International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.

McMurdie, H. F. (1937). *J. Res. Nat. Bur. Stand.* **18**, 475. (R. P. 987.)

Malquori, G. L. & Cirilli, V. (1952). *Proc. International Symposium on the Chemistry of Cement*, p. 120. London.

Midgley, H. G. (1952). *Proc. International Symposium on the Chemistry of Cement*, p. 140. London.

Midgley, H. G. (1957). *Mag. Concrete Res.* **9**, 17.

Midgley, H. G. (1958). *Mag. Concrete Res.* **10**, 13.

Newkirk, T. F. & Thwaite, R. D. (1958). *J. Res. Nat. Bur. Stand.* **61**, 233. (R. P. 2900.)

Swayze, M. A. (1946). *Amer. J. Sci.* **244**, 65.

Toropov, N. A. & Boikova, A. I. (1955). *Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci.*, p. 887.

Toropov, N. A. & Boikova, A. I. (1956). *Z. neorg. khimii*, **1**, 2106.

Yamauchi, T. (1937). *J. Japan. Ceram. Soc.* **45**, 880.

Acta Cryst. (1962). **15**, 1152

Structure of Mesomorphic Phases

By A. J. Mabis

The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati 39, *Ohio, U.S.A.*

(*Received* 10 *July* 1961)

The classification scheme of Hermann (1931) for mesomorphic phases has been extended by illustrations of the possible structures in both real and reciprocal space. The X-ray diffraction patterns most likely to be obtained for monochromatic radiation are also illustrated, for both 'powder' and 'single-crystal' type specimens. By comparing observed diffraction patterns of mesomorphic phases with those predicted, it is possible, in some cases at least, to identify the structure type. Several examples of surfactant–water compositions illustrate some of the unusual diffraction patterns that are obtained, and the use of such information to indicate the structure of the phase.

Introduction

Mesomorphic or liquid-crystalline phases are observed for a number of asymmetrically shaped molecules. Classical examples include molecules like ammonium oleate, *p*-azoxyanisole, and polymeric tungstic acid (Brown & Shaw, 1957). Of more practical importance are the mesomorphic phases observed with surfactants, polymers, lipids (e.g. triglycerides), and other biological systems. The study of the structure of such phases is facilitated by a scheme for descriptive classification. Hermann (1931) proposed a classification which does not appear to have received much attention, although Bernal & Fankuchen (1941) refer to the scheme in their plant virus work. By the application of group theory and several assumptions, Hermann derived eighteen structures between classical amorphous at one end of the scale and a well ordered three-dimensional crystal at the other end. It is the purpose of this paper to amplify Hermann's description, particularly with the use of illustrations, to point out the diffraction patterns to be expected, and to show some examples of mesomorphic phases whose diffraction patterns have unique features explained by this classification scheme.

Assumptions and definitions

The reader is referred to Hermann's original description for the details of his derivation. Several translation operations are defined there, which are means of bringing into congruence 'statistically, translationally equivalent' molecules or units of structure. The translation operations are briefly summarized here, with Hermann's symbols retained.

A 'statistical' translation, symbol S, is one in which the ends of the translation vectors fill space with uniform density. The translation from molecule to molecule in a gas is an example.

A 'reciprocal' translation, symbol R, is one for which the locus of the ends of the translation vectors is a set of parallel equally spaced planes.

In a 'direct' translation, symbol D, the equivalent structural units are equally spaced along parallel straight lines.

'Pseudo-direct' translations, symbols P_2, P_1, and P_0, are also defined, which are D-translations with two, one or zero degrees of freedom allowed for the directions of the D-translation. The subscripts indicate the number of degrees of freedom.

These translation types are taken in groups of three, one each for three independent directions in space, to derive possible structures. Not every possible combination of the nine symbols leads to a unique structure. Some combinations are redundant, and may be omitted. Four assumptions (Hermann, 1931), based on logical physical behavior of molecules, allow the rejection of several additional combinations. The four assumptions are:

(1) Substances containing only one kind of molecule are considered.
(2) The molecules, as well as polymeric groups of them, are equivalent, and in particular, geometrically congruent.
(3) When molecular centers are located on families of planes or along straight lines, the planar or linear density is the same on all planes or lines.
(4) The molecules are inpenetrable. Molecular centers of gravity must therefore have a finite minimum separation, and possible planes or chains cannot intersect or arbitrarily approach each other.

Furthermore, the choice of the translation types in two directions may dictate the possibilities for the third.

Table 1. *Hermann's translation types*

Symbol	Hermann no.	Fig. no.
SSS	1	(amorphous)
SSR	2	1
SSD	3	2
SSP_2	3*a*	3
SSP_1	3*b*	4
SSP_0	3*c*	5
$SS(RD)$	4	6
$SS(RP_1)$	4*a*	7
$SS(RP_0)$	4*b*	8
RDS	5	9
RP_1S	5*a*	10
RP_0S	5*b*	11
RRD	6	12
DDR	7	13
DP_0R	7*a*	14
P_1P_0R	7*b*	—
P_0P_0R	7*c*	—
$DR(RD)$	8	—
$DR(RP_0)$	8*a*	—
$(RD)(RD)(RD)$	9	(crystal)

There results a group of twenty possible translation types, enumerated in Table 1. The first of these, *SSS*, is the truly amorphous structure, and will not be dealt with further. The last, *(RD)(RD)(RD)*, is a three-dimensional crystal lattice, and will likewise be ignored in this discussion. Furthermore, several of the types may be treated better as disordered crystal lattices, rather than as highly ordered mesomorphic structures. For this reason they have not been illustrated, but are mentioned in the discussion to follow.

Illustrations

The drawings (Figs. 1–14) each have three parts. First is an illustration of the structure in real space. Blue balls are used to indicate molecular centers. No implications are made about the actual molecular shape, except that an asymmetric molecule is normally expected. The arrangement of molecular centers in planes ('reciprocal' translation) or along lines ('direct' or 'pseudo direct' translations) are indicated by shaded planes and straight lines.

The second part of each drawing is an illustration of reciprocal space. Actually, only the geometrical features of reciprocal space are considered, since the absence of assumptions about the shape and constitution of molecules leads to ignorance about the structure factors which in any actual case will modify the intensity distribution in reciprocal space. In some examples the zero-order reciprocal lattice features have been omitted.

The third part of the diagram indicates one or more of the diffraction pattern types to be expected. In deriving the expected diffraction patterns two kinds of specimen are considered. By analogy with diffraction by crystal lattices, these are called 'powder' and 'single crystal.' By the first of these terms is meant a sample consisting of many small regions, each region being a homogeneous volume of the structure type under consideration, but with the regions randomly oriented. By 'single crystal' is meant a specimen in which the structure is oriented in the same way throughout. Obviously, intermediate orientations are being ignored, but the expected diffraction patterns may be easily derived from the reciprocal space illustrations. The situation is partially covered since both rotation and stationary 'single-crystal' patterns are discussed. Only those diffraction effects from monochromatic radiation have been considered. Laue patterns have been discussed to some degree by Hermann (1931).

Description of structures

SSR (Fig. 1). Molecular centers are located on a set of parallel, equally-spaced planes, with the packing in the planes completely random, and no alignment from plane to plane. The reciprocal lattice consists of a single row of equally-spaced points, normal to the real-space planes. Three possible diffraction patterns are illustrated. Left to right they represent (1) the 'powder' pattern, (2) a rotation 'single-crystal' pattern with the rotation axis perpendicular to the reciprocal lattice point row, and (3) a rotation 'single-crystal' pattern with the rotation axis inclined at an acute angle to the reciprocal lattice point row. An example of the second of these patterns is shown in Fig. 18 and discussed below.

