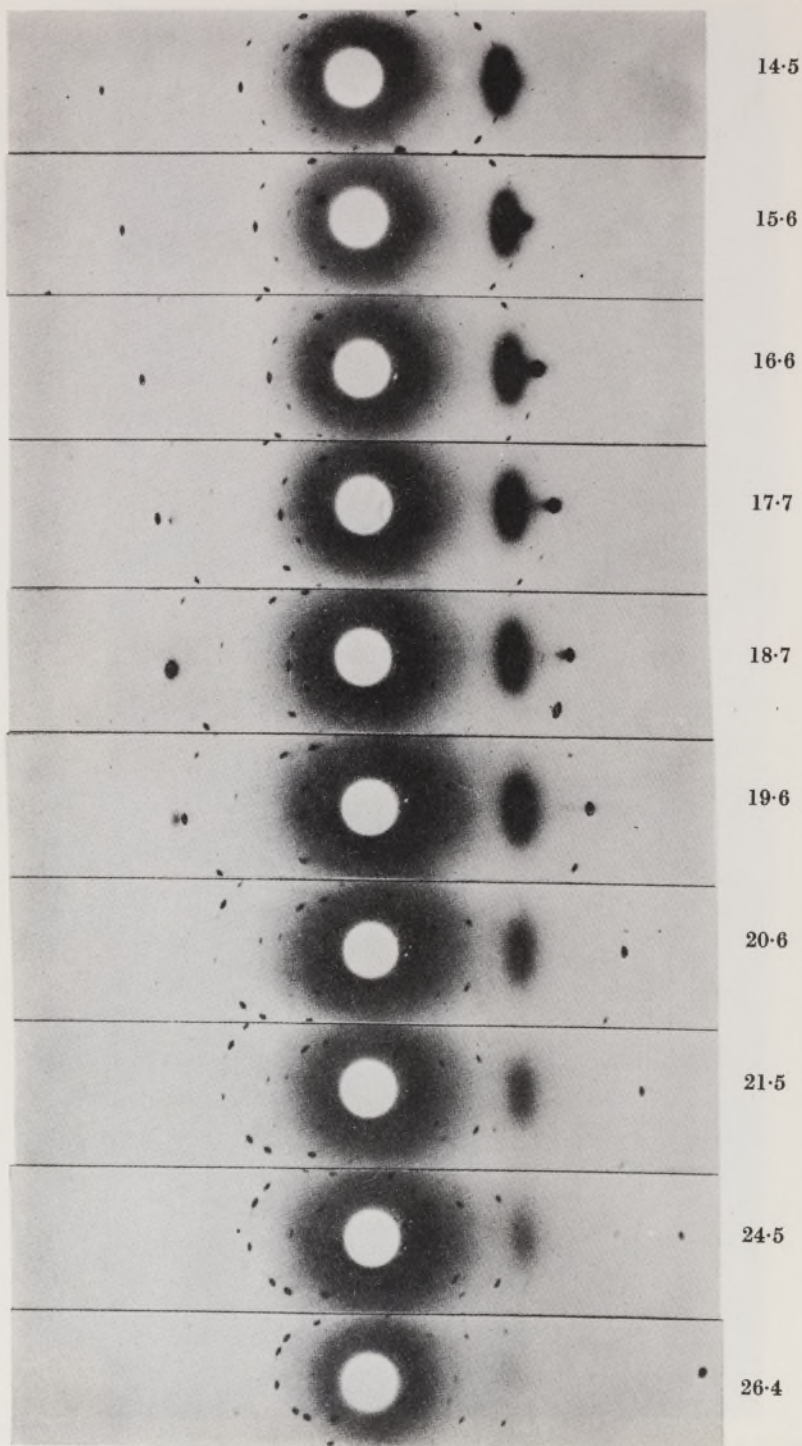


(b)

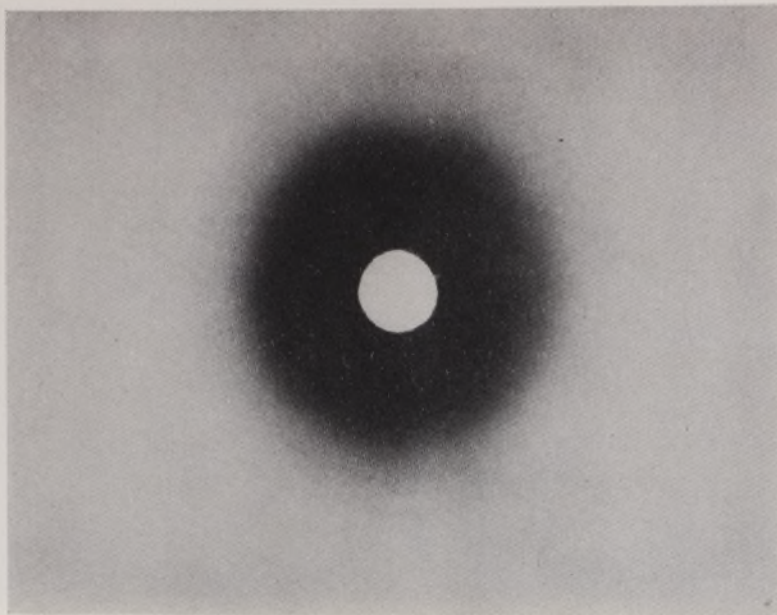
Sorbic acid: filtered Cu radiation: 6 cm. Same setting as 12a; exposure 4 times as long. Note increase of size of both Laue and diffuse spots.





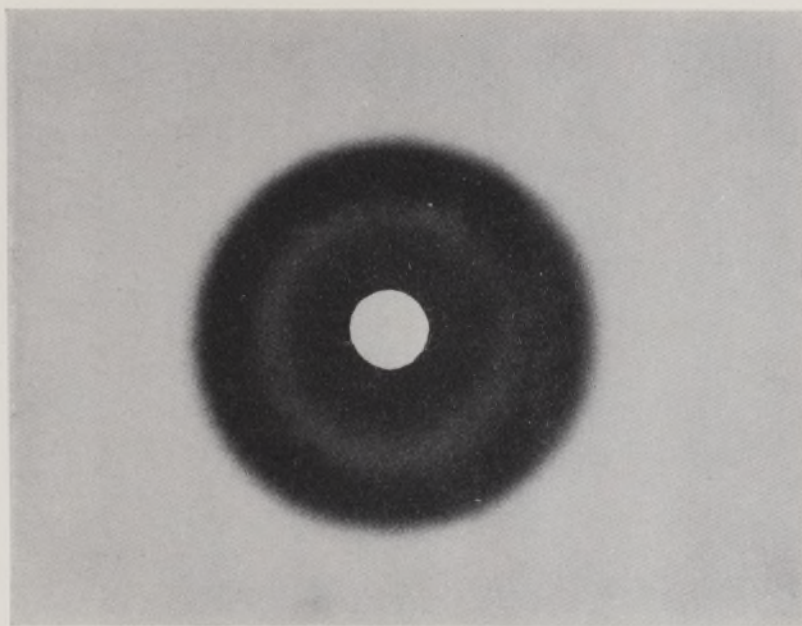






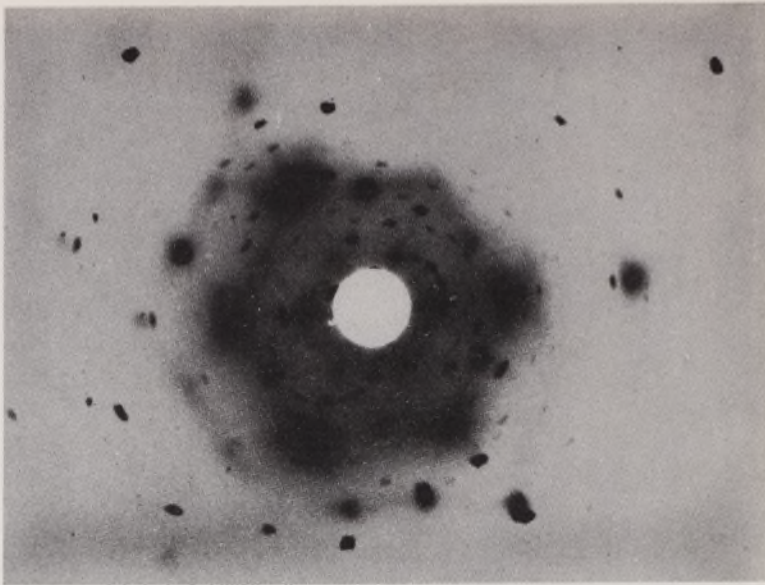
(a)

Empty cellophane tube: unfiltered Cu radiation: 4 cm.



