THE STRUCTURE AND OPTICAL BEHAVIOUR OF IRIDESCENT CRYSTALS OF POTASSIUM CHLORATE

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Received September 20, 1953

1. Introduction

The iridescent crystals of potassium chlorate which exhibit monochromatic extinctions and reflections form admirable material for a study of the optical behaviour of regularly stratified media. The fact that we had at our disposal a fine collection of these crystals led us to undertake a thorough study of the phenomena which they exhibit, and this brought to light a feature of importance which had been overlooked by the earlier investigators in the field, *viz.*, the variation of the spectral character of the iridescent reflections with the azimuth of the plane of incidence, and also revealed the existence of discrete polarised components in the spectra of such reflections. Our findings were reported in a memoir published in the November 1952 issue of these *Proceedings*. Shortly afterwards we found it possible to develop theoretical considerations which satisfactorily accounted for the facts. These, together with some further experimental results, were published in the following issue of the same *Proceedings*. A summarising article also appeared in *Current Science* for December 1952.

Fresh developments have since resulted from further investigations undertaken by us. The most striking of the new results which we wish to report in the present paper is the discovery of *the geometric patterns of reflection and extinction* which iridescent crystals of potassium chlorate exhibit when an extended source of monochromatic light is viewed by reflection at or transmission through the crystals. Typical examples of such patterns are reproduced in Figs. 3 to 10 in Plate XIX and Plate XX accompanying the paper. They show at a glance the whole group of phenomena reported in our earlier papers. Two further topics of interest are also dealt with in the present paper. A study of the conoscopic patterns exhibited by the iridescent crystals on the stage of a polarising microscope with monochromatic light reveals a rich variety of forms which are of interest in themselves and also help to elucidate the structure of the polysynthetic twins. Finally, the paper also records the interesting fact that the iridescent crystals of potassium chlorate function as diffraction gratings and give polarised spectra when traversed by a beam of light in a direction parallel to the composition planes of twinning.

We have thought it advisable in preparing this paper to deal with the subject in such manner that it would be intelligible even to one who had not studied our earlier publications.

2. THE STRUCTURE OF THE POLYSYNTHETIC TWINS

Potassium chlorate is a strongly birefringent crystal belonging to the holohedral class of the monoclinic system and possessing a two-fold axis of symmetry as well as a plane of symmetry normal to that axis. The crystals are usually forthcoming in tablet-shaped forms. Examination of an untwinned crystal of that form on the stage of a polarising microscope makes it evident that the faces of the tablets contain the two-fold axis of symmetry and are perpendicular to the plane of symmetry. The iridescent crystals also appear in tablet-shaped forms and similar observations made with them indicate that they are polysynthetically twinned in such manner that all the components have a common direction for the two-fold axis of symmetry and a common plane of symmetry, and further that the alternate layers of the structure are so related that they can be obtained one from the other by a rotation of 180° about the normal to the faces of the tablet.

The foregoing description of the iridescent crystals as inferred from their optical behaviour is very elegantly confirmed by the two X-ray diffraction patterns reproduced as Figs. 1 and 2 respectively in Plate XVIII, the first referring to an untwinned crystal and the latter to an iridescent tablet, the crystal in each case having been set precisely normal to the X-ray beam. We are indebted for these beautiful records to Mr. A. Jayaraman of this Institute. It will be seen that the pattern of the untwinned crystal is symmetric about a line running diagonally across the picture through its centre, and that on the other hand, the pattern of the iridescent crystal exhibits geometric symmetry about *two* directions, one of which is the same as for the untwinned crystal while the other is perpendicular to it. The number of spots seen in the pattern of the iridescent crystal is, except along the axis of two-fold symmetry of the structure, twice as large as for the untwinned crystal.

3. NATURE OF THE TWIN-PLANE REFLECTIONS

The clue to an understanding of the optical effects exhibited by the iridescent crystals is furnished by considerations regarding the intensity and state of polarisation of the light reflected at the composition planes of twinning. Such reflections cannot arise if the plane of incidence of the light coincides with the plane of symmetry; for, the well-known optical principle of reversibility indicates that the reflection coefficients should be of opposite sign for incidence on the two sides of the boundary, whereas the structures on either side being mirror images of each other, the coefficients should necessarily be the same in both cases—contradictory assertions which are reconcilable only when the coefficient is itself zero. But the reflections would reappear, though only feebly, when the plane of incidence deviates even slightly from the plane of symmetry. Such reappearance being a consequence of a difference only in direction and not of magnitude of the optical polarisations on the two sides of the boundary, there would ensue a rotation of the plane of polarisation of the incident light through 90° in the act of reflection. In other words, a light wave polarised in the plane of incidence would be reflected as a wave polarised in a perpendicular plane; and *vice-versa*. With increasing deviation of the plane of incidence from the plane of symmetry the two streams of light with reversed polarisation thus arising would rapidly gain in intensity, while at the same time the two streams of reflected light polarised in the same manner as the components in the incident light wave, which are absent in the first instance, would come into evidence and ultimately reach a strength comparable with the reflections of the other type. Thus, there would, in general, be four streams of reflected light emerging from the crystal, two with reversed and two with normal polarisation, their relative and absolute intensities being determined by the plane of incidence as also by the angle of incidence in that plane.

4. SPECTRAL CHARACTER OF THE REFLECTION

The considerations set forth above enable us to infer the spectral character of the integrated reflection given by the entire crystal when observed with incident white light. For any given angle of incidence, the intensity of reflection would be a maximum for the wavelength at which the reflections by the successive stratifications reinforce each other by reason of agreement in phase. Since there are, as we have seen, four reflected streams of light, there would, in general, be also four wavelengths of maximum intensity in the spectrum resulting therefrom, their positions being determined by the respective optical paths. Each principal maximum would be accompanied by a set of secondary maxima in the region of wavelengths for which the reflections by the successive stratifications only partially reinforce each other. Of the four principal maxima of intensity, two would be polarised in the normal manner and two in the reversed fashion. Their relative intensities would vary with the angle which the plane of incidence makes with the plane of symmetry. When this angle is small, there would only be two maxima of the latter type, while if the angle is large all four would appear with comparable intensities.

