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THE STRUCTURE AND OPTICAL BEHAVIOUR OF CHALCEDONY

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1. INTRODUCTION

CHALCEDONY is a cryptocrystalline variety of silica occurring in a massive form and exhibiting a waxy lustre. It is only slightly inferior to quartz in hardness and has a density lying between 2·60 to 2·64. A small percentage of water may often be found in the material. The refractive index averages at 1·537 and is thus not very different from that of quartz. Thin sections exhibit a fibrous character under the microscope and the material shows a distinct birefringence which is of the same order of magnitude as that of quartz.

Mineralogists formerly regarded chalcedony as a distinct crystalline species of silica and classed it under the orthorhombic system. But the X-ray pattern of powdered chalcedony is identical with that of quartz, as was first reported by Washburne and Navias[1] and later confirmed by Rinne,[2] thus demonstrating that chalcedony is composed of crystallites of quartz. The fibrous character of the material and the birefringence exhibited by it indicate that the crystallites have preferred orientations. Correns and Nagelschmidt[3] showed that such orientation is actually observable in the X-ray patterns of unpowdered chalcedony. The crystallites were found to be orientated around the $[1\bar{1}00]$ direction in a specimen from Olomuczan and around the $[11\bar{2}0]$ direction in a specimen from Iceland. More recently, Novak[4] has reported that the fibres of chalcedony are usually elongated along the *c*-axis or the *a*-axis of quartz.

In a recent paper[5] by Sir C. V. Raman and the present writer in these *Proceedings*, investigations on the origin of the iridescence exhibited by certain varieties of agate have been reported. By detailed optical and X-ray studies it was shown that the banded structure in iridescent agate responsible for the diffraction effects is a result of the orientation of the quartz crystallites with their *a*-axes common and the *c*-axes lying in the plane of banding in a periodic manner. It was thought worthwhile, in this connection, to apply similar optical and X-ray methods to the case of common chalcedony. The results are presented in the following pages.

2. SOME THEORETICAL CONSIDERATIONS

Before proceeding to describe the results of the present investigation, it is useful to set out here some considerations of a general character regarding the optical behaviour of a medium consisting of crystallites of birefringent material. As is well known, quartz is a uniaxial positive crystal, the optic axis being coincident with its *c*-axis. The two refractive indices for the sodium light are respectively $n_e = 1 \cdot 553$ and $n_o = 1 \cdot 544$. Though this birefringence is small, it is nevertheless large enough to profoundly influence the propagation of light through the medium, as we shall proceed to show.

We shall consider first the case of a completely random orientation of the crystallites. This situation would result in a beam of light entering the material being rapidly extinguished by the process of diffusion in its passage, unless the crystallites are exceedingly small or the total optical path very short. This can be demonstrated by the following argument. Consider a plane-polarised beam of light incident on a thin lamina of the material. For simplicity, we shall assume the crystallites to lie with their *c*-axis parallel to the vibration of the incident light over some parts of the area of the lamina, while in the other parts they lie with their *a*-axis parallel to the vibration direction. The light wave passing through the two different sets of areas will travel with different velocities, thus giving rise to differences in phase. As in the theory of the Christiansen experiment discussed in these *Proceedings* by Sir C. V. Raman,[6] these differences in phase and the interferences resulting therefrom would cause a diminution in the intensity of the transmitted light. When numerous such laminæ are present following each other, the process is repeated, and if the total optical path is sufficiently large, the whole of the incident light would be diffused in its passage through the medium.