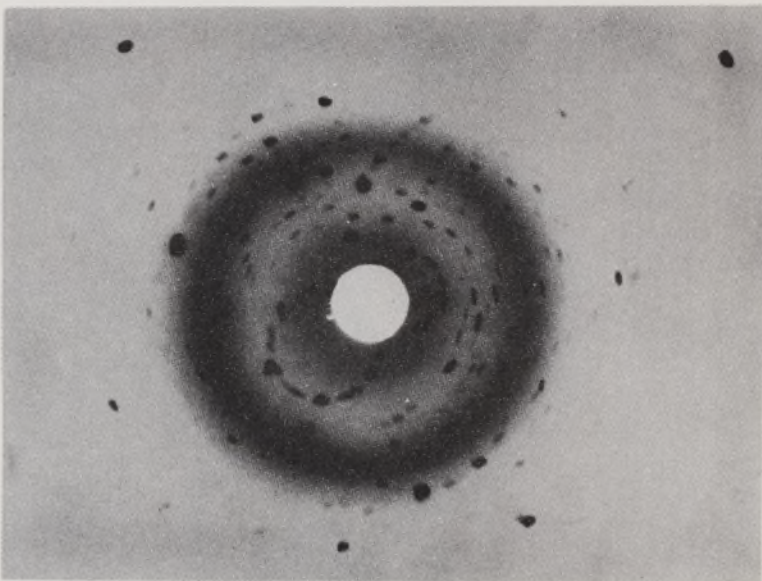
(b)

Liquid air streaming over empty cellophane tube: unfiltered Cu radiation: 4 cm.



(a)

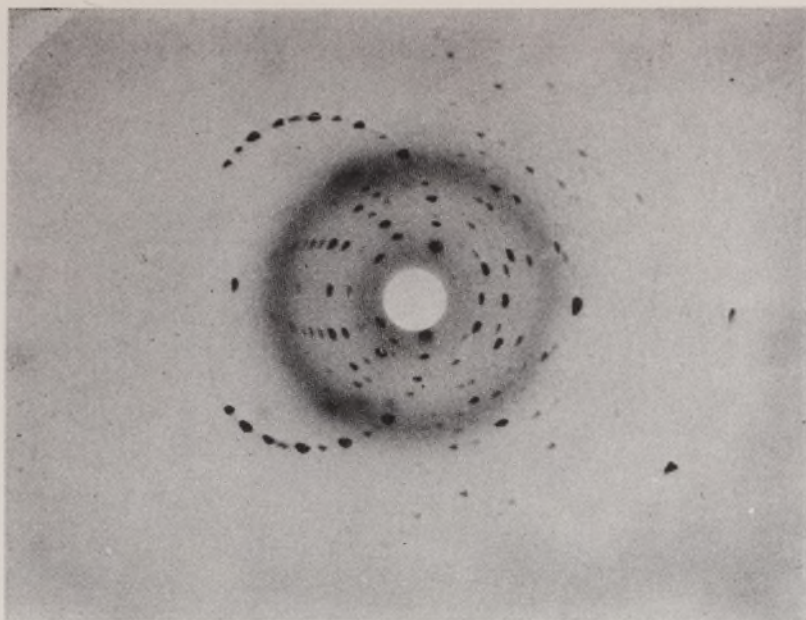
Benzil: filtered Cu radiation at about  $7^\circ$  to  $[0001]$ : 4 cm.; room temperature; photographs taken before and after liquid air experiment are identical.



(b)

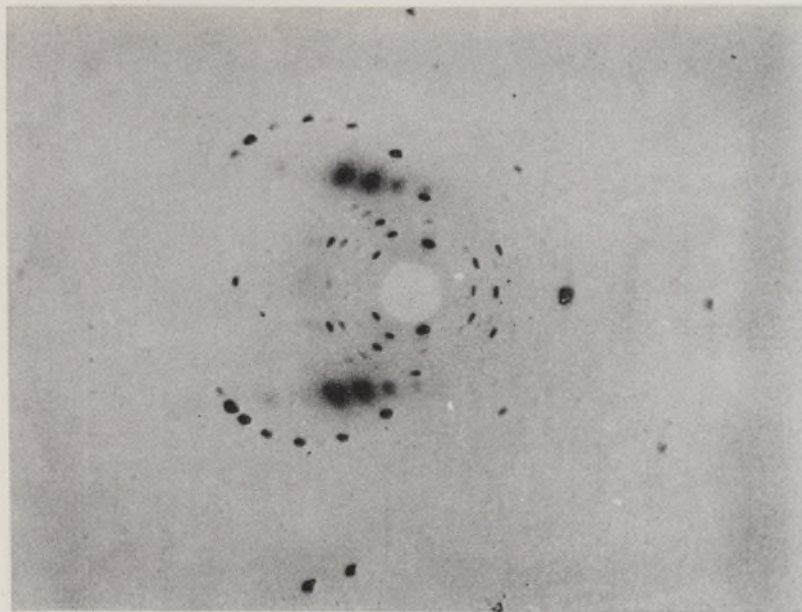
Benzil: same exposure and setting at liquid air temperature,  $\sim -180^\circ \text{C}$ . Only a trace of the strongest diffuse spots remains; many more Laue spots visible.





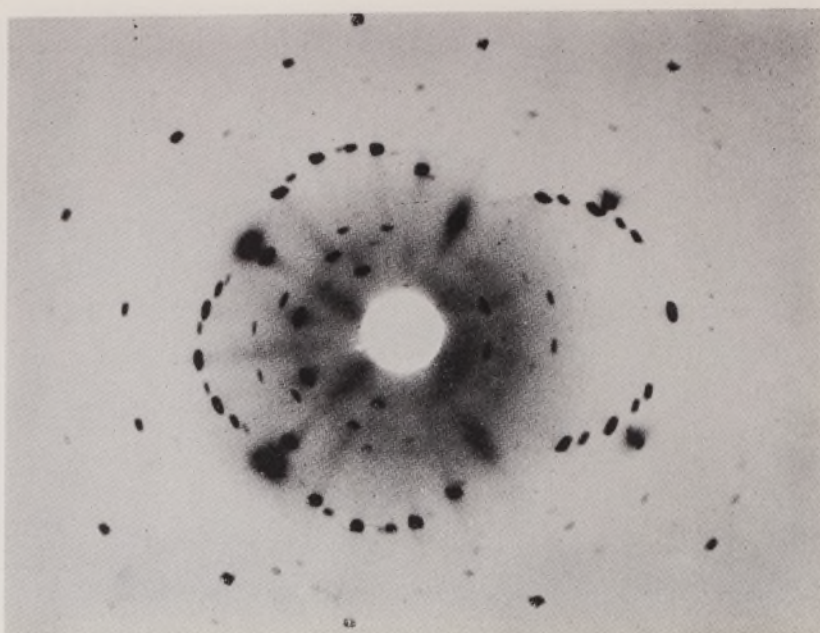
(a)

Sorbic acid: filtered Cu radiation; 3.2 cm.;  $17\frac{1}{2}$  min. exposure at liquid air temperature. Only a trace of diffuse spots present.