It can easily be shown that when the plane of incidence is perpendicular to the plane of symmetry, the optical paths for the two streams of light which emerge after reflection with reversed polarisation would be identical irrespective of the angle of incidence; for, in such a case, considerations of symmetry permit us to exchange the paths of the incident and reflected streams of light and thereby reverse the roles which they respectively play without altering the total optical paths. It follows that two out of the four maxima of intensity of reflection would then overlap and appear in the same position of the spectrum. It can be shown further that if the alternate layers in the twinning are of equal thickness, the optical retardations for the two streams of light emerging after reflection with reversed polarisation would also be identical in all cases. There would then be three maxima of intensity at the most and not four. Thus the presence of four spectral maxima would be evidence that the alternate layers of the twinning are *not* of equal thickness; the greater their difference the wider would be the spectral separation of the components exhibiting reversed polarisation.

5. STRATIFIED MEDIA IN MONOCHROMATIC LIGHT

Instead of allowing a pencil of white light to fall upon the medium in some specified direction and viewing the transmitted or reflected light through a spectroscope, a different procedure which in some respects proves itself to be far more convenient and powerful is to allow diffuse monochromatic light to be incident on the medium simultaneously in all directions and to view the reflected or transmitted light without spectroscopic aid. It is useful in this connection to recall the well-known interferences exhibited in similar circumstances of observation by a plane-parallel glass plate, or better still, by a sheet of a birefringent crystal such as mica: interferences appear which in the case of an isotropic plate are concentric circular rings, whereas in the case of a birefringent plate two distinct sets of rings appear which to a first order of approximation are both elliptic in shape. In the case of a regularly stratified medium we are concerned with the integrated effect of the reflections by a whole series of regularly-spaced laminæ: their resultant effect would evidently be to give a total reflection in the directions along which all of them reinforce each other by reason of agreement in phase. For any particular order of interference, such directions would lie along the generators of a cone whose cross-sections would be circles if the stratified medium is isotropic, and ellipses if it is birefringent. Since as we have seen, there are four streams of reflected light arising from within the twinned crystal of potassium chlorate, there would be four cones of total reflection of elliptic shape, two having the normal type of polarisation and two of the reversed type. Further, each cone of total reflection would have running parallel to it on either side a series of fainter cones due to the secondary maxima of interference. Likewise, in the transmitted light we would have for each order of interference, four cones of maximum extinction accompanied by their respective secondaries.

6. GEOMETRIC PATTERNS OF REFLECTION AND EXTINCTION

Very simple arrangements suffice for observing the phenomena indicated above. A translucent sheet of plexiglass is illuminated from behind by a sodium vapour lamp or alternatively by a mercury arc. The crystal is held as close as possible to the observer's eye or to the lens of the camera. If the illuminated screen be viewed through the crystal, the extinction bands of the latter are seen in the field of view; with sodium light they appear as dark bands on a bright field, while with the mercury arc which is a multichromatic source the extinction bands exhibit subtraction colours. The reflection spectra of the crystal, on the other hand, appear as bright curves on a dark field. With the mercury arc, the reflection patterns for its different radiations are seen well separated from each other; even the patterns due to the two yellow rays are seen clearly resolved. With some of the crystals also, more than one set of reflection and extinction patterns is observed, evidently corresponding to different orders of interference.

A great variety of patterns could be observed visually, their angular dimensions as well as the nature of the pattern depending very much on the particular crystal employed. A characteristic feature observed in all cases is that the pattern vanishes in the symmetry plane of the crystal and is seen with maximum clearness in the perpendicular plane. Besides the primary extinction or reflection bands the secondaries accompanying them could also be seen. The simplest type of pattern and one which is frequently observed is that of two semi-circular crescents facing each other with their tips narrowing to sharp points near their terminations in the symmetry plane of the crystal.

In Plate XIX, Figs. 3 and 4, we reproduce the extinction patterns and in Figs. 5 and 6 the reflection patterns for a typical and most general case where, as will be seen from the figures, there are four principal bands. In Figs. 4 and 6 the portions of the patterns near the symmetry plane are reproduced, while Figs. 3 and 5 exhibit the portion of the pattern near the perpendicular plane. It will be seen that the two outer bands which have a more or less constant angular separation become sharper and also fade off in intensity as we approach the symmetry plane. On the other hand, the two inner components are most widely separated and also sharper in the vicinity of the symmetry plane: they approach each other and cross at the perpendicular plane.

Of the four components of the extinction and reflection bands, two are polarised with their vibration directions parallel to the symmetry plane and two others perpendicular thereto. This state of affairs is demonstrated by the four photographs reproduced as Figs. 7, 8, 9 and 10 respectively in Plate XX, the two former referring to the extinction and the two latter to the reflection pattern of the crystal. The figures were recorded by placing a polaroid sheet between the wide-angle lens and the photographic film, the polaroid being orientated with its vibration directions respectively parallel and perpendicular to the symmetry plane. It will be seen that in each case two out of the four bands in the pattern have vanished, leaving the other two in possession of the field. It should be mentioned that the birefringence of the untwinned layers of the crystal gave no trouble as they were placed so as to face away from the camera lens while the iridescent layer faced towards it.

It should be mentioned that reflection and extinction patterns of varied character are also observed in monochromatic light using crystals in which the stratifications due to twinning are far from being regular. They are however much less conspicuous than in the case of the specimens possessing a periodic structure which exhibit intense monochromatic iridescence.

7. COMPARISON WITH THE SPECTROSCOPIC OBSERVATIONS

In the Plates illustrating our earlier papers, the spectrograms reproduced had been grouped together for each particular crystal so as to exhibit the effect of varying the angle of incidence of the light. This arrangement was not altogether satisfactory, since the effect of varying the azimuth of incidence, keeping the angle of incidence constant is much more interesting from the standpoint of optical theory. The geometric patterns of reflection and extinction observed with monochromatic light exhibit the latter effect in a very vivid manner and we have now found it possible to illustrate the same effect also with the aid of spectrograms in which the angle of incidence is kept constant while the azimuth is varied in steps.

Figs. 11, 12, 13 and 14 in Plate XXI reproduce the spectrograms of the light reflected by a particular crystal. The angle of incidence is progressively increased as we pass from one figure to the next in the series, while in each figure the angle of incidence is kept constant and the azimuth of incidence is varied in steps, commencing from a setting nearly coinciding with the plane of symmetry and ending with one perpendicular to it. Figs. 15, 16 and 17 in Plate XXII reproduce similar sets of spectrograms for a second crystal. Fig. 18 in Plate XXII refers to a third crystal in which the spectra exhibit the effect of the change of azimuth very clearly and is of particular interest since it was the identical crystal with which the geometric reflection patterns in Figs. 5 and 6 of Plate XIX have been recorded with sodium light and their polarisation exhibited in Figs. 9 and 10 of Plate XX. Comparison of the reflection patterns observed with monochromatic light with the spectral patterns obtained with white light for various azimuths of incidence reveals a remarkably perfect concordance. The transition from a doublet near the plane of symmetry to a quartet and thence to a triplet in the perpendicular plane are shown equally well in both sets of figures. The variations in the sharpness and intensity of the components and the secondaries accompanying them are also very clearly seen in both.

