X-RAY ANALYSIS OF THE STRUCTURE OF IRIDESCENT SHELLS.

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1. Introduction.

THE study of the iridescence of the nacreous layer of the shell of the pearl oyster and other molluscan shells has engaged a good deal of attention and the pioneer investigations of Brewster in this line are common knowledge to students of physical optics. More recently Pfund[1] and Lord Rayleigh[2] have carried out further investigations connected with this problem. In the more recent investigations of Sir C. V. Raman[3] the subject has been placed on a broader foundation by a fuller study and the discovery of several interesting features which had not been noticed by previous authors.

A study of the structure of the shells from the point of view of the X-ray crystallographer becomes highly interesting because of the regular orientation of the crystallites of calcite or aragonite forming the various layers in these shells. Shaxby,[4] Dauvillier[5] and others[6] have made some interesting studies on these lines confining their attention, however, mainly to the nacreous layer of shell of the pearl-oyster. Investigations such as these have led to methods of distinguishing "real" from "culture" pearls.[7, 8] They all find that the minute crystals of aragonite of which the nacreous layer consists, are arranged fibrously with the pseudohexagonal c axis normal to the surface of the shell. Dauvillier[9] assumes that the nacreous layer in

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[1] A. H. Pfund, *Jour. Frank. Inst.*, 1917, **183**, 453.

[2] Lord Rayleigh, *Proc. Roy. Soc.* A, 1923, **102**, 674.

[3] Sir C. V. Raman, *Proc. Ind. Acad. Sci.* A, 1934, **1**, 567; and *Proc. Ind. Acad. Sci.* A, 1934, **1**, 574.

[4] J. H. Shaxby, *Phil. Mag.*, 1925, **49**, 1201–1206. See also *Comptes Rendus*, 1924, **179**, 1602–1603.

[5] Dauvillier, *Comptes Rendus*, 1924, **179**, 819.

[6] W. V. Mayneord, *Brit. Jour. Radiology*, 1927, **23**, 19–30; Tsutsumi, *Kyoto Coll. Sci. Mem.*, 1928, **11**, 217–221; and *Kyoto Coll. Sci. Mem.*, 1928, **11**, 401–405.

[7] J. Gaiborg and F. Ryziger, *Rev. d'Optique*, 1927, **6**, 97–133. See also *Comptes Rendus*, 1926, **183**, 960–962.

[8] B. W. Anderson, *Brit. Jour. Radiology*, 1932, **5**, 57–64.

[9] *Loc. cit.*

the shell of the pearl-oyster consists of triple twin crystals of aragonite deposited in a honeycombed skeleton of conchyolin built up by the epithelial cells of the mollusc. From examination of the shells with the polarising microscope, Schmidt[10] has put forward the view that the aragonite crystals in the nacreous layer have their *c* axes normal to the surface of the shell and are cemented together with conchyolin. Other iridescent shells, a complete description of which has been given by Sir C. V. Raman,[11] have not been studied, however, by X-ray methods. The present investigation was taken up in order to find out whether the orientation and other characteristics of the aragonite crystals in these shells are the same as those in the shell of the pearl-oyster or present any differences. It was also thought desirable to investigate as to how perfect is the orientation of the crystals in the shells and also to obtain an idea of their average size. The shells examined were—*Pinctada* (*Margaratifera*) *vulgaris*, *Nautilus pompilius*, *Turbo* sp., *Trochus* sp., and *Mytilus viridis*.

2. *Method of Examination.*

Two methods of examination with X-rays were adopted. In the first method, photographs of the diffraction pattern produced by a monochromatic X-ray beam incident normal to the surface of the shell were obtained. In the second method similar photographs were obtained with the X-ray beam parallel to the surface of the shell. Suitable specimens for examination were obtained by cutting pieces from the shells either normal to the lines of growth or parallel to the lines of growth. These were ground or filed after mounting suitably in order to get a thin portion of the nacreous layer only. The thickness of the prepared specimens varied from 0·6 to 0·1 mm. depending upon the thickness of the nacreous layer. For examination with the X-ray beam normal to the surface of the shell the specimens were about three or four millimetres long and about half a millimetre wide.

For obtaining photographs with the X-ray beam normal to the surface of the shell, the longer specimens were mounted on the goniometer table of an X-ray goniometer camera and adjusted by using a carbon arc in the place of the X-ray tube. The specimen was so adjusted as to reflect the beam of light coming from the lead slit of the camera, back into the slit. Thus the specimen was set perpendicular to the axis of the camera ensuring normal incidence of the X-ray beam on its surface during the exposure.

For examination with the X-ray beam along the surface of the shell, specimens of about a millimetre or so in length were cut from those used

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[10] W. J. Schmidt, *Die Bausteine Des Tierkorpers in Polarisertem Lichte,* F. Cohen, Bonn, 1924.

[11] *Loc. cit.*

for the first method. These were mounted on a glass rod about a millimetre in diameter and 3 or 4 mm. long with a trace of canada-balsam so that the glass rod was as nearly normal to the shell surface as possible. The glass rod was mounted on the previously mentioned X-ray goniometer camera and adjusted so that the surface of the shell was perpendicular to the vertical rotation axis of the goniometer. In order to facilitate the accurate mounting of the specimen the goniometer camera was placed in front of a carbon arc as before, so that the light from the arc, after passing through the lead slit of the camera, fell on the film cassette in the position of the directly incident X-ray beam. In a goniometer camera the X-ray beam is coincident with the axis of the camera which is itself perpendicular to the vertical rotation axis of the goniometer. Consequently, when the surface of the specimen is perpendicular to the vertical rotation axis, the beam of light from the arc is parallel to the shell surface and is not reflected. But if the specimen is ever so little inclined the spot of light reflected by it appears on the film cassette. The specimen was so adjusted as to eliminate this reflection for all settings of the goniometer about its vertical rotation axis. By rotation of the goniometer about the vertical axis the specimen could be adjusted with the lines of growth on it making any specified angle with the X-ray beam which however would always be incident parallel to the shell surface. Photographs were taken with the X-ray beam perpendicular or parallel to the lines of growth. Various other settings of the goniometer were also chosen thus keeping the lines of growth inclined at various angles with the X-ray beam.

