ON THE OPTICAL BEHAVIOUR OF CRYPTO-CRYSTALLINE QUARTZ

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1. INTRODUCTION

THE present paper may be regarded as a sequel to two earlier communications[1, 2] by the present authors in these *Proceedings* which dealt with the structure and optical behaviour of iridescent agate and of the commoner forms of chalcedony. We have felt it desirable to supplement those two papers by a somewhat fuller description and discussion of the optical phenomena presented by these materials. Of particular interest is the property exhibited by the relatively more transparent specimens of chalcedony of polarising the light transmitted by them perfectly. This phenomenon is illustrated in a striking manner by Figs. 1 and 2 reproduced in Plate I; these are photographs of the entrance to the building of this Institute and of the landscape beyond as viewed through a plate of chalcedony about a millimetre thick on which was superposed a polaroid sheet. In Fig. 1, the building and landscape are seen clearly, while in Fig. 2 they are completely smudged out. In the former case, the polaroid had its vibration direction parallel to the fibres of quartz composing the chalcedony, while in the latter the vibration direction of the polaroid was transverse to the fibres. Similar effects are exhibited by Figs. 3 and 4 which are photographs of a sodium vapour lamp recorded in analogous circumstances. Polarisation effects of the same nature are also observed in the transmitted light which appears along with the diffraction spectra exhibited by iridescent agate. We shall return to these phenomena later in the paper.

An interesting and important aspect of the present subject is the close correlation which exists between the optical phenomena and the structure of the materials as revealed by X-ray diffraction studies. Large variations in structure are evident from the series of twelve X-ray diagrams reproduced in Plate III and Plate IV, and they correspond to striking differences in optical behaviour.

2. SOME THEORETICAL CONSIDERATIONS

The phenomena exhibited by chalcedony and agate in varied circumstances are best elucidated by first considering a few idealised cases in the light of a simplified geometric theory. We may assume the material to be composed of crystallites of quartz completely filling its volume. Had the material been optically isotropic, light would freely pass through the polycrystalline aggregate. Actually, the birefringence of the quartz is sufficient to ensure the total diffusion of the light in its passage through a plate of the material as a result of the refractions at the inter-crystalline boundaries, provided that the optic orientation of the crystallites is assumed to be entirely at random. A distant source of light viewed through such a plate would be invisible; a diffuse halo of light would be observed in the same general direction which would exhibit no observable polarisation even if the incident light be fully polarised.

It is evident from the foregoing that a preferred orientation of the crystallites is a *sine qua non* in order that any observable fraction of the light be regularly transmitted through the material. Indeed, the geometric theory demands a perfectly ordered orientation of the crystallites for an optical image of a light source to be visible through a plate of the substance. The maximum transmission would occur if the crystallites were so arranged that the principal optical axis of quartz, *viz.*, the *c*-axis were aligned in perfect parallelism for all of them. Actually, we have not encountered a case of this kind in our studies, though an approximation to it has been noticed in some specimens of fibrous quartz.[3] On the other hand, chalcedony consisting of crystallites of quartz with some direction perpendicular to the *c*-axis such as $[1\bar{1}00]$ or $[11\bar{2}0]$ set more or less perfectly parallel for all of them appears to be fairly common. In such an arrangement, the orientation of the *c*-axis would vary from one crystallite to another.

3. THE X-RAY DIFFRACTION PATTERNS

The foregoing remarks are illustrated by Figs. 1 to 6 in Plate III and Figs. 1 to 6 in Plate IV. Fig. 1 in Plate III is the X-ray diffraction pattern of agate recorded for a region exhibiting brilliant iridescence and using unfiltered MO radiation. It is seen that the pattern is a fibre diagram in which the crystallites are orientated with fair precision in a direction parallel to the *a*-axis of quartz, while their *c*-axes are orientated in all possible directions perpendicular thereto. Fig. 2 in the same Plate was also recorded with another piece of agate exhibiting iridescence; it shows a lesser precision in the orientation of the crystallites but which is of the same kind. Still less well defined is the orientation of the crystallites of the same nature seen in Fig. 3. This was obtained with a polished plate of chalcedony exhibiting a fair measure of transparency.

