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The optical behaviour of polycrystalline solids

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ABSTRACT

The paper discusses the influence of the factors which determine the penetration of light into a polycrystalline solid, viz. the birefringence of the crystallites, their size and shape and their relative orientations. The results of the theoretical discussions are compared with the facts of observation. Five X-ray diagrams are also reproduced which exhibit the relation between the structure and optical behaviour of polycrystalline media in particular cases of interest.

1. Introduction

As examples of polycrystalline solids, which by reason of the desirable properties they possess have been extensively used for the fashioning of works of art, may be mentioned especially the following minerals: marble, alabaster, chalcedony and jade. Visual observations supplemented, where necessary, by examination of thin slices under the polarisation microscope and the use of X-ray diffraction techniques reveal that individual specimens of these minerals may be widely different in regard to the size and shape of the crystallites of which they are composed and the manner in which these crystallites are disposed within the solid. Alongside of these differences and obviously related to them are noticed some striking differences in the optical characters of the specimens. As the external appearance of a finished work of art is influenced a good deal by such differences, it is not without interest to discuss in some detail the nature of the relationship between the structure and the optical behaviour of polycrystalline solids in general.

In all the cases mentioned, the basic substance is a transparent crystalline solid and accordingly the aggregate could also have been expected to be free from colour. Though this is so in some instances, it is not always the case. Indeed, the presence of some favoured colours often enhances the value of the material very greatly. The nature of the intrusive material responsible for such colour and the manner in which it is diffused through the substance and influences its optical behaviour are questions of considerable interest, but we shall not enter into them here.

It should be mentioned that the structure of polycrystalline solids and its relation to their optical behaviour has been the subject of both theoretical and experimental investigations by the present writer and his collaborators and the results have been reported in detail in some earlier memoirs of this Institute. In the present publication it is proposed to summarise broadly the results which have emerged from these studies and in addition to present some fresh observational material.

The five illustrations accompanying the present paper are X-ray-diffraction photographs of some interesting specimens recorded by Mr A Jayaraman at this Institute. In each case, the structure revealed by the X-ray diagram is found to be very clearly related to the optical characters exhibited by the specimen. We shall return to these diagrams and their significance later in the paper.

2. Theoretical considerations

If no extraneous material be present in a polycrystalline solid and its optical heterogeneity arises solely by reason of the varying orientations of the crystallites, the birefringences of the latter would give rise to a diffusion of the light in its passage through the material. At each incidence of the light on an intercrystalline boundary, it would be reflected and refracted and hence all trace of the original direction of propagation of the light would quickly disappear. After the passage of the light through a sufficient number of crystallites, a state of affairs would establish itself in which we have a diffusion in all directions, forwards and backwards as well as laterally. The greater the birefringence of the material, the fewer would be the number of intercrystalline boundaries needed for such a situation to establish itself. We may visualize the resulting phenomena by imagining a pencil of light to fall normally on a restricted area in the plane face of a block of the material. The observable results would then depend upon the various factors involved, namely the thickness of the block, the size of the crystallites and the magnitude of their birefringence. In the absence of any absorbing material and if the thickness of the block be sufficiently great, all of the incident light must necessarily be turned back towards the original source of light and would re-emerge from the same face spread out from a much larger area than that on which it is originally incident. On the other hand, if the thickness of the block be not too great, part of the incident radiation would also emerge from the rear face of the block spread out over a large area. In each case, the observable effects would be profoundly influenced by the size of the crystallites. The smaller the crystallites are, the more quickly would the incident light be turned back towards the source and the less, therefore, would be the depth of the penetration of the light into the medium. The presence of any absorbing material in the solid would necessarily modify the observable results to a very great extent.

3. Diffraction phenomena

While the arguments set forth above based on geometrical optics may be adequate when the crystallites are of sufficiently large dimensions and the birefringence of the material is also fairly large, they would cease to be adequate and would fail to describe what is actually observed when the reverse is the case, i.e., when the crystallites are of small dimensions and the birefringence which they exhibit is also small. In the latter circumstances, the matter has necessarily to be considered from the standpoint of the wave theory of light, and the results indicated by such theory are very different indeed from those indicated by geometrical optics.