In the above methods of setting it is assumed that the laminations are nearly parallel to the surface, so that the X-ray beam is adjusted either normal to the laminations or parallel to them. But the laminations are not parallel to the surface of the shell as shown by Sir C. V. Raman.[12] The resulting error in setting the specimen in the goniometer could be eliminated by considering the iridescent reflection from the laminations instead of the regular white reflection from the surface. This was done for setting the specimen in all the experiments. In the case of the *Nautilus* shell however this precaution was found unnecessary due to the large error in orientation of the crystallites as discussed later. Tilting the specimen by about five or ten degrees about a horizontal axis from the correct position did not alter the nature of the pattern obtained.

Molybdenum Kα and Kβ were the radiations used and with an applied kilovoltage of 50 and a tube current of 12 to 15 milliamperes good pictures

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[12] *Loc. cit.*

could be obtained in about two hours working with a 25 cycle supply with single wave rectification. Some of the photographs obtained are reproduced in Figs. 3 to 16.

3. *Turbo and Trochus.*

Photographs obtained with finely powdered nacreous layer of *Turbo* and *Trochus* were identical with Debye-Scherrer patterns of powdered aragonite. Thus the nacreous layer in these shells consists of aragonite. Patterns obtained with the X-ray beam incident normally on the nacreous layer of these shells (Figs. 3 and 4) consist of complete circles, but with X-rays incident parallel to the laminations a spot pattern is obtained (Figs. 5 and 6). This spot pattern, however, is always the same irrespective of the direction of the X-ray beam with reference to the lines of growth in the shell. The spots in the pattern obtained lie on the layer lines of aragonite drawn for rotation about the c axis. This shows that the c axes of the crystallites are normal to the shell surface while the a and b axes are parallel to the surface and oriented at random. The diffraction spots in the above patterns are much longer than the part of the specimen which is irradiated by the X-ray beam. This is because the orientation of the c axes is by no means perfect. Half the angle subtended by the ends of the spots at the centre of the pattern is roughly equal to the maximum tilt of the c axes from the normal orientation, after allowing for the finite length of the specimen as mentioned in an earlier paper.[13] This is of the order of about 7° for *Turbo* and about 10° for *Trochus.*

The random orientation of the a and the b axes may be either a *true lack of orientation* or it may be a result of continued twinning combined with a large error in orientation. In both cases complete rings will be obtained normally to the shell and the spot patterns with different orientations of the lines of growth will be identical.

The optical diffraction haloes observed by Sir C. V. Raman[14] with thin sections of *Turbo* and *Trochus* cut parallel to the laminations are complete circles.

4. *Nautilus pompilius.*

Finely powdered nacreous layer of *Nautilus pompilius* obtained during cutting the shell with a wire saw gave a Debye-Scherrer ring pattern characteristic of powdered aragonite. Photographs were obtained by the second method starting from a position in which the lines of growth were parallel to the X-ray beam and then rotating the goniometer table in steps of 30°

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[13] S. Rama Swamy, *Proc. Phys. Soc.*, 1934, **46**, 739.

[14] Sir C. V. Raman, *Proc. Ind. Acad. Sci.*, previous paper in this number.

over one complete revolution. Patterns obtained with the lines of growth at various inclinations with the X-ray beam are given in Figs. 7 to 12. Considered as a whole the spots in the patterns obtained along the lines of growth and perpendicular to the lines of growth are different from each other (Figs. 9 and 10). They are both symmetrical about a horizontal and a vertical axis. Another interesting feature of these photographs is also to be observed. Patterns obtained with inclinations of 30° on either side of the above positions are unsymmetrical about the vertical axis and are mirror images of each other (Figs. 7, 8, 11 and 12). They are symmetrical about a horizontal axis. A consideration of the structure of the aragonite lattice shows, however, that this type of symmetry cannot be obtained with a single crystal. But a suitable arrangement of crystals consistent with the structure of aragonite can explain the nature of the patterns obtained.

The crystal structure of aragonite has been thoroughly studied by Bragg.[15] He has classed it as belonging to the holohedric group of the orthorhombic system. It belongs to the space-group Q_h^{16} according to the Schoenflies notation, with fundamental axes *a*, *b* and *c* measuring 4·94, 7·94 and 5·72 Å respectively. Aragonite twins across the plane 110. The projection of the lattice of a simple twin of aragonite on the *ab* plane, taken from the paper by Bragg, is given in Fig. 1. The unit cells in the two elements of the twin are also marked. From this figure it is easily seen that the *a*

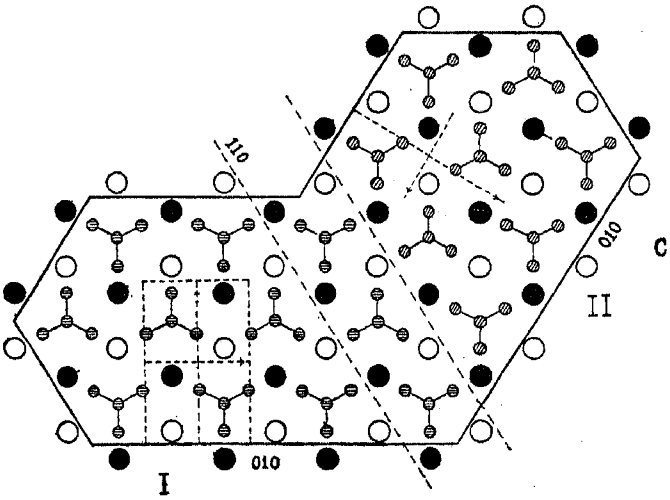

FIG. 1. Projection of lattice of simple aragonite twin on the *ab* plane.