Fig. 4 in Plate III was obtained with a polished plate of chalcedony which was remarkably transparent, being in fact the one with which the photographs reproduced in Plate I were obtained. It can be interpreted as a fibre diagram in which the fibres are parallel to the [1$\bar{1}$00] direction, while the *c*-axis takes all possible orientations perpendicular thereto. A clear indication of the same type of fibering is illustrated in Fig. 5 which was recorded with a translucent specimen of coloured agate. Fig. 6 in Plate III was recorded with the same iridescent agate as Fig. 1 but in a region exhibiting no conspicuous banding or iridescence. The figure does exhibit preferred orientation of the crystallites but not of a sharply defined character, which appears to be intermediate between the types illustrated in Figs. 1 and Fig. 5 in Plate III.

Fig. 1 in Plate IV is an X-ray diagram of powdered quartz. The remaining five figures in the Plate are diagrams of chalcedony and agate in which hardly any preferred orientation is to be noticed. Fig. 6 in Plate IV which almost resembles Fig. 1 in the same Plate was recorded with a chip of chalcedony exhibiting little transparency.

4. POLARISATION OF THE TRANSMITTED LIGHT

We may now consider the case of a plate of chalcedony assumed to be cut in such a manner that the *a*-axes of the crystallites are all parallel to each other and to the surface of the plate. If light be normally incident on such a plate with its vibration direction parallel to the common direction of the *a*-axes of the crystallites, it is evident that it would be freely transmitted by the plate. If, on the other hand, the vibration direction of the incident light be transverse to the same common direction, the variation of the direction of the *c*-axis from crystallite to crystallite would result in the light being refracted at the inter-crystalline boundaries and hence none of the incident light would be transmitted. The directions in which the light diffused would emerge and the state of its polarisation would both depend upon the orientation of the inter-crystalline boundaries, in other words on the shape of the crystallites. If the latter are elongated cylinders or fibres with their length parallel to their *a*-axes, the light diffused would appear as a fan of refracted rays lying in a plane perpendicular to the direction of the fibres: it would also be completely polarised with the vibration direction transverse to the fibres.

5. DIFFRACTION PHENOMENA

Though geometric considerations of the kind set forth above suffice to give a qualitative picture of the phenomena, they would not describe completely what is actually observed. The light rays deviated by the individual fibres would evidently be in a position to interfere with each other. Hence the fan of rays diffused by the plate should properly be regarded as due to the passage of light through an irregular phase-change grating. This would diffract the light in various directions transverse to the fibres. Further, if the length of the individual fibre were not great enough, light would also be spread out by diffraction to some extent in other directions.

The importance of the part which diffraction plays in the optical phenomena is most strikingly evident in the case of iridescent agate. As has been already remarked and illustrated in our earlier paper on the subject, the light *regularly* transmitted by iridescent agate is perfectly polarised, the only difference between the iridescent and non-iridescent regions being that the intensity of transmission is greatly enfeebled in the former by reason of the radiation energy being copiously diffracted in other directions. It is highly significant that these diffracted radiations are neither wholly nor even partly concentrated in specific directions as would be the case with ordinary gratings. The diffracted radiations in fact appear as elongated streaks, and that they are well-defined streaks is made evident by using a monochromatic light source and selected regions on the agate where the spacings are most regular. No image of the source is however seen except at the centre of the spectrum of zero order. The diffraction streaks exhibit a partial polarisation which is in the same sense as the polarisation of the regularly transmitted light near their central regions but in the opposite sense further out in the streaks on either side. This situation will be evident from the photographs reproduced as Figs. 3 and 4 in Plate II exhibiting respectively the two components of polarisation of the diffraction pattern observed with sodium light.

The explanation of the facts stated above leads us directly to the solution of the problem of the nature of the laminations in iridescent agate which we shall now proceed to consider.