We should also mention that we have made visual observations of the reflection and extinction patterns of the two other crystals whose reflection spectra have been reproduced in Plates XXI and XXII. It will be noticed that the character of the spectra recorded for these two crystals are very different in appearance. Differences of the same nature have also been observed by us in the corresponding reflection and extinction patterns.

8. THE CONOSCOPIC PATTERNS

The interference figures exhibited by twinned crystals in convergent polarised light are of considerable interest and are discussed in some detail in the well-known treatise of Pockels on crystal optics. The illustrations of such patterns reproduced as plates in his book appear to have been obtained by the rather artificial procedure of putting a plate of untwinned crystal on the mirror of a Norremberg's doubler; the two components of the synthetic twin thus obtained are necessarily of equal thickness. However, both simple and multiple twins of potassium chlorate are forthcoming in great variety as tablet-shaped crystals, and the material thus available is particularly well suited for such observations. All that is necessary is to mount the crystals with Canada balsam between a microscope slide and a thin cover-slip and to view the same on the stage of a polarising microscope. Two special settings of the specimen are of interest; in one setting the symmetry plane is parallel to the vibration-direction of either the polariser or the analyser, while in the other setting, it bisects the angle between them. In the former setting, a dark isogyre appears along the trace of the symmetry plane, while in the latter this is absent.

As potassium chlorate is strongly birefringent, it is desirable to use the monochromatic light furnished by a sodium vapour lamp, though some features of interest may be seen even with white light. In the observations with monochromatic light the iridescent crystals may be naturally expected to exhibit their extinction patterns superposed on the patterns due to birefringence, and we have found this to be actually the case. The configuration of the extinction patterns is not essentially altered by reason of the observations being made between crossed polaroids. But some curious features are noticeable in and around the regions where the patterns of birefringence and extinction cross each other; into a description of these features we do not propose here to enter.

The conoscopic figures of twinned potassium chlorate assume their simplest form when the crystal consists of only two components. They may then be described as a superposition of the birefringence patterns of the individual components, but as the result of such superposition two other sets of figures are also seen in the field which may be designated as the *differential and summational patterns* respectively. If the components of the twin are of equal thickness, the entire pattern is symmetrical with respect to the direction of the normal to the plate. If, on the other hand, the components are of unequal thickness, their individual patterns are naturally different, and their differentials and summationals drift away to one side and the pattern becomes unsymmetrical. In the normal setting of the crystal the differentials are very prominent, while in the diagonal setting the summationals dominate the picture. The former consist of a set of parallel lines, while the latter are closed curves approximately elliptic in shape. The differentials represent interferences of a lower order and may be seen as coloured bands in the appropriate parts of the field with incident white light. The foregoing remarks are illustrated in Plates XXIII and XXIV for four specimens numbered I, II, III and IV respectively, each in the two settings already specified. For these photographs we are indebted to Mr. T. K. Srinivasan by whom they were recorded in the course of an unpublished investigation at this Institute.

It is not to be expected that the conoscopic figures observed would always be of the comparatively simple types illustrated in Plates XXIII and XXIV. A form of pattern frequently noticed is that which resembles that of an untwinned crystal, but in which the successive bands exhibit periodic fluctuations of intensity. Four patterns of this type are reproduced in Plate XXV. These again were recorded by Mr. T. K. Srinivasan in the course of his examination of numerous specimens with a petrographic microscope. The detailed interpretation of these patterns awaits further investigation.

9. THE TWINNED CRYSTALS AS DIFFRACTION GRATINGS

Optical theory indicates that a regularly stratified medium can in appropriate circumstances also function as a diffraction grating and exhibit the phenomena arising therefrom. Several examples could be cited as illustrations of this statement. It is therefore not without interest to record the fact that the polysynthetically twinned crystals of potassium chlorate have actually been observed by us to exhibit such effects. For this purpose it is necessary to use a crystal in which the stratifications are not excessively fine and, in order to eliminate boundary effects as far as possible, to immerse the crystal in a cell containing liquid paraffin or other suitably chosen liquid of which the refractive index approximates to the mean index of potassium chlorate. The crystal is set in the cell in such manner that a pencil of light entering the crystal at one edge and traversing it in a direction parallel to the composition planes of twinning emerges through the opposite parallel edge and is received on an observing screen. The cleavages of potassium chlorate are good and hence with the arrangements described, disturbing effects other than those arising from the lamellar structure of the crystal are not serious.

We have made observations in the manner described above with three specimens and noticed that the emergent pencil of light is spread out by diffraction over a wide range of angles on either side of the direction of the undeviated pencil. With incident white light, coloured spectra are observed, whereas with monochromatic light the field exhibits a great many interference bands with local concentrations of intensity such as would be exhibited by a diffraction grating. The most remarkable feature, however, is that the diffraction bands observed are markedly polarised but in different ways, some concentrations in the field appearing bright for one position of the polaroid while the others disappear and *vice-versa.*

In a general way an explanation of the results observed by us is not far to seek. It is evident that except in the particular case when the light traverses the crystal along the lines of intersection of the planes of the lamination with the symmetry plane of the structure, the alternate layers of the twinning present optically different orientations to the light waves traversing them. As a consequence, the two vibration directions as well as the optical paths of the light wave would be different in the alternate layers. In these circumstances the crystal would necessarily function as a phase-change diffraction grating, the resultant spectra exhibiting polarisation effects of the character observed. Since the path differences involved are fairly large, it is necessary to use incident monochromatic light in order to reveal the resulting phenomena completely.

10. SUMMARY

Iridescent crystals of potassium chlorate exhibit geometric patterns of reflection and extinction respectively when a field of diffuse monochromatic light is viewed by reflection at or transmission through the crystal. The patterns consist in general of four closed curves, two of which are polarised with their vibration directions parallel to the plane of symmetry of the crystal and the two others perpendicular thereto. The configuration of the patterns exhibits a perfect concordance with the spectral character of the reflections or extinctions observed with incident white light at corresponding azimuths of incidence and thus furnishes a complete picture of such spectral behaviour. Photographs of the geometric patterns are reproduced with the paper as also of the conoscopic patterns exhibited by the iridescent crystals on the stage of a polarising microscope. The paper also reports the observation that the twinned crystals of potassium chlorate function as diffraction gratings and give polarised spectra when light traverses them along their composition planes of twinning.