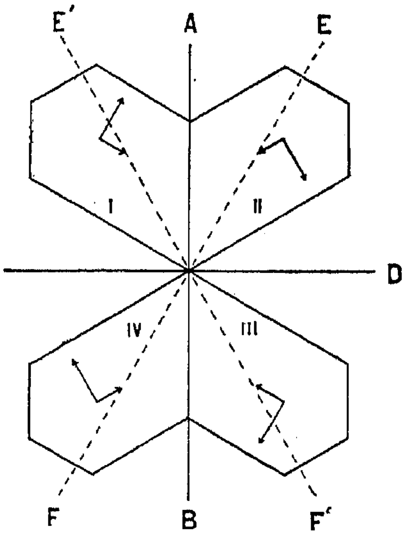

FIG. 2. Suggested arrangement of twins in *Nautilus*.

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[15] W. L. Bragg, *Proc. Roy. Soc.* A, 1924, **105**, 16–39.

and *b* axes in the lattice of the second element are inclined to the respective axes in that of the first at an angle of about 240° (or −120°). The *a* axis is normal to the 010 plane of the crystal in both cases.

An arrangement of four aragonite lattices of the type shown in Fig. 2 exhibits the kind of symmetry necessary for obtaining the patterns discussed before. This figure is a projection normal to the *c* axis and the lattice points are omitted for clearness. The outlines of the crystals (*i.e.*, the projections of the 010, 110, $1\bar{1}0$, planes) and the positive directions of the *a* and *b* axes only are drawn. Such an arrangement is provided by a set of simple twins pointing one way in some layers and the opposite way in others. Thus in Fig. 2, *I* and *II* represent a twin in one layer and *III* and *IV* represent a twin in another layer, presumably the next. This arrangement of aragonite lattices is symmetrical about *AB* and *CD* (Fig. 2). Thus diffraction patterns obtained with the X-ray beam along *AB* and *CD* will be symmetrical about the horizontal and the vertical axes. But they will be different since the inclinations of the axes and hence the reflecting planes, with *AB* are not the same as with *CD*. Also the pattern obtained with the X-ray beam along a direction *EF* will be a mirror image about *AB* of that obtained about *E'F'* where *EF* and *E'F'* are equally inclined to *AB*. A similar thing holds for directions equally inclined on either side of *CD*. This is found to be the case with X-ray patterns of *Nautilus*. It follows from this reasoning that one of the two directions *AB* and *CD* in the above arrangement is to be identified with the directions of the lines of growth. The pattern obtained with X-rays incident normally on the shell surface also exhibits the symmetry of Fig. 2, and is given in Fig. 15. The error in the orientation of the *a* and *b* axes is of the order of 15°.

The optical diffraction halo observed by Sir C. V. Raman for a thin section of this shell consists of two arcs on either side, which roughly subtend an angle of 60° at the centre. The line joining the centres of the two arcs is perpendicular to the lines of growth.

5. *Pinctada* (*Margaratifera*) *vulgaris and Mytilus viridis.*

The diffraction pattern of the nacreous layer of *Margaratifera vulgaris* obtained with an X-ray beam incident normally is given in Fig. 16. The arrangement of the spots in this pattern is seen to be unsymmetrical and the error in orientation of the plane of the *a* and *b* axes obtained from these is of the order of about 5° or 6°, which is much smaller than for *Nautilus*. The patterns obtained by the second method with the lines of growth perpendicular and parallel to the X-ray beam are given in Figs. 13 and 14.

These patterns are also unsymmetrical. Other photographs obtained with the lines of growth inclined at different angles to the X-ray beam are also found to be unsymmetrical and different from one another. This may be due to the existence of untwinned crystals in the shell since the characteristics of the patterns mentioned are all to be found in a single aragonite lattice. The error in the orientation of the *c* axis obtained from these photographs is of the order of 10°. *Mytilus viridis* has a highly iridescent nacreous layer which is less than a quarter of a millimetre thick. Specimens of this shell had, therefore, to be ground to about 0·2 mm. or less. The patterns obtained show the same general characteristics as those of *Margaratifera vulgaris.* The optical diffraction haloes obtained by Sir C. V. Raman with thin sections of these two shells consist of two spots, the line joining them being perpendicular to the lines of growth.

6. *Conclusion.*

It is significant that there is a close correspondence between the results of the X-ray investigation and the diffraction haloes observed by Sir C. V. Raman. The diffusion haloes for shells of the species *Turbo* and *Trochus* obtained with a pencil of light incident normal to the laminations are complete circles. The corresponding X-ray diffraction patterns with a normally incident pencil are also complete circles. These results can be explained by the assumption of crystallites whose *a* and *b* axes are oriented at random. But the *c* axis is normal to the laminations and hence a spot pattern is obtained with the X-ray beam parallel to them. Since the *a* and *b* axes have no preferential orientation such an arrangement is in effect equivalent to a single crystal rotating about the *c* axis. A pencil of light incident on such an arrangement of crystallites would also produce a circular diffraction halo.