We may here broadly indicate the lines on which the problem can be handled on the basis of the wave theory. If the birefringence of the material be sufficiently small, the diffusion of light in its passage through it may be considered as arising from the varying retardations in phase of the light waves in traversing the differently oriented crystallites. Provided that the product of the linear dimension of each crystallite and of its birefringence is sufficiently small, we can regard the waves as moving undisturbed through the medium except for the changes of phase occurring over different areas of the wave-front; such changes may be regarded as being additive in depth and hence capable of being summed up over the whole of the path through a slab of the material, provided that the thickness of the latter is not too great. The wave-front emerging at the rear surface of the block would thus exhibit fluctuations in phase over its area. The final observable effect may then be determined by the usual methods of diffraction theory.

The foregoing brief exposition ignores certain difficulties, namely, that inside each crystallite there would be two possible directions of vibration for which the refractive indices are different and these two directions would vary from crystallite to crystallite owing to their random orientations. This difficulty, however, may be circumvented by assuming that the light incident on the block is plane-polarised and that all the crystallites are so orientated that this original direction of vibration in the wave-front is preserved in its passage through the block, the operative refractive index for any one crystallite being one of its three principal values chosen at random. Such an assumption has the great advantage that it greatly simplifies the formulation and solution of the problem while retaining its essential features. Further, by assuming the probabilities of the three different orientations to be different, we can also determine the optical behaviour of polycrystalline solids in which the crystallites are not orientated at random but prefer certain directions. What the solution of the problem gives us is the intensity of the light regularly transmitted through the polycrystalline plate. This appears as an exponential function in which the argument has a negative sign and is directly proportional to the thickness of the plate and to the size of the crystallites and also to a quantity depending on the differences between the three refractive indices which is a measure of the birefringence; it is also inversely proportional to the square of the wavelength of the light. From the theory it follows that the light emerging from the block would be polarised in the same fashion as the light incident on the first face. The theory also shows that if the crystallites have no preferred orientation, the transmission coefficient is independent of the direction of vibration in the incident light. If, however, the crystallites are preferentially orientated, the intensity of the light emerging from the plate would vary with the circumstances, viz., with the relative probabilities of the three permitted orientations. In particular cases of this kind, e.g., when all the crystallites are orientated along a fibre axis which is also the optical vibration direction, the transmission may be actually complete.

We may summarise the foregoing by stating that on the basis of the assumptions made, the light incident on a plate of polycrystalline material would emerge from it greatly enfeebled in intensity but retaining its primitive state of polarisation. The fraction of the light regularly transmitted for a given thickness of the material would increase with diminishing size of the crystallites and would reach the limiting value of unity if they are sufficiently small. This result is precisely the opposite of that indicated by the geometrical theory according to which diminishing particle size would result in greater opacity. These two contrasting results may be regarded as valid respectively in the limiting cases of a very weak and of a very strong birefringence.

The energy that disappears from the regularly transmitted light would appear as diffracted radiation. Its distribution of intensity in different directions would be determined by the factors entering into the problem, namely, the size of the crystallites, the thickness of the plate, the birefringence of the material and finally the wavelength of the light. It is a consequence of the special assumptions made regarding the orientation of the crystallites that the diffracted radiation would be polarised in the same manner as the incident and emerging pencils. It is not, however, to be expected that this particular result would represent the actual facts of the case. As a consequence of the unrestricted randomness of the orientation of the crystallites, the diffused or diffracted radiation would necessarily be depolarised to a greater or less extent. The greater the birefringence of the material or the thickness of the plate traversed, the more complete would be such depolarisation.

It is a particular consequence of the theory that if unpolarised light be incident on a plate of material having a fibrous structure and of sufficient thickness, the regularly transmitted beam would be completely polarised on emergence, while the rest of the light would appear as a fan of diffracted rays in the plane perpendicular to the fibre axis and polarised predominantly in the perpendicular direction. It has also to be remarked that a fibrous structure of the medium is favourable to the appearance of a regularly transmitted pencil. The same material with crystallites randomly orientated might not exhibit any transmission at all, but only a diffusion of light in various directions surrounding that of the incident pencil. Finally, we may remark that since these phenomena arise by reason of wave-optical considerations depending on the wavelength of the light, the transmitted light whenever it is observable should exhibit a reddening which increases progressively with the thickness of the material traversed.