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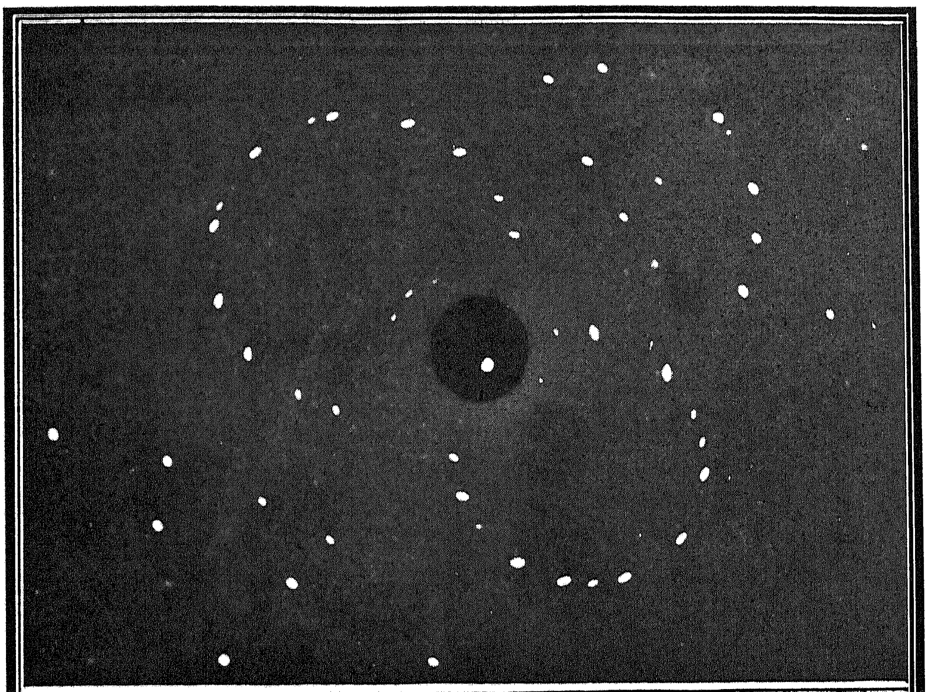