The effects observed with the *Nautilus pompilius* are particularly interesting. The results of the X-ray analysis indicate an arrangement of twinned crystals, of the type discussed previously (Fig. 2). If this arrangement were perfect and did not have an error of orientation, the corresponding optical diffusion halo would not be a complete circle but consist of four spots, at the corners of a rectangle the shorter sides of which subtend an angle of 60° at the centre. But the existence of the error in orientation results in a fusion of these spots to form two arcs which subtend nearly the same angle at the centre. This has been observed by Sir C. V. Raman.

The other two shells in which presumably there are no twins but oriented single crystals also show a similar correspondence between the optical and X-ray results. Single crystals arranged parallel to each other form parallel fibres, the optical diffusion halo from which will consist of two spots. The haloes observed by Sir C. V. Raman with *Mytilus viridis* and *Pinctada*

(*Margaratifera*) *vulgaris* are of this type. The X-ray results are in agreement with this observation.

Thus it is found that the structure of the nacreous layer is not the same in all the shells. It is of the simplest type in *Pinctada* (*Margaratifera*) *vulgaris* and *Mytilus viridis* and much more complex in *Nautilus*, *Turbo* and *Trochus*. *Margaratifera vulgaris* and *Mytilus viridis* may be considered to approximate to a single crystal. *Turbo* will be at the other end of the scale with random orientation in the plane perpendicular to the pseudo-hexagonal *c* axis. *Nautilus* occupies a position midway between these two. Another significant fact is that in all cases the spots in the patterns with the X-rays normal to the shell are much longer than those in the other patterns. This indicates a greater error of orientation in the *ab* plane than normal to it. Presumably, during the formation of the shell the aragonite crystals are restricted from an upward or downward tilt by layers below or above them much more than from a slight rotation about an axis normal to the shell surface. From photometric measurements of the widths of the diffraction spots or rings it is possible to get an idea of the size of the crystals in the shells. This will form the subject of another paper along with more accurate measurements of the error in orientation.

I take this opportunity to express my sincere thanks to Sir C. V. Raman, KT., F.R.S., N.L., for suggesting the above investigation and for his continued interest in its progress. I am very grateful to him for permitting me the use of specimens from his collection of beautiful shells. I wish also to thank Professor L. Rama Rao for the gift of an aragonite crystal which was used for taking powder patterns of aragonite.

7. *Summary.*

X-ray diffraction patterns of the nacreous layer of iridescent shells have been obtained using a monochromatic X-ray beam incident along various directions. From a study of these patterns it is found that the nacreous layers of all the shells consist of aragonite crystals orientated with their *c* axes normal to the surface. But the orientations of the other two axes vary with the particular kind of shell examined. For instance, the *ab* plane is randomly orientated in *Trochus* and *Turbo*. In *Nautilus* evidence for twinning is found combined with a specific orientation of the *ab* plane. The *ab* planes of the crystals in *Mytilus viridis* and *Margaratifera vulgaris* are found to exhibit specific orientation with respect to the lines of growth. The error in orientation is also much smaller than in *Nautilus pompilius*. The results obtained closely correspond with the optical observations of Sir C. V. Raman.

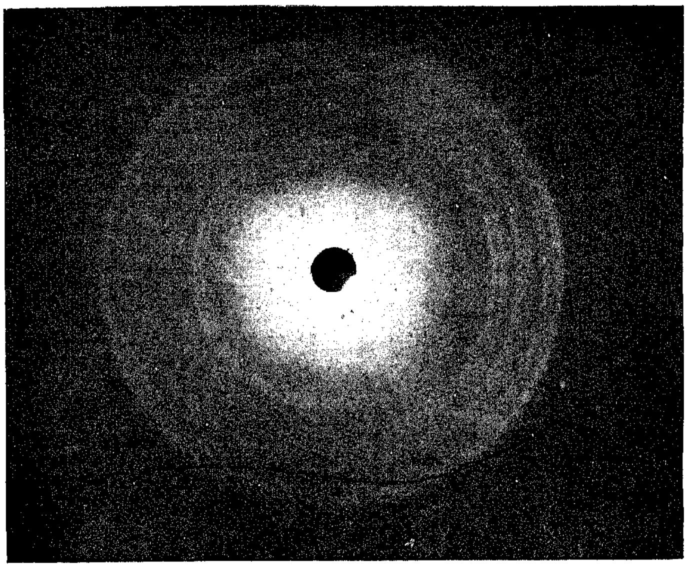

Fig. 3.

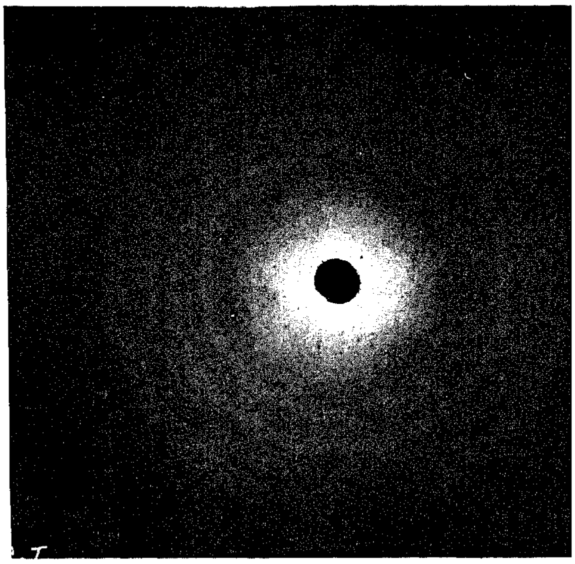

Fig. 4.