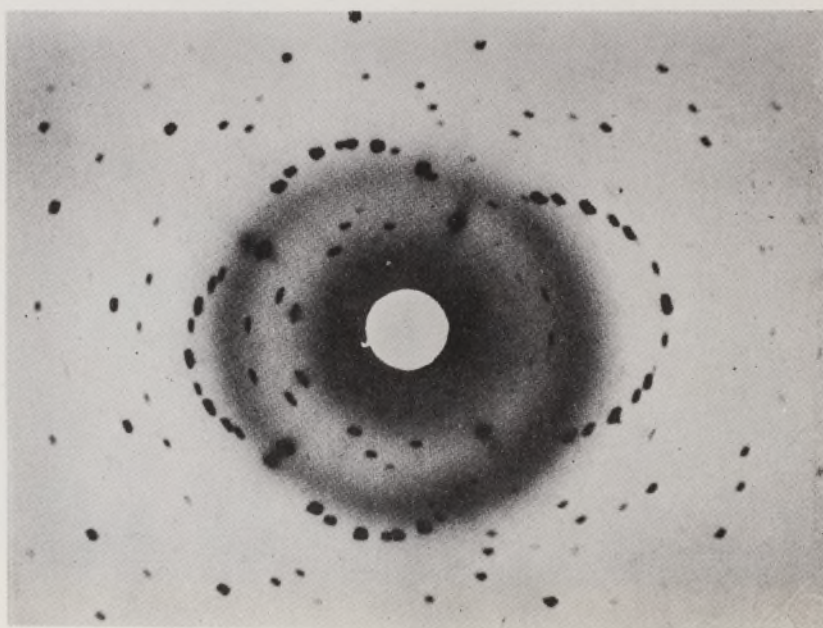
(b)

Sorbic acid: setting as above; filtered Cu radiation; 3.2 cm.; 10 min. exposure at room temperature. Many diffuse spots visible, but Laue pattern not so good as at low temperature.



(a)

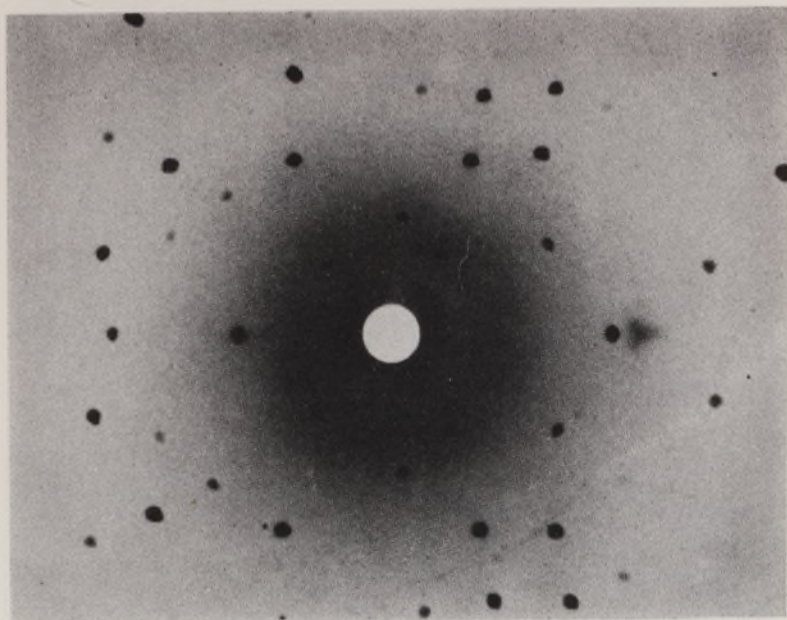
$\text{NaNO}_3$ : filtered Cu radiation nearly normal to cleavage plane: 4 cm.; 10 min. exposure at  $25^\circ \text{C}$ . Photographs before and after liquid air experiment were identical.



(b)

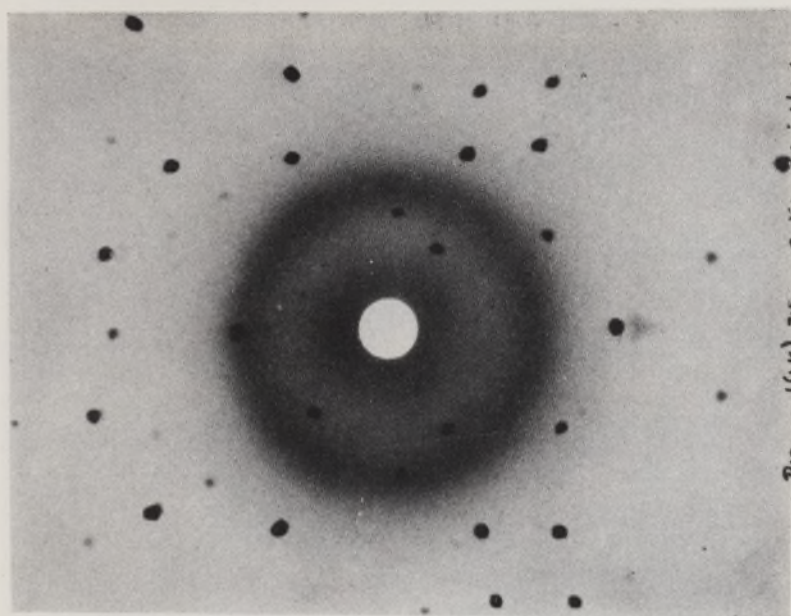
$\text{NaNO}_3$ : same setting and exposure as above, but at liquid air temperature,  $\sim -180^\circ \text{C}$ . Laue pattern much improved, but only a trace of diffuse spots or streaks remains.





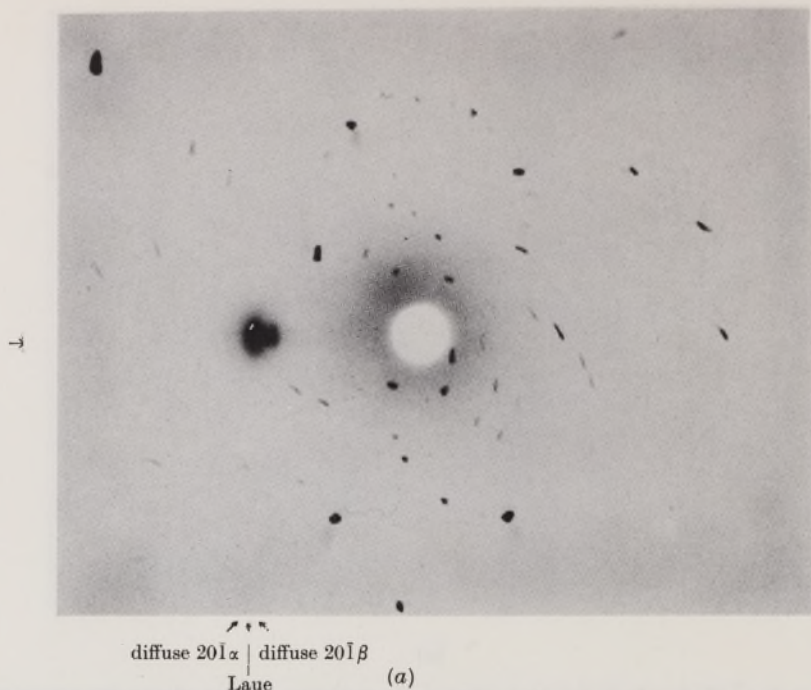
(a)

Diamond: [110] vertical; 3.5 cm.; filtered Cu radiation, giving triangular group of 111 diffuse spots, at room temperature. Photographs before and after liquid air experimental identical.