We may go a little further and describe the position in a semi-quantitative fashion by taking over the formula derived in the theory of the Christiansen experiment for the transmitted radiation, namely $I = I_0 \cdot e^{-\pi^2 (\mu_1 - \mu_2)^2 . \Delta . z / \lambda^2}$. Here μ_1 and μ_2 are respectively the maximum and the minimum refractive indices of quartz for the wavelength λ, Δ is the size of the individual crystallite, and z is the total optical path traversed. The influence of these variables Δ, z and λ on the transmission may be illustrated by a few calculations made on the basis of the above formula. Thus for example, taking $\Delta = 1\,\mu$, $z = 1$ mm. and $\lambda = 0 \cdot 7\,\mu$ or $0 \cdot 4\,\mu$, the transmission is 18% and 1% respectively for the two wavelengths. Thus there would be a marked reddening of the light as it penetrates through the material. The influence of the size of the crystallites is shown by the following calculation. When $z = 1$ mm., $\lambda = 0 \cdot 5\,\mu$ and $\Delta = \frac{1}{2}\,\mu$ or $2\,\mu$, the transmission is 20% and 0·2% respectively showing that it falls off very rapidly with increasing size of crystallites. Increasing the length of the optical path from $z = 1$ mm. to $z = 2$ mms., for $\Delta = \frac{1}{2}\,\mu$, and $\lambda = 0 \cdot 5\,\mu$ similarly results in a marked decrease of transmission from 20% to 4%. It should be remarked that the light which disappears from the incident beam would appear as diffused or diffracted radiation in various directions sorrounding the direction of the incident beam. From the arguments stated, it is clear that with incident unpolarised light, the transmitted light, if any, would also be unpolarised, and so also the diffused radiation.

The situation is totally different when we consider the case where the crystallites are all orientated with their *c*-axes as a common direction but, with their *a*-axes lying in a random manner in a perpendicular plane. The uniaxial character of quartz would result in the material exhibiting perfect transparency, irrespective of whether the direction of propagation is along the orientation axis or in the perpendicular direction, since the randomness in the positions of the *a*-axes leaves the principal optical vibration directions unaltered. The material would, in fact, be optically equivalent to a single crystal of quartz.

Another type of ordering of the crystallites requiring consideration is the *a*-axis orientation. Here the crystallites may be thought of as forming elongated fibres with their *a*-axes lying parallel to the length of the same but with their *c*-axes differently orientated. Consider a plate which is made up of a bundle of such fibres running parallel to each other and also to the surface of the plate. The fact that all the crystallites of quartz are orientated with their *a*-axes common would fix the positions of the fast optic vibration direction, which would be identical for all the crystallites, and as such the material would behave as an optically homogeneous medium for a light wave vibrating along the length of the fibres. Consequently, a plane polarised light wave incident normally on the plate of the material with its vibration direction parallel to the length of the fibres would be freely transmitted. On the other hand, if the light vibrates transversely to the length of the fibres, it would be strongly diffused. This follows from a consideration of the fact that the orientation of the *c*-axis alters as the light wave advances from one crystallite to the other, thus giving rise to fluctuations in the refractive indices. The size of the individual crystallites and the thickness of the plate would influence its behaviour for this direction of incident vibration in the same manner as that considered earlier for the case of random orientation. Hence, if unpolarised light is incident normally on the plate and if the same is sufficiently thick, the light transmitted would be completely polarised with its vibration parallel to the length of the fibres, while the light diffused would appear as a brush of light drawn out in directions transverse to the fibre length, and would be polarised with its vibration normal to the fibre length. The transmitted light would however exhibit partial polarisation if the plate is thin, since the component vibrating transversely to the fibres would also then be transmitted to some extent.

We now proceed to consider the optical behaviour of a plate of the material which is assumed to have a laminated structure, the planes of lamination being perpendicular to the surface of the plate. The crystallites of quartz composing the material are further assumed to be orientated with their *a*-axes parallel to the common normal to the laminæ, while the *c*-axes in each individual lamina has everywhere the same orientation, this however being different for the different laminæ. If plane-polarised light wave is incident on the plate normally, the optical behaviour exhibited by it would depend on whether the vibration direction of the incident wave coincides with the common direction of the *a*-axis or is perpendicular to it. In the former case, it is at once evident that the material would behave as if it were optically homogeneous and the emergent light wave would have the same phase retardation over the entire area of the plate. If on the other hand, the incident light vibrates perpendicular to the common direction of the *a*-axis, it would be freely transmitted by each lamina, because of the identical orientations of the *c*-axes of the crystallites in it; but the light emerging from the different laminæ would be retarded to different extents, in view of the fact that the orientation of the *c*-axis varies from lamina to lamina. Thus, differences in phase would be introduced and these would be of the order of several wavelengths even for plates only a fraction of a millimetre in thickness. In consequence, the light would be diffracted away in various directions lying in a plane perpendicular to the laminæ. In the particular case where the orientations of the *c*-axes in the laminæ are repeated at regular intervals, the plate would function as a phase-change diffraction grating giving several orders of spectra. The laminated structure would accordingly be visible if the plate be viewed with incident polarised light vibrating in the plane of the laminæ, but would disappear when viewed with light vibrating in a perpendicular direction.