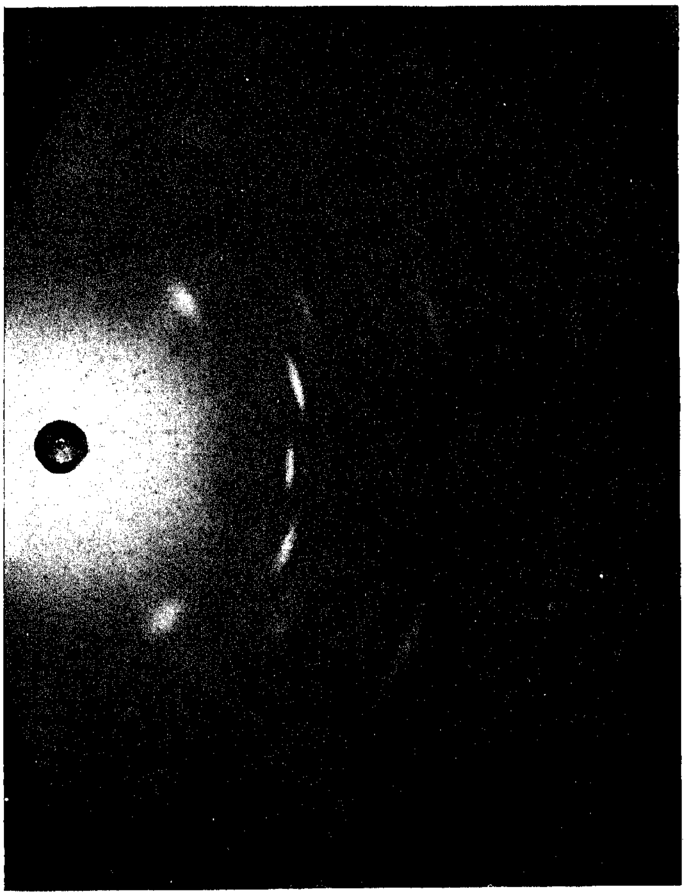

Fig. 5.

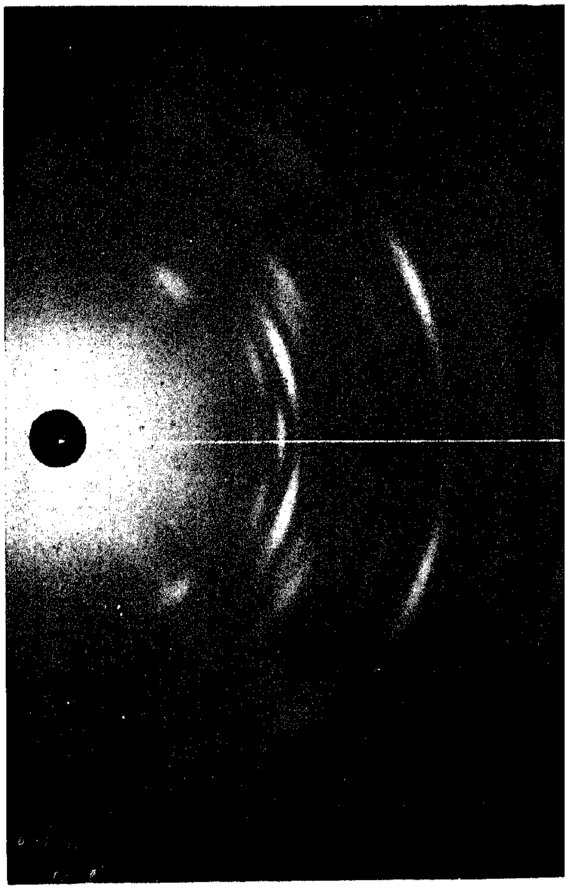

Fig. 6.

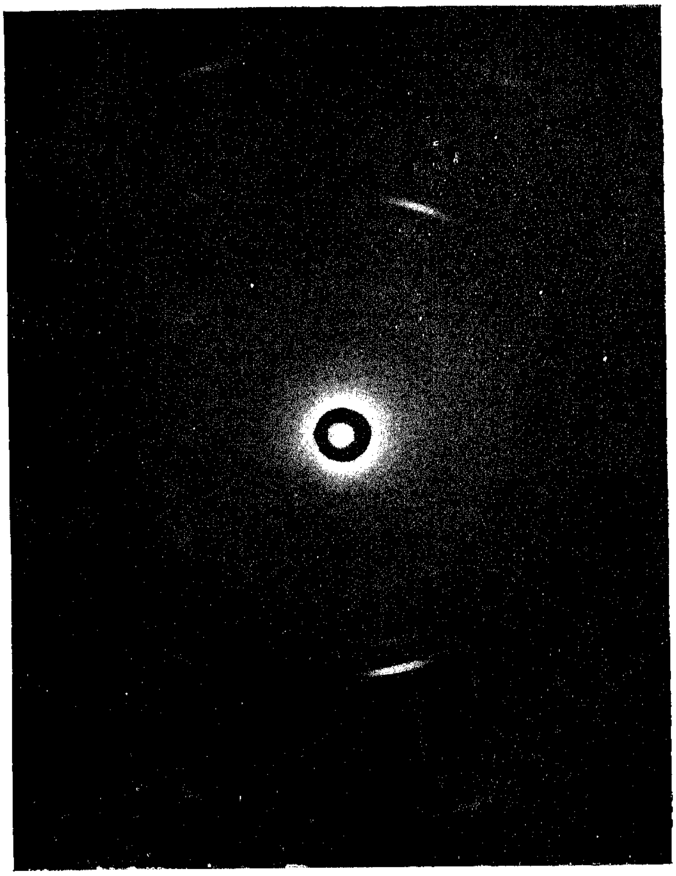

FIG. 7.

