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ON THE OPTICAL BEHAVIOUR OF CRYPTO-CRYSTALLINE QUARTZ

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(Memoir No. 64 of the Raman Research Institute, Bangalore)

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 orienta-

FIG. 1

FIG. 2

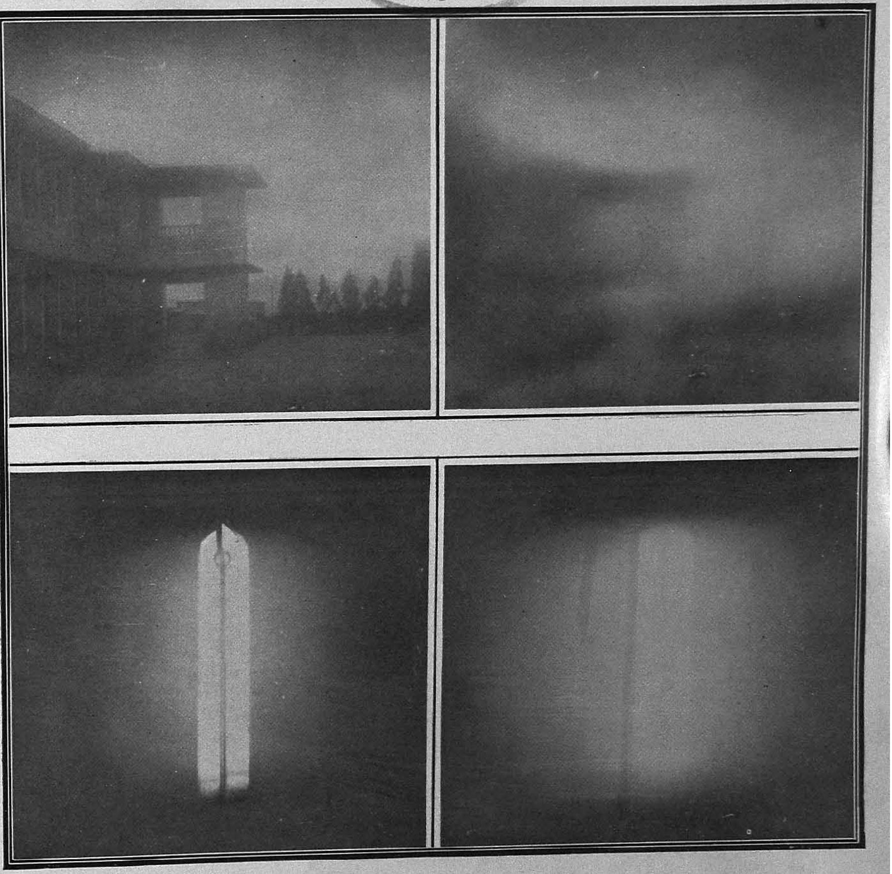

FIG. 3

FIG. 4

Polarisation of Light by Chalcedony

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and A. Jayaraman

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FIG. 1

FIG. 2

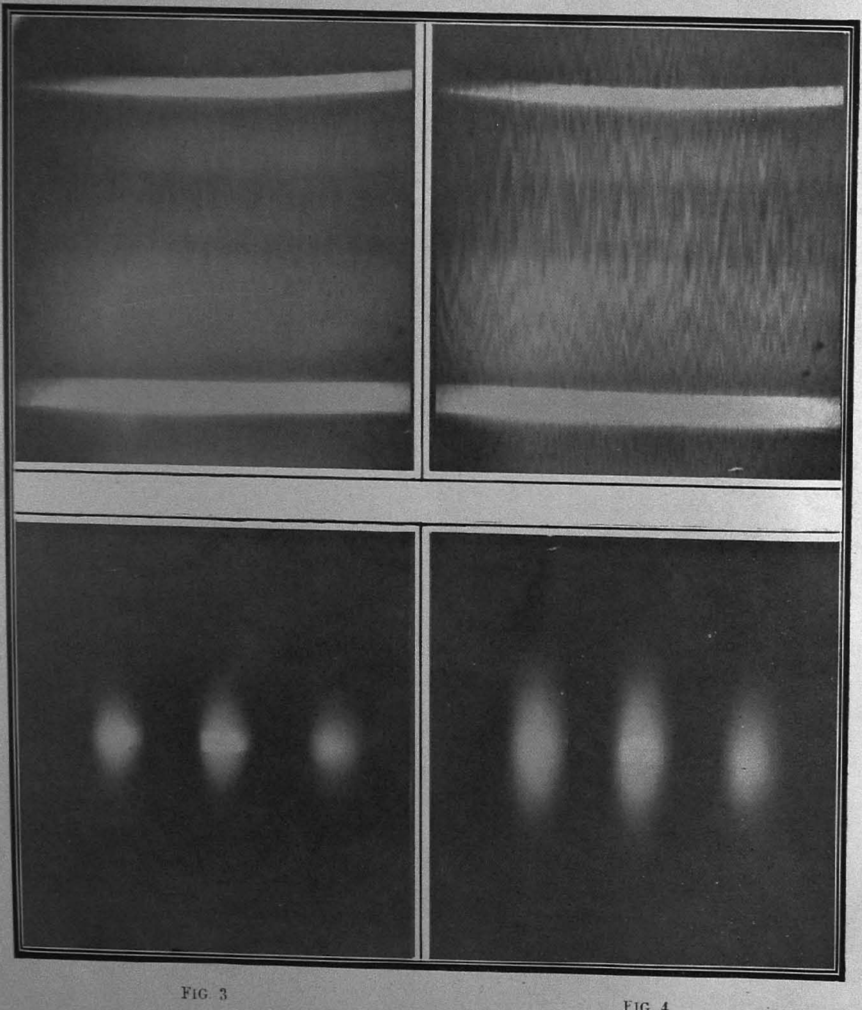

FIG. 3

FIG. 4

Polarisation of Light by Iridescent Agate

Sir C. V. Raman
and A. Jayaraman

Proc. Ind. Acad. Sci., A, vol. XLI, Pl. III

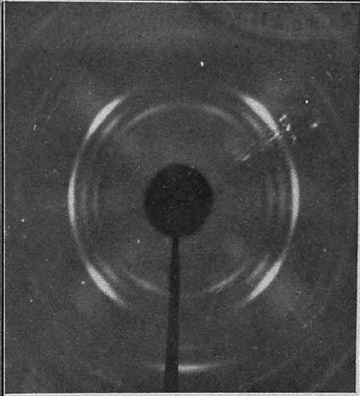

FIG. 1

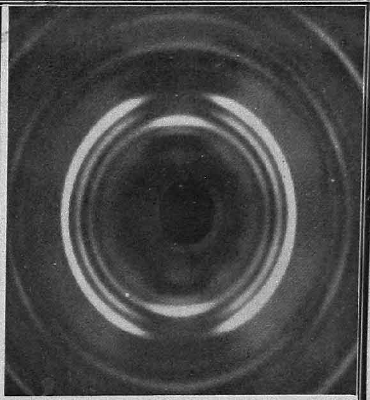

FIG. 4

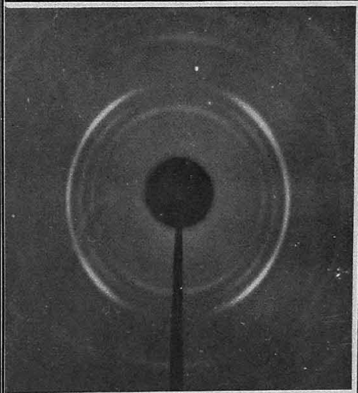

FIG. 2

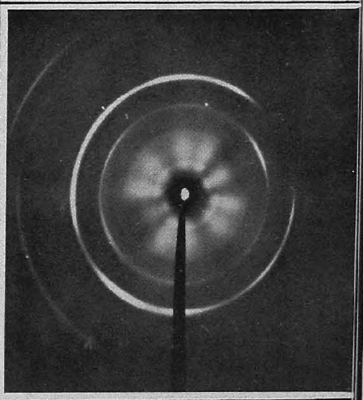

FIG. 5

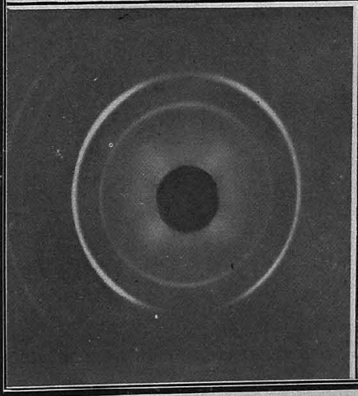

FIG. 3

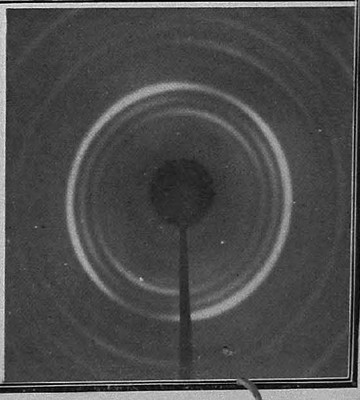

FIG. 6

X-Ray Diffraction Patterns

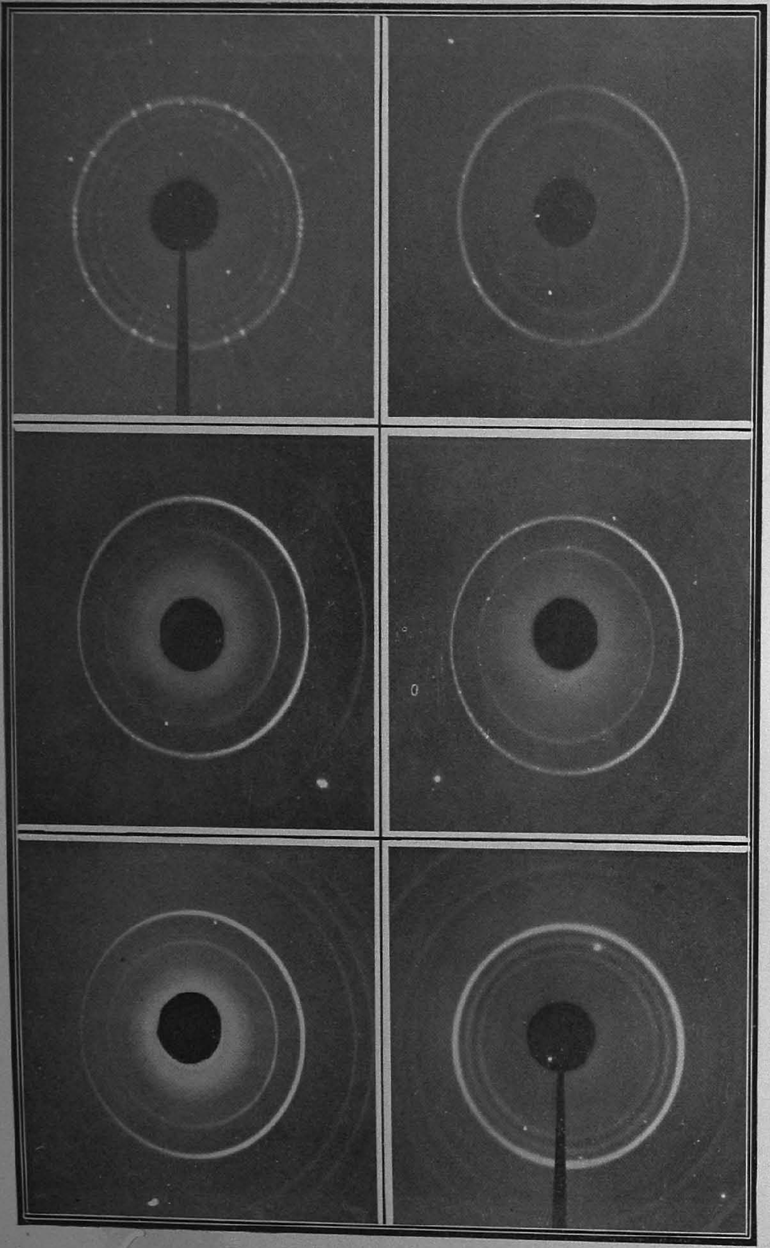

FIG. 1

FIG. 4

FIG. 2

FIG. 5

FIG. 3

FIG. 6

X-Ray Diffraction Patterns

tion 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.

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RAMAN SPECTRA OF BORAX, KERNITE AND COLEMANITE

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(*Memoir No. 65 from the Raman Research Institute, Bangalore*)

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1. INTRODUCTION

THE Raman effect in boric acid and its derivatives and the glasses associated with them has been studied by several investigators. A brief summary of the results appears in Hibben's treatise on "The Raman Effect and its Chemical Applications". The Raman spectrum of borax ($Na_2 B_4O_7 \cdot 10H_2O$) has been observed by Nielsen (*vide* Hibben's treatise, p. 433) and has been found to consist of seven frequencies at 578 (1), 853 (1), 891 (1), 942 (1), 3340 (1), 3455 (1) and 3574 (1) cm.$^{-1}$. Kernite ($Na_2B_4O_7 \cdot 4H_2O$) was investigated by Hibben (1937) who reports ten frequencies at 500 (2), 575 (0), 735 (3), 850 (0), 934 (6), 1100 (?), 3269 (2), 3343 (3), 3425 (2) and 3552 (10) cm.$^{-1}$ Gross and Vuks have reported in borax glass diffuse bands in the regions 430–535 (0), 950–1000 (0), 1077–1127 (0), and 1310–1520 (0) and a strong line at 760 (5) cm.$^{-1}$ It is rather surprising that Nielsen did not notice any shift corresponding to 760 cm.$^{-1}$ in borax. The Raman spectrum of colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$) has not so far been investigated. In view of the interest attached to these substances and the fact that the low frequency spectra of these have not so far been reported, it appeared to be desirable to investigate the spectra of these substances. The paper reports the findings from the study.

2. EXPERIMENTAL DETAILS

The Raman spectra were recorded with a Hilger medium quartz spectrograph having a dispersion of 140 cm.$^{-1}$ per mm. in the λ 2536·5 region. A quartz mercury arc of the sealed type with mercury pools as electrodes was immersed in a trough of running water and an electromagnet was used to deflect the discharge towards the top wall of the arc. With a current of 3 amperes this arrangement constituted to give an intense source of λ 2536·5. The crystals were kept quite close to the arc and the scattered radiations from the crystal were focussed on the slit of the spectrograph with a quartz condenser. Two mercury dishes were placed inside the spectrograph one at the collimator side and the other at the plate-holder side. The mercury vapour inside the spectrograph was sufficient to effectively suppress the exciting λ 2536·5 radiation so that in the spectrograms obtained, it appeared much feebler than its satellite λ 2534·8.

The crystals of borax which were rather small were efflorescent and as such fresh crystals had to be used periodically. A large specimen of kernite in the form of a thick plate was available and it was possible to record in this case a very intense spectrum. The specimen of colemanite which was somewhat smaller in size had well-developed faces forming a pyramid, but was intensely luminescent under near ultraviolet radiations. Kernite was also slightly luminescent. This fact coupled with the feeble scattering in these crystals made it impossible to record their Raman spectra with λ 4358 in the visible. In the ultraviolet region on the other hand, because of the large scattering power of the λ 2536·5 radiations the luminescence did not overpower the scattering. With a slit width of 0·045 mm. and an exposure of the order of 16 hours it was possible to obtain reasonably intense spectrograms. The complete spectrum of borax could not be obtained since the crystals grown by the method of slow evaporation were small.

3. RESULTS

Figures 1 (*b*), 1 (*c*), 1 (*d*) in the accompanying plate reproduce the Raman spectra of borax, kernite and colemanite respectively while Figs. 1 (*a*), and 1 (*e*) reproduce the spectrum of the mercury arc for comparison. In some cases the lines were rather weak and diffuse or else were partially overlapping on a mercury line and the frequency shifts of these were estimated by comparison with the position of the iron arc lines.

Borax exhibits seven lines at 159 (*w*), 349 (*w*), 458 (*m*), 572 (*m*), 753 (*w*), 847 (*v. w*), and 944 (*s*) cm.$^{-1}$ and four bands due to water at 3325, 3444, 3500 and 3577 cm.$^{-1}$ Of these the frequency at 3577 cm.$^{-1}$ is very intense and comparatively sharp. Nielsen has not reported the faint band at 3500 cm.$^{-1}$ The line reported at 891 cm.$^{-1}$ by Nielsen has not been recorded and only a trace of a line could be noticed at about 847 cm.$^{-1}$

Table I presents the data in the case of kernite and colemanite and the general correspondence between the two spectra can be noticed. In the case of colemanite, the intense frequency shift at 940 cm.$^{-1}$ observed in kernite and borax has not been recorded.

The spectrum due to water shows striking variations in its structure and in particular the frequency shift of the sharp and intense band corresponding to the hydroxyl group changes from 3552 cm.$^{-1}$ in kernite to 3577 cm.$^{-1}$ in borax and to 3605 cm.$^{-1}$ in colemanite.