4. Some illustrations of the theory

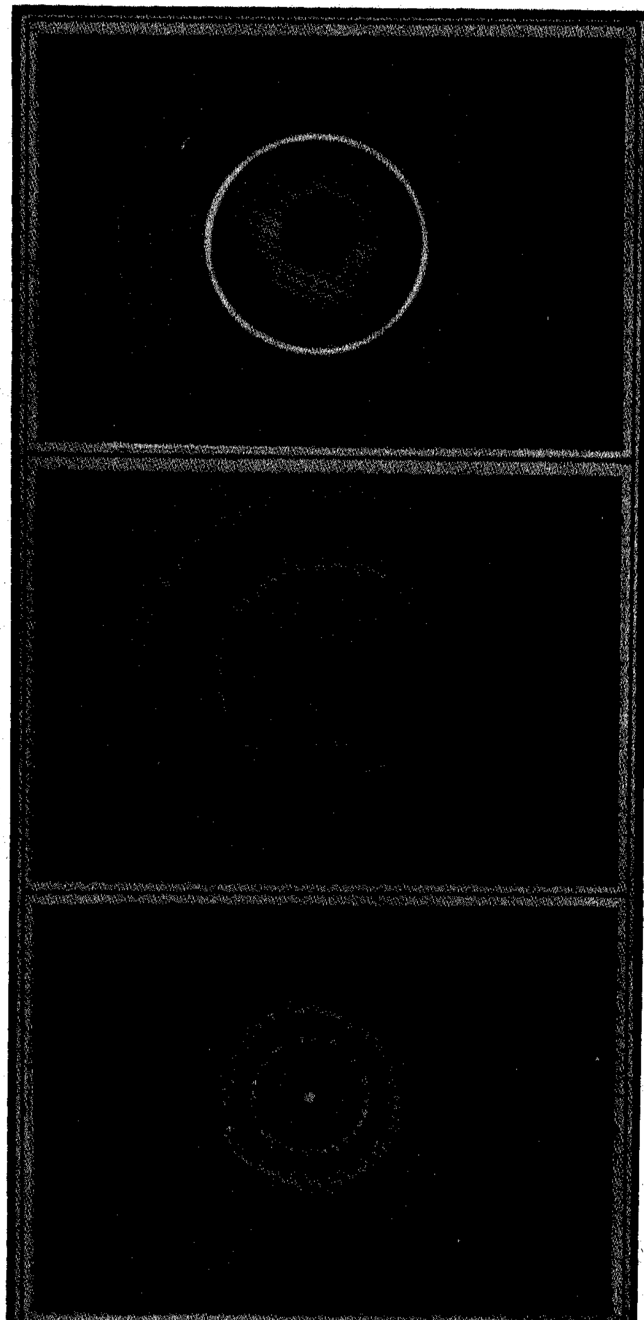
Marble which in its purest forms consists of calcite furnishes excellent illustrations of the optical behaviour of a polycrystalline medium consisting of strongly birefringent crystallites. The influence of the grain size on the penetration of light into the material indicated by the theory is readily confirmed by observations with different specimens. A very interesting fact is that the light diffused by marble both backwards and forwards exhibits a surprisingly rich redness even when the marble itself is only of a faintly pinkish colour.

Alabaster which consists of randomly orientated crystallites of gypsum affords good illustrations of the behaviour of a polycrystalline medium in which the crystallites have only a feeble birefringence. The size of the crystallites can of course be readily determined by cutting a thin section and viewing it under a polarising microscope. The relationship between the size of the crystallites and the optical behaviour of the material can be readily confirmed by viewing a bright source of light through a slice of alabaster mounted between microscope cover-slips with a little Canada balsam. Only with the thinnest sections is a true optical transmission observable. This appears surrounded by a diffusion halo exhibiting streaky colours in white light. The depolarisation of the halo and the polarisation of the regularly transmitted light when the incident light is polarised are also readily confirmed by observation.

The X-ray diffraction diagram of alabaster depends very much on the size of the crystallites which it contains. Unless the alabaster is very fine-grained, a collection of spots only vaguely indicative of a ring pattern is obtained. Very different is the picture shown in figure 3 in plate I which shows a readily recognizable ring system, though spotty in character. This was obtained with a very fine museum piece exhibiting a remarkably high degree of translucency.