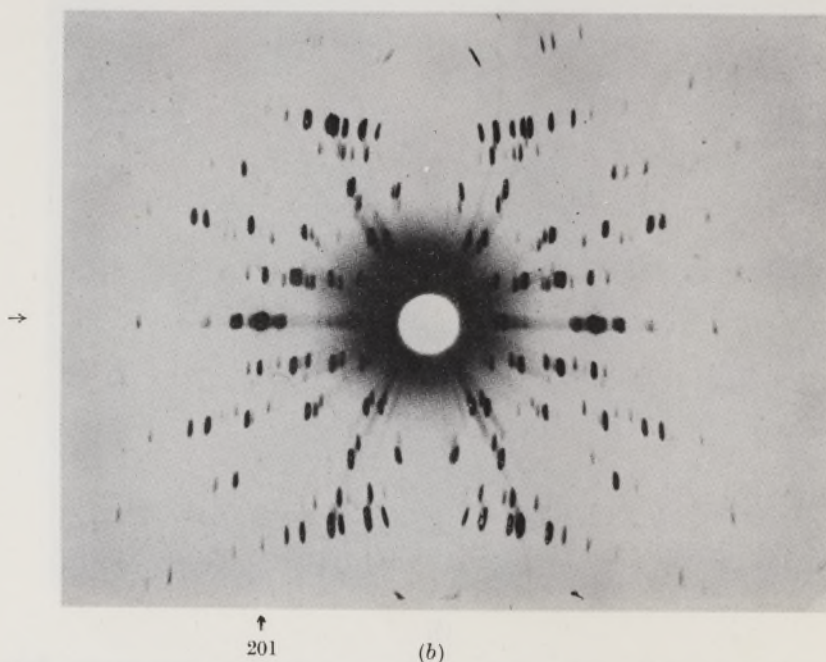


(b)

Diamond: same setting and exposure as above, at liquid air temperature. Very little change either in Laue pattern or in intensity of diffuse group. The latter appears to be slightly diminished.

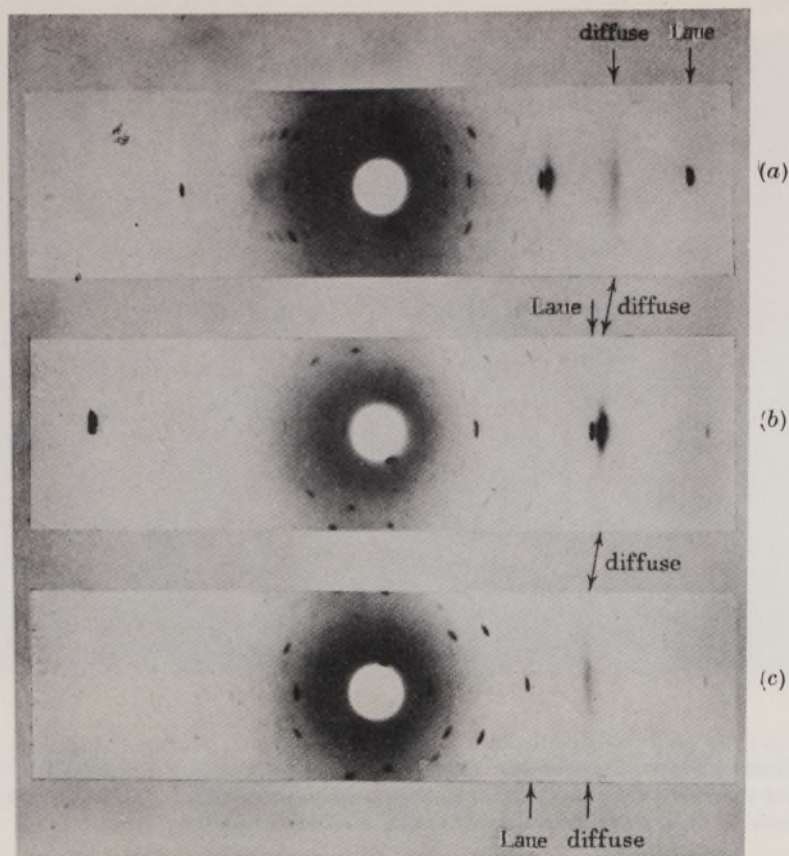


Urea oxalate: (010) ( $20I$ ) planes vertical: unfiltered Cu radiation at  $14^\circ.1$  to  $[010]$ . Sharply sloping  $20I$  Laue spot lies between corresponding diffuse spots due to Cu  $K\alpha$  and  $\beta$  radiations respectively.

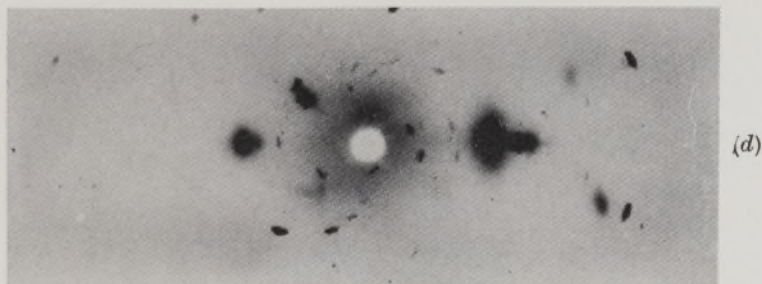


Urea oxalate: (010) ( $20I$ ) planes vertical: rotation, using unfiltered Cu radiation, about needle axis of crystal. Compare shape of spots with those in Laue photograph above.





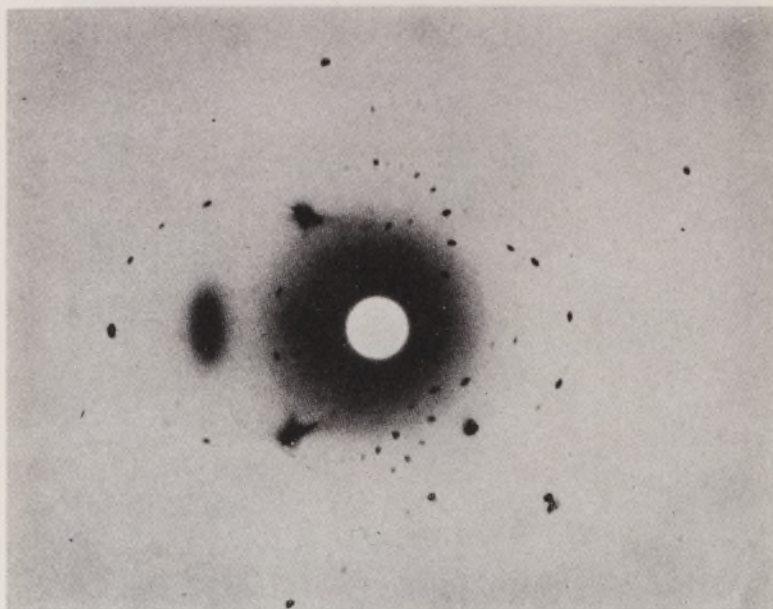
Sorbic acid: showing changes in position, intensity and shape of 604 diffuse spot as angle of incidence changes.



Hexamethylbenzene: [010] vertical; 4 cm.; unfiltered Cu radiation; showing intense diffuse spot corresponding to layer plane (001); small angle of missetting.

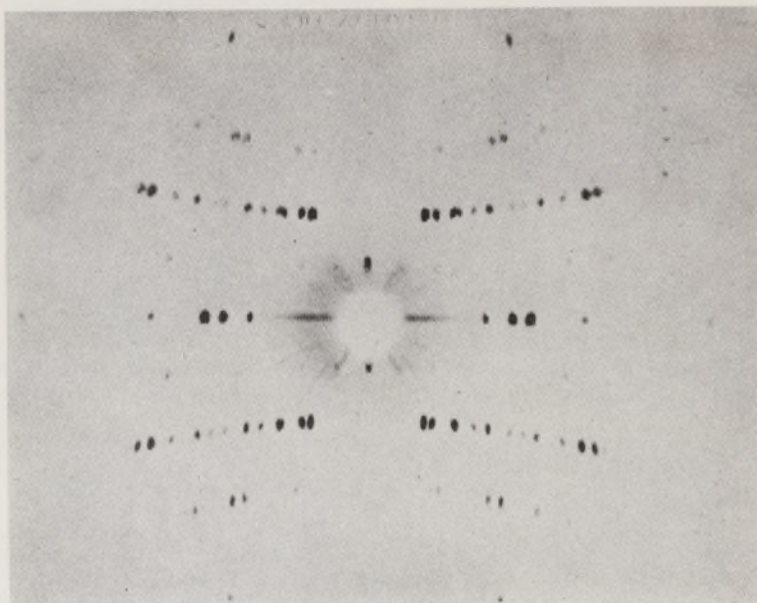


Hexamethylbenzene: [010] vertical; 4 cm.; unfiltered Cu radiation; showing strong 002 diffuse spot at a small angle of missetting and very weak 001 diffuse spot at a large angle of missetting, both to right of central spot.