TABLE I

Frequency Shifts

Kernite cm.^{-1}	Colemanite cm.^{-1}	Kernite cm.^{-1}	Colemanite cm.^{-1}
55 *s.*		806 *m.*	786 *w.*
82 *v.s.*	..	846 *m.*	∼ 870 *w.*
104 *s.*	95 *v.s.*	932 *v.s.*	..
127 *s.*	..	951 *v.w.*	∼ 982 *v.w.*
152 *w.*	148 *m.*	∼ 1028 *m.*	..
184 *s.*	181 *s.*	1087 *s.*	1078 *m.*
∼ 215 *v.w.*	223 *m.*	1135 *m.*	∼ 1150 *w.*
258 *s.*	251 *m.*	1321 *s*	∼ 1252 *w.*
		1375 *v.w.*	∼ 1310 *w.*
315 *w.*	318 *s.*	1448 *w.*	..
346 *w.*	..	∼ 1480 *v.w.*	..
371 ∼ 391 *b.m.*	..	∼ 3000 *s.*	..
426 *v.w.*	..	3248 *s.*	∼ 3310 *s.*
459 *m.*	∼ 450 *v.w.*	∼ 3305 *s.*	..
498 *v.s.*	∼ 490 *v.w.*	∼ 3360 *s.*	..
541 ? *v.w.*	538 *s.*	∼ 3425 *s.*	
562 *w.*	565 *s.*	3548 *v.s.*	∼ 3520 *s.*
..	670 *s.*	..	3605 *v.s.*
739 *v.s.*	745 *v.s.*	..	

s. strong; *w.* weak; *m.* moderate; *v.s.* very strong; *v.w.* very weak; *b.* broad. ∼ value of frequencies estimated by comparison with position of adjacent iron arc lines.

4. DISCUSSION

Borax, kernite and colemanite crystallize in the holohedral class of the monoclinic system and have been assigned to the space groups C2/c, P2/c and $P2_1/a$ respectively [*Structure Reports*, Vol. 11, pp. 428–31 and Christ, Clark and Evans (1954)]. The existence of a centre of symmetry in all these cases precludes the possibility of observing any of these lines in infra-red absorption also. Reference to the literature has revealed that no infra-red absorption studies have so far been made with borax and kernite. However, the infra-red spectrum of metallic orthoborates have been studied by Sen and Sen-Gupta (1935) in the near infra-red by transmission, by Parodi (1937) in the far infra-red both by reflection and transmission, and lately extensively by Lecomte and Duval (1952) in the near infra-red by transmission. For calcium borate [$Ca_3(BO_3)_2$] they observe maxima at 676, 734, 784, 814, 876, 922, 1000, 1100, 1168, 1340 and 1412 cm.^{-1} Parodi reports in the far infra-red for calcium borate frequencies at 365, 325, 250 and 192 cm.^{-1}

Lecomte and Duval have discussed in detail the origin of such a large number of frequencies since an ordinary planar BO_3 group should possess only four vibration frequencies. They attribute the large number of frequencies to the coupling of BO_3 groups and they calculate that two such groups coupled would give rise to eighteen vibration frequencies, the totally symmetric valence vibration frequency being in the region 909–934 cm.$^{-1}$ The structure of borax is reported to consist of BO_3 triangles sharing common vertices and forming an infinite chain along the *c*-axis consisting of B_4O_7 rings. Kernite on the other hand, is supposed to be made up of B_3O_6 rings formed by three BO_3 triangles sharing vertices, coupled together by B_2O_3 groups from two BO_3 triangles, thus forming an infinite B_4O_7 zig-zag chain along the *b*-axis. The vibrations of such a structure consisting of coupled BO_3 triangles would give rise to a large number of frequencies and it is possible here to identify only the frequency at 932 cm.$^{-1}$ in kernite and at 944 cm.$^{-1}$ in borax as due to the valence oscillation of the borons and oxygens.

The structure of colemanite recently determined by Christ, Clark and Evans (1954) is reported to consist of infinite boron-oxygen chains running parallel to the *a*-axis, the chain element being constituted by a BO_3 triangle and two BO_4 tetrahedra forming a ring, the chain element having the composition $[B_3O_4(OH)_3]^{-2}$. It has also been found by them that the B—O bond lengths in the tetrahedra are larger than the bond lengths in the triangles. Again, since colemanite also possesses a centre of symmetry no correspondence could be normally expected between the data from Raman and infra-red spectra. But the studies of Coblentz (1906) on the infra-red reflection spectrum of colemanite reveal the existence of frequencies at 1370, 1316 (?), 1064, 943 and 893 cm.$^{-1}$, which have nearly corresponding frequencies at 1310, 1078, 982 and 870 cm.$^{-1}$ in Raman effect. It is rather surprising that there is no Raman frequency in colemanite corresponding to the 940 cm.$^{-1}$ shift in borax and kernite. If the vibrating structure in colemanite consists of BO_3 triangles coupled to BO_4 tetrahedra having different bond lengths, as has been suggested by Christ, Clark and Evans, the principal vibration frequency of this system might be different from what has been observed in kernite and borax.

The existence of the O—H group in the chain element of colemanite is consistent with the observation in Raman effect of an intense and sharp band at 3605 cm.$^{-1}$ and corresponding to the hydroxyl group frequency. Though the reported structures of kernite and borax do not contemplate the existence of the hydroxyl group in them, the observation of sharp and intense bands at 3548 and 3577 cm.$^{-1}$ in their respective Raman spectra indicate the existence

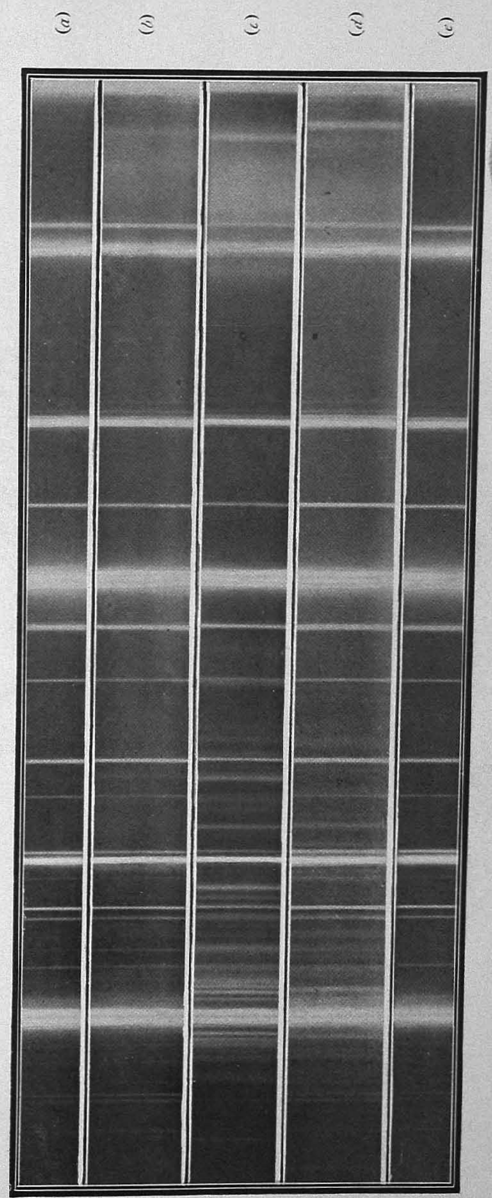

FIG. 1. Raman Spectra of Borax, Kernite and Colemanite

(a) Mercury arc. (b) Borax. (c) Kernite. (d) Colemanite. (e) Mercury arc.

of such groups in their structures. It is hoped that polarisation and orientation studies would help towards a more detailed analysis of the observed spectra of these chain structures.

The author's grateful thanks are due to Prof. Sir C. V. Raman, F.R.S., N.L., for suggesting this investigation and the encouraging interest that he took in it.

SUMMARY

The Raman spectra of borax, ($Na_2B_4O_7\cdot 10H_2O$), kernite ($Na_2B_4O_7\cdot 4H_2O$) and colemanite ($Ca_2B_6O_{11}\cdot 5H_2O$) have been investigated using λ 2536·5 as exciting radiation. The spectrum of colemanite is reported for the first time. Many additional lines hitherto unreported have been found in the case of kernite and borax. The spectrum of borax exhibits seven lines, besides four bands due to water of crystallisation while the spectrum of kernite is found to consist of twenty-eight lines and six water bands. Colemanite exhibits nineteen Raman lines, and three bands due to water of crystallization. The observed spectra are discussed in relation to the known structures of the substances.

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THE THEORY OF THE PROPAGATION OF LIGHT IN POLYCRYSTALLINE MEDIA

BY SIR C. V. RAMAN AND K. S. VISWANATHAN
(*Memoir No. 66 of the Raman Research Institute, Bangalore*)

Received February 8, 1955

1. INTRODUCTION

MANY common minerals occur in nature as polycrystalline aggregates. For example, quartz, calcite and gypsum appear in massive form respectively as quartzite, marble and alabaster, and on examining thin sections of these materials under the polarisation microscope, it is found that they consist of great numbers of crystallites variously orientated and firmly adherent to each other so as to form a coherent solid. The size, shape and manner of orientation of the crystallites may differ enormously in individual cases. Some minerals are indeed cryptocrystalline, in other words, the particles are so small that they cannot be identified by the usual polariscopic methods and require the aid of X-ray analysis to enable their true nature to be determined.

The foregoing is by way of stressing the importance alike to the mineralogist and to the physicist of a study of the physical properties of polycrystalline aggregates. It is obvious that the optical properties of the single crystal and especially its birefringence and pleochroism (if any) would play a dominant role in determining the optical characters of the polycrystalline aggregate. Considering the matter from the standpoint of geometrical optics, it is evident that when light enters a polycrystalline aggregate, it would suffer reflection at the intercrystalline boundaries. The stronger the birefringence, the greater would be the coefficient of reflection at these boundaries and hence the more quickly would the incident light be returned back towards the source. The brilliant whiteness of pure marble is thus a recognisable consequence of the strong birefringence of calcite. On the other hand, if the birefringence be feeble as in the case of quartz and gypsum, the incident light would penetrate far more deeply into the aggregate. Ultimately, all the light would necessarily be turned back provided that a sufficient thickness of the material be available and that no absorption intervenes. If the thickness of the material be insufficient, a part of the light would diffuse out—a phenomenon readily observed with various materials. Light so emerging would be depolarised even if the light incident on the plate were fully polarised in the first instance.

Various considerations indicate that a purely geometric theory is inadequate to cover all the optical phenomena actually exhibited by polycrystalline media. It will suffice to mention here the question of the influence of the size of the crystallites. Geometric considerations would suggest that the smaller the crystallites, the more numerous would be the reflections and refractions at the intercrystalline boundaries, and hence the more rapidly would the incident light be diffused and extinguished in its passage through the medium. Experience however suggests that the contrary may actually be the case, and that the more fine-grained the material is, the more deeply would the light penetrate into it. Various minerals, *e.g.*, alabaster and jade, which exhibit marked translucency, are usually fine-grained; the finer the grain, the more deeply does light penetrate into them. This suggests that the optical problems presented by polycrystalline aggregates require to be considered from the standpoint of the wave-theory of light. That indeed is the object of the present paper.

2. A SIMPLIFIED MODEL

To obtain some results of physical interest and also with a view to simplify the mathematics, we shall here restrict ourselves to the case of a feebly birefringent material and consider the case in which light is incident normally on a plate with parallel faces; this is assumed to be sufficiently thick to include a great many individual crystallites but not so thick that the incident light is completely extinguished before it can emerge at the rear face. We may disregard the geometric course of the individual rays of light and view the matter purely from the wave-theoretical standpoint. Owing to the varying orientation of the individual crystallites, the waves of light entering the plate would be retarded to different extents in passing through them. To enable the resulting total retardation to be evaluated, we use a simplified model and assume the plate to be an assembly of a great number of small cubical blocks each having a common edge-length Δ and completely filling up the available space. Each block is assumed to be a single crystallite, and the three edges of each cube to be parallel to the three optic directions for which the refractive indices are μ_1, μ_2 and μ_3 respectively. To introduce the idea of varying orientation and to take account of its influence on the propagation of light through the material, we assume the incident light-beam to be plane-polarised with its vibration direction parallel to one set of edges of the cubical blocks; on the other hand, the operative refractive index of any one block may be either μ_1 or μ_2 or μ_3, the respective probabilities for these being p_1, p_2, p_3. The case where the three probabilities are equal would correspond to a random orientation of the crystallites in the present restricted sense of that term. More generally, by giving appropriate values to p_1, p_2, p_3 such that their sum remains equal to unity, we obtain a representation of a polycrystalline aggregate with any desired measure of preferred orientation along the particular direction under consideration. If, for example, we put $p_1 = 1$ while p_2 and p_3 are zero, it would mean that all the particles of the aggregate have a common refractive index for the particular direction of vibration, though the indices may be different in the perpendicular direction.

On the assumptions stated, the incident plane-polarised disturbance would remain plane-polarised in its passage through the plate, though subject to phase retardations of varying extents. The situation would no doubt be different for any actual polycrystalline material, since the incident plane-vibration would be transformed to an elliptic vibration and the parameters describing the ellipticity would alter as the disturbance passes from crystallite to crystallite. While it would no doubt be possible to deal mathematically with this general case, a very considerable simplification is effected by our present assumptions, and as we shall see, the usefulness of the results obtained is not affected thereby.

A further question needing consideration is the effect of the reflections which would occur at the boundary between every two successive blocks. This would obviously diminish the amplitude of the transmitted disturbance. As a first approximation, we may assume such diminution to be the same over all the individual elementary areas Δ^2 on the rear surface of the plate and represent it by a numerical factor of appropriate magnitude. In other words, we ignore the variation of *amplitude* over the different elementary areas Δ^2 on the rear face of the plate and consider only the variations of *phase*. The latter are in reality of much greater importance for the determination of the final observable result.

3. MATHEMATICAL FORMULATION

Let us suppose that the wave-train before entry into the plate is represented by

$$y = e^{\frac{2\pi i}{\lambda}(ct-Z)} \tag{1}$$

and that there are n cells along the direction of the thickness of the plate. We shall first consider a typical case in which the wave has passed through k_1 cells of refractive index μ_1, k_2 cells of refractive index μ_2 and k_3 cells of refractive index μ_3 before emerging from the plate. The numbers k_1, k_2 and k_3 can all vary from zero to n subject to the relation

$$k_1 + k_2 + k_3 = n \tag{2}$$

The optical path retardation of the emergent wave would then be equal to $(k_1\mu_1 + k_2\mu_2 + k_3\mu_3)\,\Delta$.

Now the number of ways in which k_1, k_2 and k_3 cells can be orientated along a row of n cells so as to have refractive indices μ_1, μ_2 and μ_3 is obviously

$$\frac{n!}{k_1!\,k_2!\,k_3!}$$

and the probability of occurrence of each one of these cases is $p_1^{k_1}p_2^{k_2}p_3^{k_3}$. Hence the proportion of the total area of the rear surface of the plate from which a wave represented by

$$e^{\frac{2\pi i}{\lambda}(ct - Z - \overline{k_1\mu_1 + k_2\mu_2 + k_3\mu_3}\,\Delta)} \tag{3}$$

emerges is equal to

$$\frac{n!}{k_1!\,k_2!\,k_3!}\,p_1^{k_1}p_2^{k_2}p_3^{k_3} \tag{4}$$

The emergent wave-train can now be obtained by summation of waves of the type (3) with their appropriate amplitudes and phases for all possible integral values of k_1, k_2 and k_3 satisfying the relation (2). We therefore have for the emergent wave

$$y = \mathrm{P}\sum_{k_1+k_2+k_3=n}\frac{n!}{k_1!\,k_2!\,k_3!}\,p_1^{k_1}p_2^{k_2}p_3^{k_3}\,e^{\frac{2\pi i}{\lambda}(ct - Z - \overline{k_1\mu_1 + k_2\mu_2 + k_3\mu_3}\,\Delta)} \tag{5}$$

where P is a factor which is introduced to take into account the loss in intensity of the light due to reflections at the intercrystalline boundaries.