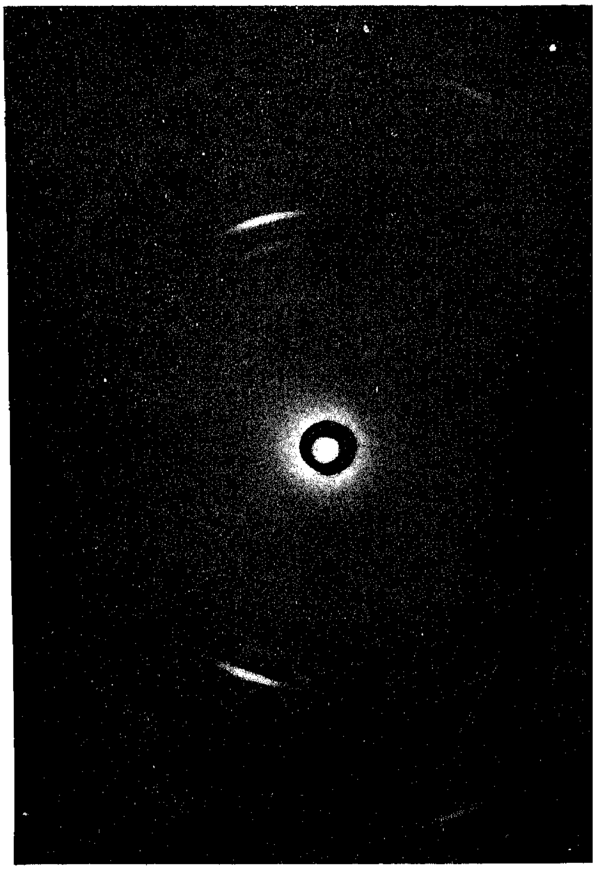

FIG. 8.

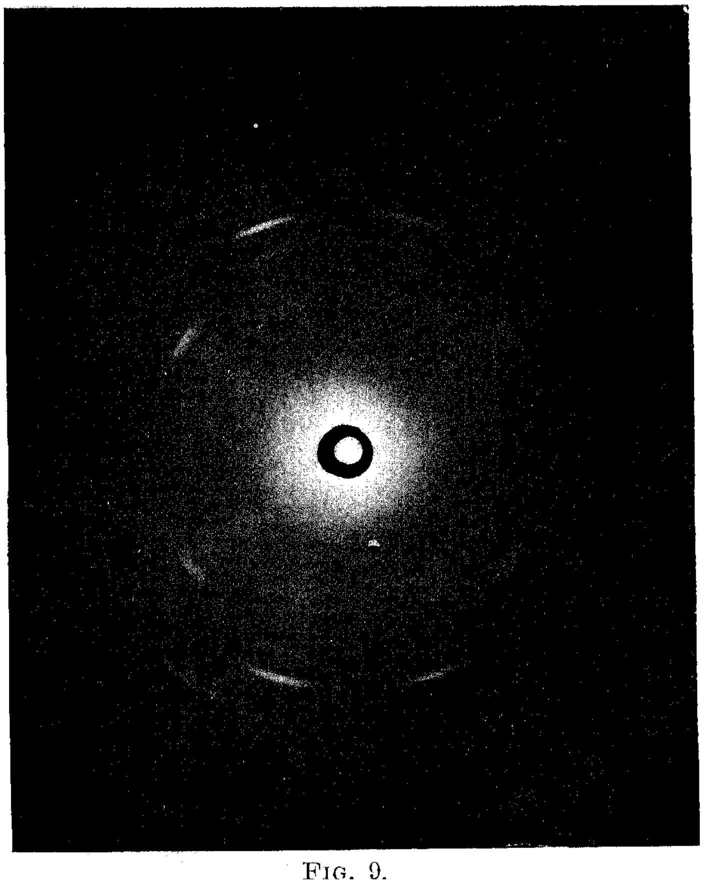

FIG. 9.

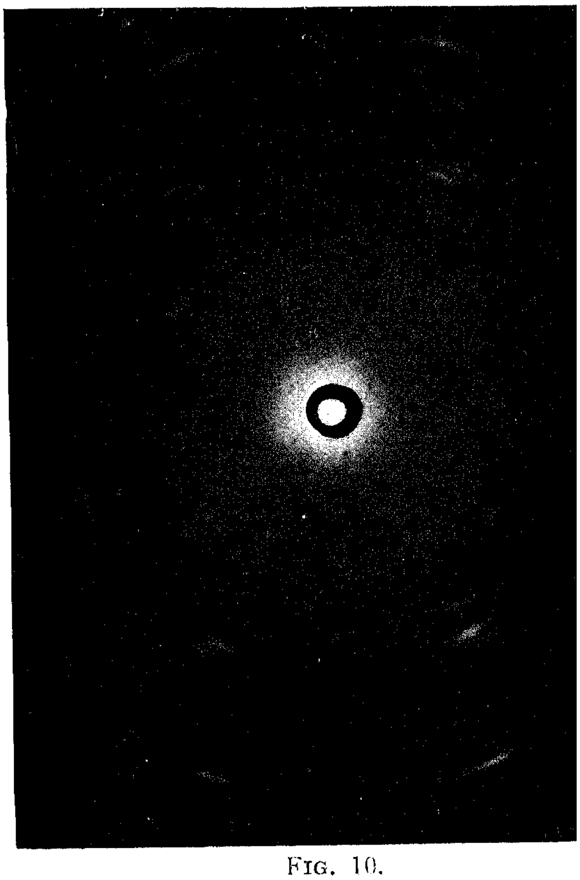

FIG. 10.