SSD (Fig. 2). Molecular centers are spaced at equal intervals along straight parallel lines. The side packing of the lines is random, and the parallel displacement of lines is random. The reciprocal lattice consists of one set of parallel equally-spaced planes. A rotation 'single-crystal' diffraction pattern is illustrated on the left, with the rotation axis parallel to the real space lines. Note that continuous layer lines will result. A 'powder' diffraction pattern has a unique asymmetric line shape, sharp on the low angle side, illustrated as a diffractometer tracing on the right. This line shape occurs for a number of the structures, and is a result of a tangential orientation of planes in reciprocal space. Examples, with additional features, are shown in Figs. 15 and 16, and are discussed below.

SSP$_2$ (Fig. 3). Molecular centers are again equally spaced along straight lines, but the two degrees of freedom allow the lines to take all directions. For each line, there is in reciprocal space a set of parallel planes. The whole reciprocal lattice consists of such sets of planes randomly oriented, but spaced at regular and equal intervals from the origin. They are therefore tangent to a set of concentric spheres (illustrated) whose radii are multiples of the reciprocal spacing. The diffraction patterns for *both* the 'powder' and 'single-crystal' cases are alike, and consist of asymmetric lines, whose *d* values are equal to and submultiples of the distance between molecular centers.

SSP$_1$ (Fig. 4). The molecular centers are again equally spaced along straight lines. The one degree of freedom restricts the line orientation to the surface of circular cones. The reciprocal lattice consists of planes spaced at regular intervals from the origin, but limited in orientation to being tangent to sets of coaxial cones. In a special case the real space cone degenerates to a plane, and the corresponding reciprocal lattice is a set of coaxial cylinders. 'Single-crystal' diffraction patterns are illustrated on the left for the case of the incident radiation parallel to the cone axis, and in the center for a random arrangement. The 'powder' pattern will have asymmetrically shaped lines, just as in the *SSP*$_2$ case.

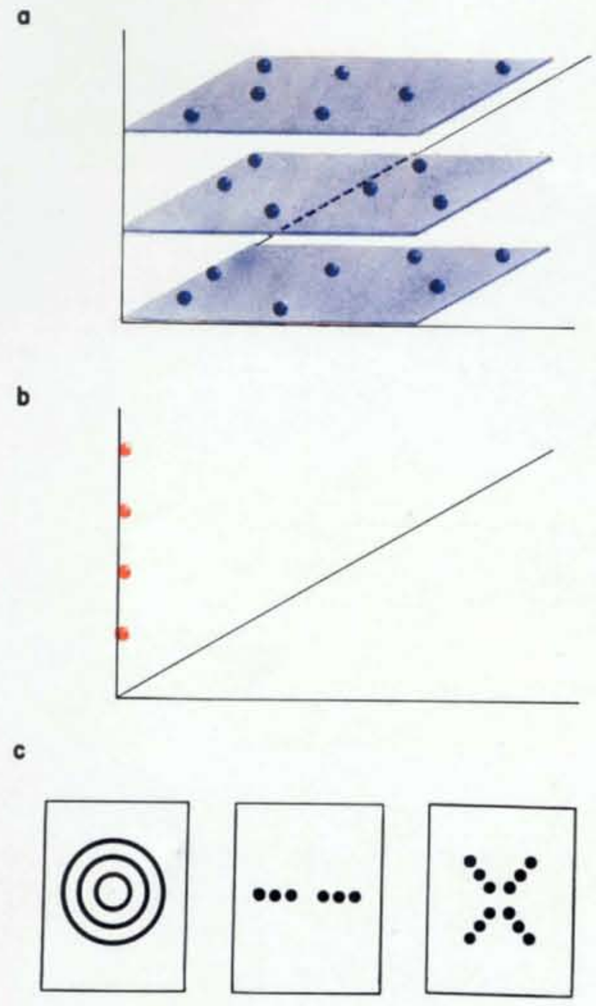
SSP$_0$ (Fig. 5). The molecular centers are equally spaced along straight lines, with their orientation limited to a small finite number of directions. (Two are illustrated.) This case differs from *SSD* only in that more than one, but still a small number, of directions are allowed for the straight lines. Reciprocal space contains a set of parallel planes perpendicular to each allowed line direction. A 'single-crystal' diffraction pattern with the beam perpendicular to one of the sets of real space lines will have continuous layer lines, plus ellipses or hyperbolas corresponding to the intersections of the second set of reciprocal lattice planes with the sphere of reflections, and is illustrated on the left. On rotation about an axis parallel to one of the real space set of lines, only the continuous layer lines will be seen, the remaining features becoming background scattering, as illustrated on the right. The 'powder' diffraction pattern will be identical with that for the *SSD* structure.

SS(*RD*) (Fig. 6). Molecular centers are not only equally spaced along parallel straight lines (*D* translation), but are also on parallel equidistant planes (*R* translation in the same direction). It is not required that the *D* translation be perpendicular to the *R* planes, but it cannot be parallel to the *R* planes. The illustrations are for the case of a slight angle between the *D* translation and the normal to the *R* planes. In reciprocal space there is a set of parallel planes corresponding to the *D* translation, and a single row of points corresponding to the *R* translation. The points will always lie on the planes in reciprocal space. A rotation 'single-crystal' pattern is illustrated on the left, with the rotation axis parallel to the real space *D* translation direction. Other situations can be imagined. The 'powder' case is an interesting one, for it leads to the superposition of a symmetric diffraction line on an asymmetric one. If the *D* translation is perpendicular to the *R* planes, the two lines coincide at the maximum of the asymmetric line. If the *D* translation is tilted with respect to the *R* planes, the symmetric line will be displaced, always to higher angles, as illustrated. Both cases have been observed, are illustrated in Figs. 15 and 16, and are discussed below.

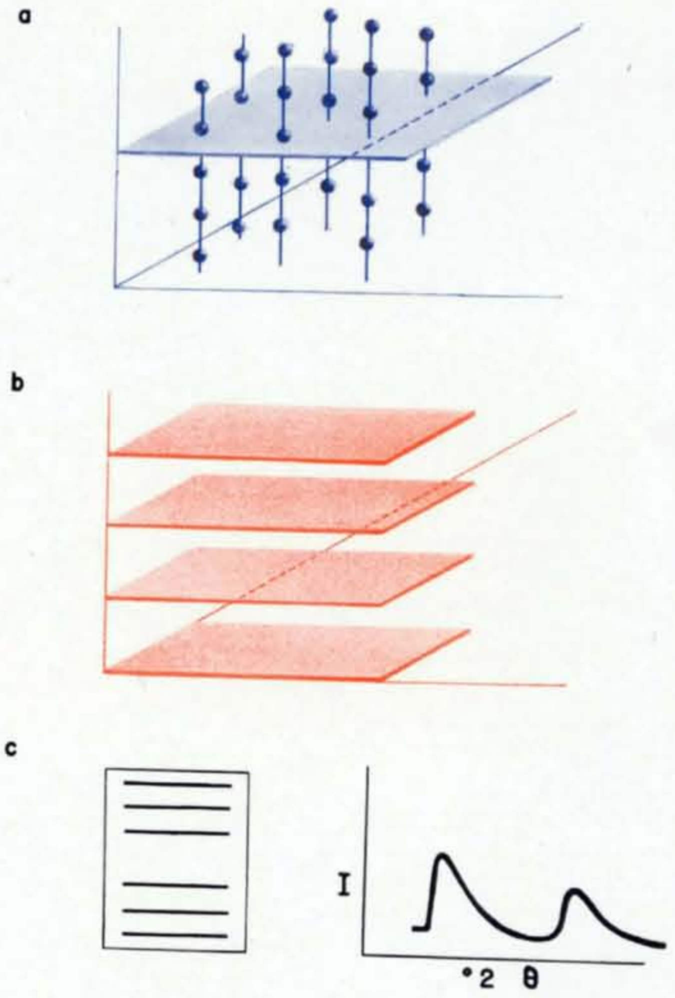
SS(*RP*$_1$) (Fig. 7). This structure consists of parallel equidistant *R* planes, with one degree of freedom allowed to the direction of the *D* translation. As a result, the straight lines along which molecular centers are located are on the surface of a cone, whose axis must be perpendicular to the *R* planes. In reciprocal space a set of cones as in *SSP*$_1$ (Fig. 4) results, with the exception that a set of points, reciprocal to the *R* planes, is located at the cone apices. Diffraction patterns similar to those for *SSP*$_1$ may therefore be expected for the 'single-crystal' case. The 'powder' pattern will have both a set of asymmetrically shaped lines and a set of symmetrically shaped lines, with the first order of the asymmetric line being at lower angle than the first order of the symmetric line.