In view of the multinomial theorem, equation (5) may be rewritten as

$$y = \mathrm{P}\,e^{\frac{2\pi i}{\lambda}(ct-Z)}\left(p_1 e^{\frac{-2\pi i\mu_1\Delta}{\lambda}} + p_2\,e^{\frac{-2\pi i\mu_2\Delta}{\lambda}} + p_3 e^{\frac{-2\pi i\mu_3\Delta}{\lambda}}\right)^n \tag{6}$$

The average refractive index of the medium is clearly

$$\mu = (p_1\mu_1 + p_2\mu_2 + p_3\mu_3) \tag{7}$$

If therefore we set $\nu_1 = (\mu_2 - \mu_3)$; $\nu_2 = (\mu_3 - \mu_1)$; and $\nu_3 = (\mu_1 - \mu_2)$, we can then express μ_1, μ_2 and μ_3 as

$$\begin{aligned}\mu_1 &= \mu + (p_2\nu_3 - p_3\nu_2)\\ \mu_2 &= \mu + (p_3\nu_1 - p_1\nu_3)\\ \mu_3 &= \mu + (p_1\nu_2 - p_2\nu_1)\end{aligned} \tag{8}$$

Further, the thickness of the plate is given by $d = n\Delta$. Hence substituting the relations (8) in (6) and expanding the exponential terms in power series of their arguments, one obtains

$$y = \mathrm{P}\, e^{\frac{2\pi i}{\lambda}(ct - Z - \mu d)} \times \left\{ 1 - \frac{2\pi^2\Delta^2}{\lambda^2} \Sigma p_1 (p_2\nu_3 - p_3\nu_2)^2 \right\}^n \tag{9}$$

As the birefringence is assumed to be small, we have ignored terms of third and higher powers of $(\mu_1 - \mu_2)$, $(\mu_2 - \mu_3)$ and $(\mu_3 - \mu_1)$ in (9). Also by means of a small simplification, it can be verified that

$$\Sigma p_1 (p_2\nu_3 - p_3\nu_2)^2 = \Sigma p_2 p_3 \nu_1^2$$

Hence, we can rewrite (9) as

$$y = \mathrm{P}\, e^{\frac{2\pi i}{\lambda}(ct - Z - \mu d)} \left\{ 1 - \frac{1}{n} \times \frac{2\pi^2\Delta d}{\lambda^2} \Sigma p_2 p_3 \nu_1^2 \right\}^n$$

$$= \mathrm{PR}\, e^{\frac{2\pi i}{\lambda}(ct - Z - \mu d)}$$

where

$$\mathrm{R} = e^{\frac{-2\pi^2\Delta d}{\lambda^2} \Sigma p_2 p_3 \nu_1^2} \quad \text{as } n \text{ is large.}$$

The ratio of the intensity of the transmitted light to that of the incident radiation is therefore given by

$$\frac{\mathrm{I}}{\mathrm{I}_0} = \mathrm{P}^2\mathrm{R}^2 = \mathrm{P}^2\, e^{\frac{-4\pi^2\Delta d}{\lambda^2} \Sigma p_2 p_3 (\mu_2 - \mu_3)^2} \tag{10}$$

If the three optic axes of any cube have the same probability of being orientated in the direction of the incident light, then $p_1 = p_2 = p_3 = \frac{1}{3}$ and (10) reduces to

$$\frac{\mathrm{I}}{\mathrm{I}_0} = \mathrm{P}^2\, e^{\frac{-8\pi^2\Delta d}{9\lambda^2} (\Sigma \mu_1^2 - \Sigma \mu_2\mu_3)} \tag{11}$$

4. SIGNIFICANCE OF THE RESULTS

The physical meaning of the result stated in (10) is that the plane-polarised waves incident on the front of the plate emerge from the rear face of the plate also as a plane-polarised vibration but with an attenuated amplitude determined by an exponential factor involving four variables, namely the size of the particles, the thickness of the plate, the wave-length of the light and a quantity which is a measure of the birefringence of the material, since it vanishes when the three indices μ_1, μ_2, μ_3 are all equal. The appearance of λ^2 in the denominator indicates that white light entering the plate would emerge enfeebled but with the longest waves predominant, in other words, much reddened in colour. Since the wave-length λ is a small quantity, the actual intensity of the emerging light would be negligible if both Δ and d are large. The individual crystallites have, in fact, to be quite small and the total thickness traversed should be moderate if any observable fraction of the light is to emerge as a coherent optical beam. We have already assumed the birefringence to be small and the need for such assumption is reinforced by our final result which indicates that unless the three indices μ_1, μ_2, μ_3 differ from each other by quantities which are small fractions of their absolute magnitudes, no light can emerge from the rear of the plate.

We may illustrate the foregoing remarks by the case of a plate of alabaster 1 mm. thick taking λ and Δ equal to 5896 A.U. and $1\,\mu$ respectively; the three indices for gypsum are $\mu_1 = 1{\cdot}520$, $\mu_2 = 1{\cdot}523$ and $\mu_3 = 1{\cdot}530$. The percentage of transmission then comes out as 13·5% but increases to 37% and 82% if $\Delta = 0{\cdot}5\,\mu$ and $0{\cdot}1\,\mu$ respectively. Thus, the formula indicates that a plate of alabaster approaches practically complete transparency as the crystallites of which it is composed approach colloidal dimensions.

The case of preferred orientations is also of interest in view of the known optical behaviour of chalcedony and of certain forms of gypsum. Taking now the general formula (10), if we put $p_1 = 1$ while p_2 and p_3 are both zero, the formula indicates that the transmission becomes complete. In other words, if the crystallites are so orientated that all of them have a common refractive index for the direction of vibration of the incident light, then we have a complete transmission of the incident light wave. But the position would be totally different for a perpendicular direction of vibration if the refractive indices for the latter direction differ from crystallite to crystallite. The general formula (10) would then show only a partial transmission depending upon the actual values of the probabilities and the refractive indices for that direction. Since the latter transmission would depend upon the thickness d, it would follow that if the light incident upon the plate be unpolarised, the state of polarisation of the emerging light would vary with the thickness of the plate. Formula (7) also indicates that the effective refractive index of the medium would be different for the two directions of vibration under consideration. Light which is plane-polarised in any arbitrary azimuth when incident on the plate, would emerge as elliptically polarised light, the parameters describing such ellipticity varying with the thickness of the plate—a phenomena readily capable of experimental verification with materials of the nature under consideration.

5. SOME FURTHER REMARKS

The question naturally arises as to where the energy goes which disappears from the incident light according to (10). The answer to this is not far to seek. Since the reduction of amplitude is a consequence of the random variations of phase over the elementary areas of the rear face of the plate, the missing light would appear as diffracted radiation spread out in various directions surrounding the direction of the incident beam. The angular dimensions of the diffraction halo would obviously be comparable with the ratio between the wave-length λ of the light and the linear dimension Δ of the crystallites which we have assumed the material to be composed of. A diffusion halo of this type can indeed readily be observed on viewing a bright source of light through a thin plate of alabaster surrounding the sharply defined image of the source itself. According to the theory developed above, both the light emerging from the rear surface of the plate and the light appearing in the diffusion halo would be perfectly polarised if the incident light be itself plane-polarised. These results are consequences of the special assumption regarding the orientation of the crystallites which we have made. We may now ask ourselves whether they would continue to be true if the particles are orientated truly at random. The answer to this question is most readily ascertained by making a few actual observations with a plate of alabaster sufficiently thin to give a true transmission. It is then observed that the true transmission is completely polarised while the diffraction halo seen overlying it is imperfectly polarised. A more complete mathematical theory which takes account of the ellipticity resulting from the passage of light through an arbitrarily orientated crystal block would no doubt yield results in agreement with these facts of observation. It is clear, however, that the present theory suffices to indicate the state of polarisation of the transmitted light correctly and also its intensity, at least as regards the order of magnitude. But the theory fails to indicate the state of polarisation of the diffracted light accurately, since it ignores the ellipticity produced by the passage of light through a birefringent crystal in an arbitrary orientation; such ellipticity would obviously result in diverting some of the incident energy into the perpendicular component of vibration as diffracted radiation.

SUMMARY

A formula based on wave-theoretical considerations is deduced which gives the coefficient of extinction of plane-polarised light traversing a polycrystalline aggregate in terms of the wave-length of the light, the size of the particles and their birefringence. The general formula covers the case where the particles have preferred orientation expressible by three different probability numbers for three mutually perpendicular directions, and the special case of isotropic orientation is readily derivable therefrom. The significance of the results is discussed in relation to the facts of observation.

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A GENERALISED THEORY OF THE CHRISTIANSEN EXPERIMENT

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1. Introduction

In a paper[1] published in these *Proceedings* nearly six years ago, the theory of the well-known Christiansen experiment was discussed on a wave-optical basis. The expression derived in that paper for the transmission coefficient of a Christiansen light filter showed it to be an exponential function involving five variables, namely the wave-length of the light, the thickness of the cell, the size of the individual particles of the powder, the difference between the refractive indices of the powder and the surrounding liquid and finally also the proportions of the volume of the cell occupied respectively by the liquid and by the particles of the powder. In the present paper, it is proposed to deal with the more general case in which the particles of the powder are *birefringent* and hence their refractive index varies with the orientation of the crystallites within the cell. The mathematical treatment adopted is on much the same lines as that followed by us in discussing the theory of the propagation of light in polycrystalline media.[2] The only difference, in fact, is that some of the cubical elements of volume each of edgelength Δ which we imagine the cell to consist of must now be considered as being filled either by the liquid of refractive index μ_l or by the crystallites. These latter are assumed to be of cubical shape and to have their edges parallel to the three optic directions for which the refractive indices are μ_1, μ_2 and μ_3 respectively. We also assume the incident light beam to be plane-polarised with its vibration direction parallel to one set of edges of the cubical blocks and that the operative refractive index of any one block may be either μ_1, μ_2 or μ_3 with equal probabilities if it is a crystallite or μ_l if it is filled with the liquid.

2. Mathematical Formulation

We shall denote by p and q the respective probabilities of a cubical block having anyone of the three principal refractive indices μ_1, μ_2, μ_3 of the crystallites and of the refractive index μ_l of the liquid. Then $3p$ and q would represent the proportion of solid and liquid elements in the Christiansen filter and therefore

$$3p + q = 1 \tag{1}$$

As before, we consider a typical case in which the incident wave-train which we shall represent by

$$y = e^{\frac{2\pi i}{\lambda}(ct-Z)} \tag{2}$$

encounters in its passage through the Christiansen cell $(n-m)$ elementary cells of solid blocks and m cells of liquid elements. The probability of the occurrence of this event is obviously

$$\frac{n!}{(n-m)!\, m!}\,(3\,p)^{n-m}\,q^{m} \tag{3}$$

If further in any specification of the state of orientation of the crystallites inside the filter, k_1, k_2 and k_3 of the $(n-m)$ cubical blocks considered above have refractive indices μ_1, μ_2 abd μ_3 respectively, then the optical path retardation of the emergent wave for this configuration is $(k_1\mu_1+k_2\mu_2+k_3\mu_3)\,\Delta + m\mu_l\Delta$. We have in addition

$$(k_1 + k_2 + k_3) = (n-m) \tag{4}$$

Also, the probability of occurrence of a state in which k_1, k_2 and k_3 cells in a row of $(n-m)$ cells can be orientated so as to have refractive indices μ_1, μ_2 and μ_3 is

$$\frac{(n-m!)}{k_1!\,k_2!\,k_3!}\left(\frac{1}{3}\right)^{n-m} \tag{5}$$

Combining (3) and (5) we find that the proportion of area of the rear surface of the filter from which an emergent wave described by

$$e^{\frac{2\pi i}{\lambda}\left(ct-Z-\overline{k_1\mu_1+k_2\mu_2+k_3\mu_3+m\mu_l\Delta}\right)} \tag{6}$$

proceeds is equal to

$$\frac{n!}{k_1!\,k_2!\,k_3!\,m!}\,p^{n-m}\,q^{m} \tag{7}$$

The disturbance emerging from the Christiansen cell can now be obtained by a superposition of all the different wave functions of the type (6) multiplied by suitable weight factors of which (7) is a typical example. Hence,

$$y = \sum_{k_1,\,k_2,\,k_3,\,m} \frac{n!}{k_1!\,k_2!\,k_3!\,m!}\,p^{n-m}\,q^{m}\,exp\,\frac{2\pi i}{\lambda}\left(ct - Z - \overline{k_1\mu_1+k_2\mu_2+k_3\mu_3+m\mu_l\Delta}\right)$$

$$= e^{\frac{2\pi i}{\lambda}(ct-Z)}\left\{p\left(e^{\frac{-2\pi i}{\lambda}\mu_1\Delta} + e^{\frac{-2\pi i}{\lambda}\mu_2\Delta} + e^{\frac{-2\pi i}{\lambda}\mu_3\Delta}\right) + qe^{\frac{-2\pi i}{\lambda}\mu_l\Delta}\right\}^{n} \tag{8}$$

The average refractive index of the medium is now

$$\mu = p(\mu_1 + \mu_2 + \mu_3) + q\mu_l \tag{9}$$

If the birefringence of the crystalline particles is small and if further the three refractive indices of the solid powder do not differ much from the index of the liquid, then an approximation for (8) for large values of n can be effected by proceeding exactly as in the preceding paper. Denoting by d the total thickness of the cell, and neglecting terms of order higher than two in the differences between the various refractive indices, we can rewrite (8) as

$$y = e^{\frac{2\pi i}{\lambda}(ct-Z-\mu d)}\left[1 - \frac{2\pi^2\Delta^2}{\lambda^2}\left\{\sum_{r=1}^{3} p_r(\mu_r-\mu)^2 + q(\mu_l-\mu)^2\right\}\right]^n \tag{10 a}$$

Now if $\mu_1, \mu_2 \ldots \mu_n$ are n quantities having the respective probabilities of occurrence $p_1, p_2 \ldots p_n$ in any observation, then

$$\begin{aligned}\sum_{\substack{r,s\\ r<s}} p_r p_s(\mu_r-\mu_s)^2 &= \tfrac{1}{2}\sum_{r,s=1}^{n} p_r p_s(\mu_r-\mu_s)^2\\ &= \sum_s p_s\Big(\sum_r p_r\mu_r^2\Big) - \Big(\sum_r p_r\mu_r\Big)^2\\ &= \sum_r p_r\mu_r^2 - \mu^2\\ &= \sum_r p_r(\mu_r-\mu)^2\end{aligned}$$

where μ is the average of the n quantities $\mu_1, \mu_2, \ldots \mu_n$.

Applying the above result to (10) we find that for large values of n

$$y = \mathrm{R}e^{\frac{2\pi i}{\lambda}(ct-Z-\mu d)} \tag{10 b}$$

where

$$\mathrm{R} = exp\,\frac{-2\pi^2\Delta d}{\lambda^2}\{p^2\,\Sigma(\mu_2-\mu_3)^2 + pq\,\Sigma(\mu_1-\mu_l)^2\} \tag{11}$$

The ratio of the intensity of the transmitted light to that of the incident radiation is therefore given by

$$\frac{\mathrm{I}}{\mathrm{I}_0} = \mathrm{R}^2 = exp\,\frac{-4\pi^2\Delta d}{\lambda^2}\{p^2\,\Sigma(\mu_2-\mu_3)^2 + pq\,\Sigma(\mu_1-\mu_l)^2\} \tag{12}$$

Formula (12) expresses the extinction coefficient of light in its passage through the Christiansen cell in terms of several variables, namely, the wave-length of the light employed, the thickness of the cell, the size of the crystalline particles, the birefringence of the same and the three differences between the refractive index and the three principal indices of the birefringent material, and finally the proportion of the liquid and solid elements in the cell. By giving suitable values to p, q, μ_1, μ_2 and μ_3, several interesting cases of special importance can be deduced from (12). Thus we observe that the case of the polycrystalline aggregate considered earlier follows readily from (12) if $q = 0$ and $p = \frac{1}{3}$. Again, by writing $\mu_1 = \mu_2 = \mu_3$; $p = \frac{\sigma}{3}$ and $q = (1 - \sigma)$ which corresponds to the case of a Christiansen cell composed of isotropic particles mixed in a liquid in the proportion $\sigma : (1 - \sigma)$, we obtain the result

$$I = I_0 \, exp \frac{- 4\sigma (1 - \sigma) \pi^2 \Delta d}{\lambda^2} (\mu_1 - \mu_l)^2 \tag{13}$$

derived earlier by one of us[1] on different theoretical grounds. By writing $\mu_1 = \mu_2 = \mu_3$; $p = \frac{1}{6}$ and $q = \frac{1}{2}$ in (12) or $\sigma = \frac{1}{2}$ in (13) we get the expression

$$I = I_0 \, exp \frac{- \pi^2 \Delta d}{\lambda^2} (\mu_1 - \mu_l)^2 \tag{14}$$

for transmission by a cell composed of isotropic particles and a liquid of nearly the same refractive index mixed in equal proportions.

3. SOME FURTHER REMARKS

Considering once again the general formula (12), we may draw attention to certain features which we may expect to observe in the Christiansen experiment with birefringent powders differing from those noticeable when isotropic powders are employed. In the latter case, the transmission would be complete for the particular wave-length for which the solid and liquid have equal refractive indices and would fall off rapidly on either side of such wave-length. The light not transmitted by the cell would appear as a diffusion halo surrounding the direction of the optical image of the source as seen through the cell. Brilliant chromatic effects are accordingly to be expected and are indeed observed with isotropic powders in the experiment.

Formula (12) shows clearly that the effect of the birefriengence of the powder is to diminish the intensity of the transmitted light for all wave-lengths, and we cannot therefore, expect any observable transmission through the cell with strongly birefringent powders, unless the size of the particles be very small and the thickness of the cell be reduced to a minimum. In such cases the colour of the transmitted light would be determined predominantly by the factor $1/\lambda^3$ appearing in the argument of the exponential. Hence, it would be reddish in colour and the chromatic effects observed with isotropic powders would be absent. In these circumstances, the liquid in the cell serves only to secure optical continuity between the discrete particles contained in the cell. On the other hand, if the birefringence be small, one may expect to observe chromatic effects similar to those observed with isotropic powders. It would be necessary, however, to work with fairly fine powders and moderate cell thickness for noticeable transmission to occur. The formula also shows that the maximum transmission in these circumstances would be exhibited for those wave-lengths for which the refractive index of the liquid is most nearly equal to a species of average of the three indices of the crystal. But this is not the average index in the ordinary sense of the word.

Another important consequence of the formula is that even if the birefringence of the powder be not very small, chromatic effects would be observable when the proportion of the volume in the cell occupied by the powder is sufficiently small. In the usual form of the Christiansen experiment, the particles are allowed to settle down and form a compact aggregate at the bottom of the cell. To observe the effects now contemplated, the contents of the cell should be stirred up; alternatively the particles should be so small that they remain suspended for a long time within the liquid. In other words, dilute suspensions of strongly birefringent powders may be expected to give brilliant chromatic effects in a Christiansen cell. However, our theory could hardly be expected to give more than a qualitative indication of the phenomena then noticeable.