FIG. 1

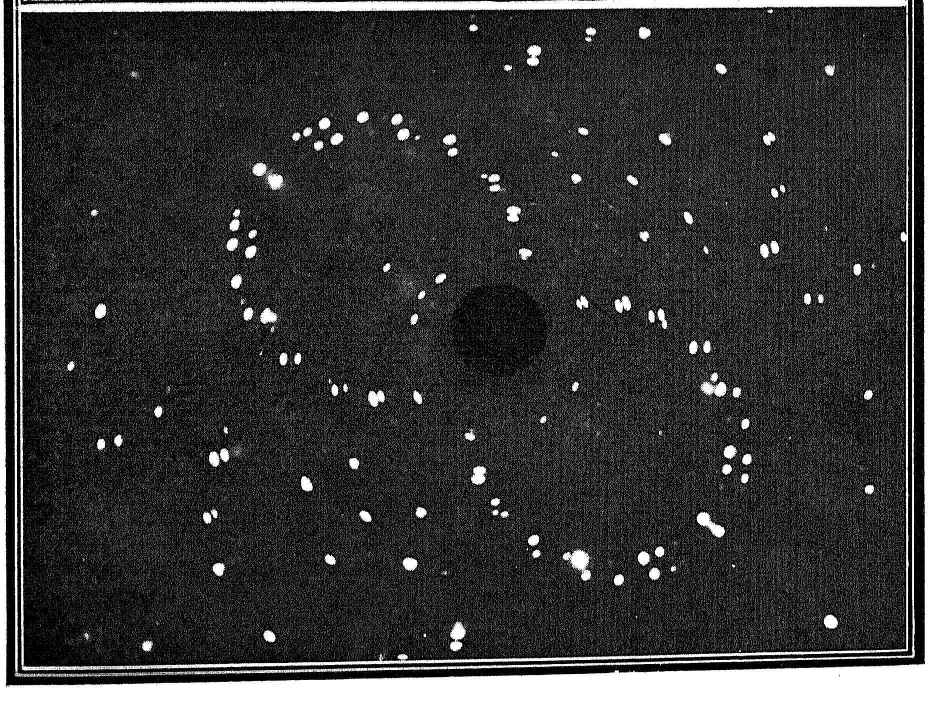

FIG. 2

X-ray Diffraction by Untwinned and by Iridescent Crystals

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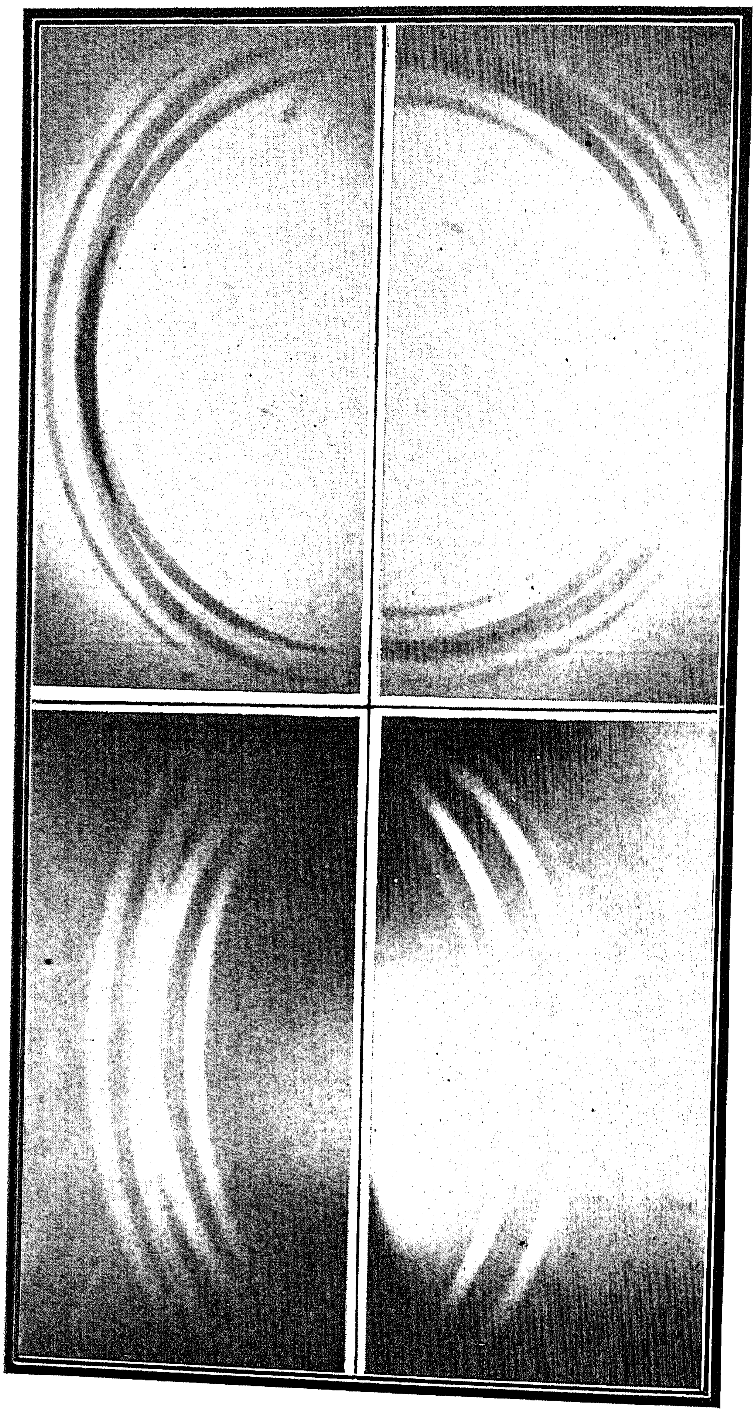