3. TRANSMISSION AND DIFFUSION OF LIGHT

The theoretical considerations set forth in the preceding section clearly indicate that the optical behaviour of a medium consisting of crystallites of quartz would be very much influenced by its thickness. Accordingly, five plates of different thicknesses ranging from 2 mms., down to about 0·15 mm. were cut and polished out of translucent and colourless agate or chalcedony, specimens of which were available in the Museum of the Institute. We now proceed to describe and illustrate the various optical effects exhibited by a typical specimen.

The particular plate was sliced out of a lump of colourless, translucent agate, and measured 2 cms. in length, 1·5 cm. in width, and 1 mm. in thickness. When viewed directly against a lighted window, it exhibits a characteristic structure, the transparency of the plate varying enormously over its area. Certain regions appear bright while others are seen as dark cloudy patches. The situation however is completely different when the specimen is viewed against a dark background with the light falling on it rather obliquely; the dark portions now appear bright and *vice versa*. This is illustrated in the photographs reproduced as Figs. 1 and 2 in Plate XXXIII taken respectively by direct and by diffracted light. Their complementarity is particularly evident on a comparison of the areas depicted on the right of Figs. 1 and 2; the dark patches in the one appear as bright patches in the other. The region to the extreme left in Fig. 1 which is seen in the photograph as a dark area is actually very bright when the plate is viewed directly against an extended source of light.

The optical behaviour of the different parts of the specimen is better appreciated when a narrow bright source of light is viewed through the plate with the latter held close to the eye of the observer. When thus examined, the light source itself cannot be seen through the areas depicted on the right-hand side of Fig. 2; only an extended patch of diffuse light is observed. On the other hand, the light source is seen well defined, though somewhat diminished in intensity, if the plate is viewed through the area appearing dark towards the left of Fig. 2. The light source, however, appears overlaid by a narrow brush of diffused light, which extends on either side of it through a considerable range of angles. A remarkable feature of the light regularly transmitted by the plate is that it is fully polarised and therefore totally extinguished by a polaroid appropriately orientated and placed in the path of the light. When the vibration direction of the polaroid is parallel to the brush of diffuse light, the transmitted light is cut off. The diffused light also exhibits a high degree of polarisation, its intensity being a minimum when the vibration direction of the polaroid is perpendicular to the extension of the brush, thus indicating that the latter is polarised in the opposite sense to the transmitted light.

The observations described above are illustrated in Figs. 6 and 7 of Plate XXXIV. Fig. 6 was recorded with the specimen mounted inside a camera, the latter focussing a brightly illuminated circular aperture placed at a distance from the camera lens. The plate was kept 4 cms. away from the photographic film and the entire beam passed through the region of the specimen already referred to. It will be noticed on an inspection of Fig. 6 that the light transmitted appears as a well-focussed central image, overlaid by a diffuse brush of light. The photograph reproduced as Fig. 7 was recorded with the same arrangements but with a double-image prism of quartz placed in front of the camera lens. As a result of this combination, the incident beam of light is split into two polarised components vibrating in perpendicular directions. The plate was suitably orientated so as to exhibit the polarisation of the transmitted light and the diffuse brush most clearly. The two images appearing in Fig. 7 represent respectively the components vibrating perpendicular and parallel to the diffuse brush. It will be noticed that the image of the light source is clearly seen in the former and is invisible in the latter. *Per contra*, the diffuse brush is more intense in the latter than in the former. These observations described are in full agreement with the behaviour envisaged in Section 2 above for a medium consisting of crystallites of quartz orientated with their *a*-axes common. It may therefore be inferred that the material has a fibrous structure and that the crystallites of quartz are orientated with their *a*-axes along the length of the fibres.