Finally, we come to the question of the state of polarisation of the transmitted light as also of the diffracted light when observed with birefringent powders. The present theory indicates that if the light incident on the cell be plane-polarised, both the transmitted and the diffracted light should also be perfectly plane-polarised. So far as the transmitted light is concerned, there can be no doubt that the theoretical result is correct. For, any ellipticity consequent on the passage of light through an arbitrarily orientated crystallite would give rise to a component perpendicular to the original vibration direction in the diffracted light. But such components cannot appear in the light transmitted by the cell in the true optical sense. Indeed, provided the birefringence is small and the size of the particles and the thickness of the cell are moderate we may expect also to find that the diffraction halo is itself strongly polarised. In other circumstances, however, especially when the particles are strongly birefringent, the diffracted light would exhibit a marked imperfection of polarisation by reason of the ellipticity effects which have dropped out of consideration in the present treatment of the problem.

SUMMARY

A formula is derived for the transmission coefficient of a Christiansen cell containing particles of a birefringent material whose interstices are filled up by a liquid of suitably adjusted refractive index. The consequences of the formula and especially the influence of the birefringence on the spectral character of the transmitted light are discussed.

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THE CHRISTIANSEN EXPERIMENT WITH BIREFRINGENT POWDERS

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1. INTRODUCTION

IN the well-known experiment due to Christiansen which has been applied in the construction of monochromatic light-filters, an isotropic transparent solid, *e.g.*, optical glass, is powdered and placed inside a flat-sided glass cell and the latter is then filled up by a liquid whose refractive index is adjusted to equality with that of the solid for some particular wave-length in the spectrum. Christiansen himself tried using powdered quartz in the experiment, and found that it did not prove a success. The light entered the cell and was diffused by the powder-liquid mixture, but the source of light could not itself be seen through the mixture. Considered from the standpoint of geometrical optics, this result is not surprising, since the refractive index of the particles of a birefringent powder would depend on their orientation within the cell and hence would vary from particle to particle.

However, geometrical optics does not correctly describe what is actually observed in the Christiansen experiment even with optically isotropic powders,[1, 2] and hence there is no reason to believe that it would be any more successful in the case of birefringent powders. In another paper[3] appearing in the present issue of these *Proceedings*, a general theory has been developed which indicates that chromatic effects analogous to those observed with isotropic powders should also be capable of appearing with birefringent powders in appropriate circumstances. The manner in which the birefringence would modify the observed effects has also been discussed in that paper.

It is proposed in what follows to place on record some observations which we have made broadly confirming the indications of the general theory. It has been found that provided the birefringence is fairly small and the material is in a finely subdivided state, it is possible to obtain a true transmission exhibiting brilliant colours. It is also found that the light so transmitted is not greatly inferior in the degree of its monochromatism to that observed with isotropic material in similar circumstances. Another noteworthy feature is that if the light incident on the cell is plane-polarised, the light transmitted by it is also completely plane-polarised. This might seem paradoxical when it is recalled that the light has had to pass through considerable thicknesses of a birefringent material; nevertheless the observation is in strict accord with the theory. On the other hand, the diffusion halo appearing in directions surrounding the regularly transmitted light exhibits imperfect polarisation to an extent depending on the fineness of the subdivision of the material. The colours exhibited by the diffusion halo are also found to be markedly different for the components of the light vibration respectively parallel and perpendicular to that in the incident light.

2. SOME GENERAL OBSERVATIONS

Besides the factors which determine the transmission coefficient with isotropic powders, an additional factor appears in the present case, namely the magnitude of the birefringence of the material. The importance of this relatively to the differences in the refractive indices of the solid and liquid varies with the proportion of the volumes occupied respectively by the powder and the liquid in the cell. By varying this proportion, we may pass from one extreme case of a polycrystalline aggregate in which the liquid serves merely to secure optical continuity between the particles of the powder to the other extreme case in which the liquid occupies the whole volume except for the particles of solid held in suspension. The most interesting cases are however those in which the two components are present in nearly the same proportions. To observe chromatic effects in such cases, it is necessary to use material which is not too highly birefringent and which is in a fine state of subdivision. The latter condition is most conveniently secured by using a substance which is commercially obtainable in the state of a fine powder and hence does not need any further preparation. We shall content ourselves here by mentioning three such substances which we have found to work very well in the experiment.

Barium sulphate can be used with success in a cell from five to ten millimetres thick with carbon disulphide as the liquid filling it up. The addition of a few drops of benzene shifts the transmission from the yellow towards the violet end of the spectrum. Precipitated calcium sulphate in the form of gypsum also gives good results, the appropriate liquid in this case being monochlorobenzene; a drop or two of carbon disulphide shifts the transmission towards the red, while the addition of a few drops of benzene shifts it towards the violet. Magnesium fluoride also serves admirably; the appropriate liquid to use in this case is acetone, the addition to which of benzene causes the transmission to appear first at the violet end of the spectrum and shifts it step by step toward the red.

3. POLARISATION PHENOMENA

In all the three cases mentioned, beautiful chromatic haloes are observed surrounding the direction of the transmitted light. The colour of the halo varies with the direction of observation and also alters when the spectral region of transmission is shifted. Viewing a bright and well-defined light source through the cell held before the eye of the observer, with one polaroid inserted between the source and the cell and a second polaroid between the cell and the observer's eye, striking polarisation phenomena may be observed. In all cases, the image of the light source is itself completely extinguished when the two polaroids are crossed. But the diffusion halo seen surrounding the light-source shows imperfect polarisation. The magnitude of this imperfection differs very much in the case of the three substances mentioned above. With magnesium fluoride the halo disappears almost completely when the polaroids are crossed. With barium sulphate its extinction is less complete, and the diffusion halo remains observable in directions adjacent to the source and gives indications of a bright cross with its arms bisecting the angle between the vibration directions of polariser and analyser. The extinction of the diffused light is least perfect in the case of calcium sulphate and the halo remains observable over the whole area of the field even with the polaroids crossed.

4. OBSERVATIONS WITH POWDERED QUARTZ

The following method was adopted to prepare quartz in a state of fine subdivision but uncontaminated by extraneous material. A transparent piece of crystalline quartz was heated and dropped into cold distilled water. The fragments into which it broke as the result of this treatment were heated in a silica dish and then again dropped into cold distilled water. Repetition of this procedure reduced the substance to a state of powder and the material thus obtained was then ground up very fine between two quartz crystals with flat faces and finally separated into four grades by elutriation in distilled water. The two finest grades thus obtained were those which remained in suspension in a tall beaker of distilled water for ten and twenty minutes respectively.

The optical effects exhibited by the four grades of quartz when placed in a cell and filled up with a mixture of benzyl alcohol and carbon disulphide were found to be very different. The first or roughest grade gave only a diffusion halo without any regular transmission even with a cell only one millimetre thick. With the second grade of powder and the same thickness of cell, a very weak transmission can be glimpsed, the bright diffusion halo overlying it making the observation rather difficult. On the other hand, the two finer grades when allowed to settle down in a cell two millimetres thick show brilliantly coloured transmitted images of the source. With a cell only one millimetre thick, the transmission is even more brilliant, but its colour is then less saturated.

In all cases, if a transmission is obtained at all, it is completely extinguished when the cell is placed between two crossed polaroids. On the other hand, the appearance of the diffusion halo as well as its state of polarisation shows remarkable variations with the grade of powder and the thickness of cell employed. With the coarser grades of material, the halo is found to be completely depolarised. On the other hand, with the finer grades the halo shows a very marked degree of polarisation. Not merely the brightness of the halo but also the distribution of colour in it is strikingly different when the polaroids are respectively parallel and crossed. This difference is best described by the statement that when the polaroids are crossed, the halo exhibits colours similar to those of the transmitted light (which is extinguished in the same circumstances); *per contra,* with the polaroids parallel, the colour of the halo is complementary to that of the transmitted light. These changes were most striking when observed with the cells of smaller thickness. For, with such cells, the colour of the halo over its whole area is markedly different from that of the transmitted light and exhibits its complementary character most clearly. The changes produced by the rotation of the analyser are therefore particularly striking.

5. OBSERVATIONS WITH DILUTE SUSPENSIONS

With the two finer grades of quartz powder, it is possible to use much thicker cells with success for observing the transmitted light, if they are filled with an excess of liquid in which the powder is held as a dilute suspension. By varying the thickness of the cell and the quantity of material held suspended in it, one can either increase or decrease the saturation of the colours observed in the transmitted light and in the diffusion halo. It is worthy of note that in such cases the diffusion halo exhibits a colour complementary to that of the transmitted light even in directions adjacent to the latter. This indeed is what optical theory indicates should be the case for a dilute suspension. On the other hand, multiple scattering comes into play in the case of dense aggregates, and the colour of the halo is in consequence almost indistinguishable from that of the transmitted light in closely adjoining directions and only further out changes by insensible gradations to the complementary tint.

It appears worthwhile also to record some observations made with strongly birefringent powders, calcium carbonate in the form of precipitated chalk being a typical example. It is not possible to obtain any transmission with this material in the usual form of the Christiansen experiment. But interesting effects may be observed even with cells of considerable thickness if they are filled with carbon disulphide into which a little precipitated chalk is put in and stirred so that the liquid appears as a milky-white suspension. A bright source of light can be seen through such a suspension and exhibits a deep red colour, as indeed it should according to the theory. Here again the transmitted light is completely extinguished if the cell is placed between crossed polaroids. On the other hand, the light diffused by the cell is depolarised, but if the suspension is very dilute, the cell exhibits a bright cross between crossed polaroids. If benzene is added to the suspension of chalk in carbon disulphide, thereby bringing the index of the liquid mixture nearer to the mean index of calcium carbonate, the colour of the transmitted light is shifted towards shorter wave-lengths in the spectrum.

6. DESCRIPTION OF THE FIGURES IN PLATE IX

By way of illustration of the foregoing observations, some photographs have been reproduced in Plate IX accompanying this paper. The following remarks are explanatory notes on the same.

Fig. 1 shows the appearance of a small brilliant light-source as viewed through a cell five millimetres thick containing barium sulphate in a finely subdivided state. This had settled down at the bottom of a mixture of carbon disulphide and benzene so adjusted as to transmit the green part of the spectrum. The picture clearly shows the transmitted light and the diffusion halo surrounding it.

Fig. 2 shows the same experiment with the cell placed between crossed polaroids and photographed with a much longer exposure. The source itself is extinguished in these circumstances. The halo also disappears except at its brightest part near the centre which exhibits the bright cross whose arms bisect the angle between the vibration directions of the polariser and analyser.

Fig. 3 reproduces the spectra of the light transmitted by the cell containing barium sulphate in the same circumstances. The colour of the transmitted light was shifted in steps from orange-yellow to blue by the successive additions of benzene to carbon disulphide. The lines of the mercury arc spectrum are reproduced to indicate the positions of the transmission band.

Fig. 4 is a photograph of a small bright source of light seen through a cell two millimetres thick containing the finest grade of quartz powder which had settled down at the bottom of the cell. Benzyl alcohol to which a few drops of carbon disulphide had been added was the liquid used and the mixture transmitted the yellowish-green part of the spectrum. The photograph itself was rather overexposed with the result that the transmission and the halo are not seen clearly distinguished from one another. The streaky nature of the halo is clearly shown.

Fig. 5 is a photograph of a bright source of light seen through a thin film of nitrobenzene containing fine particles of lithium carbonate in suspension and held between crossed polaroids. The dark arms of the cross seen in the diffusion-halo are parallel to the vibration directions of the polariser and analyser respectively.

7. SUMMARY

Optical effects analogous to those exhibited by isotropic materials in a Christiansen cell are also observable with birefringent materials in a fine state of subdivision. While the transmitted light is fully polarised, the diffusion halo is depolarised in part and exhibits colours between parallel and crossed polaroids which are complementary to each other.

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2. M. R. Bhat .. *Proc. Ind. Acad. Sci.*, 1953, **38 A**, 67.
3. C. V. Raman and K. S. Viswanathan .. *Ibid.*, 1955, **41 A**, 55.

FIG. 1

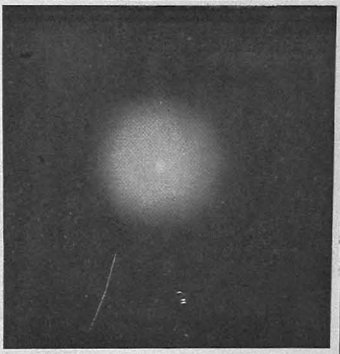


FIG. 2

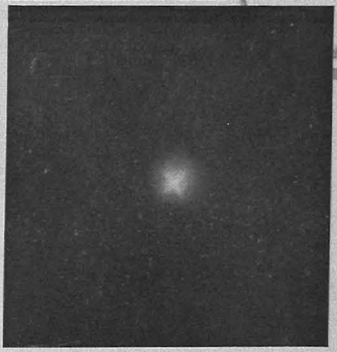
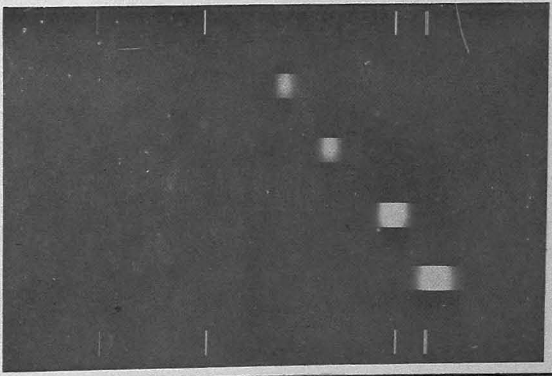


FIG. 3



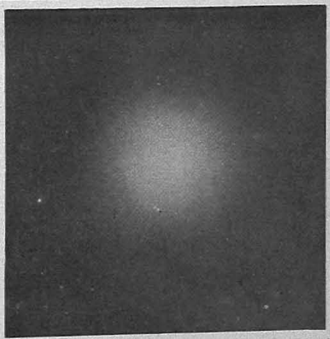


FIG. 4

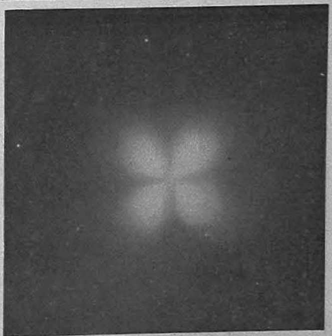


FIG. 5

Christiansen Experiment with Birefringent Powders.

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THE THEORY OF THE ELASTICITY OF CRYSTALS

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I. INTRODUCTION

THE subject of the elasticity of crystals has from its very early stages of development been approached from two distinct view-points which have resulted respectively in the phenomenological and the atomistic theories. The phenomenological theory was initiated by Green and Kelvin, and is founded on the continuum hypothesis of matter in solids. It is further built on the basis that the total energy of the solid is obtainable as the sum of the energies of the individual volume elements into which it can be subdivided. Each such volume element is supposed to possess a uniform density and the forces acting on it are assumed to be conservative, being derivable from a potential function. These remarks concerning the hypotheses underlying the phenomenological theory have been made here, in order to emphasize the limitations of the theory and to bring out the range of applicability of its results to any actual crystal composed of discrete atoms. It is obvious that these conditions can be incorporated for a crystal with a lattice structure only if the volume elements under consideration are large in comparison to the interatomic distances in the solid. The range of applicability of the phenomenological theory is therefore limited for crystals and its results can be expected to be sustainable only in relation to phenomena involving large volume elements, such as the propagation of non-dispersive waves of large wavelengths and low frequencies in the medium.

A fundamental problem of solid state physics is to interpret the macroscopic behaviour of crystals in terms of the constants characterising the lattice structure and the mutual interactions between pairs of atoms of the crystal. The importance of such an atomistic theory is mainly three-fold. Firstly, it enables us to examine the question whether the two theories would lead to identical results even in the range wherein the phenomenological theory is expected to be applicable. Secondly, it elucidates the nature of the vibrations in a crystal in regions that fall definitely outside the scope of the ordinary theory of elasticity, as in the case of dispersive waves in the medium. Finally, it holds out the hope of computing theoretically the numerical values of the macroscopic constants. This is rendered possible because every crystal possesses a set of stationary normal modes of vibration whose frequencies are obtainable from spectroscopic data. The frequencies of these vibrations are also expressible in terms of the force-constants of the crystal. By a comparison of these two, the numerical values of at least a few of the force-constants can be ascertained and thus a possibility is opened up whereby the numerical values of the elastic constants become accessible to theoretical calculations as well.

The earliest attempt to provide an atomistic theory of elasticity is due to Cauchy. The investigations of Cauchy were however based on a somewhat outdated model of a solid, in which each atom is a centre of symmetry for the structure and the interatomic forces are strictly central. A direct consequence of these assumptions is that only fifteen among the twenty-one elastic constants emerging from Green's theory are independent, this reduction being effected by means of six relations that are generally known after Cauchy's name. Recent experiments have however proved that the Cauchy relations[2] are violated by a great number of crystals, even by most of the simplest variety of them, *viz.*, the cubic crystals. The failure of the Cauchy relations is clearly due to the assumption of central interactions among the atoms of the crystal, which might be true if each atom is simply an ion attracting the others in accordance with a law of force of the Coulomb type. But in any solid, the nucleii are all surrounded by clouds of electronic charges and any deformation of the substance would tend to change the energy of the electron cloud as well, thus producing forces that are non-central in character.

In order to be able to arrive at results that are in agreement with experimental data, it is therefore essential to start with a system of forces more general than a central force-scheme to represent the interatomic force-field inside crystals. An atomistic theory of elasticity based on such general system of forces was first provided by Begbie and Born[6, 7] and by Kun Huang.[5] By comparing the equations of long acoustic waves of low frequencies obtained from the atomistic theory with the equations of wave-propagation of the elasticity theory, these authors deduced expressions for the elastic constants of the crystal in terms of the force-constants. But the process of identification of the two sets of equations in their theories necessitated the assumption of a few relations among the force-constants which would be strictly true for central force systems only. Thus in spite of the formalism using a general force-scheme, the theories so far provided are reliable only for central interactions among the atoms of the crystal and do not adequately take account of the force-field existing inside crystals.