Figure 2 in plate I is an X-ray diagram recorded with a dish of Chinese origin stated to be of jade, but not really so. The material was colourless and exhibited a high degree of translucency. The extremely small size of the crystallites of which it is composed is evident from the X-ray diagram.

Figure 1 in the same plate is the X-ray diagram obtained by passing a beam of X-rays through a plate of a white porcelain-like material which was cut out from a block of agate and which was identified as α-cristobalite by its X-ray pattern. The extreme fineness of the particles of the material is evident from the X-ray diagram. A source of white light seen through the plate is visible, but appears of a deep red colour. The material thus furnishes an excellent example of a polycrystalline

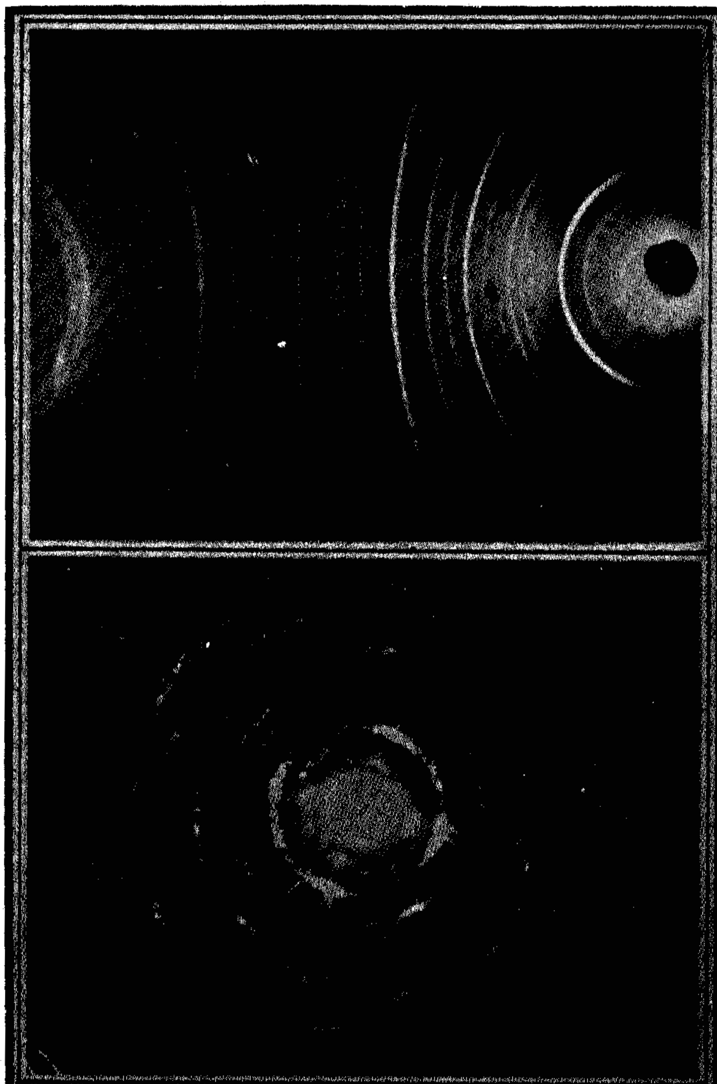


(1)

(2)

(3)

Plate I



(4)

(5)

Plate II

medium consisting of a birefringent material which nevertheless exhibits a true optical transmission by reason of the small size of the crystallites.

The phenomena arising from the propagation of light through a medium with a fibrous structure are beautifully illustrated by observing a source of light through a polished plate of chalcedony. They exhibit in a very conspicuous manner the various features indicated by the theory. It should be emphasized that chalcedony exhibits large variations in its structure and these correspond to striking differences in optical behaviour. Two extreme cases are illustrated respectively by figures 4 and 5 in plate II. The first is an X-ray diagram recorded with a specimen of agate which exhibited only translucency but no real transmission of light. It will be seen from the X-ray diagram that this material consisted of extremely fine particles. Figure 5, on the other hand, is an X-ray diagram of a specimen of chalcedony showing a coarsely fibrous structure. A source of light could easily be seen in perfect focus through the plate though much dimmed in intensity and reddened in colour. The transmitted light was found to be completely polarised, and this was evidently a consequence of the fibrous structure revealed by the X-ray pattern and also evidenced by the streams of diffracted light seen surrounding the image of the source.