(a)

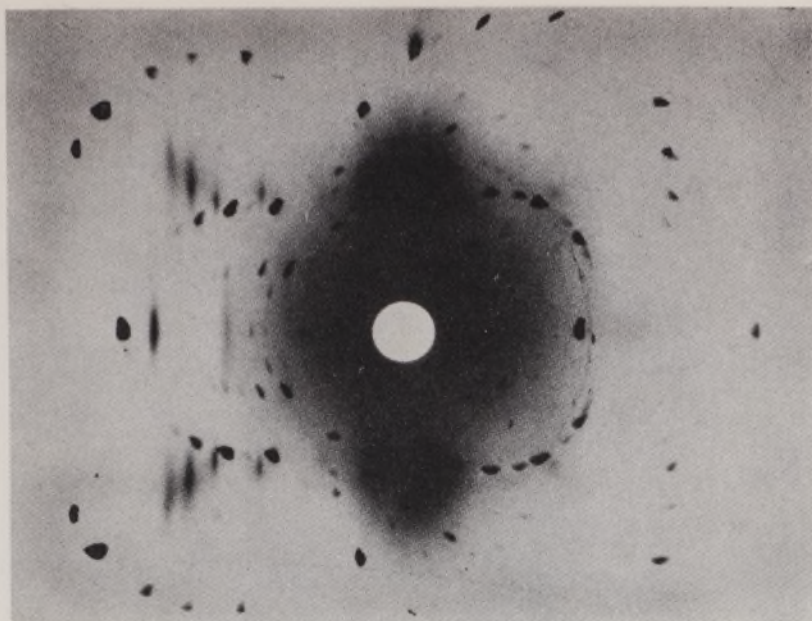
Urea nitrate: filtered Cu radiation; showing how diffuse spot corresponding to (002) layer plane stands out, even for a large angle of missetting. Other diffuse spots, nearer to their appropriate Laue spots, are much smaller.



(b)

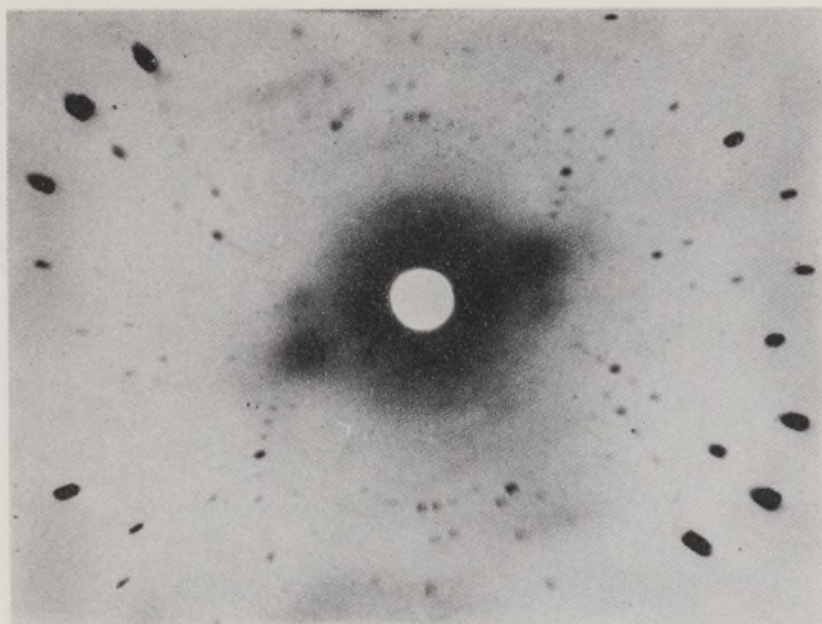
Urea nitrate: filtered Cu radiation; [100] rotation, corresponding to Laue photograph above. No outstanding reflexion from layer plane for moderate exposure.





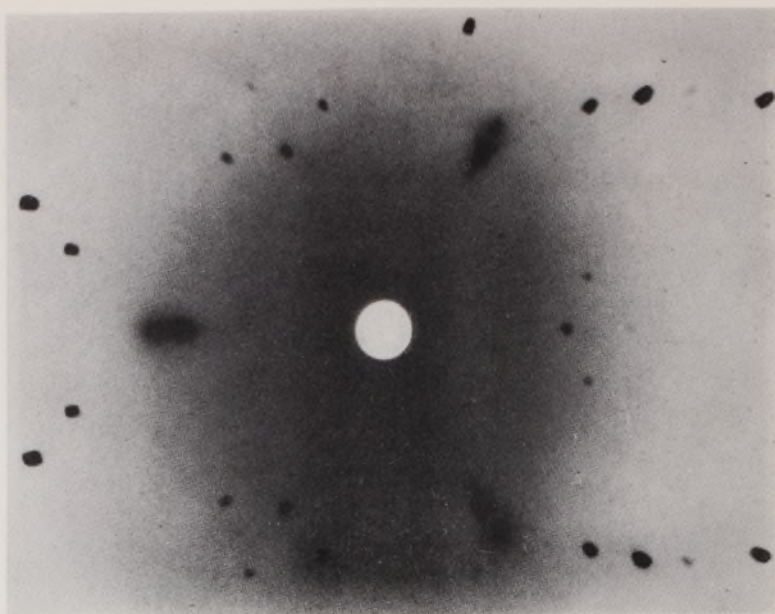
(a)

Sorbic acid: [010] vertical; 4 cm.; unfiltered Cu radiation at  $20^{\circ}6$  to [001] in obtuse  $\beta$ . Note the two types of diffuse spot; intense and broad on the one hand, comparatively weak and elongated on the other.



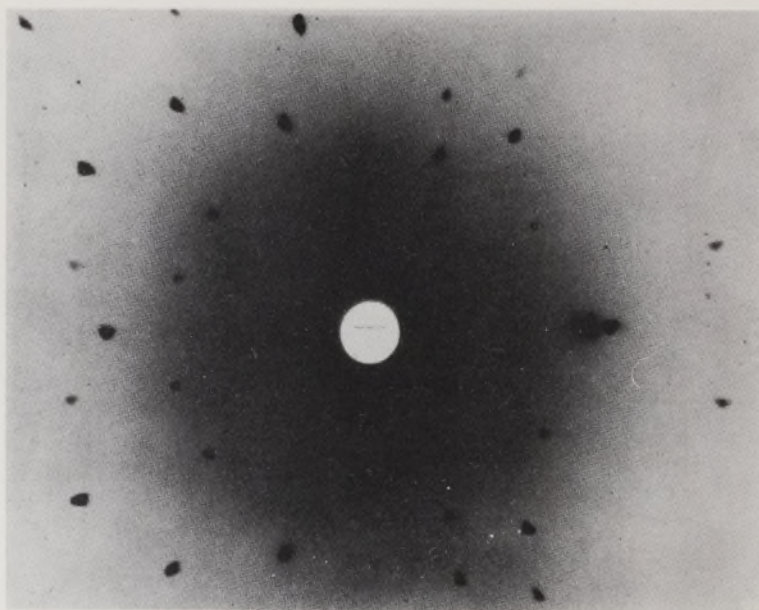
(b)

Sorbic acid: [100] vertical; 4 cm.; filtered Cu radiation along [010] axis. Projected length of molecule lies parallel to plane  $(20\bar{4})$ , giving very intense  $20\bar{4}$  diffuse spots. Lengths of streaky spots are perpendicular to this direction (cf. figure 2).