FIG. 3

FIG. 4

FIG. 5

FIG. 6

Geometric Patterns of Extinction and Reflection

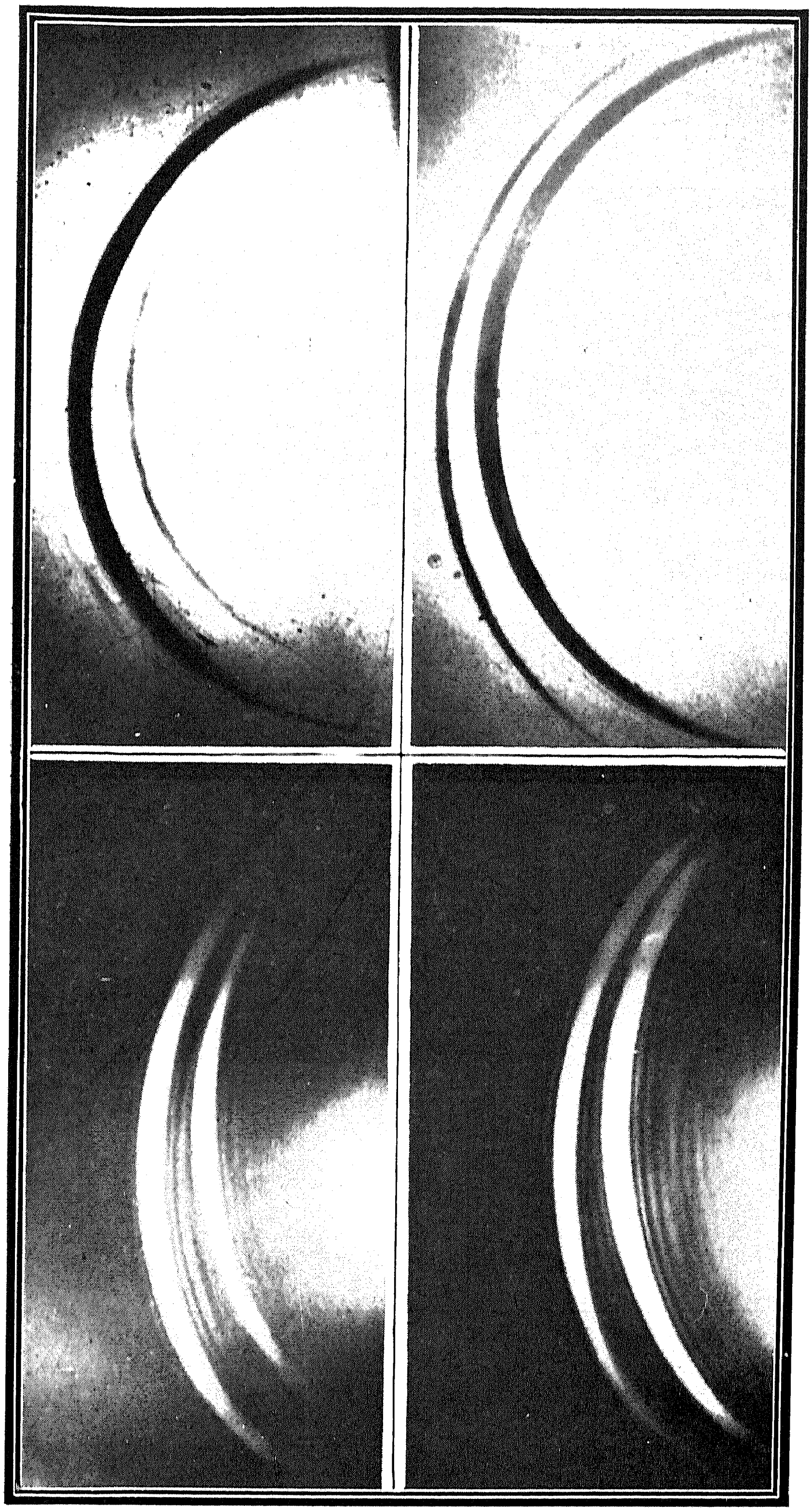

FIG. 7

FIG. 8

FIG. 9

FIG. 10

Polarisation of the Patterns

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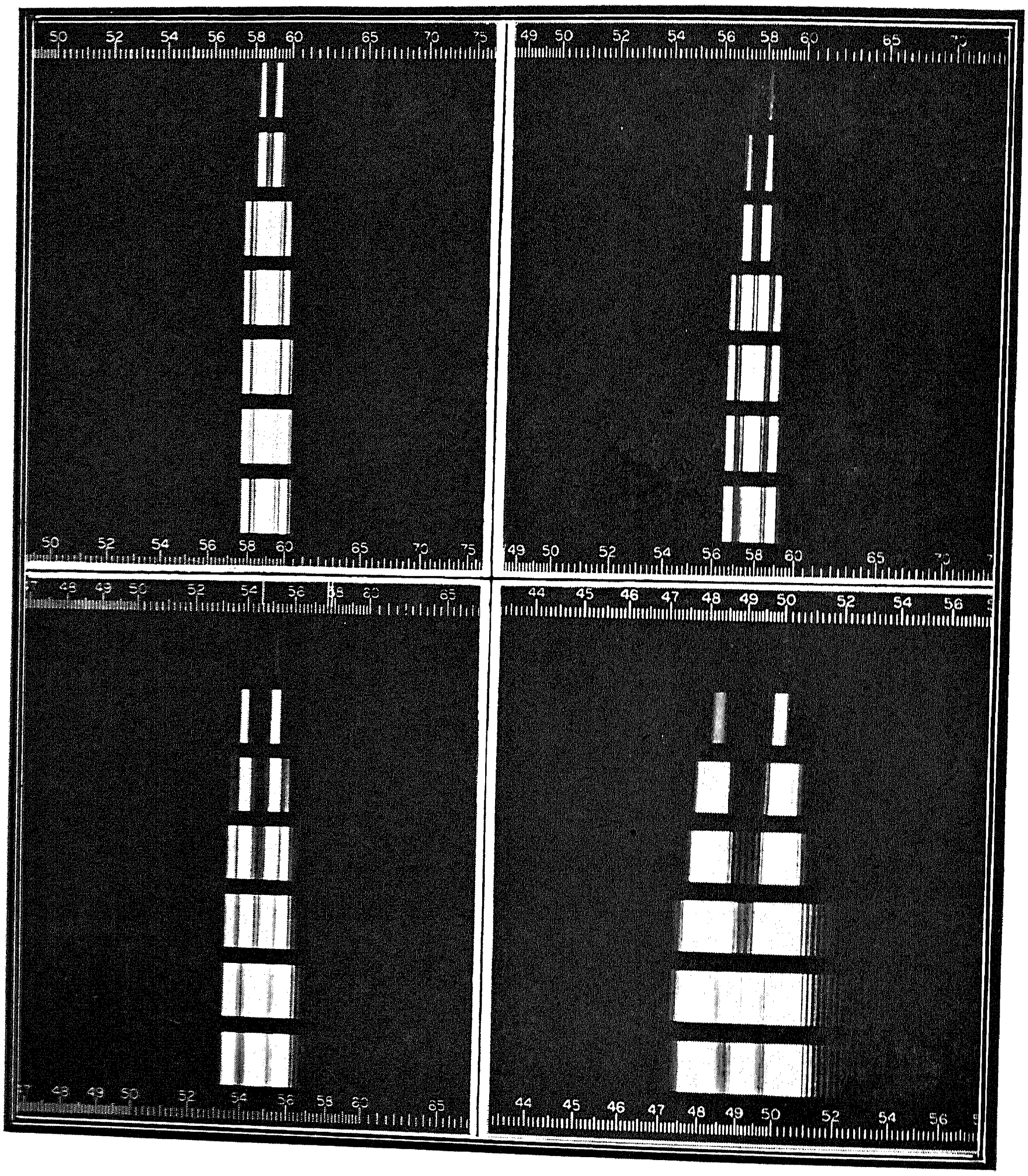