In this review, an attempt is made to present coherently the facts relating to the nature of the atomic vibrations inside crystals, and the general character of elastic deformations and wave-propagation inside crystals. A substantial part of the review is drawn from material contained in two papers already published by the author but it is made self-contained as far as possible. The contents of it are arranged in seven sections. Section one describes the notation adopted in the paper and introduces the basic concepts regarding wave-propagation in crystal structures. In Section II, we consider the state of movements of the atoms of the crystal arising from a disturbance confined initially to a small region of it. It is shown here that any arbitrary disturbance resolves itself into a superposition of the $(24p-3)$ harmonic vibrations predicted by the thoery of Sir C. V. Raman, and an elastic wave-motion that moves away from the region of the initial disturbance. In any region, the former modes are the only vibrations that possess significant amplitudes after a long time, and further these are independent of the conditions of the boundary of the crystal. Section III is devoted to a discussion of the long waves of low frequency inside the crystal, which are the analogue of the non-dispersive waves contemplated in the elasticity theory. Section IV concerns itself with the evaluation of the strain-energy function in the atomistic theory. An important fact emerging from this section is that the strain-energy function derived from the atomistic theory differs from the energy function of Green in that the former contains terms in the three rotational components of the strain also and thus involves forty-five independent elastic constants. A comparison of the two theories is possible only for the case of static strains which are strictly homogeneous or strictly irrotational. In these circumstances, expressions for the elastic constants as defined in the phenomenological theory can be obtained in terms of the atomic force-constants. Section VI deals again with wave-propagation inside crystals and it is shown here that except in the case of longitudinal waves, the equations of wave motion and the velocities of propagation of the elastic waves would be different in the two theories. Finally, the consequences of the forty-five constant theory as regards the stress-strain relations inside the crystal are discussed in Section VII.

I. PRELIMINARY CONCEPTS

We shall suppose that an unit cell of the crystal contains p atoms, and denote the three primitive translational vectors of the lattice by $\mathbf{d}_1$, $\mathbf{d}_2$ and $\mathbf{d}_3$. If the positions of the p atoms, which we can number as $1, 2, 3, \ldots . p$, are all known inside any unit cell, then the structure of the crystal is completely specified. We denote by $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ the three primitive translational vectors which generate the reciprocal lattice of the crystal. These are then determined from the relations

$$\mathbf{b}_i \cdot \mathbf{d}_j = \delta_{ij} \tag{1}$$

where δ_{ij} is the Kronecker delta symbol. Any vector **a** of the reciprocal lattice is therefore expressible as

$$\mathbf{a} = \theta_1\mathbf{b}_1 + \theta_2\mathbf{b}_2 + \theta_3\mathbf{b}_3 \tag{2}$$

Further, we use in the sequel the letters r and ρ as general symbols to represent any of the p atoms in the unit cell, and likewise denote by s and σ a general cell of the crystal lattice.

Taking any three mutually orthogonal axes x, y and z we represent the components of the displacements of the atom (r, s) from its equilibrium position by q_{xrs}, q_{yrs} and q_{zrs}. If however the letters x or y occur under a summation sign in any expression, they should be understood as general summational indices that cover all the three directions of the co-ordinate axes of the system.

The expressions for the kinetic and potential energies of the crystal can now be written down. Denoting by m_1, m_2, ...m_p the masses of the p different atoms in the unit cell, we can write them as

$$2\mathrm{T} = \sum_{xrs} m_r \dot{q}^2{}_{xrs} \tag{3}$$

and

$$2\mathrm{V} = \sum_{xrs} \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs} \, q_{xrs} \, q_{y\rho\sigma} \tag{4}$$

The equations of motion of the atoms of the crystal can be derived from (3) and (4) by means of a Lagrangian formulation. They are given by

$$- m_r \ddot{q}_{xrs} = \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs} \, q_{y\rho\sigma} \tag{5}$$

The force-constants occurring in the above equations are not all entirely independent, but are connected to each other by means of a few relations which express the invariance conditions of the potential energy under pure translations. If the entire crystal is translated by an amount specified by the vector $\mathbf{u} = (u_x, u_y, u_z)$, then the left-hand side of the equation (5) should vanish and one therefore gets

$$\sum_{y\rho\sigma} u_y \, k^{y\rho\sigma}_{xrs} = 0 \tag{6}$$

As the vector **u** is arbitrary it follows that

$$\sum_{\rho\sigma} k^{y\rho\sigma}_{xrs} = 0 \ (x, y = x, y, z) \tag{7}$$

Substituting the relations (7) in (5) we can rewrite the latter as

$$- m_r \ddot{q}_{xrs} = \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs} (q_{y\rho\sigma} - q_{yrs}) \tag{5'}$$

The above equation expresses the fact that the total force acting in the x-direction on the atom (r, s) is a linear sum of the forces due to the displacements of its neighbours, the force exerted by (ρ, σ) alone being equal to $- \sum_{y} k^{y\rho\sigma}_{xrs} (q_{y\rho\sigma} - q_{yrs})$. The force-constant $k^{y\rho\sigma}_{xrs}$ can therefore be interpreted as the x-component of the force exerted by (ρ, σ) on the atom (r, s) per unit relative displacement of these two atoms parallel to the y-direction.

Since the crystal is composed of p different homogeneous lattices, we shall suppose that a wave of given frequency and wave-length is propagated with different amplitudes inside the different Bravais lattices and that no damping of the waves occurs anywhere inside the crystal. The displacement of any atom caused by the propagation of a wave of frequency ν and wave-length λ travelling in the direction of the vector **e** through it is then expressible in the form

$$\mathbf{q}_{rs} = \mathbf{A}_r \, e^{2\pi i \left(\nu t - \frac{e.s}{\lambda}\right)} \qquad \text{or}$$

$$\mathbf{q}_{rs} = \mathbf{A}_r \, e^{i(\omega t - a.s)} \tag{8}$$

where

$$\omega = 2\pi\nu \text{ and } \mathbf{a} = \frac{2\pi}{\lambda}\mathbf{e}$$

By substituting these wave solutions in the equations of motions of the atoms of the crystal, we can now obtain a set of $3p$ linear equations in the $3p$ amplitudes A_r^x, A_r^y, A_r^z ($r = 1, 2, \ldots. p$). A process of elimination of these amplitudes from these homogeneous equations then leads to the determinental equation

$$|A - M\omega^2)| = 0 \tag{9}$$

in which the elements of the matrix (A) composed of $3p$ rows and columns are the coefficients of the $3p$ amplitudes in the $3p$ sets of equations.

Equation (9) can also be rewritten in the form

$$s_0 \omega^{6p} + s_1 \omega^{6p-2} + \ldots. + s_{3p} = 0 \tag{9'}$$

The coefficients $s_1, s_2 \ldots s_{3p}$ are functions of the wave vector $\mathbf{a}$. The frequencies of the waves in the crystal are therefore dependent on their wavelengths, or the waves are dispersive. Further, there are $3p$ waves with a given wavelength, whose frequencies are the roots of (9) which correspond to this wave-vector.

II. Effect of an Arbitrary Disturbance

This section deals with the spreading of a disturbance, initially confined to a small region of the crystal, into its undisturbed portions at later instants of time. In view of the interaction among the atoms of the crystals, any local disturbance will gradually spread into the other regions of the lattice also, the rate of spreading depending on the strength of coupling between the various atoms of the crystal. To make the problem specific, we shall suppose that initially all the atoms in the cell (0, 0, 0) with index zero are displaced by small amounts and that the velocities of all other atoms are zero. In other words, the initial state of movements of the atoms is described by

$$\mathbf{q}_{rs}(0) = \frac{1}{8\pi^3 c} \int_{\Delta} \mathbf{u}_r \, e^{ia.s} \, dV = \mathbf{u}_r \, \delta_{so} \tag{10}$$

and

$$\dot{q}_{rs}(0) = 0 \tag{11}$$

Here dV denotes the element of volume in the reciprocal space. If a_1, a_2, a_3 are the components of the wave vector in any three orthogonal directions and if c denotes the determinant of the transformation $a_i = \sum_j c_{ij} \theta_j (i, j = 1, 2, 3)$ where $\theta_1, \theta_2, \theta_3$ are the components of the wave vector along the directions of the axes of the primitive vectors of the reciprocal lattice, then $dV = da_1 \, da_2 \, da_3 = c \, d\theta_1 \, d\theta_2 \, d\theta_3$. Further Δ denotes the volume of the parallelopiped whose corners are given by $\pi (\pm \mathbf{b}_1 \pm \mathbf{b}_2 \pm \mathbf{b}_3)$.

The displacements of the atoms of the crystal from their equilibrium positions at a later instant can be determined by superposing waves of type (8) for all possible wavelengths and frequencies so that the final result reduces to the equations (10) and (11) for the case $t = 0$. If therefore we denote by $\omega_1^2, \omega_2^2, \ldots \omega_{3p}^2$ the $3p$ different roots of (9) and their associated amplitudes by $\mathbf{A}_{r,1} \, \mathbf{A}_{r,2} \ldots \mathbf{A}_{r,3p}$ $(r = 1, 2, \ldots 3p)$, then by choosing the amplitude functions so as to satisfy the relation

$$\sum_{k=1}^{3p} \mathbf{A}_{r,k} = \mathbf{u}_r \tag{12}$$

we can represent the state of movements of the atoms of the crystal at any later instant by

$$\mathbf{q}_{rs}(t) = \frac{1}{16\pi^3 c} \sum_{k=1}^{3p} \int_{\Delta} \mathbf{A}_{r,k} \left(e^{i\omega_k t} + e^{-i\omega_k t} \right) e^{ia.s} \, dV \tag{13}$$

A discussion of the above sum of $3p$ integrals for different values of t and s would reveal the nature of the disturbance at different instants and in the different regions of the crystal. We here consider only a simple and interesting case, namely the value of the above sum for large values of t.

This is done with the aid of the method of stationary phases introduced by Kelvin. The principle of Kelvin asserts that the value of an integral of the type

$$\mathrm{I} = \int_{\Delta} f(\mathbf{x}) \exp i \{\omega(x)\, t - s \cdot x\} \, dV \tag{14}$$

for large values of t arises only from the neighbourhood of points at which the function $\omega(x)$ is stationary. Such points are known as *saddle points.* We shall denote the stationary points of the function ω in the region of integration by $x_0, x_1 \ldots x_i$. If the matrix whose elements are $a_{rs} = \left(\frac{\partial^2 w}{\partial x_r \partial x_s} \right)_{x=x_0}$ is denoted by $\Delta(x_0)$ and k denotes the difference between the number of positive eigenvalues of $\Delta(x_0)$ and the number of its negative eigenvalues, then the asymptotic value itself is given by

$$\mathrm{I} \sim \left(\frac{2\pi}{t} \right)^{3/2} \sum_{x_0} \frac{f(x_0)}{|\Delta(x_0)|^{\frac{1}{2}}} \exp i \{\omega(x_0)\, t - s \cdot x_0 + k\pi/4\} \tag{15}$$

the summation being over all the stationary points of the function ω inside the region of integration.

The above expression in fact denotes the first term in the asymptotic expansion of (14) in inverse powers of t and will represent integral (14) very closely if t is sufficiently large. It can be supposed to provide a fairly good estimate of (14) for all values of t greater than or equal to $\mathrm{K}\, |\, \mathrm{s}\, |^2$, where K is a constant of the dimensions of Time, for in this case $\omega(x)\, t$ is a quantity of second-order in largeness compared to the factor $\mathrm{s} \cdot \mathrm{x}$ occurring in the exponential of the integral.

The saddle points for the $3p$ integrals occurring in equation (13) are clearly the solution of the equations $\frac{d\omega_k}{da} = 0$ $(k = 1, 2 \ldots 3p)$. In any dispersive medium, the expression $\frac{d\omega}{da}$ represents the group velocity of the waves traversing it. Thus the saddle points correspond to waves for which the group velocity is identically equal to zero. It has now been shown elsewhere[10] that there are eight points in the reciprocal space for which the group velocities of waves traversing the crystal are equal to zero and for these, the components θ_1, θ_2 and θ_3 of the wave-vector **a** are all equal to either zero or π. Explicitly, these points are given by $\mathbf{a}^1 = (0, 0, 0)$; $\mathbf{a}^2 = (\pi, 0, 0)$; $\mathbf{a}^3 = (0, \pi, 0)$; $\mathbf{a}^4 = (0, 0, \pi)$; $\mathbf{a}^5 = (0, \pi, \pi)$; $\mathbf{a}^6 = (\pi, 0, \pi)$; $\mathbf{a}^7 = (\pi, \pi, 0)$; and $\mathbf{a}^8 = (\pi, \pi, \pi)$.

Considering first the vector $\mathbf{a}^1 = (0, 0, 0)$, it is readily observed from (8) that this corresponds to waves of infinite wave-length inside the lattice. It can be shown that for this case three of the roots of (9) vanish and that $\frac{d\omega_k}{da} \neq 0$ for these three frequency branches. Long waves associated with these three branches correspond to the elastic vibrations of the crystal and will be discussed later. For the remaining $(3p - 3)$ frequencies associated with this vector, as also for the $21p$ frequencies that are yielded by the seven other points listed above, the expression $\frac{d\omega_k}{da}$ vanishes. Thus we see that for a crystal containing p atoms in each of its unit cells, there are $(24p - 3)$ frequencies for which the group velocity of the waves vanishes.

Returning to the evaluation of (13) for large values of t, we note that the functions $\mathrm{A}_{r,k}$ and ω_k occurring in the $3p$ integrals are all periodic functions of the wave-vector **a** with periods equal to 2π for their components θ_1, θ_2 and θ_3 in the reciprocal lattice, and the region of integration of the integrals can therefore be slightly shifted about the origin without affecting their values so that it completely encloses all these eight saddle points. Then, denoting by $\triangle^a{}_k$, $\nu^a{}_k$ and $\mathrm{A}^a{}_{r,k}$ the values of the functions $\triangle_k$, ω_k and $\mathrm{A}_{r,k}$ at the eight saddle points, we can write the asymptotic value of the displacement of the atom $(r, \mathbf{s})$ as

$$\mathbf{q}_{rs}(t) = \frac{1}{c\,(2\pi t)^{3/2}} \sum_{k=4}^{3p} \frac{\mathrm{A}_{r,k}(1)}{|\triangle^1{}_k|^{\frac{1}{2}}} \cos\left(\nu^1{}_k t + k^1\pi/4\right)$$

$$+ \frac{1}{c\,(2\pi t)^{3/2}} \sum_{a=2}^{8} \sum_{k=1}^{3p} \frac{\mathrm{A}_{r,k}{}^{(a)}}{|\triangle_k{}^a|^{\frac{1}{2}}} \cos\left(\nu_k{}^a t + \mathbf{a}^a \cdot \mathbf{s} + k^a\pi/4\right) \tag{16}$$

The above expression can be considered to give a good approximation of $\mathbf{q}_{rs}(t)$ for all values of t greater than or equal to K $|s|^2$ where K is a constant characteristic of the medium having the dimensions of (Time).

Equation (16) suggests that in any region for which the above approximation is applicable, the vibrations of the atoms are all obtainable as a superposition of a set of harmonic vibrations which are characteristic of the crystal and hence may be appropriately called the characteristic vibrations of the crystal lattice. In the $(3p - 3)$ modes represented by the first sum, equivalent atoms in successive cells all vibrate with the same phase and amplitude. In the remaining $21p$ modes equivalent atoms in successive cells vibrate with the same amplitude but with opposite phases along one, two or three of the Bravais axes of the crystal, as each term in the second sum contains a factor $\cos \mathbf{a}^{a} . \mathbf{s}$ which is equal to *plus* or *minus* unity. Thus these modes are exactly identical with the stationary normal modes of vibration discussed in the dynamics of crystal lattices proposed by Sir C. V. Raman.[3-5] *Our theory therefore shows that the asymptotic nature of the vibrations of the atoms of the crystal arising from an arbitrary disturbance, confined initially to a small region of the lattice is a summation of the* $(24p - 3)$ *normal modes of vibrations recognised in Raman's theory.*

With the aid of the above results, it is possible to visualise at least qualitatively the nature of the vibration of the atoms at different instants of time and in different regions. In and very near the region of initial disturbance, the displacements of the atoms are representable by (16) even for small values of t and the disturbance therefore resolves itself into a superposition of the $(24p - 3)$ characteristic vibrations of the crystal almost immediately. In the farther off regions the disturbance spreads in the form of waves of which the fastest groups correspond to the elastic vibrations of the crystal. Since no atom can acquire a sensible amplitude until the fastest group reaches that lattice point, the maximum amplitude of any atom is attained only after a certain instant of time which depends on the velocity of propagation of the elastic waves in the medium. The value of the maximum amplitude can further be estimated to be of the order of t^{-1}, if we consider the elastic vibrations as surface waves divulging from a point whose energy is concentrated in a thin spherical shell only. The amplitudes of the atom thereafter fall away and for sufficiently large values of time comparable in magnitude with the square of the distance of any atom in a given region from the origin, the vibration of the atoms in this region consist of a superposition of the characteristic vibrations of the crystal with time-dependent amplitudes. At these instants, the elastic waves would have completely moved away from the region under consideration, and their effects on the vibration of the atoms is therefore negligible, as can otherwise also be seen from the fact that the contributions of the elastic waves to the displacements of the atoms are infinitesimals of order higher than $t^{-3/2}$ and are therefore ignorable. Thus asymptotically in any region the characteristic modes of the crystal are the only vibrations that possess physically significant amplitudes, and the elastic waves which form a low frequency residue to them contribute none other than second order perturbation terms to the actual displacements of the atoms.