(a)

Diamond:  $[\bar{1}10]$  vertical; 3.2 cm.; unfiltered Cu radiation nearly normal to a (111) plane. Note nearly circular diffuse spots accompanied by streamers; also relative sizes of Cu  $K\alpha$  and  $\beta$  diffuse spots.

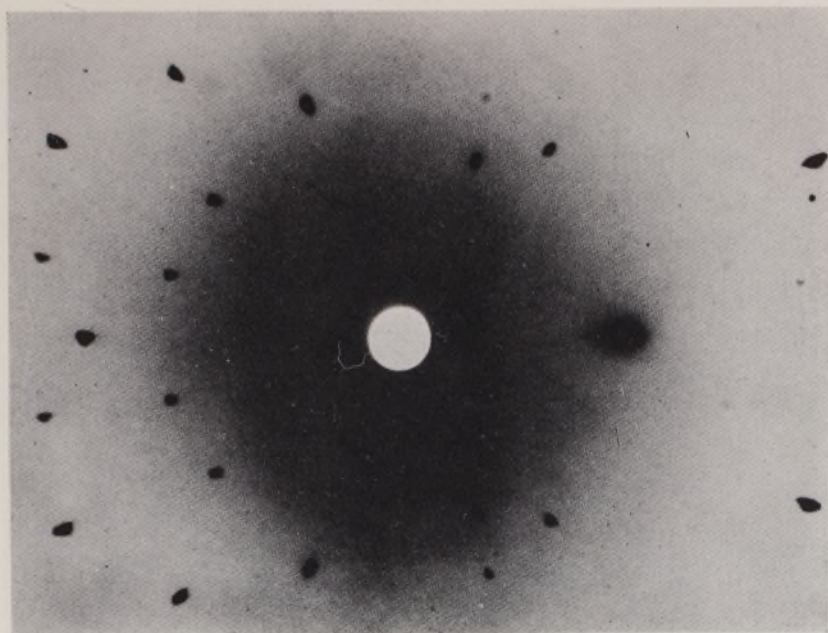


(b)

diffuse group  $\uparrow \uparrow$  Laue

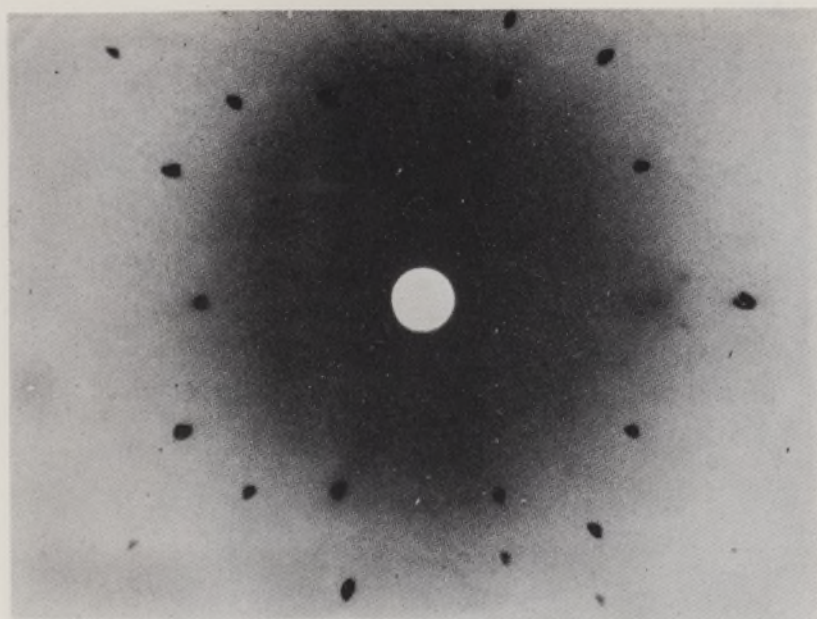
Diamond:  $[\bar{1}10]$  vertical; 2.97 cm.; unfiltered Cu radiation at  $-23^\circ.75$  and  $+46^\circ.75$  to  $\{111\}$  planes. Note triangular group of diffuse spots with apex away from 111 Laue spot; compare plate 19.





(a)

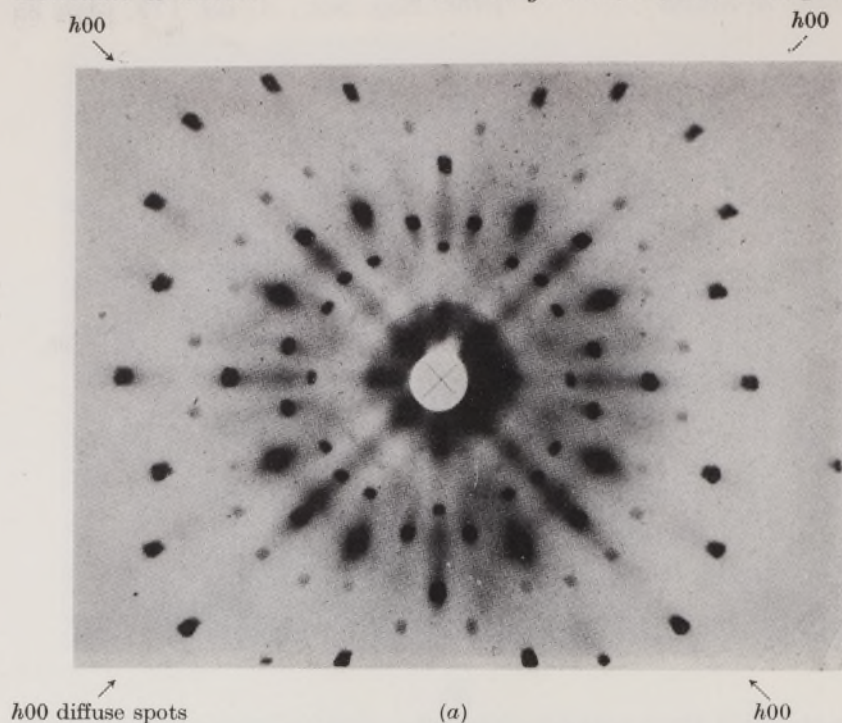
Diamond: [110] vertical; 2.97 cm.; unfiltered Cu radiation at  $-21^{\circ}.9$  and  $+48^{\circ}.6$  to {111} planes. Diffuse Cu  $K\alpha$  spot coincides with Laue spot; weak triangular group of  $\beta$  diffuse spots clearly visible on original film.



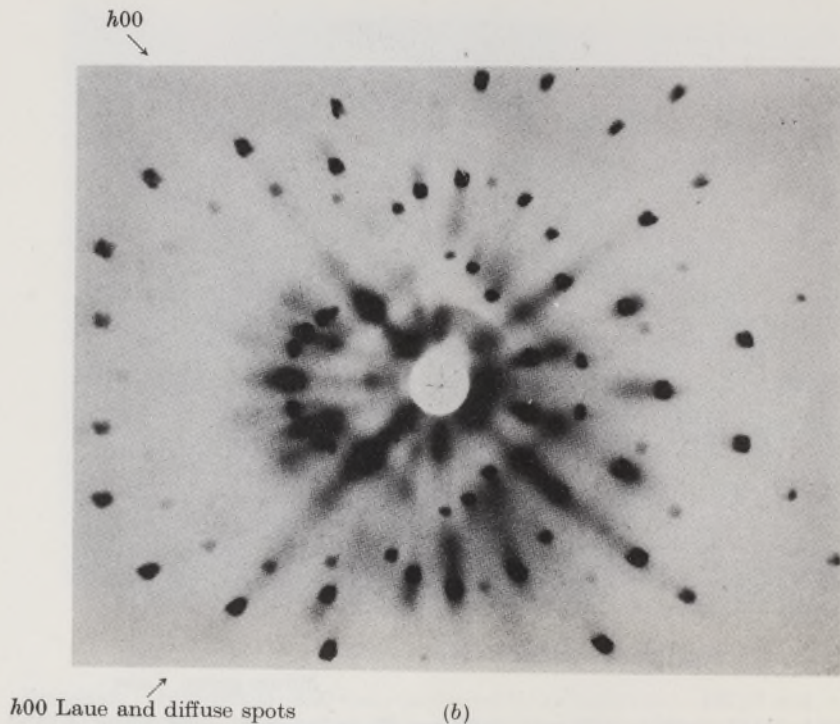
(b)

↑  
diffuse group    Laue

Diamond: [110] vertical; 3.03 cm.; unfiltered Cu radiation at  $-26^{\circ}.8$  and  $+43^{\circ}.7$  to {111} planes. Note wide separation of components of Cu  $K\alpha$  diffuse group, and sharpness of definition of the three outer spots.