FIG. 11

FIG. 12

FIG. 13

FIG. 14

Reflection Spectra of Iridescent Crystals

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FIG. 15 FIG. 16

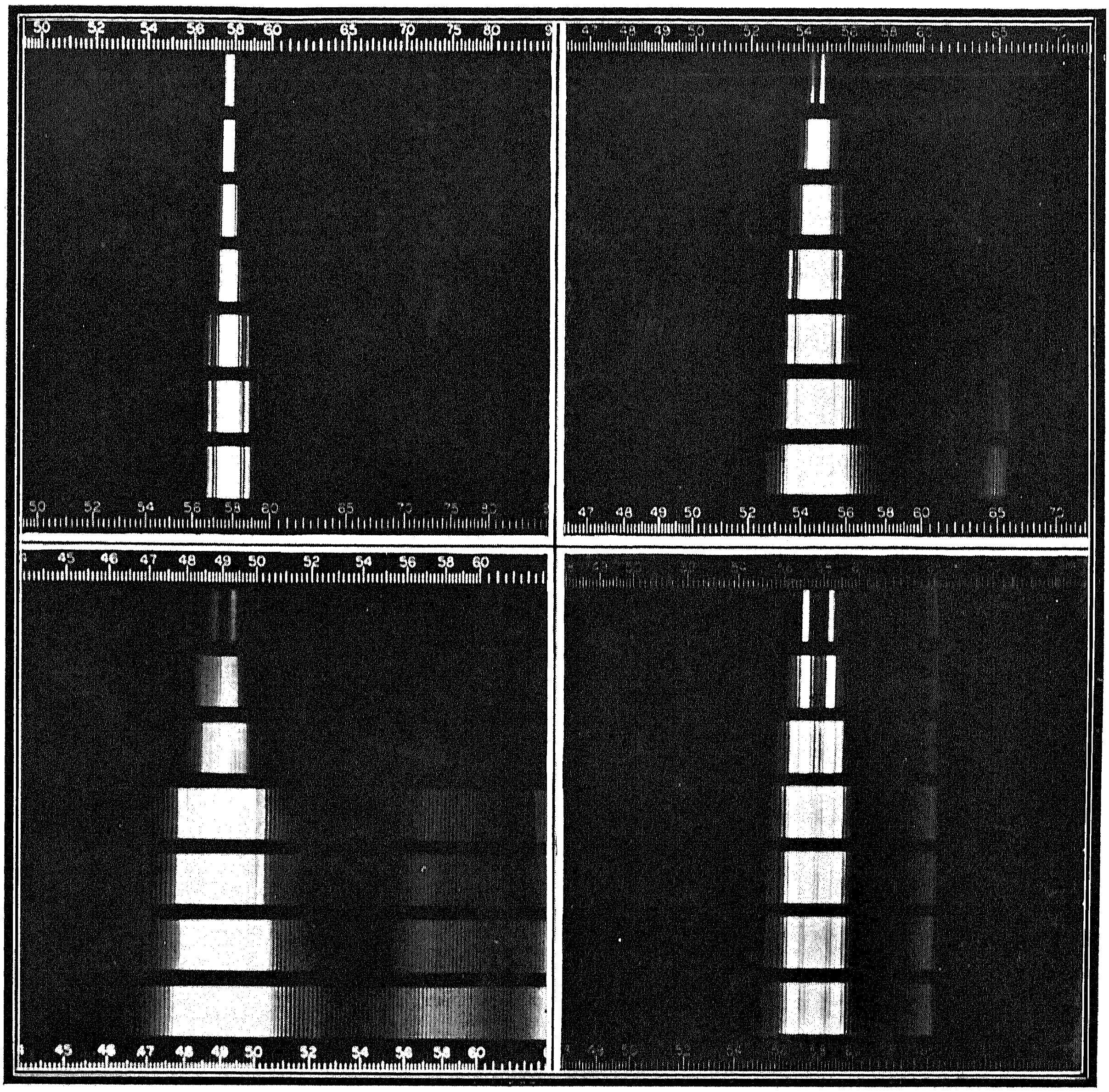

FIG. 17 FIG. 18

Reflection Spectra of Iridescent Crystals

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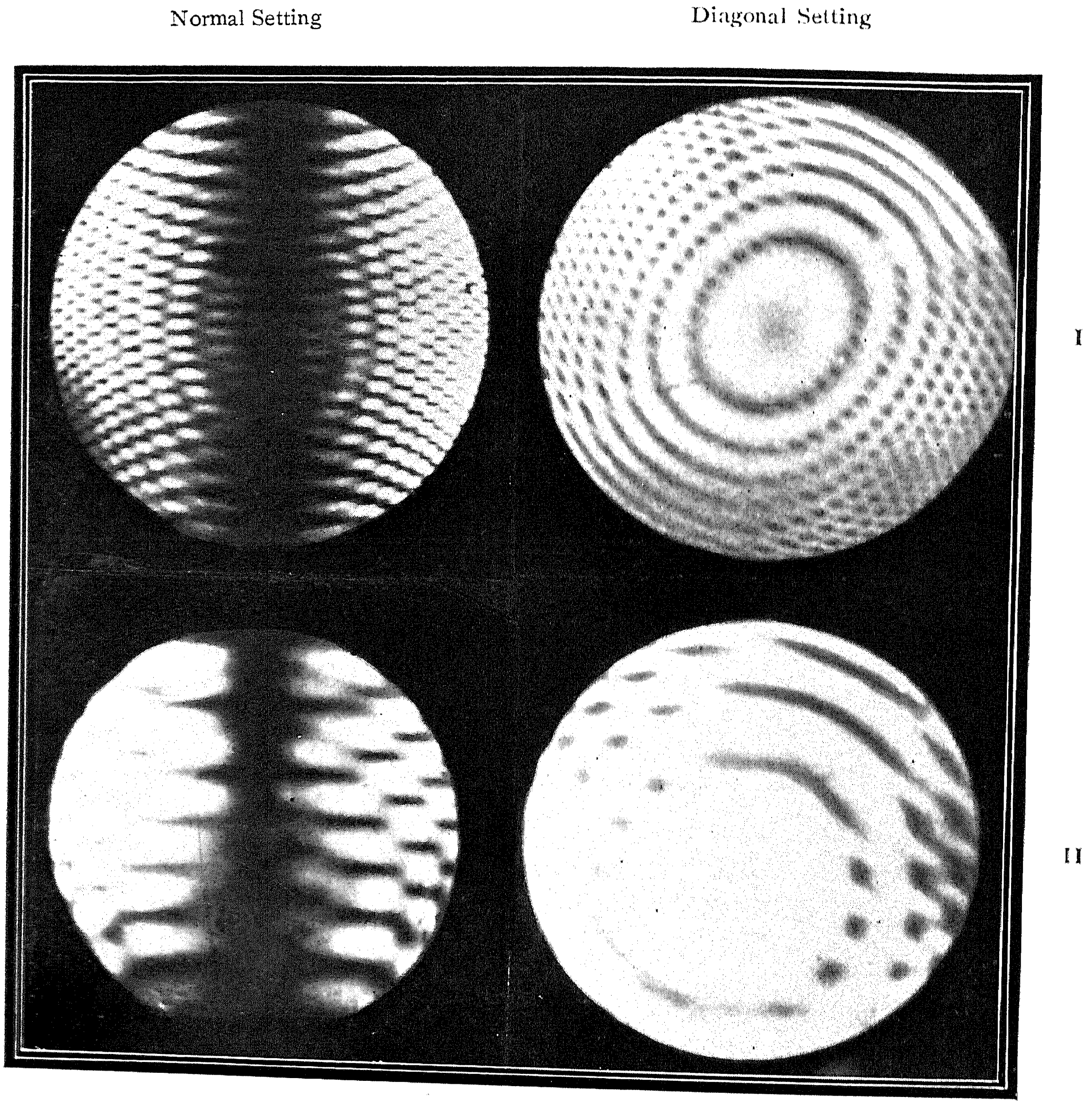