If the characteristic vibrations are assumed to settle in any region after an interval of time of the order r^2 where r is the distance of the region from the origin, then the rate of spreading of the disturbance $\frac{dr}{dt}$ at any point is inversely proportional to its distance from the centre. The vibrations therefore spread rapidly in the regions near the centre of disturbance but their rate of spreading diminishes for points in the farther off regions of the crystal. Another significant result that deserves mention is the dependence of the amplitudes of these vibrations on time, which indicates that these modes diffuse slowly into the volume of the crystal and do not travel outwards like elastic wave propagation in a medium. Further by the time these vibrations take to reach the external boundary of the crystal, their amplitudes would have become insignificant infinitesimals. Hence the characteristic vibrations are entirely uninfluenced by the boundary conditions of the crystal, and in discussing them all reference to its size and shape can be completely left out of account.

III. THE ELASTIC WAVES IN THE CRYSTAL LATTICE

We have already mentioned that three roots of equation (9) tend to zero in the limiting case of waves of infinite wave-length. Vibrations associated with these three roots of the secular equation (9) represent the elastic wave-motions inside the lattice and are propagated without any dispersion. For such vibrations, since $\underset{a\to 0}{\mathrm{Lt}} \frac{\omega_k}{a} = \frac{d\omega_k}{da}$ the group and wave velocities become identical with the velocity of propagation of the elastic waves inside the crystal.

As in the classical elasticity theory, there can progress in any direction three types of elastic waves whose vibration directions are mutually orthogonal. Denoting by y and e the velocity and direction of propagation of sound waves, it can be shown[11] that the velocity of the three different waves travelling in the direction of the unit vector **e** are given by the roots of the cubic equation

$$720\,a_0 y^3 + 360\,a_1 y^2 + 30\,a_2 y + a_3 = 0 \tag{17}$$

The coefficients a_0, a_1, a_2 and a_3 in the above equation are functions of the force-constants and are equal to the derivatives of s_{3p-3}, s_{3p-2}, s_{3p-1} and s_{3p} with respect to the variable a of orders 0, 2, 4 and 6 respectively. The velocities of the sound waves in crystals are therefore functions of the force-constants, which are the roots of the equation (17).

IV. THE DEFORMATION ENERGY FOR CRYSTALS

To obtain an expression for the deformation energy of the crystal, we first try to calculate the mutual energy between pairs of atoms of the crystal. The energy stored in any unit cell can then be obtained by summing up the mutual energy of interactions of the atoms in that cell with all the atoms of the crystal. We have already shown in Section I that the force exerted on the atom (r, s) in the x-direction by the displacement of the atom (ρ, σ) is equal to $-\sum_{y} k^{y\rho\sigma}_{xrs}\,(q_{y\rho\sigma} - q_{yrs})$. The mutual energy of this pair $(V^{\rho\sigma}_{rs})$ is obtained by multiplying the force by the relative displacement of the atoms, and dividing the result by two. Hence we have

$$V^{\rho\sigma}_{rs} = -\tfrac{1}{2}\sum_{xy} k^{y\rho\sigma}_{xrs}\,(q_{y\rho\sigma} - q_{yrs})\,(q_{x\rho\sigma} - q_{xrs}) \tag{18}$$

If $\triangle$ denotes the volume of the unit cell, the deformation energy stored in the cell s is given by

$$\triangle U = \tfrac{1}{2}\sum_{r}\sum_{\rho\sigma} V^{\rho\sigma}_{rs}$$

or

$$-4\triangle U = \sum_{xr}\sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\,(q_{y\rho\sigma} - q_{yrs})\,(q_{x\rho\sigma} - q_{xrs}) \tag{19}$$

Now each atom of the crystal should be in equilibrium in the deformed state also and hence one gets

$$\sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\,q_{y\rho\sigma} = 0 \tag{20}$$

With the aid of (20) we can rewrite (19) also in the form

$$-4\triangle U = \sum_{xr}\sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\,q_{x\rho\sigma}\,q_{y\rho\sigma} \tag{21}$$

Any deformation of the crystal can be analysed into two parts: a part which denotes the mutual displacements with respect to each other of the p

interpenetrating Bravais lattices and which is thus the same for all the atoms in the same lattice of the crystal; and another part which corresponds to the usual elastic deformations, denoting the continuous change in the relative displacements of the points of the body due to the strain. The former are generally known as the *inner displacements.*

Denoting now by k_{xr}, k_{yr}, k_{zr} the components of the inner displacements of the rth lattice, by x_{rs}, y_{rs}, z_{rs} the co-ordinates of the atom (r, s) in the underformed state and by u_{xy} $\left(=\frac{\partial u_x}{\partial y}\right)$ the components of the strain, we can represent displacement components of the atoms due to the deformation by

$$q_{xrs} = k_{xr} + \sum_{\bar{x}} u_{x\bar{x}}\, \bar{x}_{rs} \tag{22}$$

Substituting (22) in (21) we can rewrite the energy expression as

$$-2\mathrm{U} = \sum_{x\rho}\sum_{y\bar{y}} \left\{ {\rho \atop xy\bar{y}} \right\} k_{x\rho}\, u_{y\bar{y}} + \sum_{x\bar{x}}\sum_{y\bar{y}} [x\bar{x},\ y\bar{y}]\ u_{x\bar{x}}\, u_{y\bar{y}} \tag{23}$$

where

$$\left\{ {\rho \atop xy\bar{y}} \right\} = \frac{1}{\Delta} \sum_{r\sigma} k^{y\rho\sigma}_{xrs}\ \bar{y}_{\rho\sigma}$$

and

$$[x\bar{x},\ y\bar{y}] = \frac{1}{2\Delta} \sum_{r\rho\sigma} k^{y\rho\sigma}_{xrs}\ \bar{x}_{\rho\sigma}\, \bar{y}_{\rho\sigma} \tag{24}$$

The inner displacements can now be eliminated from the energy expression which can thus be expressed as a function of the strain variables only. The equations determining them are obtained by substituting (22) in (20) and are given by

$$\sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\ k_{y\rho} = -\sum_{y\bar{y}} u_{y\bar{y}} \left(\sum_{\rho\sigma} k^{y\rho\sigma}_{xrs}\ \bar{y}_{\rho\sigma}\right) \tag{25}$$

These are a set of $3p$ equations in the $3p$ unknowns $k_{y\rho}$, etc., of which only $(3p - 3)$ can be linearly independent since the matrix multiplying them in the left-hand side is singular and is of rank $(3p - 3)$. Assuming that these equations are consistent and solvable and denoting by Γ the matrix that would multiply the column vector on the right-hand side in the solution of these equations, we can find the expressions for the inner displacements as

$$k_{xr} = -\sum_{y\rho}\sum_{x'y'}\sum_{\rho'\sigma'} u_{x'y'}\, \Gamma^{y\rho}_{xr}\ k^{x'\rho'\sigma'}_{y\rho s}\ y'_{\rho'\sigma'} \tag{26}$$

Substituting (26) in (23) one gets

$$2U = \sum_{x\bar{x}} \sum_{y\bar{y}} d_{x\bar{x},\, y\bar{y}}\; u_{x\bar{x}}\, u_{y\bar{y}} \tag{27}$$

where

$$d_{x\bar{x},\, y\bar{y}} = -\,[x\bar{x},\; y\bar{y}] + (x\bar{x},\; y\bar{y}) \tag{28}$$

with

$$(x\bar{x},\; y\bar{y}) = \frac{1}{\Delta} \sum_{x'\rho} \sum_{r\sigma} \sum_{y'\rho'} \sum_{\rho_1\sigma_1} k^{y\rho\sigma}_{x'rs}\, \bar{y}_{\rho\sigma}\, \Gamma^{y'\rho'}_{x'\rho}\, k^{x_1\rho_1\sigma_1}_{y'\rho's}\, \bar{x}_{\rho_1\sigma_1} \tag{29}$$

Equation (27) gives the energy expression in the atomistic theory, and the constants multiplying the various quadratic terms in it are functions of the force-constants and the lattice parameters. We note that both the bracket expressions in (28) are symmetric in the pairs $x\bar{x}$, $y\bar{y}$. The round brackets are further invariant under a permutation of the symbols x and $\bar{x}$, or of y and $\bar{y}$, while the square brackets do not possess such a symmetry except in the special case of a central force system.

V. THE ELASTIC CONSTANTS OF CRYSTALS[12]

If we write $e_{x\bar{x}} = (u_{x\bar{x}} + u_{\bar{x}x})$ for $\bar{x} \neq x$ and $e_{xx} = u_{xx}$ then the deformation energy obtained from the elasticity theory is a general quadratic in the six strain components e_{xx}, e_{yy}, e_{zz}, e_{yz}, e_{zx} and e_{xy}. Using the notation of Voigt in which the numbers (1, 2, 3, 4, 5, 6) replace respectively the symbols (xx, yy, zz, yz, zx, xy) the strain energy function of the elasticity theory can be written in either of these two forms

$$2U = \sum_{r,s} \sum_{=1}^{6} c_{rs}\, e_r\, e_s \tag{30}$$

$$= \sum_{x\bar{x}} \sum_{y\bar{y}} c_{x\bar{x},\, y\bar{y}}\; u_{x\bar{x}}\, u_{y\bar{y}}$$

The second form of the energy expression contains forty-five terms and the constants $c_{x\bar{x},\, y\bar{y}}$ are therefore subjected to the symmetry relations

$$c_{x\bar{x},\, y\bar{y}} = c_{x\bar{x},\, \bar{y}y} = c_{\bar{x}x,\, y\bar{y}} = c_{\bar{x}x,\, \bar{y}y} \tag{31}$$

so that it might become identical with the first one.

The expression (27) for the energy expression obtained from the atomistic theory can also be written in the form (30) provided the constants $d_{x\bar{x},\, y\bar{y}}$ also satisfy the same symmetry laws as the elastic constants, *i.e.*, if they are invariant under a permutation of the letters x and $\bar{x}$ or y and $\bar{y}$. But this is by no means the case, for these constants are functions of the force-constants defined in accordance with the relations (24) and (29), and any assumption of such symmetry requirements can be shown to be equivalent to the assumption of a central force scheme for the interactions among the atoms of the crystal. As a central force interaction is not obeyed by a number of crystals, there is no justification whatsoever to suppose that these constants are also governed by relations (31) with the *c*'s replaced by the *d*'s.

The atomistic theory thus involves 45 independent constants for the case of a general strain* as had been stressed recently by Laval[9] and the present writer.[10] In order to derive expressions for the elastic constants in terms of the force-constants, it is therefore necessary to investigate the circumstances or conditions of strains under which expression (27) might reduce to the same mathematical form as that of (30) and which might thus enable us to identify the two. Obviously both these expressions reduce to the same form if

$$u_{xy} = u_{yx} \tag{32}$$

The above relation is clearly satisfied by irrotational strains. There is another type of strain which is important from the experimental standpoint, and which conforms to the above condition. These are the infinitesmal homogeneous deformations for which all the nine strain components are constants throughout the volume of the crystal. Any small homogeneous strain can now be analysed into a pure strain followed by a rotation about a suitable axis. By a proper choice of the co-ordinate axes it is always possible to make the rotational part of the strain vanish, and thus the relation (32) holds good for homogeneous strains also. By substituting (32) in (27) and comparing it with (30) we can now obtain expressions for the elastic constants determined by static homogeneous strains in terms of the force-constants, and they are given by

$$c_{x\bar{x},\, y\bar{y}} = \tfrac{1}{4}\,[d_{x\bar{x},\, y\bar{y}} + d_{\bar{x}x,\, y\bar{y}} + d_{\bar{x}x,\, \bar{y}y} + d_{x\bar{x},\, \bar{y}y}] \tag{33}$$

The constants appearing on the right-hand side of the above equation reduce to a fewer number than forty-five for crystals possessing symmetry. We shall consider the explicit relations following from (33) for crystals possessing the symmetry of the cubic class. If, as before, we introduce the convention of replacing the letter pairs (*xx*, *yy*, *zz*, *yz*, *zy*, *zx*, *xz*, *xy*, *yx*)

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* Cases in which the energy function is a quadratic expression in the nine strain components have been considered in the phenomenological theory also, as can be inferred from a reference to a paper by Macdonald (*London Math. Soc. Proc.*, 1900, **32**, 311) given in Chapter VII of Love's book. Since this paper is not available to the author, it has not been possible to discuss the results contained therein in this article.

wherever they occur into the numbers (1, 2, 3, 4, 5, 6, 7, 8, 9), it can be shown that there are only four independent constants d_{11}, d_{12}, d_{44} and d_{45} for cubic crystals. The relations (33) reduce in this case to

$$\begin{aligned} c_{11} &= d_{11}; \\ c_{12} &= d_{12}; \\ c_{44} &= \tfrac{1}{2}(d_{44} + d_{45}) \end{aligned} \tag{34}$$

VI. WAVE-PROPAGATION INSIDE CRYSTALS

In this section we consider the nature of wave-propagation inside the crystal assuming that the strain produced by the propagation of a wave-front inside the crystal is very general and that the energy of the wave motion involves all the nine components of strain being given by the function (27). We shall assume all the nine strain components $u_{xy} = \frac{\partial u_x}{\partial y}$ are linearly independent functions of variables x, y and z. Then the equations of motions of the various elements of the crystal can be derived from the variational principle

$$\delta \int (\mathrm{T} - \mathrm{U})\, dt + \int \delta \mathrm{W}\, dt = 0 \tag{35}$$

in which U stands for the potential energy function (27) and T and W denote respectively the total kinetic energy of the solid and the work done by the external forces on the solid.

In the absence of body forces, W is given by

$$\delta \mathrm{W} = \sum_{x} \int (\mathrm{T}_{x\nu}\, \delta u_x)\, d\mathrm{S} \tag{36}$$

if $\mathrm{T}_{x\nu}$ denotes the normal component of the surface traction of the body, and the kinetic energy T is given by the expression

$$\mathrm{T} = \int \rho\, (\dot{u}_x{}^2 + \dot{u}_y{}^2 + \dot{u}_z{}^2)\, d\mathrm{V} \tag{37}$$

where ρ is the density of the medium.

The variational equations of (35) can now be written down and they are given by

$$\rho \frac{\partial^2 u_x}{\partial t^2} = \sum_{\bar{x}} \frac{\partial}{\partial \bar{x}} \left(\frac{\partial \mathrm{U}}{\partial u_{x\bar{x}}} \right) \qquad (x \rightarrow x,\ y,\ z) \tag{38}$$

for interior points of the solid, and

$$T_{x\nu} = \sum_{y} \frac{\partial U}{\partial u_{xy}} \cos(y, \nu) \tag{39}$$

for points on the surface of the crystal.

We now seek to find out solutions of the above equations which are in the form of plane waves of the type

$$u_x = A^x \exp. \frac{2\pi i}{\lambda}(\nu t - e.r) \qquad (x \to x, y, z) \tag{40}$$

Substituting (40) in (38) one gets

$$\rho v^2 A^x = \sum_{x} \sum_{y\bar{y}} d_{x\bar{x}, y\bar{y}}\, e_{\bar{x}}\, e_{\bar{y}}\, A^y \qquad (x \to x, y, z) \tag{41}$$

If we write $A = (A^x, A^y, A^z)$ and $D_{xy} = \sum_{\bar{x}\bar{y}} d_{x\bar{x}, y\bar{y}}\, e_{\bar{x}}\, e_{\bar{y}}$ then the above equations can be rewritten as $(D - \rho v^2) A = 0$. The matrix $D = (D_{xy})$ is symmetric and hence its eigenvalues are real. If they are distinct, the corresponding eigenvectors are mutually orthogonal. Thus there are three types of elastic waves progressing in any direction of the crystal. Their vibrations directions are mutually perpendicular to each other, but they may be obliquely inclined to their direction of propagation.

Equations (41) are the equations of wave-propagation inside a crystal lattice and were first deduced by Begbie and Born. They had subsequently been used by several authors to obtain expressions for the elastic constants in terms of the force-constants. The first set of expressions were given by Begbie and Born, who obtained the relations

$$c_{x\bar{x}, y\bar{y}} = d_{x\bar{x}, y\bar{y}} \tag{42}$$

This relation is clearly untenable in a general force-scheme, for it amounts to assuming a central force-scheme, and would lead to the Cauchy relations for crystals possessing a centre of symmetry. For such crystals, the round brackets vanish and therefore $d_{x\bar{x}, y\bar{y}} = -[x\bar{x}, y\bar{y}]$. If further the relation (42) is satisfied, then the suffixes x and y are interchangeable in the expression for $d_{xx, yy}$, and similarly x and y or z are interchangeable in $d_{xx, yz}$. Therefore it follows from (33) that

$$\begin{gathered} c_{12} = c_{66};\ \ c_{23} = c_{44};\ \ c_{31} = c_{55}; \\ c_{14} = c_{56};\ \ c_{25} = c_{46};\ \ c_{45} = c_{36} \end{gathered} \tag{43}$$

which are the Cauchy relations. Thus the expressions of Begbie and Born are true in a central force scheme only and are not valid for the case of a general force system. A second set of relations for the elastic constants were later obtained by Kun Huang whose method also consists in identifying the lattice wave equations with the wave equations of the elasticity theory. But such an identification could be done only with the aid of a few additional relations such as $[x\bar{x}, y\bar{y}] = [\bar{x}x, \bar{y}y]$ which were assumed in Kun Huang's theory, and these were interpreted as the conditions for the vanishing of the initial stresses in an infinite lattice. We may mention that there is no justification for the assumption of these relations in a general force scheme which would hold good for central interactions between the atoms only. The expressions of Kun Huang are also not reliable in a general force scheme and can be expected to hold good for the case of central force systems only.