4. Some Further Observations

Thus, as we have seen, theoretical considerations and actual observations alike demonstrate that the manner in which the crystallites of quartz are orientated in it profoundly influence the optical behaviour of chalcedony. Another factor which has to be considered and indeed is scarcely less important is the length of the optical path, in other words the thickness of the plate. A study of the behaviour of plates both thinner and thicker than that dealt with in the preceding section shows this very clearly.

As an example, we may refer to the case of a plate 0·15 mm. thick which was examined. It exhibited a notable measure of transparency over its entire area, though from the manner in which the light was diffused in passage through the plate, it was quite clear that the crystallites in it did not possess any specificity of orientation. Neither the transmitted light nor the diffused radiation exhibited any observable measure of polarisation. Examination of the piece on the stage of a polarising microscope between crossed nicols confirmed these inferences. In a number of places a radiating fibrous structure was seen exhibiting a dark cross. An example of this is illustrated in the microphotograph reproduced as Fig. 10 in Plate XXXV.

Another plate 0·3 mm. thick the optical behaviour of which was studied gave some interesting results. In many respects it resembled the 1 mm. thick plate considered in Section 3, but it was distinctly more transparent over its whole area. Nevertheless large local variations in transparency were observable. In the regions where the image of the source was seen most brightly the latter appeared overlaid by an elongated brush of diffused light. The polarisation of the transmitted light was *less* perfect, and the polarisation in the opposite sense of the brush of diffuse light *more* perfect than in the case of the 1 mm. thick plate. These features which are in agreement with the indications of theory will be evident from the photograph taken with a double image prism and reproduced as Fig. 8 of Plate XXXIV.

The decreasing transparency resulting from the increase in length of the optical path is further illustrated by observations made with a plate of 2 mms. thickness. Even in its most transparent regions, the source of light seen through it was much less intense than in the case of the 1 mm. thick plate and also showed a distinct reddish tinge. The polarisation of the transmitted light was however visibly perfect in such areas. *Per contra*, the polarisation of the brush of diffuse light was noticeably imperfect.

5. The Lamellar Structure; Its Nature and Optical Characters

A coarsely banded structure, often following in its course the naturally occurring external boundary of the material, is a very common feature exhibited by chalcedony. Examples of this are illustrated in Fig. 3, Plate XXXIII, the photograph being by transmitted light and in Figs. 4 and 5 of Plate XXXIII, taken respectively by transmitted and diffracted light. The photographs were recorded with specimens cut and polished normal to the planes of banding, the piece illustrated in Fig. 3 being 2 mms. thick and that illustrated in Figs. 4 and 5 being 1 mm. thick. The influence of the shape of the external surface of the material on the configuration of the banding is very conspicuous in Fig. 3. The complementarity of the appearance of the chalcedony as seen by transmitted and diffracted light is remarkably well shown by Figs. 4 and 5 in Plate XXXIII.

As will be seen from Figs. 3 and 4, the transparency of the material varies notably in the case of both the specimens, the most transparent area in each being a broad band running through the centre. When a distant bright source of light is viewed through this area, a well-defined image of the source can be seen, accompanied by a brush of diffuse light running in a direction parallel to the planes of banding. When the specimen is moved laterally, the direction of the brush follows the course of banding. From what has already been described in the preceding section, it is clear that the planes of banding are everywhere transverse to the length of the fibres, which as already explained are themselves parallel to the a-axis of the crystallites. Analogous features are also visible in the more heavily banded areas in which the transmitted light is very feeble. In these latter areas the coarsely fibrous structure of the material is very obvious. This can be seen from the picture reproduced as Fig. 12 in Plate XXXV which is an enlarged photograph of an area of the specimen illustrated on a smaller scale in Fig. 4. Fig. 12 also exhibits numerous closely-spaced lamellæ which are not visible in Fig. 4. This is a general feature in the case of both specimens.