SS(*RP*$_0$) (Fig. 8). This structure is very much like *SS*(*RD*), with one or more added *D* translations. The illustrations shows two *D* translations. If the *D* translations all have the same intermolecular spacing, as they should for a system of one kind of molecule, the several *D* translations must be tilted equal amounts to the *R* planes. The corresponding sets of planes in reciprocal space will likewise have equivalent spacings. The set of points reciprocal to the *R* planes must lie simultaneously on all sets of planes in reciprocal space, i.e. at their intersections. The diffraction pattern on the left is for the 'single-crystal' case, no rotation, and the beam parallel to one of the sets of planes in reciprocal space. The 'powder' pattern in the center is identical with that for *SS*(*RD*) (Fig. 6). A 'single-crystal' pattern on the right would result if the rotation axis were parallel to one of the real space *D* translations.

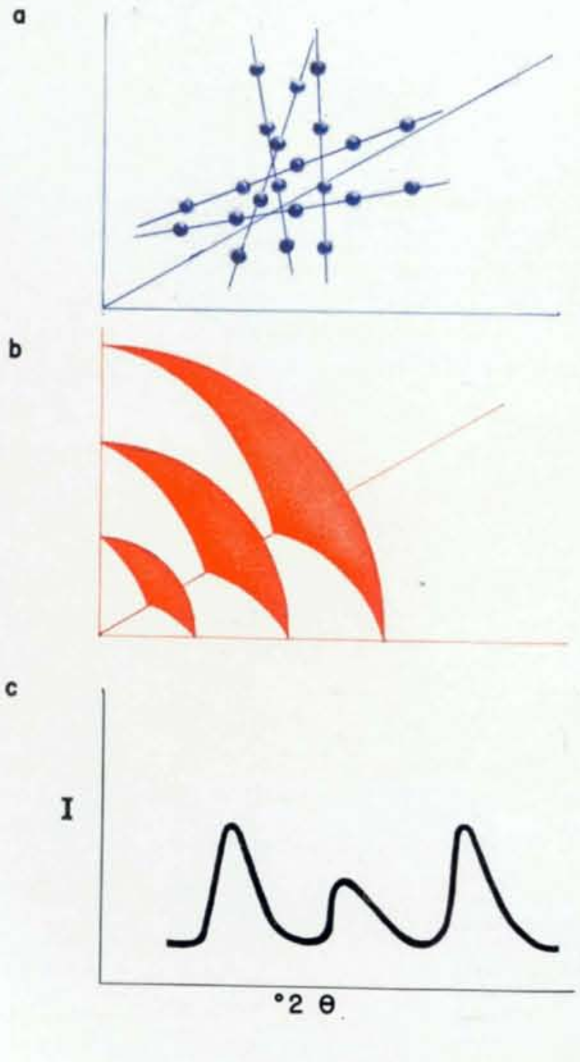
RDS (Fig. 9). In this case the set of parallel lines which are the *D* translation lie *in* the *R* planes. Parallelism of the lines is maintained from plane to plane, while the side packing of the lines in the plane is random. In reciprocal space a single row of points represents the *R* translation, and a set of planes parallel to this row corresponds to the *D* translation. A rotation 'single-crystal' pattern illustrated on the left would be obtained when the rotation axis is parallel to the *D* translation. The equatorial line in this case has discrete spots, while other layer lines are continuous. A 'powder' pattern will have asymmetrically shaped lines for the reciprocal lattice planes, and sym-