The real difficulty or source of error in identifying the lattice wave equations with those of the elasticity theory lies in the fact that they owe their origin to different potential functions in the variational method of deriving them. The former are derived from a potential function that contains the rotational part of the strain as well thus involving 45 independent constants, whereas the latter are derived from an energy expression involving 21 constants only. These two are not in general mathematically equivalent and are therefore not identifiable. For those cases of wave-propagation in which longitudinal waves moving in a certain direction alone are excited, the energy of the solid due to the wave motion will not involve the three rotational components of the strain, and in such cases both the theories would lead to identical results. But in general the equations of wave-motion and hence velocities of propagation of the waves are different in the two theories that involve twenty-one and forty-five constants respectively.

VII. THE STRESS-STRAIN RELATIONS

A natural question that arises in a forty-five constant theory is as regards the nature of the stress-strain relations in the solid. Since the potential energy of deformation in this case is a function of the nine strain variables, one can form nine quantities $T_{xy} = \frac{\partial U}{\partial u_{xy}}$ obtained by differentiating the energy expression partially with respect to the strain variables u_{xy}. If these are called the stresses acting on the body, then a striking property of the forty-five constant theory is that the stress tensor *does not* satisfy the symmetry property

$$T_{xy} = T_{yx} \tag{44}$$

If the surface tractions are the only forces acting on any volume element of the body, the result $T_{xy} = T_{yx}$ holds good at every point inside an elastic body which is under a state of stress. This is easily shown by considering the equilibrium of any small cube of volume l^3 with its centre at the origin and edges parallel to the axes and equating the total angular momentum parallel to the three axes to zero. In order to reconcile ourselves to the circumstance in which the nine stresses do not form a symmetric tensor, we shall assume that each volume element is being acted upon by a couple which tends to rotate it relative to its neighbouring elements in the solid, in addition to the surface tractions acting on it. Denoting by lW_x, lW_y, lW_z the components of the moment of the couple parallel to the three co-ordinate axes, we can obtain the equilibrium conditions of this element by equating the total angular momentum of the system to zero. This leads to

$$(T_{yx} - T_{xy}) + W_z = 0 \tag{45}$$

We shall now write

$$e_{xy} = \tfrac{1}{2}(u_{xy} + u_{yz})$$

and

$$\omega_z = \omega_{xy} = -\omega_{yx} = \tfrac{1}{2}(u_{xy} - u_{yx}).$$

Then obviously

$$T_{xy} = \frac{\partial U}{\partial u_{xy}} = \frac{1}{2}\left(\frac{\partial U}{\partial e_{xy}} + \frac{\partial U}{d\omega_z}\right) \text{ and } T_{yx} = \frac{1}{2}\left(\frac{\partial U}{\partial e_{xy}} - \frac{\partial U}{\partial \omega_z}\right).$$

Hence

$$(T_{yx} - T_{xy}) + \frac{\partial U}{\partial \omega_z} = 0 \tag{46}$$

Comparing (45) and (46) we see that the quantities $\frac{\partial U}{\partial \omega_x}, \frac{\partial U}{\partial \omega_y}, \frac{\partial U}{\partial \omega_z}$ denote respectively the components of the couple W_x, W_y, W_z acting on any small element of unit volume in the body.

We have already shown in Section IV that the quantities d_{11}, d_{12} and $\frac{1}{2}(d_{44} + d_{45})$ denote respectively the three elastic constants of cubic crystals for static homogeneous strains. A physical interpretation of the four constants occurring in the general theory will therefore be complete if it is possible to give a meaning to the quantity $(d_{44} - d_{45})$ which is independent of the above three. It then follows as a consequence of (45) applied to the case of cubic crystal that the constant $2(d_{44} - d_{45})$ is equal to the ratio of the magnitude of the couple acting on any volume element of the crystal to the magnitude of the rotation suffered by it due to the strain.

Finally, the author expresses his indebtedness to Professor Sir C. V. Raman for many of the ideas contained in this paper and for the useful discussions he had with him.

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THE STRUCTURE AND OPTICAL BEHAVIOUR OF JADEITE

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I. INTRODUCTION

JADEITE is a mineral to which much interest attaches by reason of the use which has been made of it since ancient times—especially in China—for the fabrication of works of art which have been greatly admired. It is a much rarer material than nephrite which is another mineral product to which the name jade is also commonly given; happily, the two substances are readily distinguishable from each other. In its finest forms, jadeite is known as gem-jade or imperial jade and differs from the commoner varieties in its optical characters; it exhibits a beautiful green colour resembling that of emerald and is semi-transparent instead of being cloudy or opaque. There is an extensive literature which deals with jadeite from the mineralogical point of view; works on gemmology also naturally devote a good deal of space to it. We have not however found in the literature any explanation of the optical characters which jadeite exhibits in terms of its structure. Indeed, it does not appear to have been realised that there is a problem awaiting answer in that connection. The opportunity for examining the subject presented itself to us when a collection of specimens of Burmese jade which was acquired for the Museum of this Institute became available for our studies.

2. THE STRUCTURE OF JADEITE

The chemical composition of jadeite corresponds to the formula $NaAl(SiO_3)_2$ and indicates that it belongs to the series of monoclinic pyroxenes of which diopside $CaMg(SiO_3)_2$ is a typical example. X-ray studies[1, 2, 3] support the latter conclusion, the X-ray powder diagrams of jadeite and diopside showing a close resemblance to each other. The published chemical analyses[4] show the presence in jadeite of varying proportions of other oxides, notably the oxides of calcium and magnesium, thereby indicating that diopside is present as a minor constituent in the mineral. Physically, jadeite is a polycrystalline aggregate. Examination of thin sections under the polarising microscope reveals the presence of individual crystals which are birefringent, their greatest and the least refractive indices being 1·667 and 1·654 respectively.

When light enters a polycrystalline aggregate in which the individual grains are birefringent, it would necessarily suffer reflection and refraction at the intercrystalline boundaries. The smaller the individual crystallites, the more numerous would be such reflections and refractions. Hence, on this view, none of the incident light would succeed in penetrating through the material, if it is fine-grained and also of sufficient thickness. In the absence of any absorption properly so-called, the incident light would mostly be sent back towards the source by repeated internal reflections. In other words, a fine-grained aggregate of birefringent crystals should present a high albedo by reflected light and appear opaque in transmission.

The foregoing inferences based on geometrical optics do not however represent what is actually observed in the case of jadeite. Indeed, the converse is much nearer the truth; in other words, the specimens exhibiting a coarse structure are those which are opaque to light and reflect it strongly, while the specimens which are most readily penetrated by light are those having a fine-grained structure. Why this is so is the problem considered in the present paper.

3. THE X-RAY DIFFRACTION PATTERNS

To establish the relationship between structure and optical characters briefly indicated above, we have recorded the X-ray diffraction patterns of specimens exhibiting diverse optical behaviour. Three of these diagrams which are representative of the rest are reproduced in Plate XII. The film to specimen distance was in every case 5 cm. and MOKα radiation was employed to record the patterns.

Figure 1 was recorded with a piece of jade about half a millimetre thick cut out from one of our specimens and polished flat on both sides. The X-ray pencil passed normally through the specimen. The plate exhibited a notable measure of translucency; when placed on a printed sheet of paper, the finest print could easily be read through it. The X-ray record shows clearly that the crystallites present in the specimen are of varying sizes and that crystallites of very small sizes are the most numerous; though individual bright spots appear in the pattern, there are also numerous fainter ones which run into each other and appear as continuous rings.

Figure 2 is an X-ray diagram taken with similar arrangements, the X-ray pencil now grazing the edge of a flat ellipsoidal piece of green jade. It will be seen that the pattern is of the same general nature as that reproduced in Fig. 1 except that the continuity of the rings is less evident and the spottiness more conspicuous.

Figure 3 is the pattern recorded with a greenish-white specimen which was nearly opaque to light. It will be seen that the pattern consists of a number of individual spots, some of which are very bright. But hardly anything in the nature of continuous rings can be discerned. In other words, the specimen consists of relatively large crystallites.

4. THEORETICAL CONSIDERATIONS

To understand the optical behaviour of jadeite, we have to put aside the considerations based on geometrical optics and deal with the matter from the standpoint of the wave theory of light. It is useful, in the first instance, to think of an extreme case in which the individuals in the polycrystalline aggregate are assumed to be of very small dimensions even in comparison with the wave-length of light and are also randomly orientated. Such an aggregate could obviously be regarded as equivalent to an optically isotropic medium with a refractive index which is the average of the principal refractive indices of the crystallites. A beam of light incident normally on a slab of such material would traverse it as a coherent wave-train, and emerge from the rear surface of the slab, but not the whole of the incident energy would succeed in so emerging. For, in consequence of the varying orientations of the crystallites and their birefringence, the medium would exhibit local variations in optical behaviour, and there would therefore be a diffusion of light both forwards and backwards. In the limiting case when the grains are very small, the diffusion would extend approximately with equal strength both forwards and backwards. More generally, however, there would be a concentration of the diffused radiation in the forward directions surrounding the path of the regularly transmitted light-beam. There would also be a diffusion of light backwards towards the light-source, but this would be less conspicuous.

The situation set forth above would be modified if the grains of the medium are of dimensions comparable with the wave-length of light. Nevertheless, provided the birefringence of the individual crystallites is small, we may continue to regard the aggregate as an isotropic medium which exhibits local variations in refractive index depending on the direction of vibration in the light beam traversing the material. These variations would result in the phase of light-waves passing through an individual grain being either accelerated or retarded as the case may be. The errors in phase thus resulting when summed up over the total path would tend to cancel each other out; the residual errors in phase would be the smaller relatively to the total path, the more numerous the particles are, in other words the smaller is their size. Thus, it follows that if the birefringence is not large and the material is very fine-grained, the waves of light would succeed in penetrating the medium. Nevertheless, the residual errors in phase would result in a reduction of the absolute intensity of the transmitted beam and ultimately also its total extinction. The missing energy would appear for the most part in a cone of diffuse radiation surrounding the direction of propagation of the incident light-beam.

Wave-theoretical considerations also indicate that the proportion of the incident energy sent back towards the source as a diffuse reflection by a fine-grained aggregate would be far less than that indicated by considerations based on geometrical optics. For, the phase of a reflected wave relatively to the incident wave depends on whether the first or the second medium on the two sides of the reflecting boundary has the higher index. The boundaries encountered by a light-wave traversing a polycrystalline aggregate would obviously be of both kinds and in approximately equal numbers. The reflection in the two cases being in opposite phases, their effects would tend to cancel each other more or less completely in all directions.

Thus we may sum up the situation by the statement that light would penetrate into a polycrystalline aggregate much more freely and would be reflected backwards much less freely than that might be anticipated in terms of geometrical optics, provided that the aggregate is sufficiently fine-grained. Thus, we have an explanation in general terms of the semi-transparency exhibited by the finest varieties of jadeite.

5. SUMMARY

The phenomenon of semi-transparency exhibited by the finer varieties of jadeite is discussed. X-ray diffraction studies and theoretical considerations based on wave-optics alike indicate that this is a consequence of the very small particle size of the crystallites forming the aggregate.

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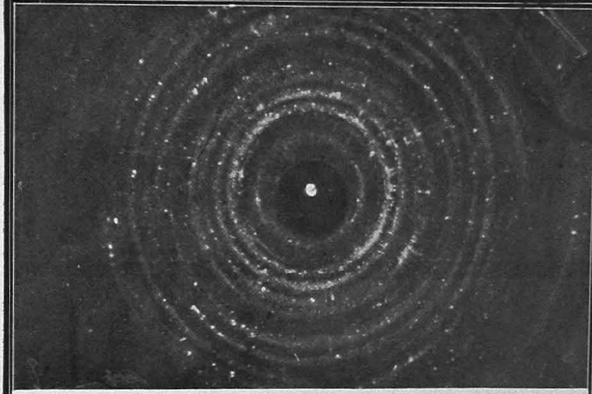

FIG. 1

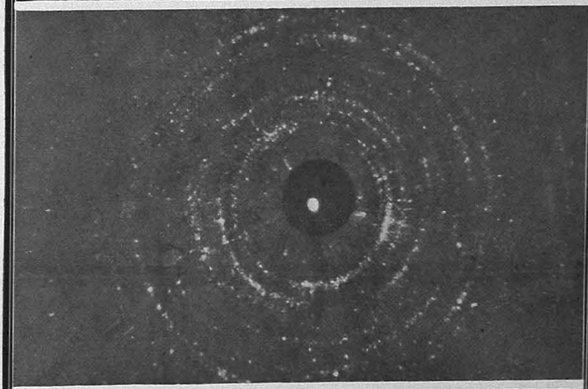

FIG. 2

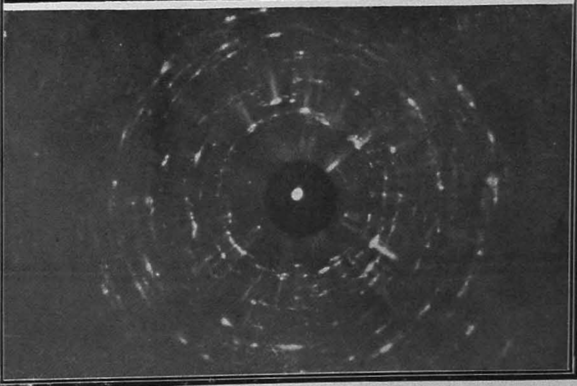

FIG. 3

X-ray Diffraction Patterns of Jadeite

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ACHROMATIC COMBINATIONS OF BIREFRINGENT PLATES

Part I. An Achromatic Circular Polarizer

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1. INTRODUCTION

WHEN polarised light of any form is incident on a birefringent plate, the phase retardation δ introduced between the two waves during their passage through the plate, is far from being the same for all wave-lengths; in fact, being given by $\delta = (2\pi/\lambda)(\mu_1 - \mu_2)\, t$, this retardation of phase varies almost inversely as the wave-length λ, that is, if the birefringence $(\mu_1 - \mu_2)$ does not disperse notably with wave-length. So much so, that what acts as a quarter-wave retardation plate for the deep red end of the spectrum will, for the wave-lengths in the deep violet, behave practically as a half-wave plate.

The question of the achromatisation of devices in this field has engaged the attention of several workers. References to their investigations may be found cited in the paper entitled, " *Réalisation d'un quart d'onde quasi-achromatique par juxtaposition de deux lames crystallines de même nature* " by Destriau and Prouteau[1]; the two plates referred to, do not, of course, have their principal planes parallel, and the 'compound plate', comprising the two superposed plates, can transform incident circularly polarised light to plane polarised light vibrating at a certain azimuth, or *vice-versa*. But the device described by these authors would more properly be called an achromatic circular polarizer (or analyser); to call it an achromatic quarter-wave plate would be incorrect since the combination does not have the usual attributes of a quarter-wave plate—it cannot, for example, be used for the analysis of elliptically polarised light in the usual manner of an ordinary $\lambda/4$ retardation plate.

Nevertheless it is as a circular polarizer or analyser that a quarter-wave plate is often used—as when it is inserted with its principal planes at an angle of 45° to those of a nicol, in a petrographic microscope. And we shall reserve for the second part, the problem of superposing birefringent plates in such a manner that the combination as a whole behaves as an achromatic quarter-wave plate. In this paper we shall describe a circular polarizer which is expected to have a much higher degree of achromatism than the one discussed in the paper quoted above. The description of the device may be found at the end of the next section; its applicability is not limited to the visible. The birefringent plates in our discussion are all of the same material; the dispersion of the birefringence of this material is not assumed to be negligible—though such an assumption would indeed be justified for plates of muscovite mica, at least for the visible and ultra-violet wave-lengths.[2]

2. THE ACHROMATIC CIRCULAR POLARIZER

The Poincaré sphere* lends itself very conveniently for the theoretical discussion of the two problems at hand—especially the one to be treated later. (As is well known, any point on the surface of this sphere, of latitude 2ω and longitude $2l$, represents an elliptic vibration of ellipticity $|\tan\omega|$ the major axis of which makes an angle l with a fixed reference direction. Passage through a birefringent plate of retardation δ, the orientation of whose principal planes are given by O and O′, is equivalent to the operation of rotating the sphere by an angle δ about the equatorial diameter OO′.)