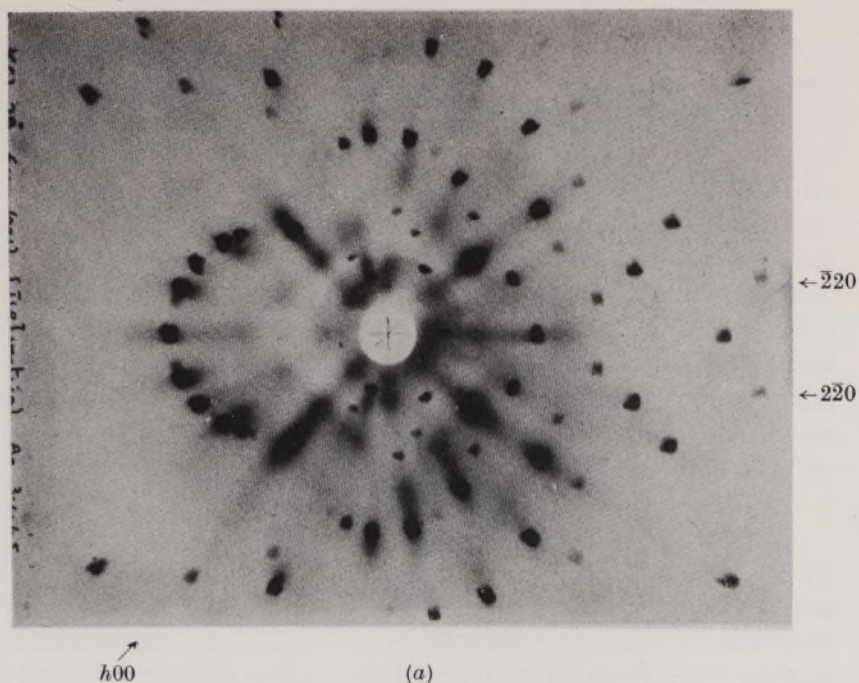


Sylvine:  $[110]$  vertical;  $\sim 3.5$  cm.; unfiltered Ag radiation along  $[001]$ . Diffuse spots corresponding to  $\{200\}$   $\{400\}$   $\{620\}$  along diagonals, and to  $\{220\}$   $\{221\}$  along vertical.

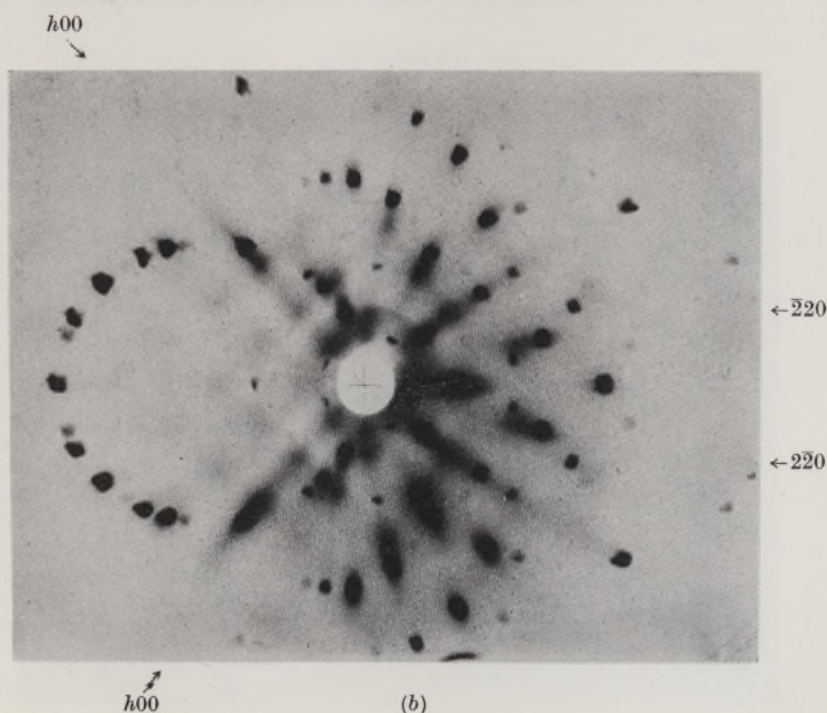


Sylvine:  $[110]$  vertical;  $\sim 3.5$  cm.; unfiltered Ag radiation at  $15^\circ$  to  $[001]$ .