The fibrous structure of chalcedony in which the a-axes of the crystallites of quartz are parallel to the fibre length is often, if not invariably, accompanied by a lamellar structure with its planes running everywhere transverse to the fibres. Such a structure is most clearly seen through a magnifier when the area under observation lies on the boundary between light and darkness, when the plate is held and viewed against a source of light. It is seen very clearly in Fig. 1, Plate XXXIII in the region to the left and in the lower parts of the figure. A remarkable characteristic of this fine lamellar structure is the appearance of numerous ripples or waves running approximately parallel to it over the area of the specimen. This feature is illustrated by micro-photographs recorded under low-magnification and reproduced as Figs. 9 and 11 respectively in Plate XXXV. The photographs were taken with a polaroid interposed between the plate and the objective of the microscope, the vibration transmitted by the polaroid being parallel to the planes of banding in Fig. 9, and being transverse to it in Fig. 11. As will be seen on a comparison of the two figures, the rippling is very clearly seen in Fig. 9 and is scarcely visible in Fig. 11. It should also be mentioned in this connection, that a small distant source of light viewed through the area exhibits, superposed on the diffuse brush of light, a series of diffraction spectra on either side. Whereas the source of light itself is almost completely extinguished when a polaroid is interposed with its vibration direction parallel to the planes of banding, the diffraction spectra referred to are not extinguished and indeed are generally better seen in that position of the polaroid.

It may be mentioned here that the light transmitted is greatly influenced by the tilt of the specimen, rapidly diminishing in intensity when the plate is tilted in such manner that the planes of banding make increasing angles with the incident beam of light.

From the foregoing observations, we are entitled to infer that the lamellar structure and the fine ripples seen accompanying it are a consequence of a