6. THE STRUCTURE OF IRIDESCENT AGATE

We shall assume that the fibres of quartz in the iridescent layers of agate have all a common direction and also a common optic orientation. That this assumption is substantially correct is evident from the complete polarisation of the light regularly transmitted through the iridescent layers and is further confirmed by the X-ray diffraction studies to which we have already referred. What then is the nature of the periodicity that gives rise to the diffraction spectra? We have already remarked that the diffraction streaks observed with fibrous chalcedony are a consequence of the varying orientation of the *c*-axis from fibre to fibre. Hence, the natural interpretation of the observed optical behaviour of the iridescent regions is that the orientation of the *c*-axis is periodic along the length of each individual fibre. In fact, one is led to that interpretation by a simple process of exclusion. What is actually observed is a diffraction of light by a phase-change grating which is irregular along the plane of the laminations but is regular and periodic in the perpendicular direction, in other words, *along* the length of the fibres. A periodicity in the orientation of the *c*-axis along the length of each fibre is just what is required to give rise to such a situation. We remark that since the change of phase affects only the vibration transverse to the fibres, it would give rise to diffracted beams polarised in that sense. But, as we have already seen, such beams are not regularly transmitted but are diffused into a fan of rays. The non-appearance of any optical images of the source in the spectra is thus explained. We do indeed observe in the spectra a region of enhanced intensity near their centres which is partially polarised in the same sense as the regularly transmitted light. But this is evidently a secondary effect arising by reason of our assumption of a perfectly orientated fibre structure being an idealisation which differs noticeably from the actual situation.

7. THE MOIRÉ PATTERNS OF IRIDESCENT AGATE

A striking confirmation of the conclusions set forth above is furnished by a study of the moiré patterns exhibited by the iridescent regions. These patterns are readily observed by merely holding up the plate against a source of light and viewing it through a magnifier. They are only seen in the regions displaying iridescence. Small tilts of the plate produce large changes in the configuration of the patterns, thereby indicating their origin, which is that the laminations in the material at different depths are not in perfect register. The introduction of a polaroid between the iridescent agate and the observer's eye produces a remarkable change in the moiré pattern. When the vibration direction of the polaroid is transverse to the laminations, in other words parallel to the fibre direction, the moiré pattern disappears practically completely. If, on the other hand, the polaroid is set with its vibration direction parallel to the laminations and hence transverse to the fibres, the moiré pattern becomes extremely conspicuous. These effects are shown in Figs. 1 and 2 in Plate II.

The interpretation of the facts is obvious, *viz.*, that the periodic changes of phase produced by the grating which progressively transform themselves to periodic variations of amplitude are operative only in respect of the optical vibrations transverse to the fibre length. This is precisely the result which would ensue as a consequence of a periodic change in the orientation of the *c*-axis along the length of each individual fibre.

Neither the observed diffraction effects nor the behaviour of the moiré patterns could be reconciled with a periodicity of structure due to a rhythmic segregation of opal as has been suggested in a recent paper[4] on iridescent agate which has been brought to our notice. Further, as has been shown elsewhere[5] by us, the opal that is actually found associated with agate is identifiable with α-cristobalite. This exhibits a very intense X-ray diffraction ring with a spacing of 4·03 A.U. Not even a trace of a ring with such a spacing is to be observed in the X-ray diagram recorded by us in the strongly iridescent regions of our agate specimens.

SUMMARY

The polarisation of the light regularly transmitted by fibrous chalcedony and the character of the diffraction spectra exhibited by iridescent agate are described and discussed. It is shown that the phenomena point conclusively to the laminations in iridescent agate responsible for the diffraction effects being a consequence of the periodic orientation of the *c*-axis of quartz along the length of the fibres. Photographs illustrative of the optical effects and of the X-ray diffraction patterns of the materials are reproduced.

REFERENCES

1.	C. V. Raman and A. Jayaraman ..	*Proc. Ind. Acad. Sci.*, 1953, **38A**, 199.
2.	A. Jayaraman ..	*Ibid.*, 1953, **38A**, 441.
3.	C. V. Raman and A. Jayaraman ..	*Ibid.*, 1954, **40A**, 107.
4.	F. T. Jones ..	*Amer. Mineral.*, 1952, 37, 578.
5.	C. V. Raman and A. Jayaraman ..	*Proc. Ind. Acad. Sci.*, 1953, **38A**, 343.