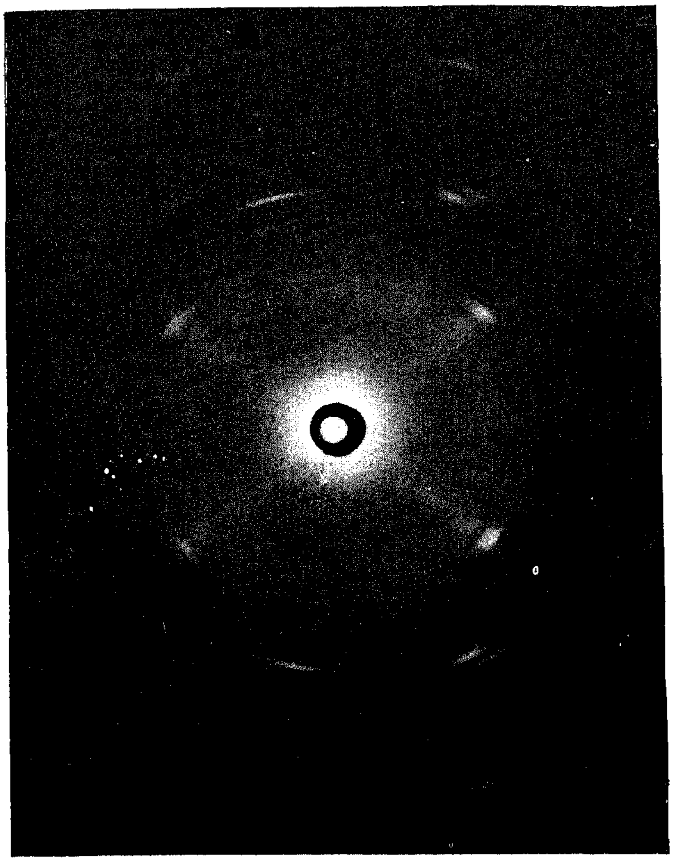

FIG. 11.

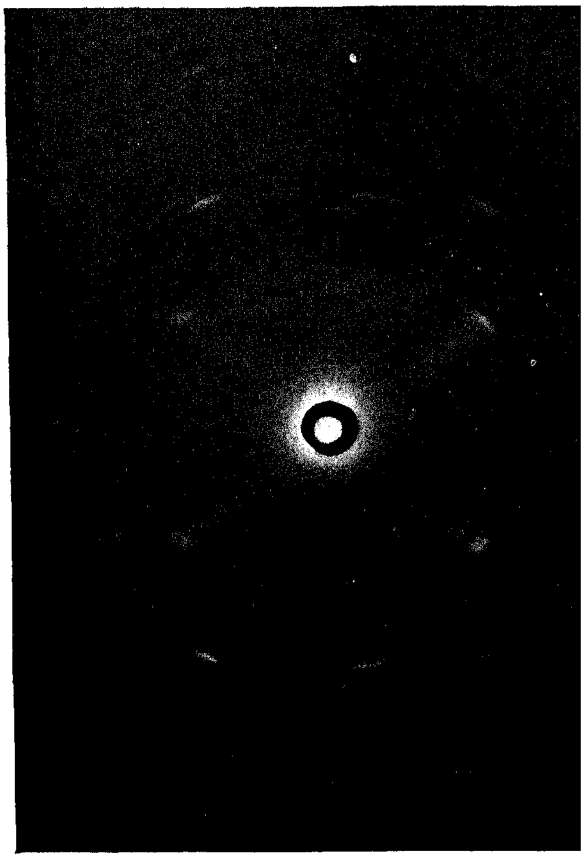

FIG. 12.

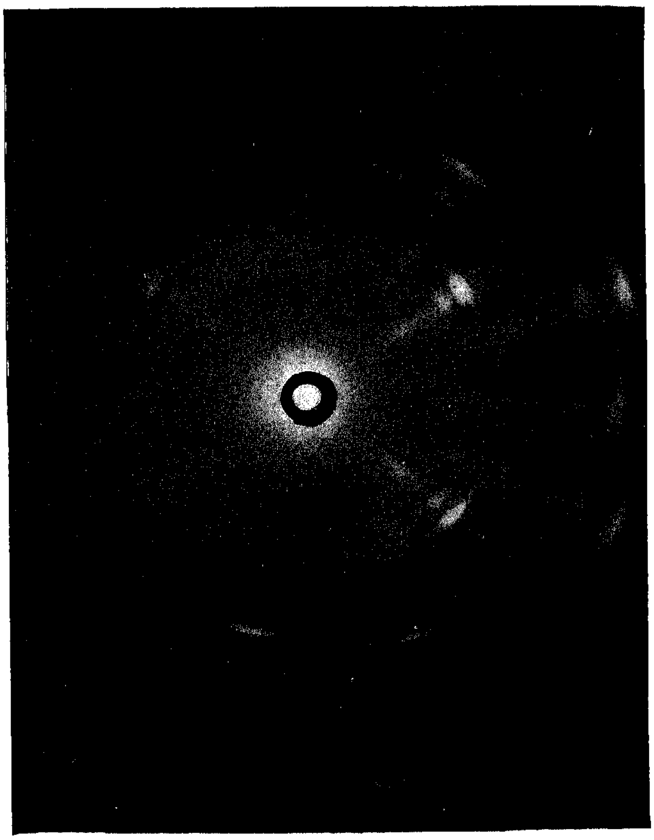

FIG. 13.