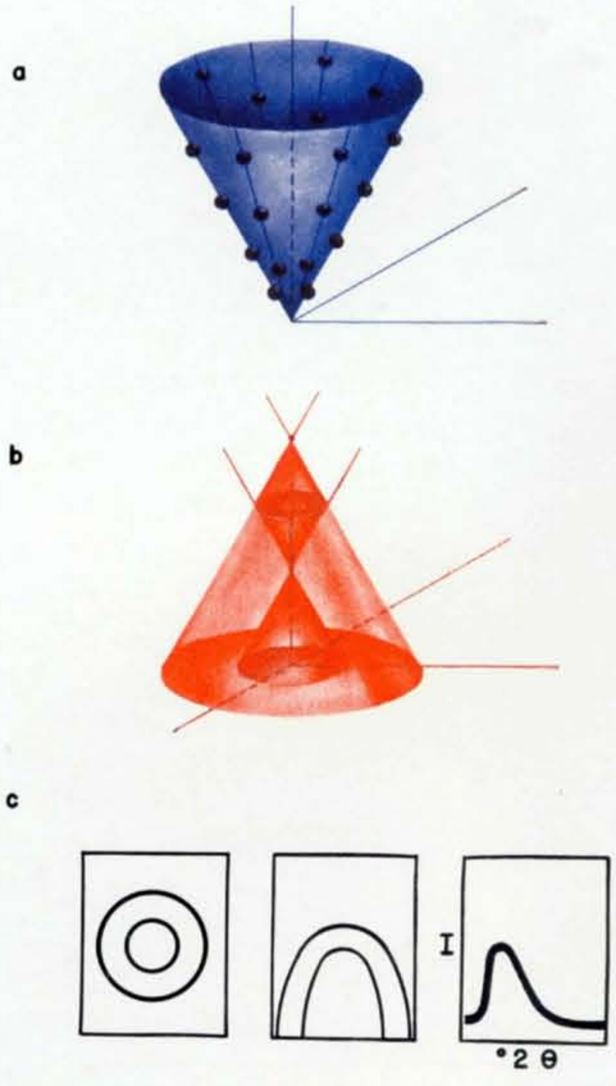
SSR FIG. 1



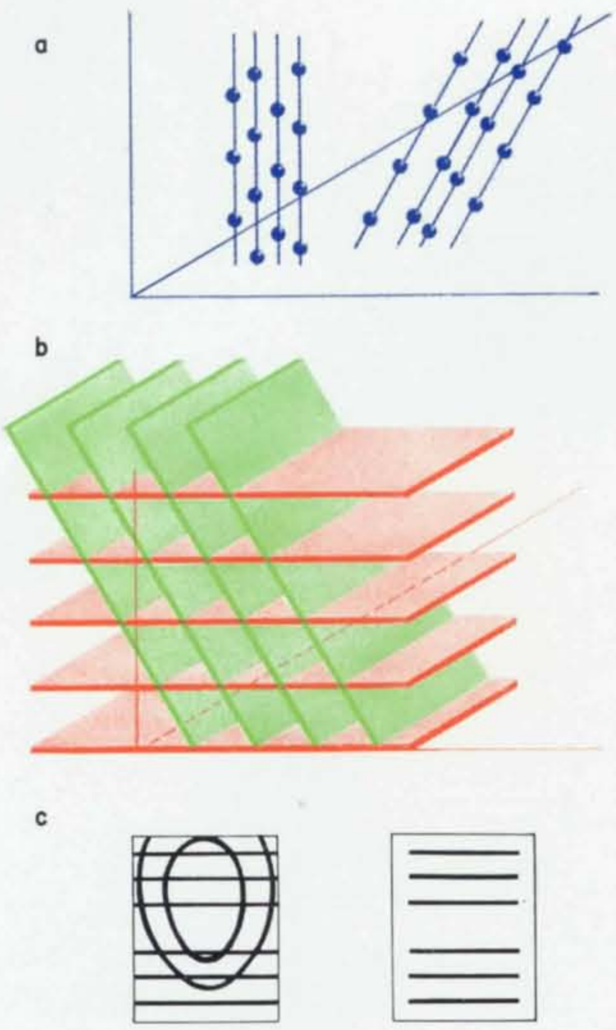
SSD FIG. 2



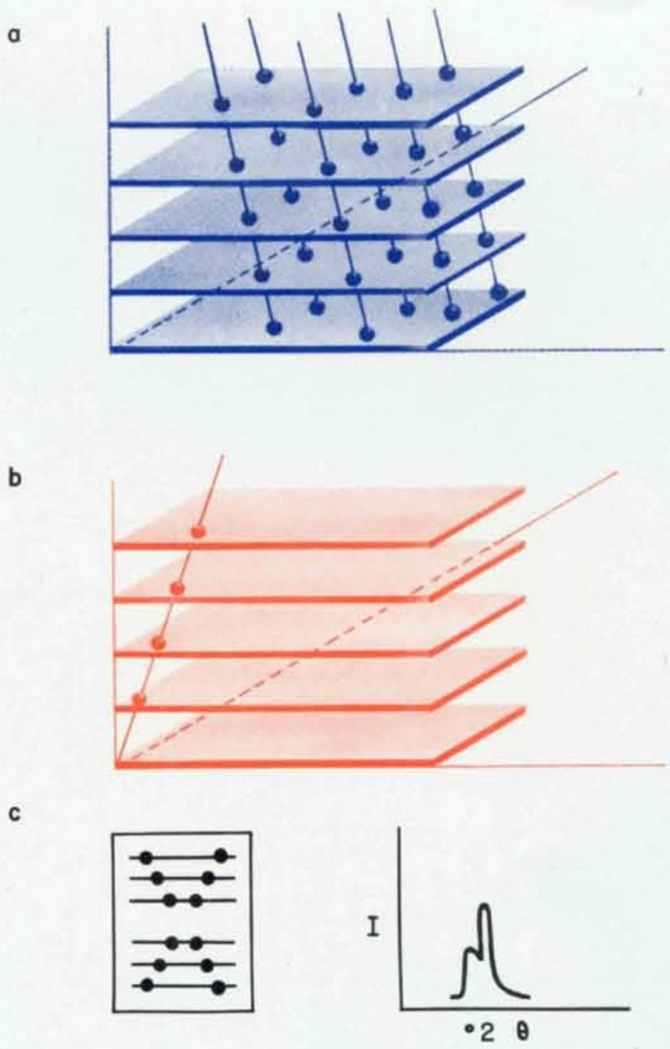
SSP$_2$ FIG. 3



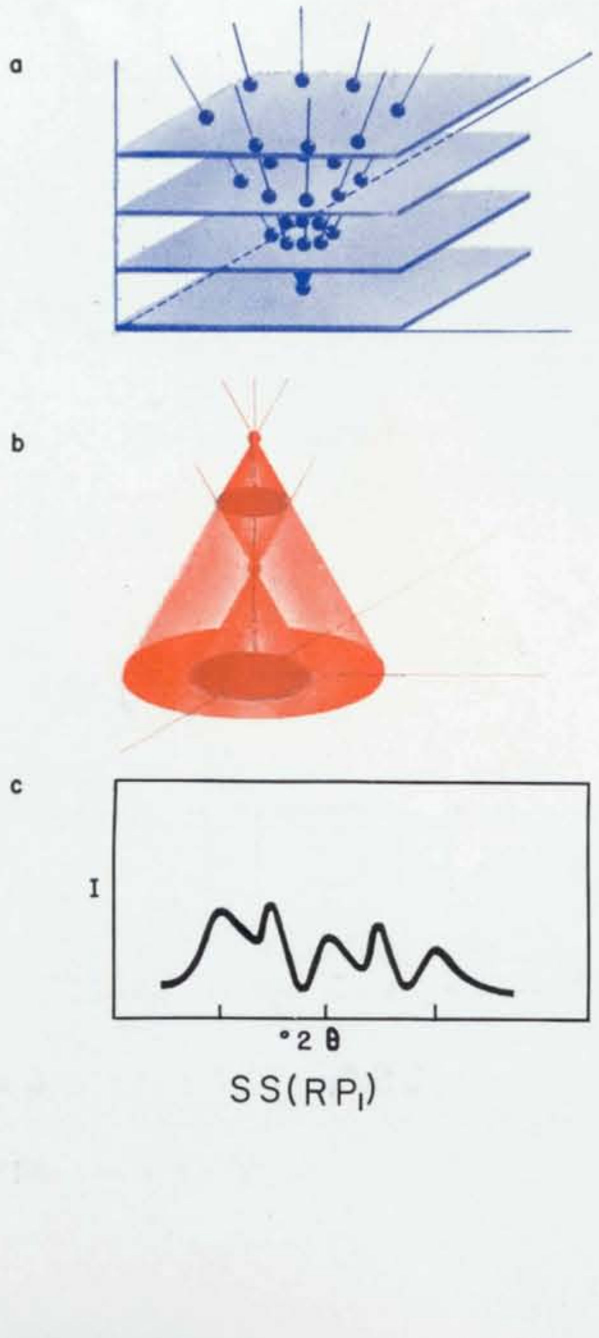
SSP$_1$ FIG. 4



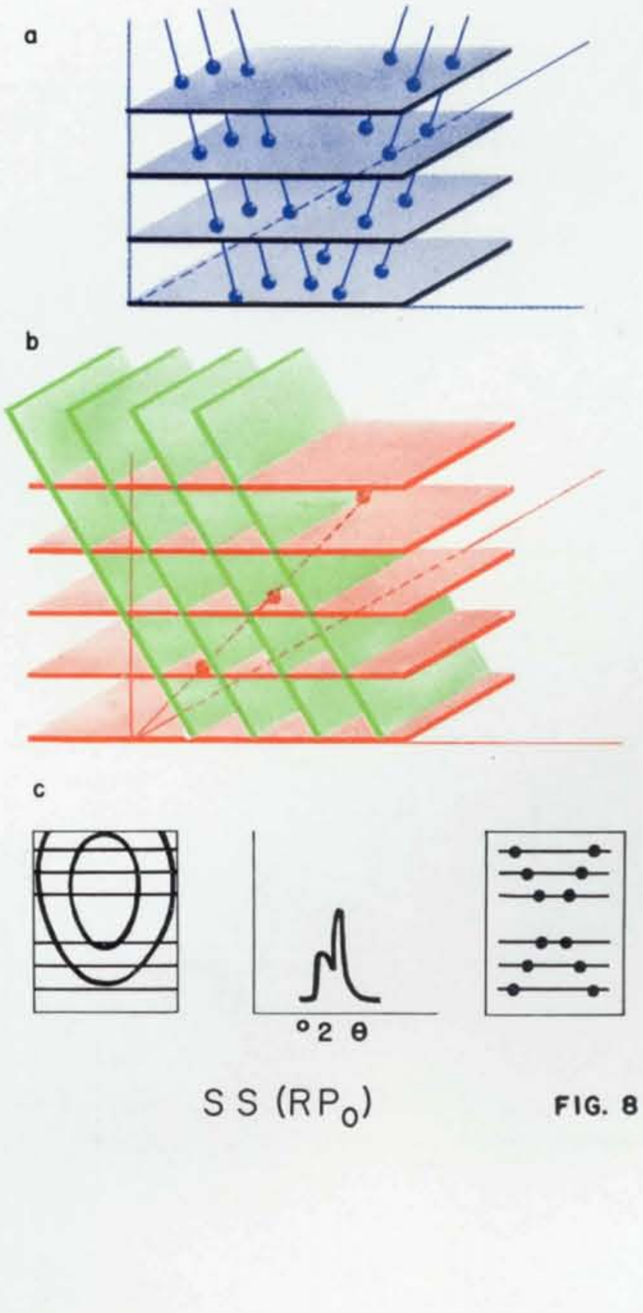
SSP$_0$ FIG. 5



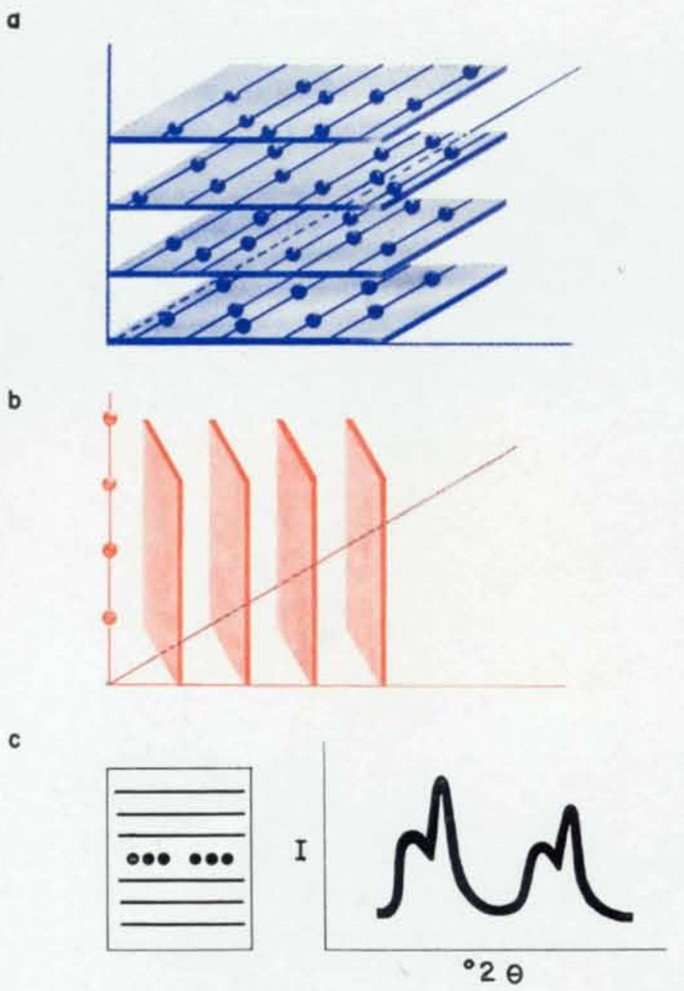
SS(RD) FIG. 6



SS(RP$_I$) FIG.7

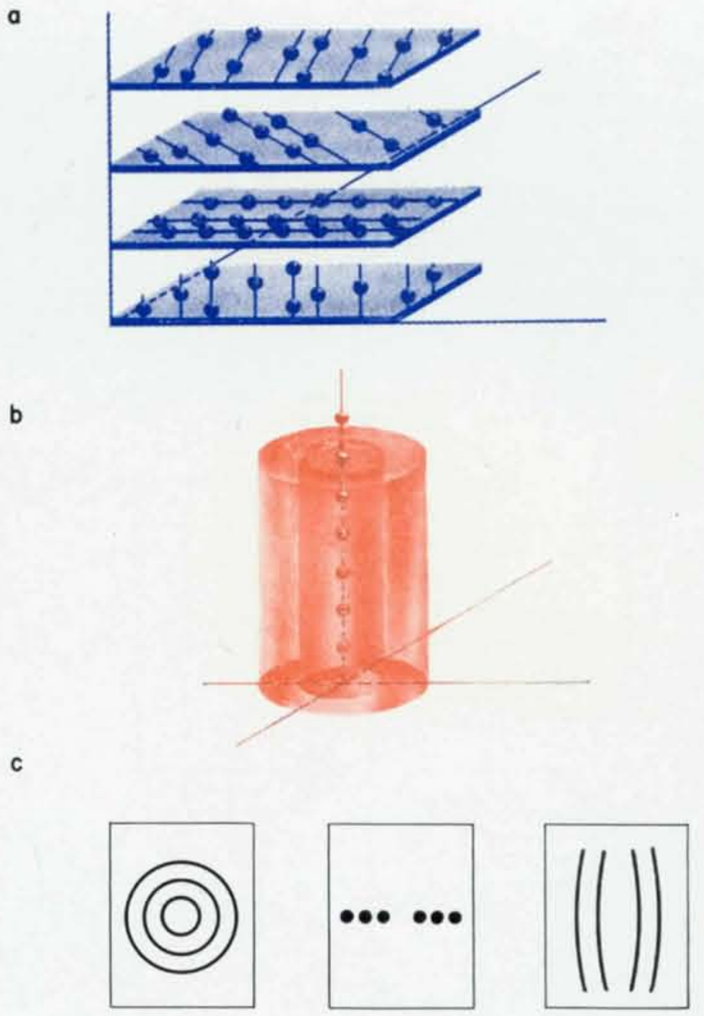


SS (RP$_0$) FIG. 8



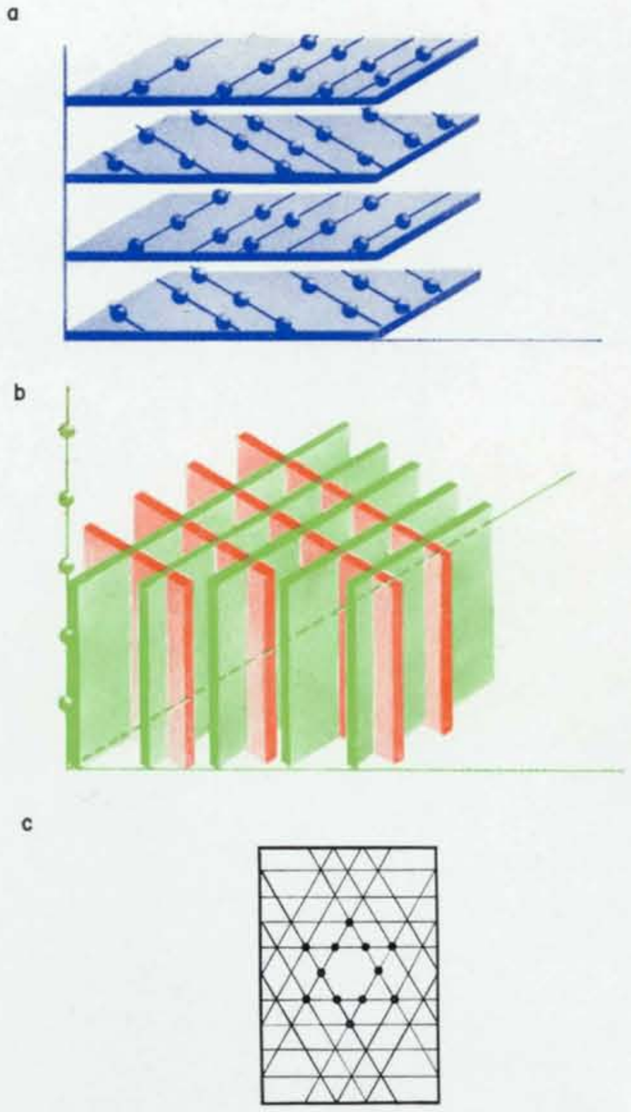
RDS

FIG. 9



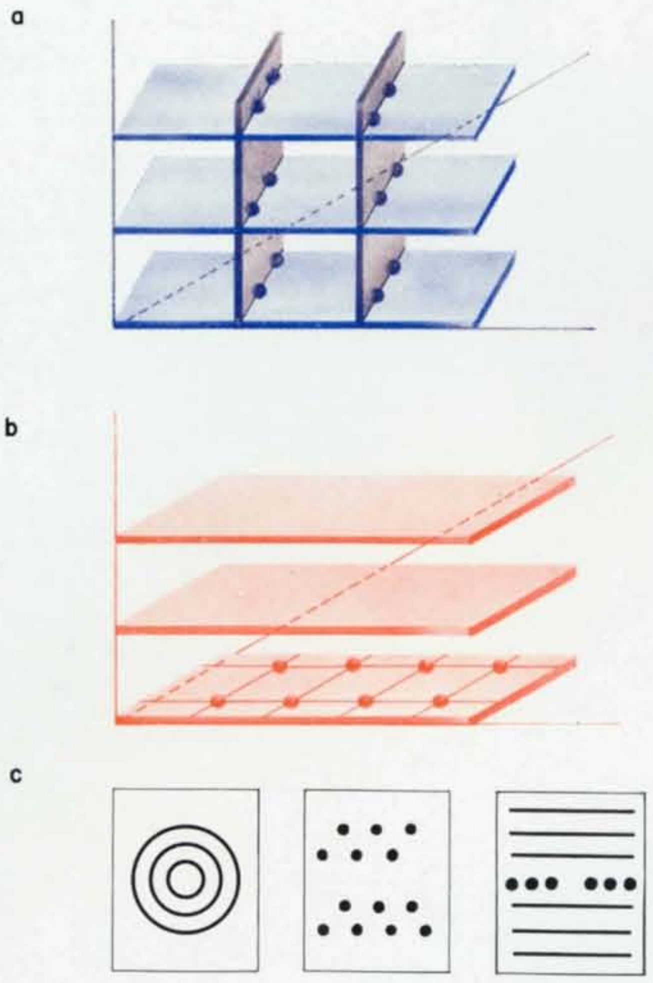
RP$_1$S

FIG. 10



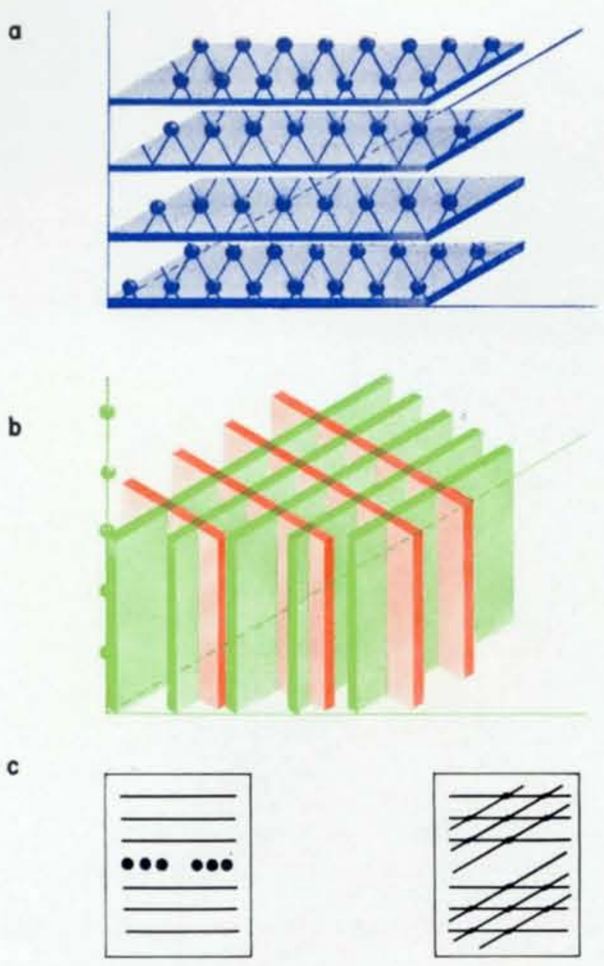
RP$_0$S

FIG. 11



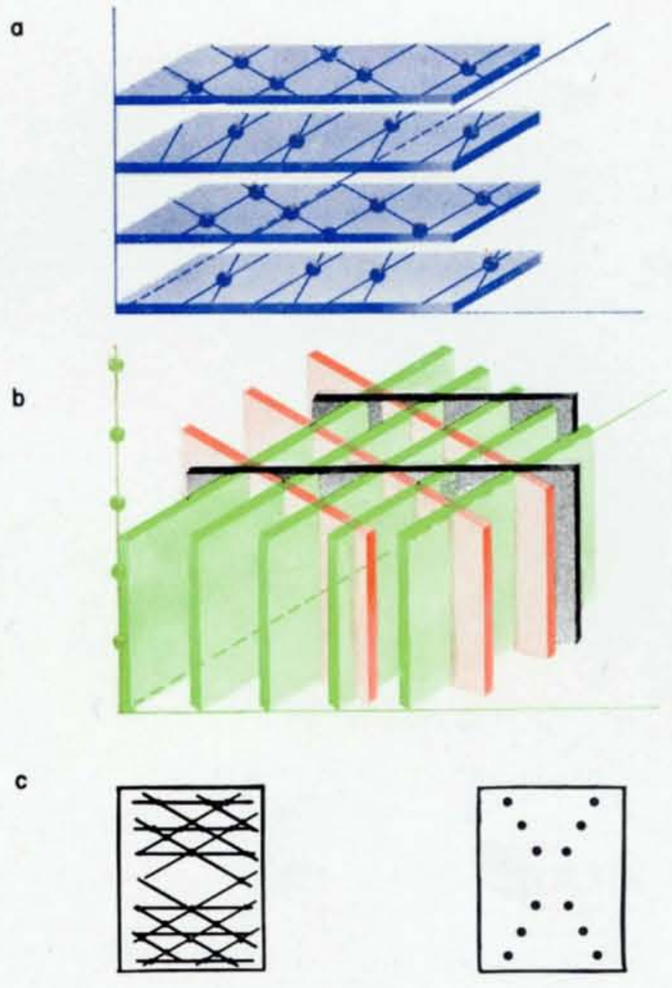
RRD

FIG. 12



DDR

FIG. 13



DP_0R

FIG. 14

metrically shaped lines for the points, illustrated on the right. It would be expected that the repeat distances for the *D* and *R* translations would be different. For polymeric chains, for example, a large *D* spacing corresponding to the repeat unit along the chain, and a small *R* spacing corresponding to side packing of chains, might result.

RP_1S (Fig. 10). This structure can be derived from *RDS* by arbitrary rotation of the *R* planes. The corresponding arbitrary directions of the *D* translations from plane to plane results from the one degree of freedom permitted for the *D* translation. As a result, in reciprocal space, the planes illustrated in Fig. 9 may now take all positions tangent to a set of concentric cylinders, which are illustrated in Fig. 10. A 'single-crystal' diffraction pattern with the beam perpendicular to the *R* planes in real space, will consist of a set of concentric, asymmetrically shaped rings, illustrated on the left. On rotation about an axis perpendicular to the beam direction the rings will disappear and a set of equatorial spots will appear, as illustrated in the center. If the beam is parallel to the *R* planes in real space, a pattern like that on the right will result, and it does not change with rotation around the normal to the *R* planes. The 'powder' pattern will be just like that for *RDS*.