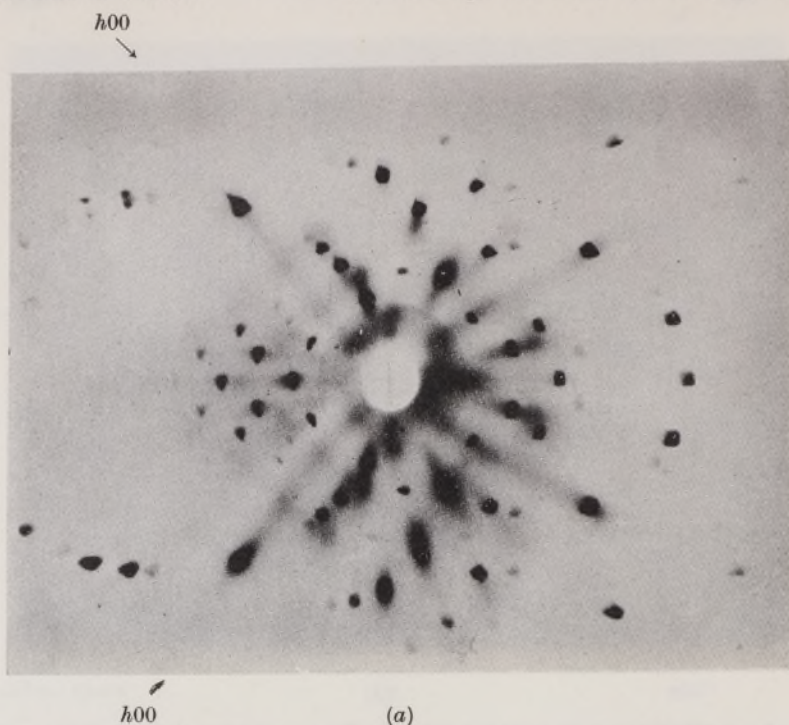




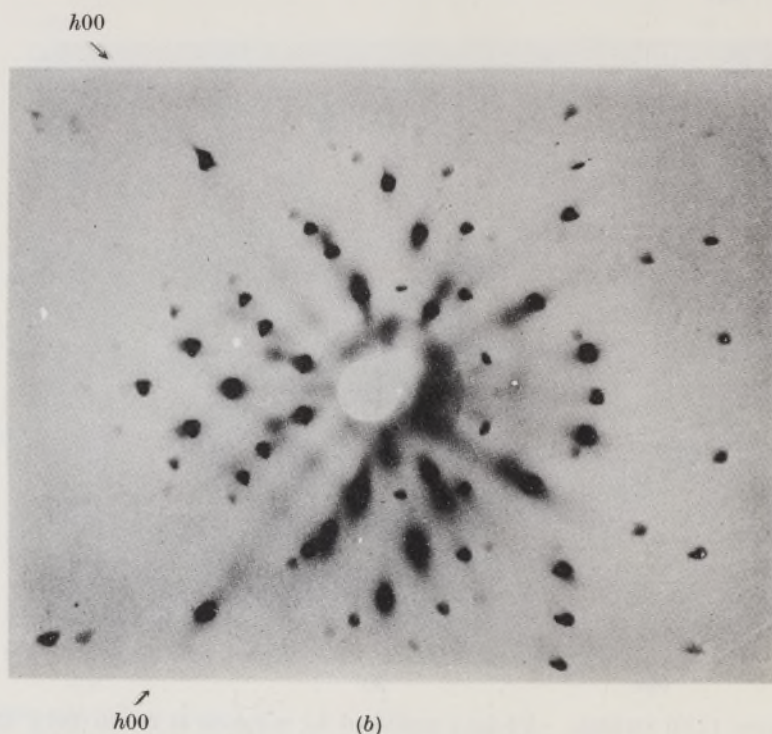
Sylvine:  $[110]$  vertical:  $\sim 3.5$  cm.; unfiltered Ag radiation at  $20^\circ$  to  $[001]$ . Note displacement of  $220$  diffuse spots out of vertical plane of incidence.



Sylvine:  $[110]$  vertical;  $\sim 3.5$  cm.; unfiltered Ag radiation at  $25^\circ$  to  $[001]$ . Diffuse spots corresponding to 200, 400, 600 reflexions seen on diagonal streaks, together with  $h00$  Laue spots.



Sylvine:  $[110]$  vertical;  $\sim 3.5$  cm.; unfiltered Ag radiation at  $30^\circ$  to  $[001]$ . Note curvature of the streak on which the 200, 400, 600, 800 diffuse spots lie.



Sylvine:  $[110]$  vertical;  $\sim 3.5$  cm.; unfiltered Ag radiation at  $35^\circ$  to  $[001]$ . Curvature of streak connecting 200, 400, 600, 800 diffuse spots is even more marked.



tion of diffuse to Bragg reflexions in reciprocal space. The diffuse reflexions correspond to points in reciprocal space, on the sphere of reflexion, which are not far from (relatively strongly reflecting) reciprocal lattice points. Thus each such reciprocal lattice point (corresponding to an infinite set of crystal planes) may be regarded as being surrounded by a cloud of reflecting points, whose physical significance is open to various interpretations. Future experiments must involve a detailed exploration of such diffusely reflecting regions, which are certainly not, in general, spherical, being extended along reciprocal lattice planes and axes. The non-radial streaks correspond to reflexion in the near neighbourhood of reciprocal lattice planes or axes, and the non-existence of monochromatic radial streaks (except for large angles of deflexion) is readily understood, since these would correspond to reflexions near to the reciprocal lattice origin, that is, to relatively large spacings.

We are indebted to the Managers of the Royal Institution for laboratory facilities and especially to Sir William Bragg for the keen interest he has taken in this research. We have derived much help from conversations with our fellow-workers in the laboratory and we are particularly grateful to Dr I. E. Knaggs for handing over to us the material indicated in the text as being her work.

#### REFERENCES

- Barrett and Geisler 1940 *J. Appl. Phys.* **11**, 733.  
 Bernal 1926 *Proc. Roy. Soc. A*, **113**, 117.  
 Bragg 1940 *Nature, Lond.*, **146**, 509.  
 Brill, Grimm, Hermann and Peters 1939 *Ann. Phys., Lpz.*, **34**, 393.  
 Brillouin 1922 *Ann. Phys., Paris*, **17**, 88.  
 Brockway and Robertson 1939 *J. Chem. Soc.* p. 1324.  
 Calvet, Jacquet and Guinier 1938 *C.R. Acad. Sci., Paris*, **206**, 1972.  
 Calvet, Jacquet and Guinier 1939 *J. Inst. Met.* **6**, 177.  
 Charlesby, Finch and Williams 1939 *Proc. Phys. Soc.* **51**, 479.  
 Clay 1934 *Proc. Phys. Soc.* **46**, 703.  
 Coven 1932 *Phys. Rev.* **41**, 422.  
 Debye 1914 *Ann. Phys., Lpz.*, **43**, 49.  
 Ewald 1940 *Proc. Phys. Soc.* **52**, 167.  
 Faxén 1923 *Z. Phys.* **17**, 266.  
 Friedrich 1913 *Phys. Z.* **14**, 1082.  
 Guinier 1938 *C.R. Acad. Sci., Paris*, **206**, 1641; *Nature, Lond.*, **142**, 569.  
 Harvey, Williams and Jauncey 1934 *Phys. Rev.* **46**, 365.  
 Jahn and Lonsdale 1941 *Nature, Lond.*, **147**, 88.  
 Jauncey 1941 *Nature, Lond.*, **147**, 146.  
 Jauncey and Baltzer 1940 *Phys. Rev.* **58**, 1116.  
 Jauncey and Pennell 1933 *Phys. Rev.* **43**, 505; **44**, 138.

- Knaggs and Lonsdale 1939 *Nature, Lond.*, **143**, 1023.  
 Knaggs, Lonsdale, Muller and Ubbelohde 1940 *Nature, Lond.*, **145**, 820.  
 Kracek, Posnjak and Hendricks 1931 *J. Amer. Chem. Soc.* **53**, 3339.  
 Laue and Riewe 1936 *Z. Kristallogr.* **95**, 408.  
 Laval 1938 *C.R. Acad. Sci., Paris*, **207**, 169.  
 Laval 1939a *C.R. Acad. Sci., Paris*, **208**, 1512.  
 Laval 1939b *Bull. Soc. franç. Minér.* **62**, 137.  
 Lonsdale 1929 *Proc. Roy. Soc. A*, **123**, 494; *Trans. Faraday Soc.* **25**, 352.  
 Lonsdale 1941 *Proc. Roy. Soc. A*, **177**, 272.  
 Lonsdale, Knaggs and Smith 1940 *Nature, Lond.*, **146**, 332.  
 Lonsdale, Robertson and Woodward 1941 *Proc. Roy. Soc. A* (in the Press).  
 Lonsdale and Smith 1939 *Phil. Mag.* **28**, 614.  
 Mauguin and Laval 1939 *C.R. Acad. Sci., Paris*, **208**, 1446.  
 Muller and Clay 1939 *J. Inst. Elect. Engrs*, **84**, 261.  
 Preston 1938 *Nature, Lond.*, **142**, 570.  
 Preston 1939 *Nature, Lond.*, **143**, 76; *Proc. Roy. Soc. A*, **172**, 116.  
 Preston 1940 *Proc. Phys. Soc.* **52**, 77.  
 Raman and Nath 1940a *Proc. Indian Acad. Sci.* **12**, 83.  
 Raman and Nath 1940b *Proc. Indian Acad. Sci.* **12**, 427.  
 Raman and Nilakantan 1940a *Nature, Lond.*, **145**, 667, 860; **146**, 523, 686; *Curr. Sci.* **9**, 165.  
 Raman and Nilakantan 1940b *Proc. Indian Acad. Sci.* **11**, 379, 389, 398.  
 Raman and Nilakantan 1940c *Proc. Indian Acad. Sci.* **12**, 141.  
 Raman and Nilakantan 1941 *Nature, Lond.*, **147**, 118.  
 Robertson 1936 *Proc. Roy. Soc. A*, **157**, 79.  
 Siegel and Zachariasen 1940 *Phys. Rev.* **57**, 795.  
 Wadlund 1938 *Phys. Rev.* **53**, 843.  
 Waller 1923 *Z. Phys.* **17**, 398.  
 Waller 1925 Dissertation: Theoretische Studien zur Interferenz- und Dispersions-  
 theorie der Röntgenstrahlen. *Uppsala Univ. Årsskr.*  
 Zachariasen 1940 *Phys. Rev.* **57**, 597; *Nature, Lond.*, **145**, 1019.