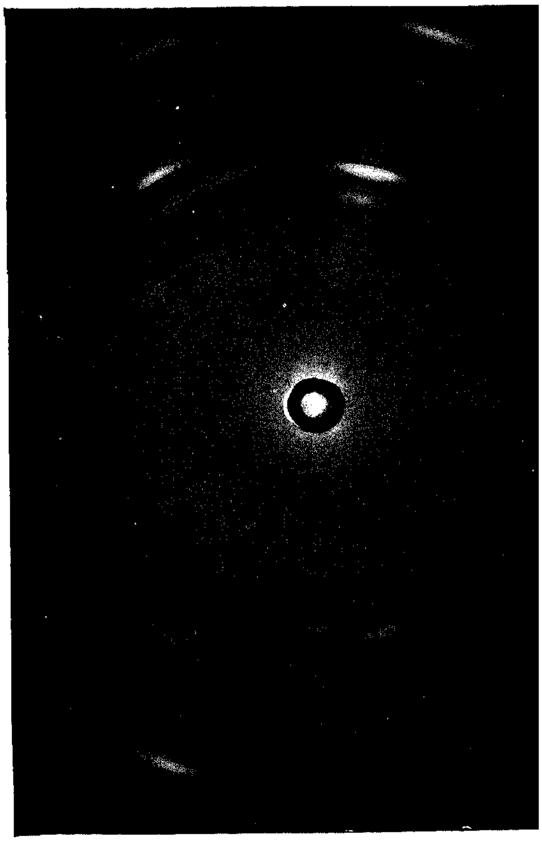

FIG. 14.

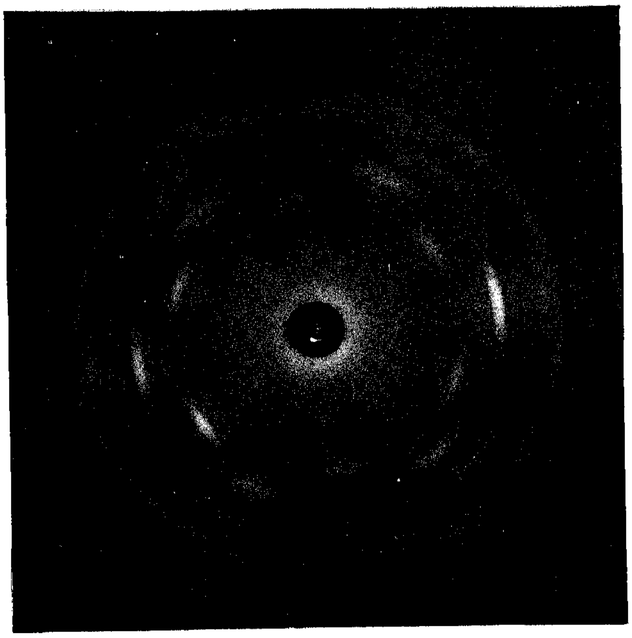

FIG. 15.

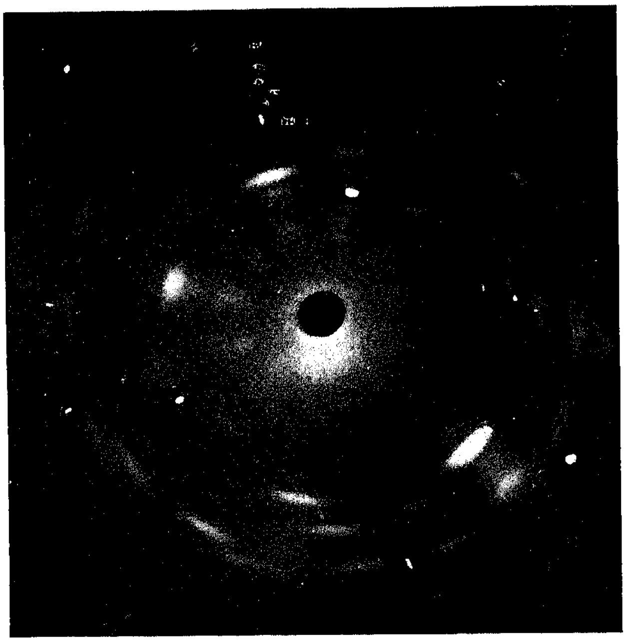

FIG. 16.

EXPLANATION OF PLATES.

Fig. 3.—*Turbo*, X-ray beam perpendicular to surface.

Fig. 4.—*Trochus*, do. do.

Fig. 5.—*Turbo*, X-ray beam parallel to surface.

Fig. 6.—*Trochus*, do. do.

Figs. 7–12.—*Nautilus*, X-ray beam parallel to surface with the following orientations.

Fig. 7.—Lines of growth set at – 30° to the X-ray beam.

Fig. 8.—Lines of growth set at 30° to the X-ray beam.

Fig. 9.—Lines of growth parallel to the X-ray beam.

Fig. 10.—Lines of growth perpendicular to the X-ray beam.

Fig. 11.—Lines of growth set at 60° to the X-ray beam.

Fig. 12.—Lines of growth set at 120° to the X-ray beam.

Fig. 13.—*Margaratifera vulgaris*, X-rays incident parallel to shell surface, lines of growth perpendicular to X-ray beam.

Fig. 14.—*Margaratifera vulgaris*, X-rays parallel to surface, lines of growth along the X-ray beam.

Fig. 15.—*Nautilus*, X-rays normal to shell surface, lines of growth almost horizontal.

Fig. 16.—*Margaratifera vulgaris*, X-rays normal to shell surface.