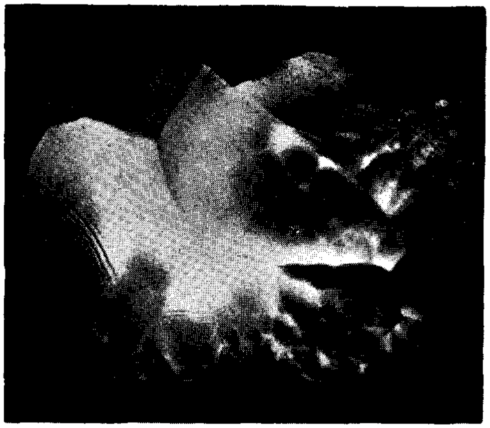

FIG. 1

FIG. 2

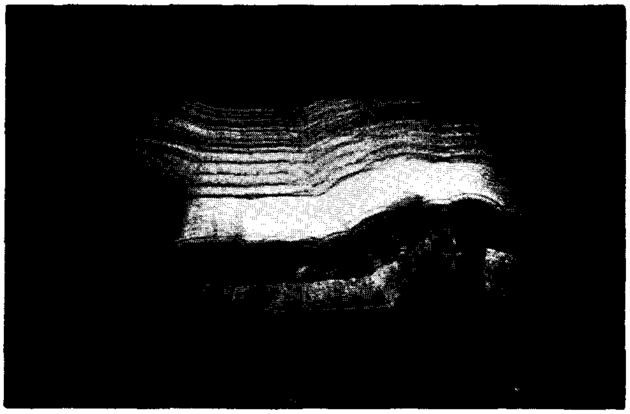

FIG. 3

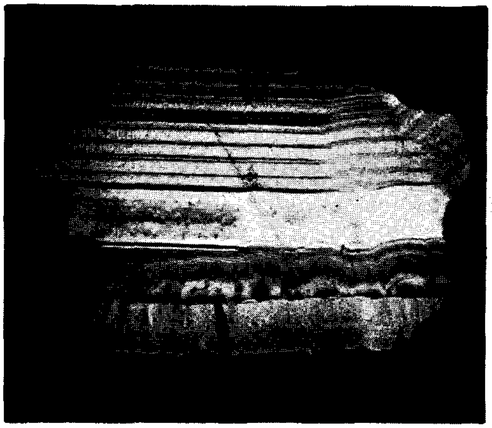

FIG. 4

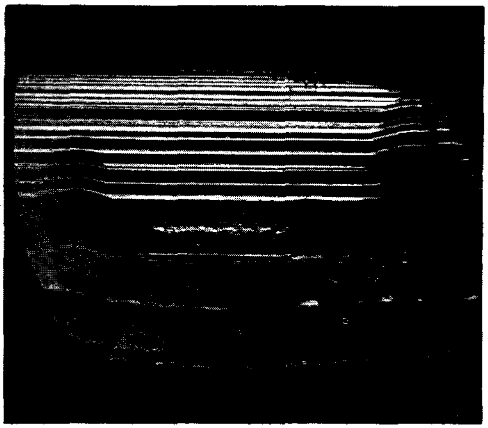

FIG. 5

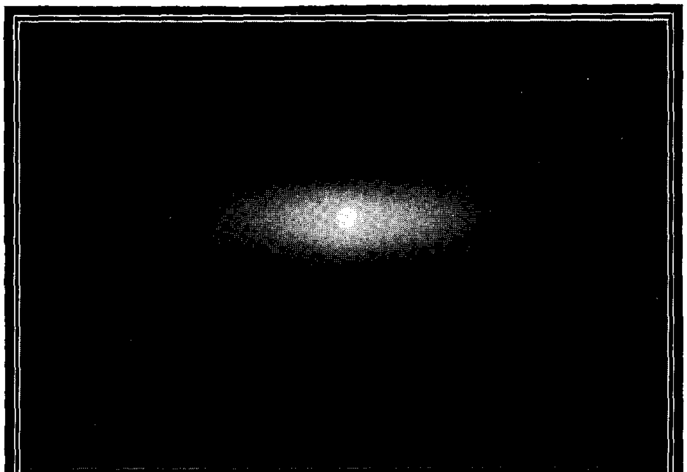

FIG. 6

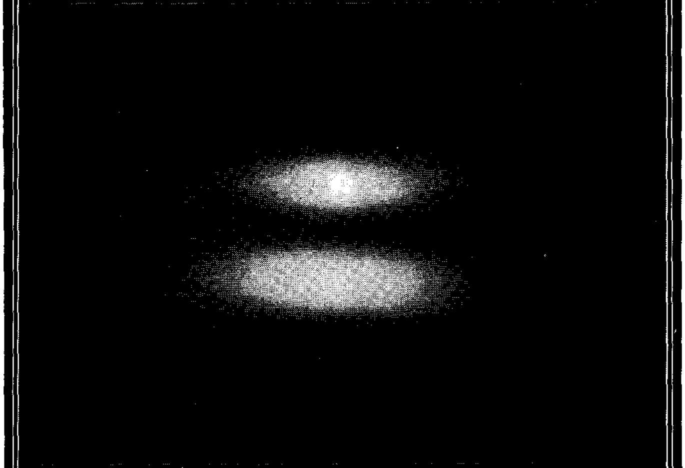

FIG. 7

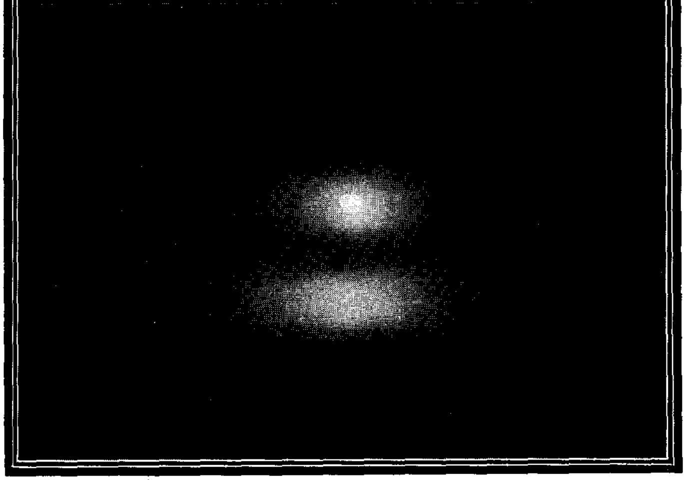

FIG. 8

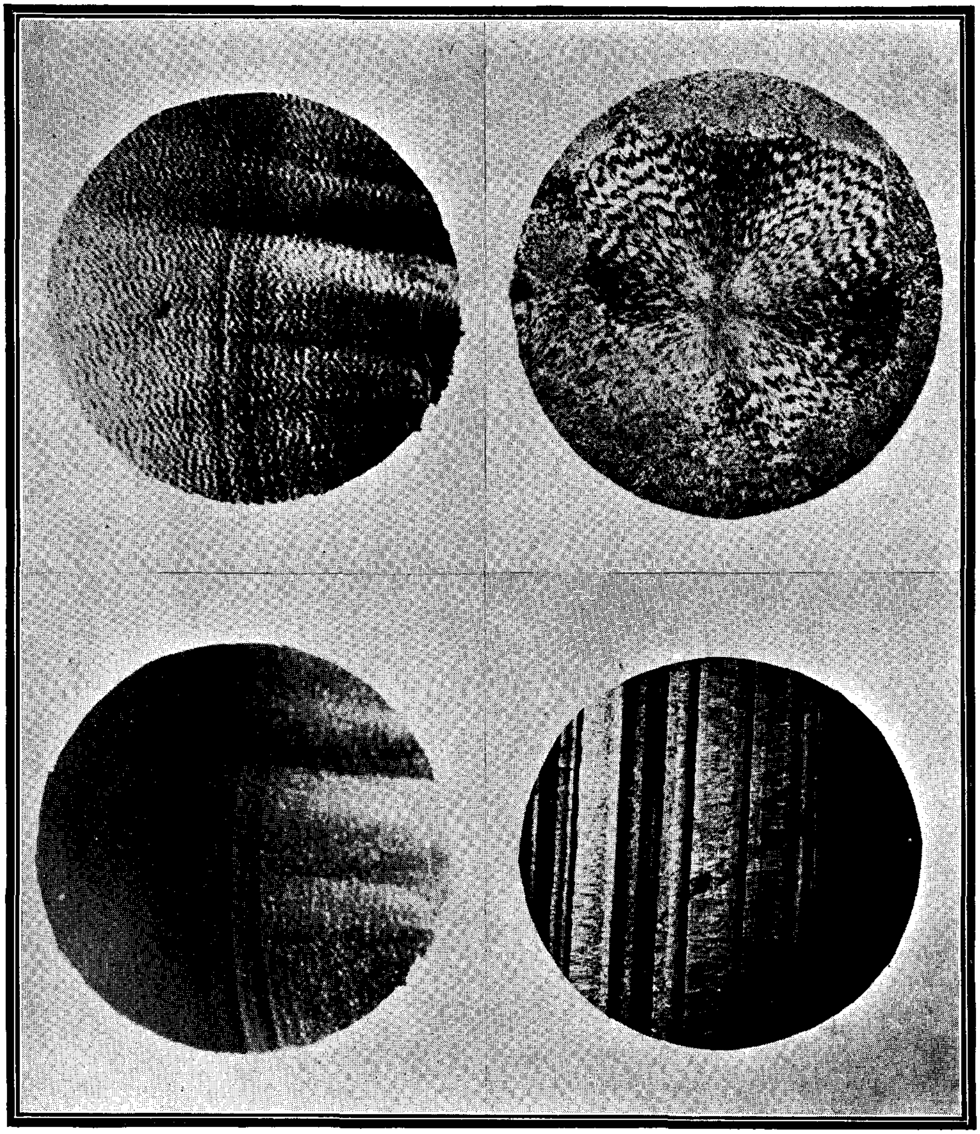

FIG. 9

FIG. 10

FIG. 11

FIG. 12

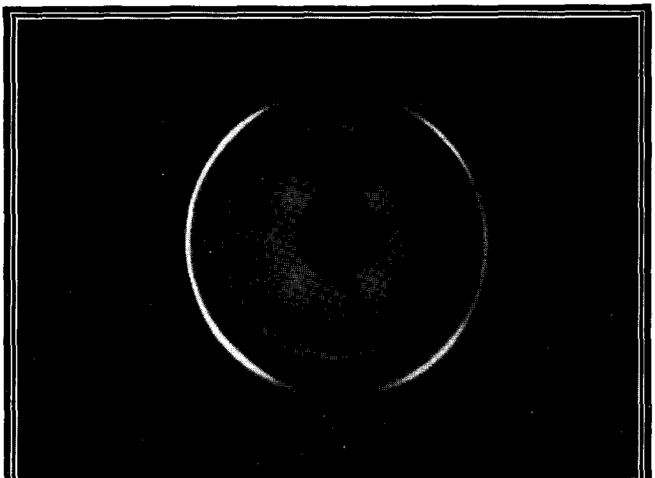

FIG. 13

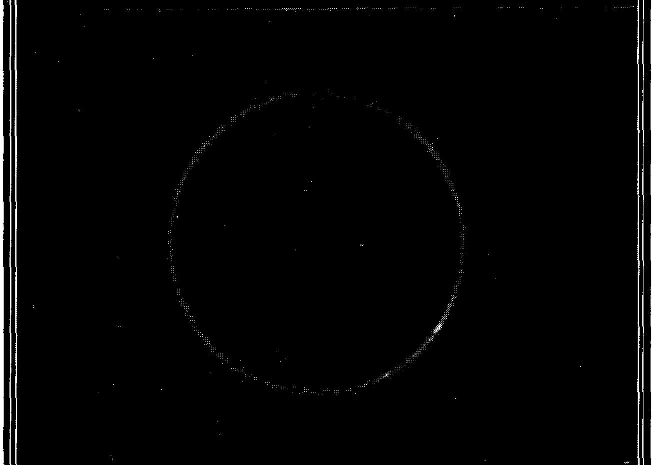

FIG. 14

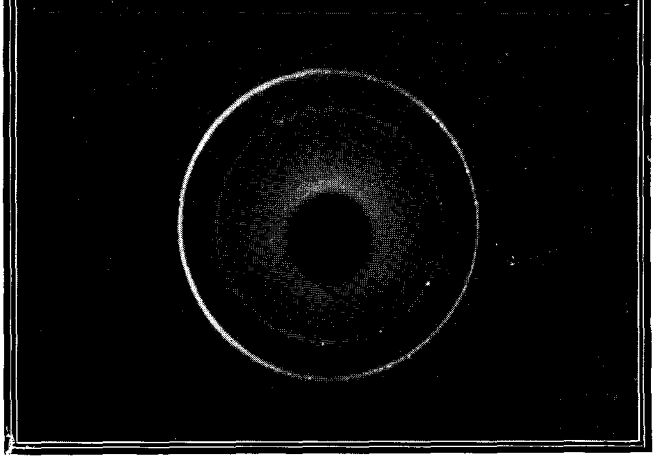

FIG. 15

variation in the orientation of the *c*-axes of the crystallites in the successive layers which are perpendicular to the length of the fibres.