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FIG. 1

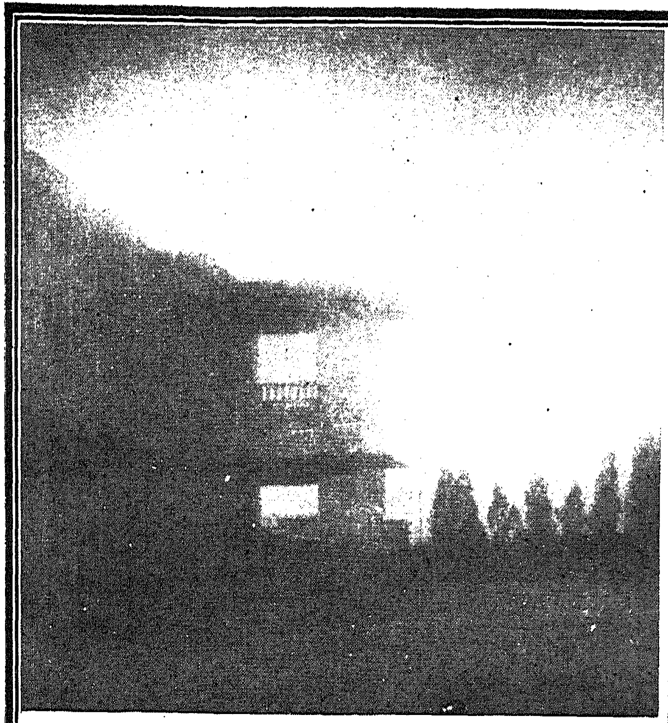
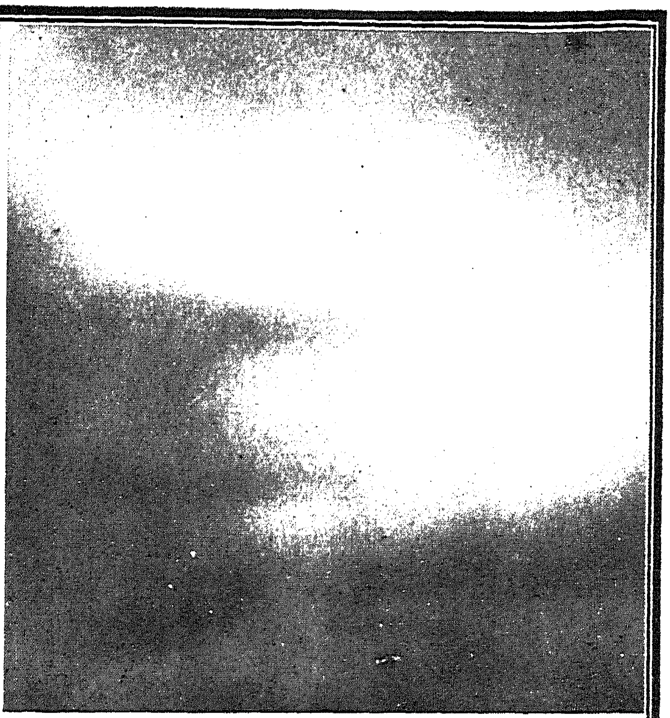