RP_0S (Fig. 11). If the *D* translations of *RDS* are allowed a small finite number of directions, this RP_0S structure results. In reciprocal space in addition to the row of points reciprocal to the *R* translation, there will be several sets of planes (two are illustrated) with equivalent spacings, one set for each of the allowed *D* translation directions. A 'single-crystal' diffraction pattern with the beam perpendicular to the *R* planes in real space will show the pattern of intersecting sets of planes. An interesting case is the one for which the *D* translations occur in three directions, making angles of 120° with each other. The end view of the reciprocal lattice then consists of continuous layer lines in the form of hexagons, as illustrated. The spots at the intersections of the corners of the hexagons are meant to call attention to the fact that an increase in intensity is expected where two or more planes intersect. The inner hexagon has regions of high intensity at the corners; the next hexagon should have continuous scattering parallel to the inner one, but the regions of higher intensity will be displaced 30° from the inner set. Such a pattern is illustrated in Fig. 17, and discussed below. On rotation, for this orientation, the described pattern will disappear and an equatorial line of discrete spots will appear. The 'powder' pattern will be like that for *RDS*.

RRD (Fig. 12). In this structure the *D* translation lies along the intersections of sets of planes. Although two sets of *R* planes are illustrated, more are permitted for this structure. A hexagonal arrangement, for example, is another possibility. The requirement is that all sets be parallel to the *D* translation direction. In reciprocal space, a set of planes corresponds to the *D* translation, and in the zero order plane of this set there is a two-dimensional lattice of points, corresponding to the *R* planes in real space. Several 'single-crystal' diffraction patterns can be imagined. If the beam is parallel to the real space *D* translation, a set of rings results from the intersection of the reciprocal space planes with the sphere of reflection, as illustrated on the left. On rotation the rings disappear and the two-dimensional network of points will give discrete spots, as illustrated in the center. If the beam is perpendicular to the real space *D* translation, continuous layer lines will be observed. If the specimen is then rotated about the *D* translation, the continuous layer lines are retained and an equatorial row of spots appears. The 'powder' pattern for this structure will have a group of symmetrically shaped lines corresponding to the $(hk0)$ reciprocal two-dimensional lattice, and a set of asymmetrically shaped lines corresponding to the reciprocal lattice planes. This structure can be derived from a three-dimensional crystal lattice by simple random and parallel displacement of all lattice rows parallel to a given direction.

DDR (Fig. 13). In this structure the molecular centers lie on *R* planes, but in each plane form a two-dimensional lattice. The axes defining the two-dimensional lattice are parallel from plane to plane, but otherwise randomly displaced. In other words, this structure may be derived from a crystal lattice by random displacement, without rotation, of all planes parallel to a reference plane. The reciprocal lattice for this structure has a row of points and two sets of planes parallel to that line. The 'powder' diffraction pattern will have a set of symmetrically shaped rings arising from the points, and sets of asymmetrically shaped rings corresponding to the planes. Two sets of continuous layer lines, as illustrated on the right, will result for the 'single-crystal' specimen if the beam is perpendicular to the real space *R* planes. Rotation about one of the *D* translation directions as an axis will add an equatorial row of discrete spots, as illustrated on the left.

DP_0R (Fig. 14). The *R* planes in this structure have one *D* translation direction in common, i.e. parallel from plane to plane. In addition, there is allowed a second *D* translation in the *R* planes, which may take several (small number) directions. Two are illustrated. In reciprocal space, a row of points again passes through the origin, and parallel to that line are the set of planes reciprocal to the real space *D* translation, and several sets of planes reciprocal to the several P_0 translations. The diffraction patterns will be very much like those for *DDR*. The 'powder' pattern will be identical to that of *DDR*; the stationary 'single-crystal' patterns will be complicated by one or more additional sets of continuous layer lines, as illustrated on the left. On the right is illustrated the type of diffraction pattern which would be obtained for the case of the beam perpendicular to the real space R planes, but with rotation about a random axis not one of the D or P_0 translation directions. Note that this pattern differs from the one illustrated in Figs. 6 and 8 in that the continuous layer lines are missing, but is like that of Fig. 1.

The remaining four structures are not illustrated, for they offer no new diffraction features. Furthermore, they are more logically treated as disordered crystal lattices, and are not so likely to be encountered in mesomorphic phase studies. A brief description of them follows.

P_1P_0R. This structure has parallel equidistant planes, each containing two sets of chains; one of these can take any orientation from plane to plane, the other is restricted to a small number of directions. Derivation from a crystal lattice may be imagined as follows: (1) All planes parallel to a reference lattice plane are arbitrarily displaced parallel to themselves; and (2) successive planes are then rotated randomly.

P_0P_0R. This structure can be derived from a crystal lattice by (1) parallel displacement of successive parallel planes in the lattice, and (2) rotation of the planes about their normal to several arbitrary positions. The angle between the two P_0 translations remains constant from plane to plane. Reciprocal space then consists of the axial row of spots, with two sets of planes taking several orientations, but always parallel to the row of spots.

$RD(RD)$. This structure is derived from a crystal lattice by random displacement, parallel to given line and without rotation, of all lattice planes which are parallel to a reference plane. If the displacement occurs parallel to the crystallographic c-axis, then reciprocal space contains a set of planes parallel to the c^*-axis, and in the zero order of this set of planes there is a two-dimensional point lattice.

$RD(RP_0)$. This structure is very similar to the previous one. In addition to its parallel displacement, each plane may be rotated about its normal to several positions.

Examples

Several of the unusual diffraction features described above have been observed. In Figs. 15 and 16 the combination of a symmetrically shaped diffraction line superimposed on an asymmetrically shaped line is illustrated. This combination was predicted for structures $SS(RD)$ and $SS(RP_0)$. Fig. 15 is a copy of the diffractometer pattern of 'neat' phase for the sodium oleate–water system, the concentration being approximately 65% sodium oleate. In this case the D translation, which is responsible for the one observed order of asymmetric line, must be perpendicular to the R planes, which are responsible for the several orders of sharp, strong, symmetric lines. In Fig. 16, the diffractometer pattern of a 60% potassium soybean-oil soap called Soluble Green, which is an example of 'viscous neat' phase (Rosevear, 1954), the symmetric line is displaced to the high angle side of the asymmetric line. The D translation in this case is therefore tilted with respect to the R planes.

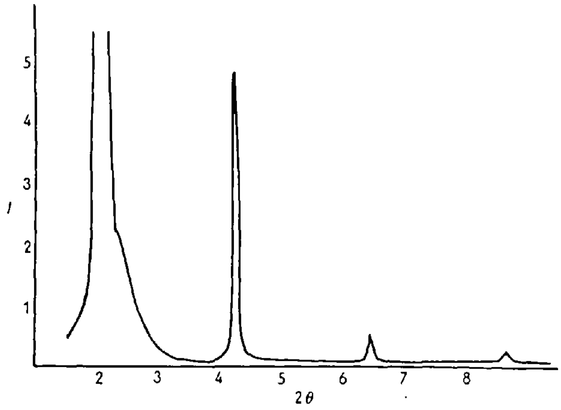


Fig. 15. Neat phase sodium oleate-H_2O.

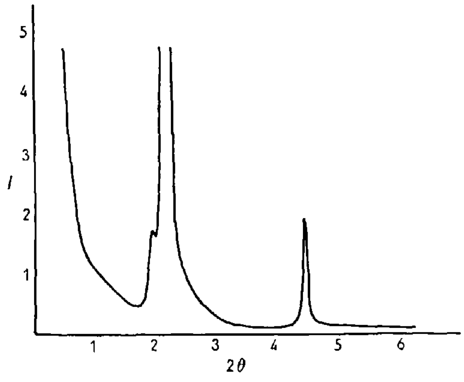


Fig. 16. Viscous-neat phase 'soluble green'.