Confirmation of the ideas regarding the structure of the material as deduced from its optical behaviour is forthcoming when the X-ray patterns of chalcedony are recorded for different regions and interpreted. In Figs. 13, 14 and 15 appearing in Plate XXXVI the X-ray patterns are reproduced. Fig. 13 is the record for a region exhibiting transparency and Figs. 14 and 15 are the records for areas exhibiting greater opacity. The X-ray pattern reproduced in Fig. 13 demonstrates that the crystallites of quartz composing the material are orientated with their *a*-axes common.

In conclusion the author wishes to express his grateful thanks to Professor Sir C. V. Raman, F.R.S., N.L., for suggesting the problem and for the valuable help and inspiring guidance that he offered during the course of this investigation.

6. Summary

Common chalcedony and agate, when examined by methods of investigation similar to that employed in the case of iridescent agate, the results of which have already been reported in these *Proceedings*, exhibit analogous features. The transmission and diffusion of light, their polarisation characters and the influence of the thickness of the medium on these features are discussed from a theoretical standpoint. The results are borne out by observations made with several specimens of agate and chalcedony. The lamellar structure which is often exhibited by chalcedony is found to arise from the orientation of the *c*-axes of the crystallites of quartz in the fibres along the banding planes which run transversely to the former. X-ray patterns of chalcedony in such regions reveal that the crystallites of quartz are orientated with their *a*-axes common along the fibre length.

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