FIG. 2



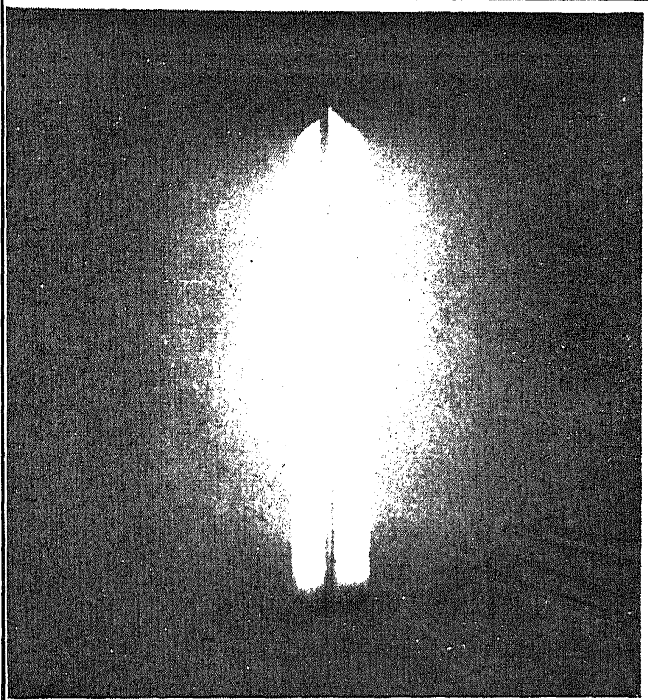


FIG. 3

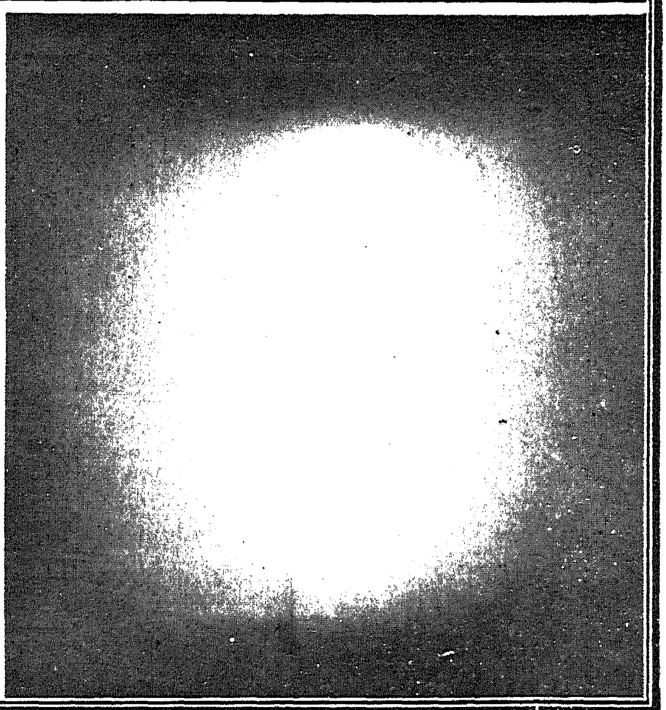


FIG. 4

Polarisation of Light by Chalcedony

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FIG. 1 FIG. 2