A very unusual diffraction pattern is illustrated in Fig. 17. This is an enlargement of the central, nickel filtered, portion of a pattern of a surfactant–electrolyte–water system. Specifically, the composition was 36% sodium dodecyl-glyceryl-ether-sulfonate, 5% sodium sulfate, and 59% water. The diffraction effects extend to a spacing (applying the Bragg formula) of approximately 20 Å. Note the two hexagonal arrays of spots, with continuous scattering from spot to spot in the inner row, while the continuous scattering in the outer ring is through the spots and parallel to the inner ring. This type of pattern is predicted for structure RP_0S. This phase has been called 'middle' because its optical properties are like those of other 'middle' phases in soap–water systems. Its structure must be different from that found for 'middle' soap by Luzzati, Mustacchi & Skoulios (1957, 1958), since their hexagonally packed cylinders of indefinite length would not produce this pattern.

An example of a single equatorial row of spots is illustrated in Fig. 18. This pattern was observed for a dilute and fluid 'solution' containing about 14%

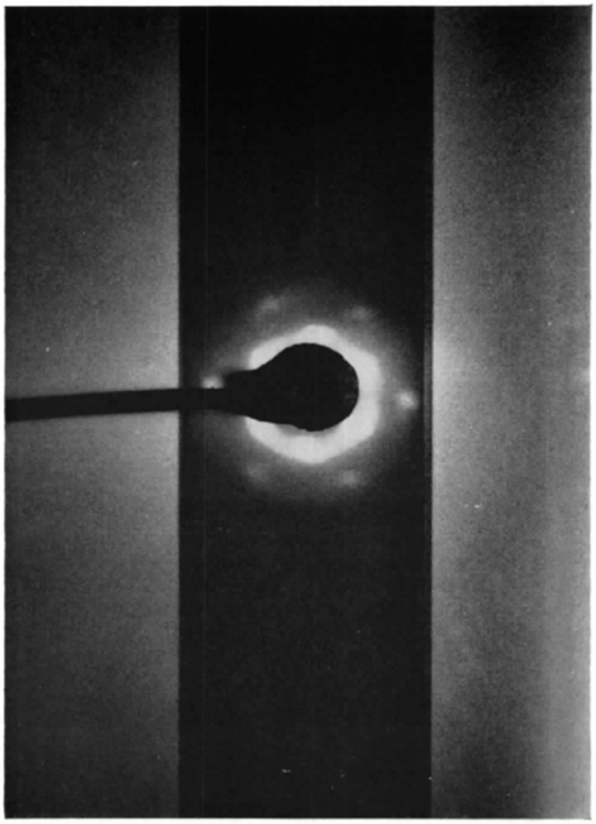


Fig. 17. Hexagonal pattern with continuous scattering.

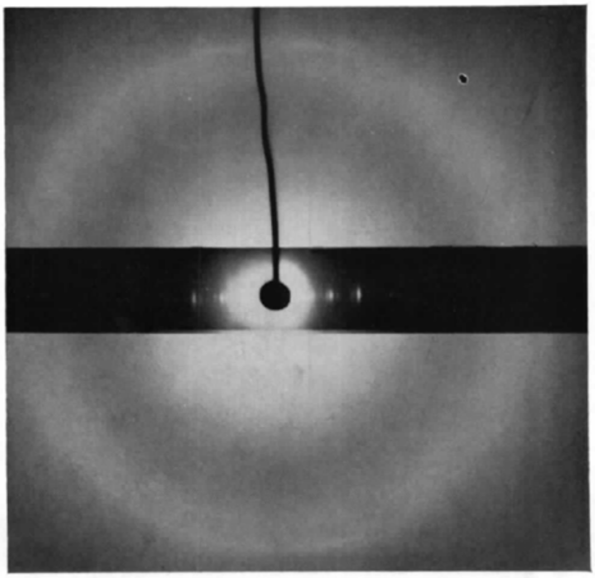


Fig. 18. Equatorial row of diffraction spots.

sodium dodecylsulfate, 4% lauryl alcohol and 82% water. The specimen was contained in a thin-walled capillary, and was taken without rotation. The structure was therefore not 'single-crystal', but was a strictly cylindrically oriented 'powder' specimen. This pattern type was predicted for structures *SSR*, RP_1S and RP_0S, and could occur for very special and unlikely rotations of SSP_1, $SS(RD)$, $SS(RP_1)$, $SS(RP_0)$, *DDR*, and DP_0R.

Conclusions

It can be seen from the above examples, that some information about the structure of mesomorphic phases can be derived from their diffraction patterns. It is obvious that one can be more specific about the classification of the structure if one can prepare both 'powder' and 'single-crystal' specimens. In addition, stationary and rotating sample techniques will help to distinguish similar structures. It is sometimes possible to orient mesomorphic systems by flow into a capillary tube, or by centrifuging in a capillary. Occasionally the container itself (e.g. a capillary) will influence the orientation of the specimen. Since many of the mesomorphic phases have high viscosities, time will usually aid the orientation process.

It is also obvious that a complete determination of the structure of any phase must include structure factor calculations so that predicted and observed intensities may be compared. As mentioned above, the present discussion completely ignores the molecular structure factor, and its influence on the intensity distribution in reciprocal space.

The help and encouragement of many colleagues at Procter and Gamble has been deeply appreciated. Special thanks are due Mr R. E. Kammann, who did the air-brush art work, and to Mr C. W. Hand, presently at Harvard University Graduate School, who helped with many of the drawings.

References

Bernal, J. D. & Fankuchen, I. (1941–2). *J. Gen. Physiol.* **25**, 111.

Brown, G. H. & Shaw, W. G. (1957). *Chem. Rev.* **57**, 1049.

Hermann, C. (1931). *Z. Kristallogr.* **79**, 186, 337.

Luzzati, V., Mustacchi, H. & Skoulios, A. (1957). *Nature, Lond.* **180**, 600.

Luzzati, V., Mustacchi, H. & Skoulios, A. (1958). *Disc. Faraday Soc.* No. **25**, 43.

Rosevear, F. B. (1954). *J. Amer. Oil Chem. Soc.* **31**, 628.

Acta Cryst. (1962). **15**, 1157

An X-ray Investigation of Wet Lysozyme Chloride Crystals. Preliminary Report on Crystals Containing Complex Ions of Niobium and Tantalum

By Robert B. Corey, R. H. Stanford, Jr., Richard E. Marsh, Yuen C. Leung* and Lois M. Kay

Gates and Crellin Laboratories of Chemistry,† California Institute of Technology, Pasadena, California, U.S.A.

(*Received* 14 *February* 1962)

Egg-white lysozyme chloride when crystallized at pH 4·5 from solutions containing the ions $Ta_6Cl_{12}^{++}$ and $Nb_6Cl_{12}^{++}$ forms crystals containing these complex ions in the amount of approximately one ion per molecule of lysozyme. These crystals have the same space group ($P4_12_1$) and approximately the same cell dimensions as those of lysozyme chloride alone.

Two-dimensional and three-dimensional Patterson diagrams ($d_{\text{min.}} = 5$ Å) indicate that these ions occupy one set of eight-fold general positions in the unit cell and establish the coordinates of the ion centers. There is good evidence that the large complex ions cause a significant alteration in the configuration of the protein molecule. Some implications of these findings are discussed with respect to further investigations of the crystals.

1. Introduction

Egg-white lysozyme has many properties that recommend it as a subject for X-ray investigation, among them being its low molecular weight (about 14,700), its relative stability and homogeneity, its availability in highly purified form, and the ease with which it can be crystallized. Crystals of the chloride grown at pH 4·5 are especially stable and yield X-ray photographs with reflections extending to a minimum

---

* Deceased, November 11, 1958.

† Contribution No. 2812 from the Gates and Crellin Laboratories of Chemistry. The work described in this article was supported principally by a Contract (Nonr-220(05)) between the Office of Naval Research and the California Institute of Technology; it was also aided by research grant No. H-2143 from the National Heart Institute, Public Health Service, and by grants Nos. G-1265 and G-9467 from the National Science Foundation.