Symmetric Conoscopic Patterns

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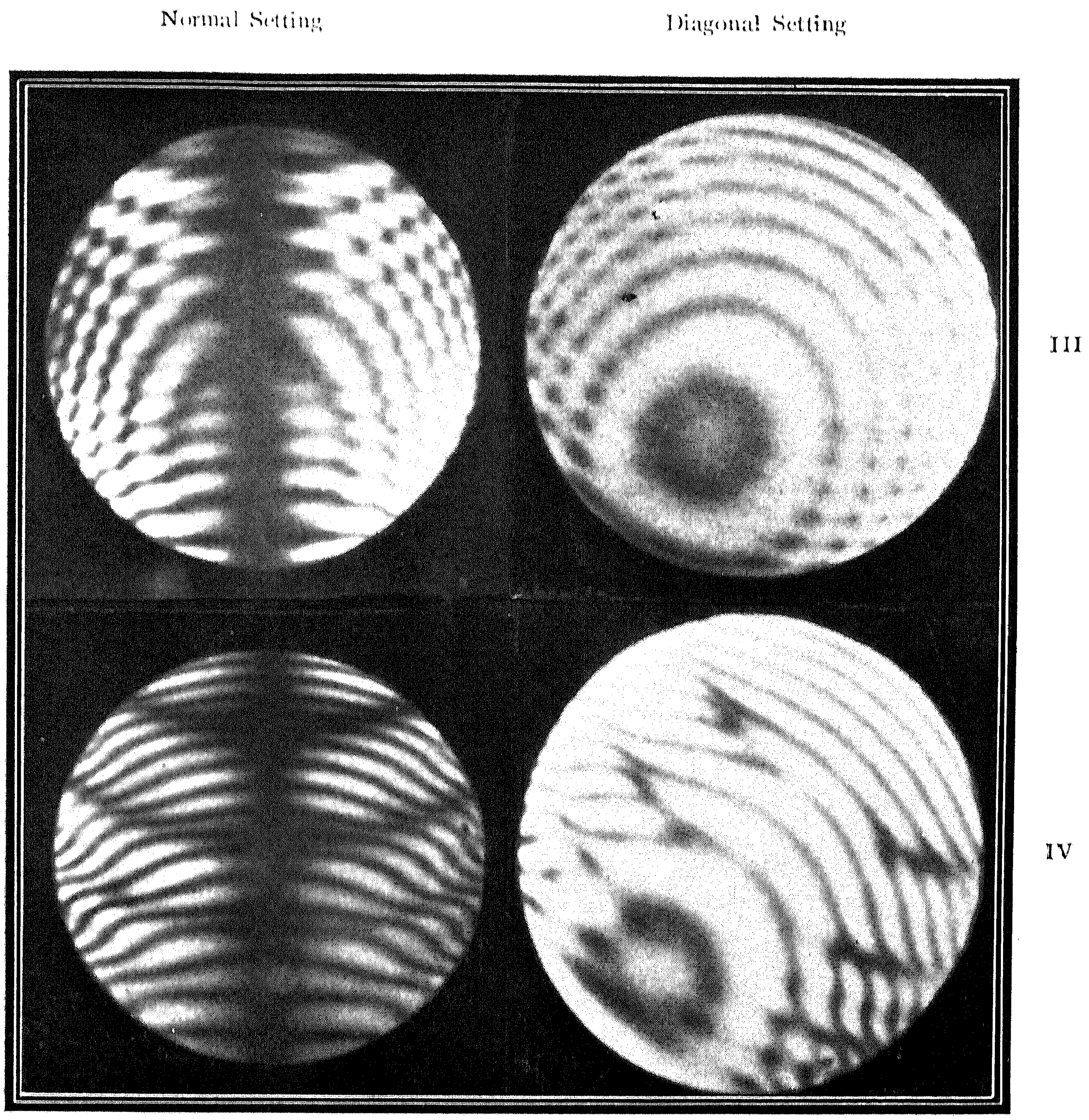
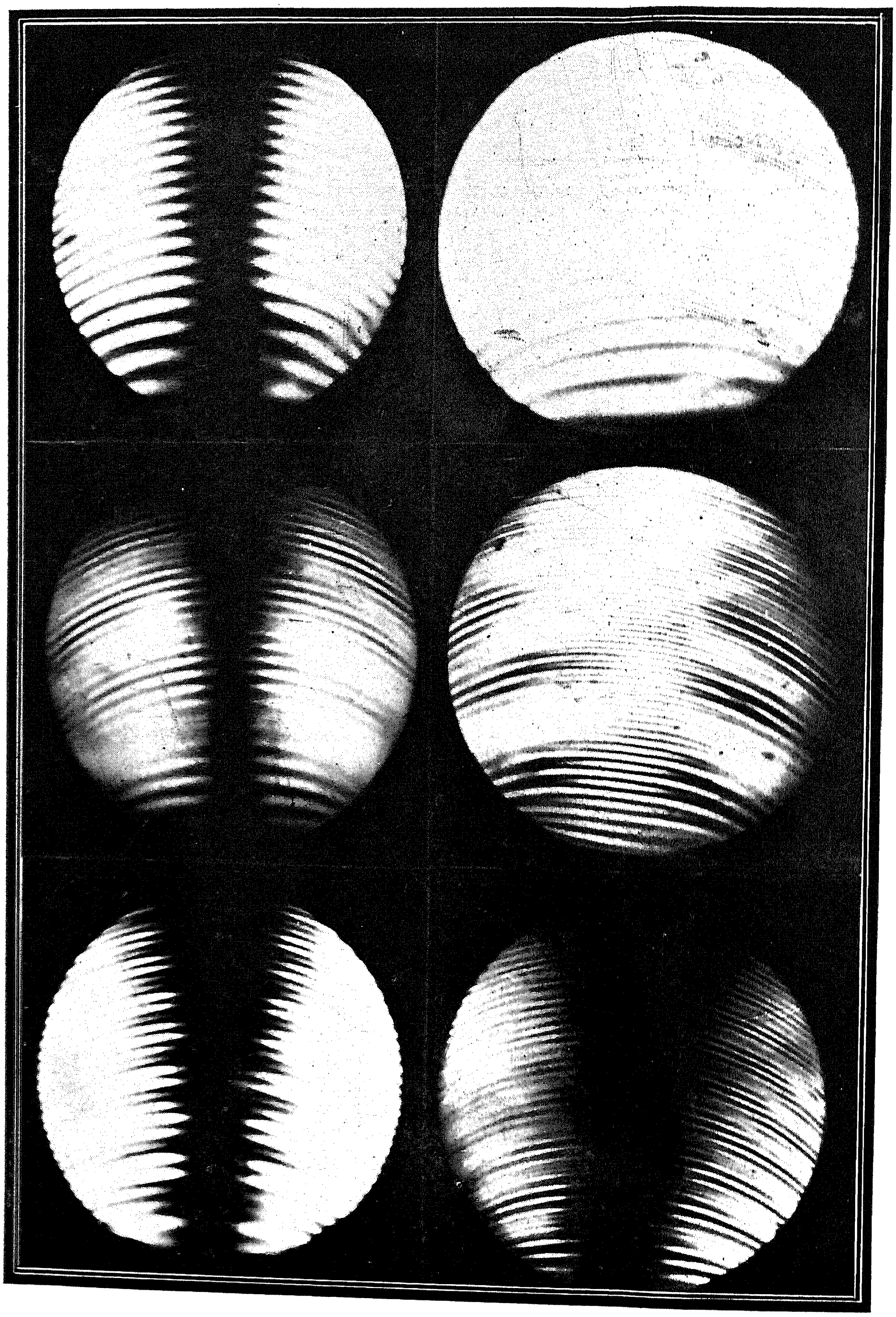


Asymmetric Conoscopic Patterns



Conoscopic Patterns of Iridescent Crystals