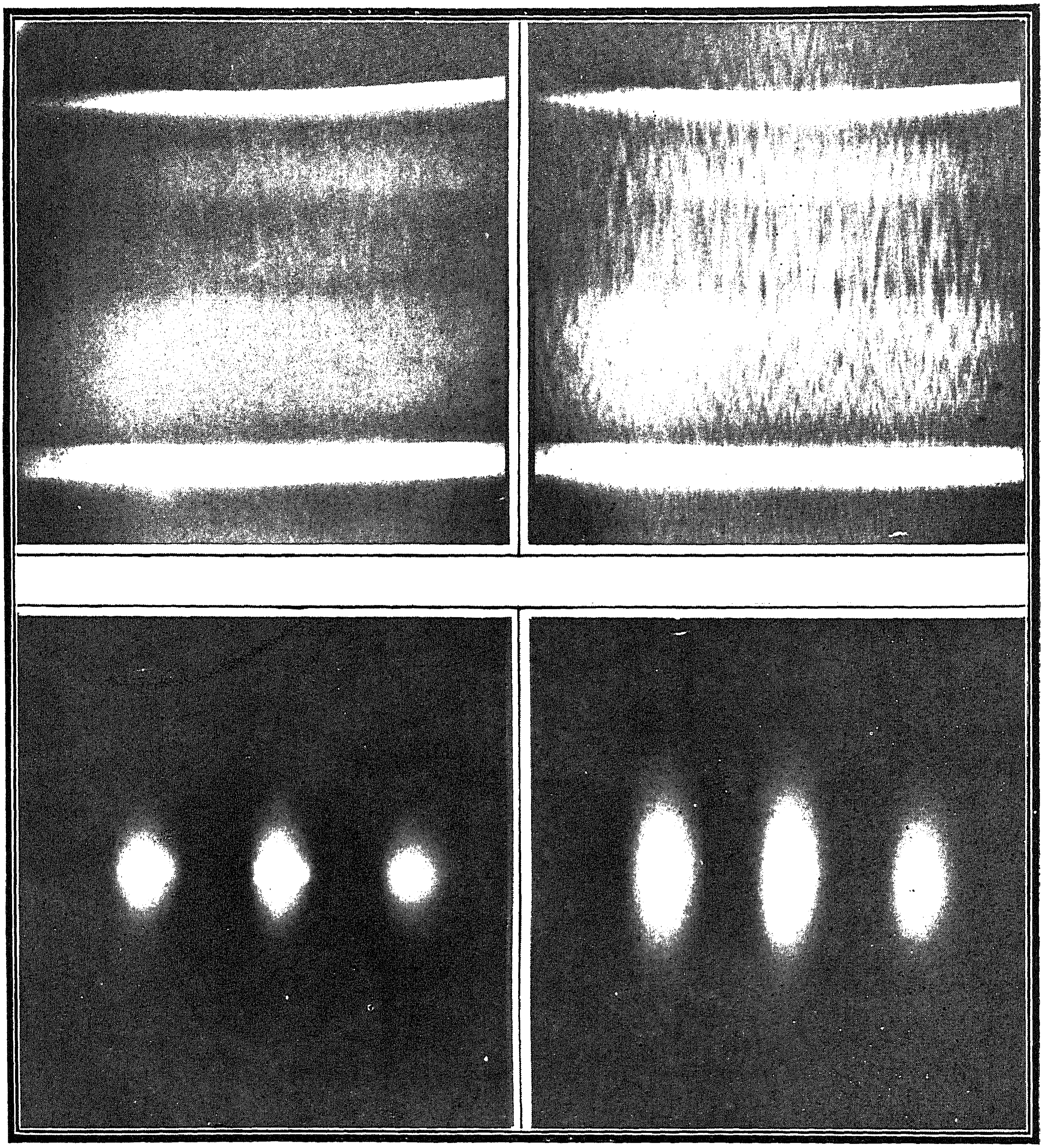

FIG. 3 FIG. 4

Polarisation of Light by Iridescent Agate

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FIG. 1

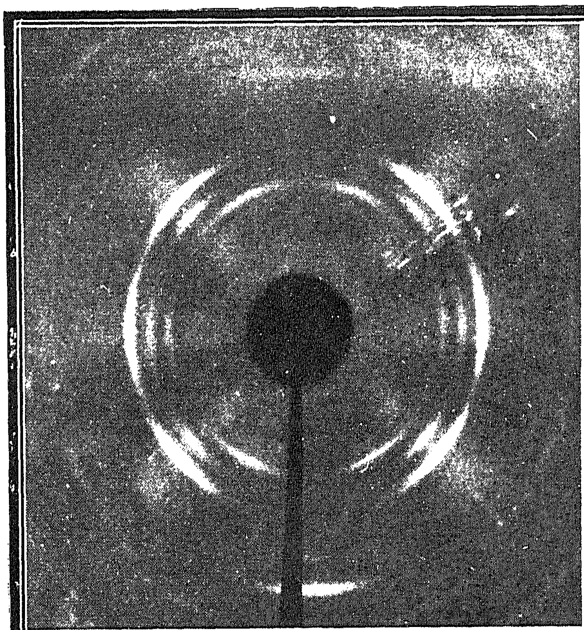


FIG. 2

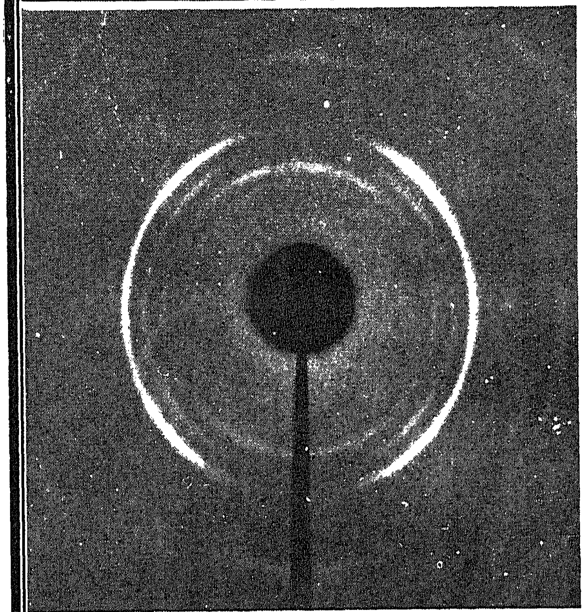


FIG. 3

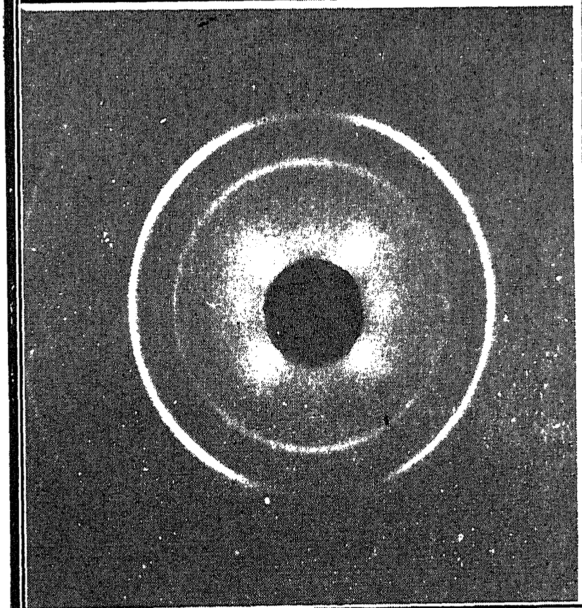


FIG. 4

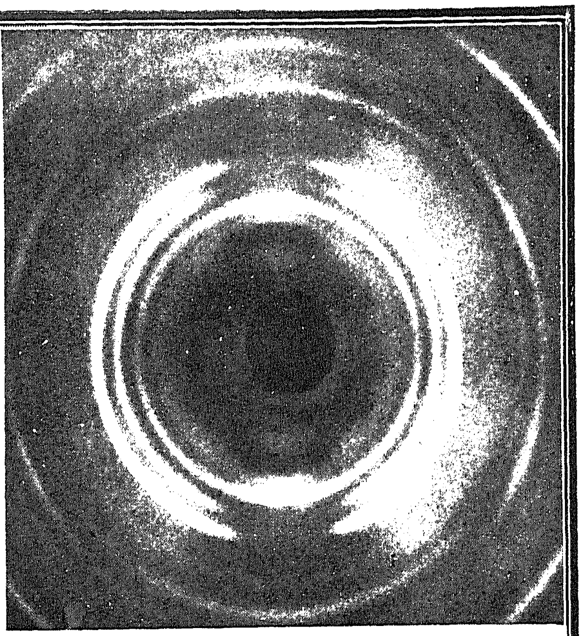


FIG. 5

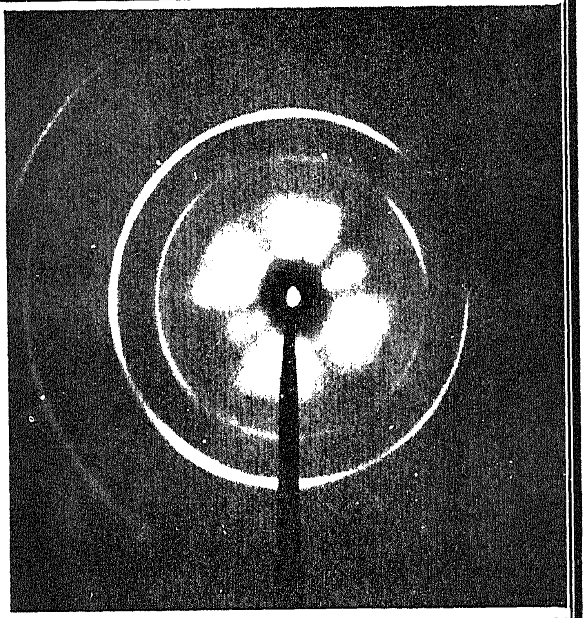
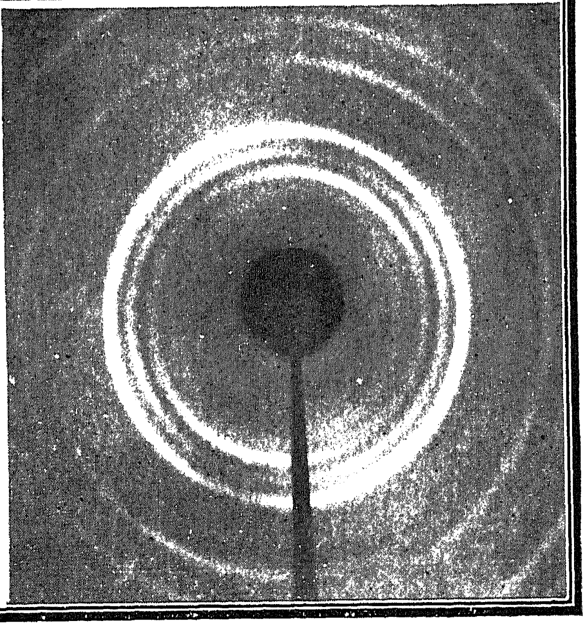


FIG.



X-Ray Diffraction Patterns

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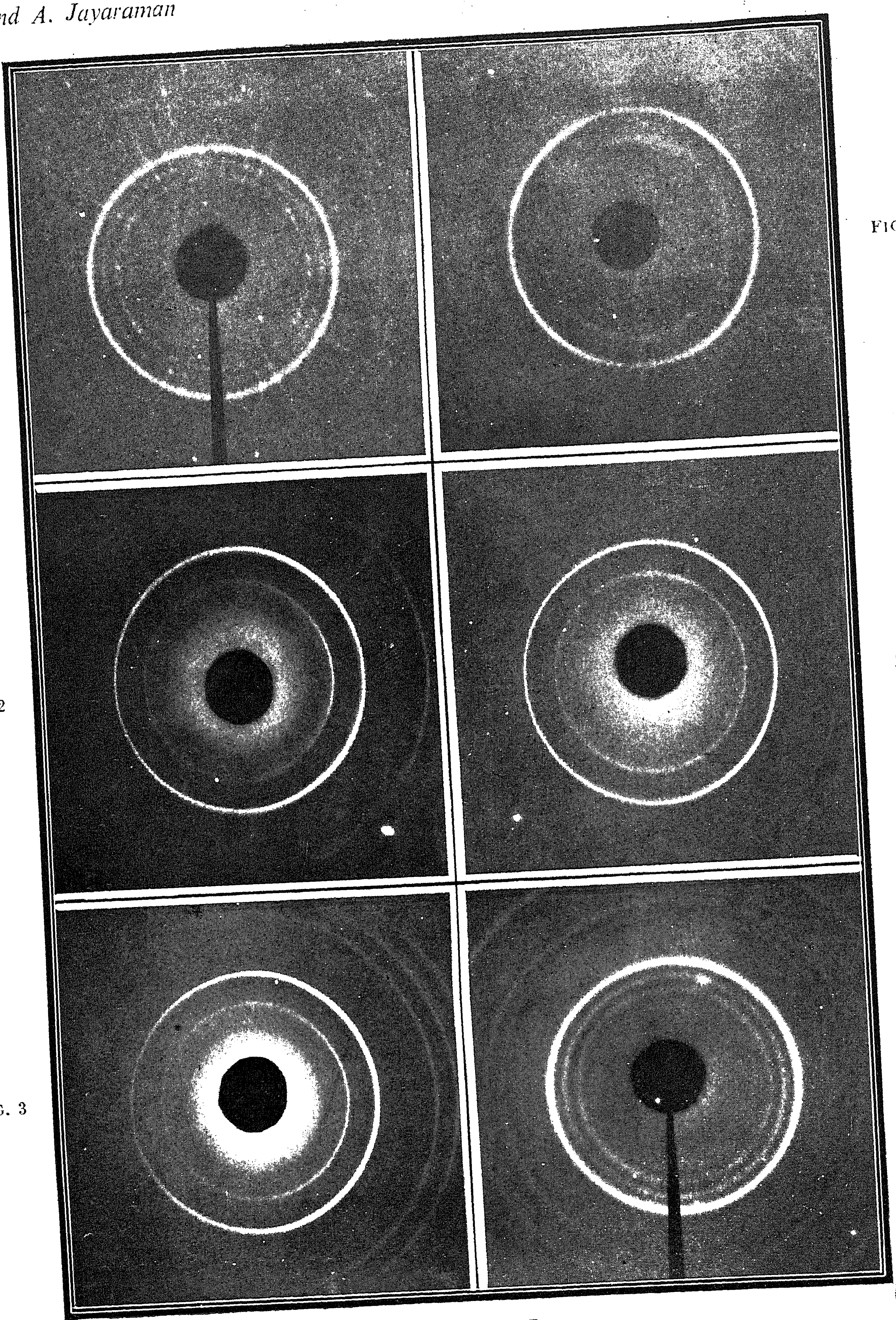

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

X-Ray Diffraction Patterns