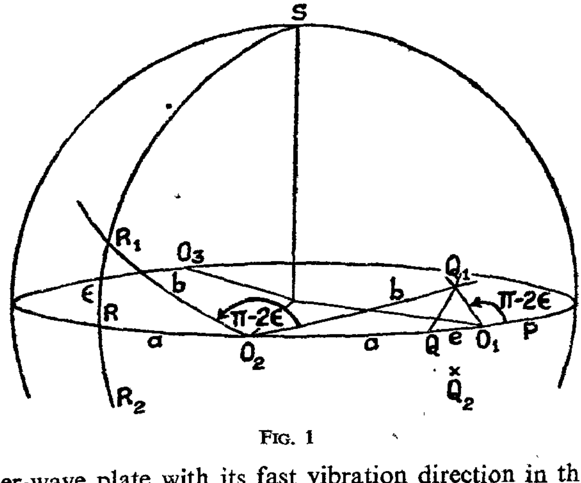

FIG. 1

A quarter-wave plate with its fast vibration direction in the orientation O_3 (Fig. 1) can transform the incident linear vibration R—inclined at 45° to the principal planes—to circularly polarised light represented by the pole S—but only for the wave-length λ for which its retardation is exactly

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* Expositions in English, of the properties of the Poincaré sphere are apparently not so common in text-books, but may be found in numerous recent articles: see *e.g.*, Ramachandran and Ramaseshan, *J. Opt. Soc. Am.*, 1952, **42**, 49.

$\pi/2$. For the wave-lengths λ_1 and λ_2 on either side of λ, for which the respective retardations are $\pi/2 - \epsilon$ and $\pi/2 + \epsilon$, the emergent light will be circularly polarised only if the incident vibrations are given respectively by R_1 and R_2; these two points lie on the meridian SR and are equidistant from R (arc $R_1R = \epsilon$). Thus if the ellipticity of the incident vibrations were dispersed roughly along R_1R_2 in a proper fashion, the quarter-wave plate would transform the vibrations for all the wave-lengths to approximately circular polarised light.

The required dispersion of the ellipticity of the vibrations incident on the quarter-wave plate, it may be seen, can be effected by allowing plane polarised light P to first pass successively through two half-wave plates, the orientation of whose fast axes are given by O_1 and O_2 respectively and are to be determined. In order that the light emerging from the third retardation plate (*i.e.*, the quarter-wave plate) should be exactly circularly polarised for all the three wave-lengths λ_1, λ and λ_2, the state of polarization of the light incident on the second half-wave plate for these three wave-lengths should be given by Q_1, Q and Q_2 respectively—got by the following construction. The point Q is marked off on the equator such that $O_2Q = O_2R$ ($= a$ say); the arc O_2Q_1 is drawn such that $R_1O_2Q_1 = \pi - 2\epsilon$, and $O_2Q_1 = O_2R_1$ ($= b$ say); Q_2 is a point symmetrically placed with respect to Q_1 on the lower hemisphere. The first half-wave plate has to be oriented in a position depending on the quantity a which determines the orientation of the second; for we must have $O_1Q_1 = O_1Q_2 = O_1Q$ ($= e$ say); and further we must choose a such that $P\hat{O}_1Q_1 = \pi - 2\epsilon$. If the plane of the incident vibration P be now set such that $O_1P = e$, then the light emerging from the combination will be circularly polarized for the three wave-lengths λ_1, λ and λ_2 for which the retardations of a quarter-wave plate would be $\pi/2 - \epsilon$, $\pi/2$, and $\pi/2 + \epsilon$ respectively; ϵ is an arbitrarily chosen parameter on which will depend the two opposing characteristics of the combination: the range and the degree of its achromatism.

By the use of spherical trigonometry we shall get an equation for a involving the parameter ϵ. Thus, from the equilateral triangle Q_1O_1Q, denoting arc Q_1Q by c

$$\cos 2\epsilon = -\cos^2 Q_1QO_1 + \sin^2 Q_1QO_1 \cos c$$

or

$$1 + \cos 2\epsilon = 2\sin^2 Q_1QO_1 \cos^2 c/2$$

From the triangle Q_1O_2Q we have, writing $Q_1O_2Q = C$,

$$\frac{\sin c}{\sin C} = \frac{\sin b}{\sin Q_1QO_1}$$

i.e.,

$$\sin Q_1QO_1 \cos\frac{c}{2} = \frac{\sin b \sin C}{2\sin\frac{c}{2}}$$

We thus obtain

$$\sin^2 b \sin^2 C = 2\sin^2\frac{c}{2}(1 + \cos 2\epsilon) \tag{1}$$

We shall express the quantities on the left-hand side in terms of a. Denoting R_1O_2R by C'

$$\sin C = \sin(2\epsilon - C') = \sin 2\epsilon \cos C' - \cos 2\epsilon \sin C' \tag{2}$$

From the right-angled triangle R_1O_2R

$$\sin C' = \frac{\sin\epsilon}{\sin b}$$

and

$$\cos C' = \frac{\cos\epsilon - \cos a \cos b}{\sin a \sin b} = \cos\epsilon \cdot \frac{\sin a}{\sin b}$$

since

$$\cos b = \cos\epsilon \cos a \tag{3}$$

Substituting the expressions obtained for $\cos C'$ and $\sin C'$ in (2)

$$\sin C = \frac{\sin\epsilon}{\sin b}(2\cos^2\epsilon \sin a - \cos 2\epsilon)$$

Introducing this in (1)

$$(2\cos^2\epsilon \sin a - \cos 2\epsilon)^2 = 2\cot^2\epsilon(1 - \cos c) \tag{4}$$

It remains to express $\cos c$ in terms of a. From triangle Q_1QO_2

$$\cos c = \cos a \cos b + \sin a \sin b \cos C$$

$$\cos C = \cos(2\epsilon - C') = \cos 2\epsilon \cos C' + \sin 2\epsilon \sin C'$$

$$= \frac{\cos\epsilon}{\sin b}(\cos 2\epsilon \sin a + 2\sin^2\epsilon)$$

Using this relation, together with (3), the expression for $\cos c$ becomes,

$$\cos c = \cos\epsilon(1 + 2\sin^2\epsilon \sin a - 2\sin^2\epsilon \sin^2 a)$$

Substituting for $\cos c$ in (4), and rearranging, we finally get an equation in $\sin a$ of the form:

$$A\sin^2 a + B\sin a + C = O \tag{I}$$

where

$$A = 4\cos^3\epsilon\,(1 - \cos\epsilon)$$

$$B = 4\cos^2\epsilon\,(\cos 2\epsilon - \cos\epsilon)$$

$$C = 2\cot^2\epsilon\,(1 - \cos\epsilon) - \cos^2 2\epsilon$$

An expression for e may be obtained from triangle Q_1O_1Q

$$\cos c = \cos^2 e + \sin^2 e \cos 2\epsilon$$

or

$$\sin^2 e = \frac{1 - \cos c}{1 - \cos 2\epsilon}$$

Using (4),

$$\sin e = \frac{2\cos^2\epsilon \sin a - \cos 2\epsilon}{2\cos\epsilon} \tag{II}$$

The combination can produce exactly circularly polarized light for three wave-lengths. If we neglect the dispersion of the birefringence, the two extreme wave-lengths will obviously be $(1 + f)\,\lambda$ and $(1 - f)\,\lambda$—where we have denoted the ratio $\epsilon : \pi/2$ by f; the achromatism of the combination may however be considered to extend up to two wave-lengths *outside* this interval, for which the deviation from circular polarisation is roughly the same as the maximum deviation attained within this interval—which latter may be expected to occur in the neighbourhood of the wave-lengths $(1 \pm \cdot 5 f)\,\lambda$. Thus we may with some arbitrariness, consider the combination to be achromatic within the range $(1 \pm 1{\cdot}25 f)\,\lambda$.

Choosing $2\epsilon = 47^\circ$ (which means $1{\cdot}25 f = \cdot 325$), equation (I) when solved gives $\sin a = \cdot 6642$ or $a = 41^\circ\, 37'$.

The corresponding value of e obtained from (II) is $e = 13^\circ\, 43'$.

On the other hand, if we choose $2\epsilon = 36^\circ$ (which means $1{\cdot}25 f = \cdot 25$) we obtain

$$a = 43^\circ\, 8'; \; e = 13^\circ.$$

Thus to summarize our results, an achromatic arrangement for producing circularly polarised light is obtained by allowing parallel plane polarised light to pass normally through a combination of three superposed plates of the same material; the first two should be half-wave plates, and the last, a quarter-wave plate for the wave-length λ in the centre of the spectral range to be covered. Let θ be the angle by which the fast vibration direction of the first plate is turned with respect to the azimuth of the incident vibration; θ_1, the angle by which the fast axis of the second plate is turned with respect to the first; and θ_2 the corresponding angle between the fast axes of the third and second plates—all the angles being measured in the same sense. The set of values

$$\theta_2 = \tfrac{1}{2}(\pi/2 + a) = 65^\circ\, 49'; \;\; \theta_1 = \tfrac{1}{2}(a + e) = 27^\circ\, 40'; \;\; \theta = \tfrac{1}{2}\, e = 6^\circ 52'$$

can be used for covering the range from $1 \cdot 325\ \lambda$ to $\cdot 675\ \lambda$ and is therefore suited for covering the entire visible spectrum if we choose $\lambda = 6000$ Å. A greater degree of achromatism can be attained at the expense of restricting the range to the major portion of the visible. Thus the set of values

$$\theta_2 = 66^\circ\, 34'; \;\; \theta_1 = 28^\circ\, 4'; \;\; \theta = 6^\circ\, 30'$$

can be used for covering the range from $1 \cdot 25\ \lambda$ to $\cdot 75\ \lambda$. If the dispersion of the birefringence of the material used is not negligible, the values given above for the range over which the combination may be considered achromatic would have to be altered.

On turning the polarizing nicol to a perpendicular position, circularly polarized light of the opposite sense is produced. In fact in passage through any succession of 'elliptically birefringent' plates, two orthogonal states of the incident polarization will correspond to two orthogonal states of the emergent polarization. This is a consequence of a more general fact; the angular separation on the Poincaré sphere of two possible states of the incident polarization will be equal to the angular separation of the two corresponding states of the emergent polarization, since angular relationships remain invariant under any number of rotations. Thus if the nicol had been turned by 45°, the emergent wave-lengths would all have been practically plane polarized, but with the azimuths of the vibrations dispersed—an interesting illustration of the fact that the combination does not have the properties of a quarter-wave plate.

3. EXPERIMENTAL VERIFICATION

Two half-wave plates and a quarter-wave plate, all prepared of mica, were cemented together (using copal varnish) with their principal planes at inclinations slightly different from the first set of values given above—in order to cover an even wider range. The combination was laid on a mirror. With the aid of another mirror, white light from a point source was made to pass normally through a polaroid and the achromatic combination, and then back again—after which it reached the eye. As the polaroid is rotated a position is reached where the image of the source is completely extinguished; this is the position where a single passage through the compound plate would give circularly polarized light, while the double passage gives plane polarized light which is crossed out by the polarizer itself. When the experiment is repeated with a single quarter-wave plate the image is never completely extinguished, but is highly coloured.

The two $\lambda/2$ retardation plates may first be cemented together at the proper angle θ_1, using the fact that the two together will rotate the plane of polarization of *any* incident linear vibration (of wave-length λ) by an angle $\pi - 2\theta_1$; (this can be proved by a construction given in Part II); the quarter-wave plate may then be cemented and adjusted, while the cement is still wet, to the position of best achromatism—as determined by the test given above.

SUMMARY

Circularly polarised light is obtained by superposing two half-wave plates and one quarter-wave plate, all of the same material, such that the fast vibration-directions of the successive plates make specific angles θ_1, θ_2, θ_3 with the azimuth of the linear vibration incident on the first plate. The required range of achromatism determines the optimum values of the angles. Thus, using mica retardation plates prepared for Na 5890, the range from 4000 Å to 7800 Å is covered with $\theta_1 = 6° 52'$, $\theta_2 = 34° 32'$, $\theta_3 = 100° 20'$; while the range 4400 Å to 7400 Å can be covered with superior achromatism by taking $\theta_1 = 6° 30'$, $\theta_2 = 34° 34'$, $\theta_3 = 101° 8'$.

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ACHROMATIC COMBINATIONS OF BIREFRINGENT PLATES

Part II. An Achromatic Quarter-Wave Plate

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1. INTRODUCTION

A COMBINATION of birefringent plates which can be used for producing circularly polarised light over a fairly large range of wave-lengths has been described in Part I. And it has there been pointed out that the arrangement cannot be properly described as an achromatic quarter-wave plate. A quarter-wave plate when rotated between crossed nicols will show two extinction positions; the achromatic combination described will show none. And to understand under what conditions a combination of plates will have the properties of a single birefringent plate—let alone a plate which is in addition achromatic—it is desirable to have a general method for combining the action of a pile of birefringent plates when their principal planes are not parallel. We shall follow a method differing slightly from that which may be found described by Pockels.[1]

2. GENERAL CONSIDERATIONS

The problem of designing an achromatic elliptic polariser is the problem of transforming a particular state of polarization represented by P_1 (on the Poincaré sphere) to another particular state P_1'. But, of an achromatic retardation plate we require that it transforms *every* P to a corresponding P′ obtained by rotating the sphere by an angle δ about an equatorial diameter.

Passage of monochromatic polarised light through a succession of birefringent plates corresponds to a succession of rotations of the Poincaré sphere about a series of equatorial diameters. Any succession of rotations of the sphere can, however, be compounded into one single resultant rotation. Hence the action of a combination of birefringent plates corresponds to a rotation ϕ of the Poincaré sphere about some diameter EE′—which will in general be inclined to the equatorial plane; this means, of course, that the combination is equivalent to a single plate having elliptic birefringence—

E and E′ being the orthogonal elliptic vibrations propagated without change of form, and between which a phase retardation ϕ is incurred.

The condition that the combination should act as a purely birefringent plate (for a particular wave-length λ) is that the axis EE′ of the resultant rotation should be on the equator; so that, if 2ω denote the lattitude of E, the faster ellipse, $2\omega = 0$. And if the retardation of the plate is to have a required value δ, the magnitude of the resultant rotation ϕ should be equated to this value.

Both the magnitude ϕ as well as the axis EE′ of the resultant rotation will in general alter with the wave-length, since the magnitudes (though not the axes) of the component rotations are a function of wave-length. Hence, for the combination to be considered achromatic in the immediate neighbourhood of the wave-length λ, some more conditions have to be imposed; when the wave-length is increased by $\Delta\lambda$ the values of the composite phase retardation ϕ, as well as the latitude 2ω and longitude $2l$ of E, should remain unaltered at least to the first order of approximation.

Instead of following matrix methods, we shall use a well-known geometrical construction (illustrated in Fig. 1) for finding the resultant of any

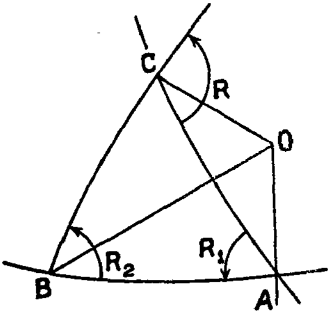

FIG. 1. Composition of Rotations: $2R_1 + 2R_2 = 2R$.

two rotations. If ABC be a spherical triangle described on a sphere whose centre is O then: *a rotation about AO through twice the internal angle at A, followed by a rotation about BO through twice the internal angle at B is equivalent to a rotation about CO through twice the external angle at C.*

3. A BIREFRINGENT COMBINATION WITH VARIABLE RETARDATION

We shall now show that a combination of three birefringent plates, the first and last of which have their corresponding principal planes parallel and their retardations identical, will behave as a single purely birefringent plate of retardation 2δ, whose fast vibration direction is inclined at an angle c_1 to that of the first plate, where 2δ and c_1 are given by:

$$\cos\delta = \cos 2\delta_1 \cos\delta_2 - \sin 2\delta_1 \sin\delta_2 \cos 2c \qquad (a)$$

and

$$\cot 2c_1 = \operatorname{cosec} 2c\,(\sin 2\delta_1 \cot\delta_2 + \cos 2\delta_1 \cos 2c) \qquad (b)$$

In the above relations $2\delta_1$ is the common retardation of the first and last plates, $2\delta_2$ that of the central plate, and c the angle between the fast vibration directions of the central plate and the other two.

Before proceeding to prove these relations, we may mention that by choosing 2 quarter-wave plates as the first and last plates, and a half-wave plate as the central plate, we can, by rotating the central plate, vary the retardation of the combination continuously from 0 to 2π; the principal planes of the combination will always be inclined at 45° to those of the first plate.

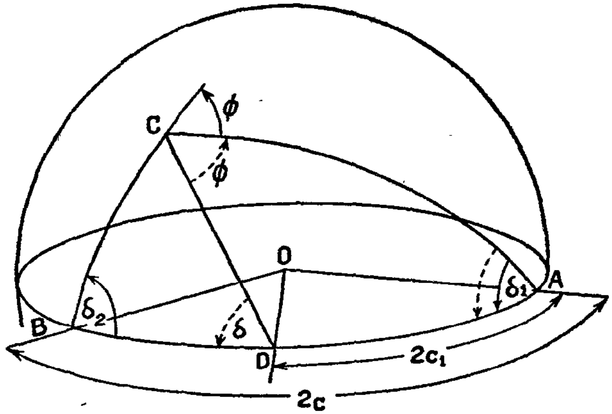

FIG 2.

Referring to Fig. 2, a rotation $2\delta_1$ about AO followed by a rotation $2\delta_2$ about BO, where A and B give the orientation of the fast axes of the first and middle plates respectively, is equivalent to a rotation 2ϕ about CO—where CAB $= \delta_1$, CBA $= \delta_2$ and $\pi -$ ACB $= \phi$. Let us draw an arc CD such that ACD $= \phi$, D being the point of intersection of this arc with the equator. Considering now the triangle ACD, the rotation 2ϕ about C (representing the combined action of the first 2 plates) followed by a rotation $2\delta_1$ about A (which now represents the action of the third plate) is equivalent to a rotation about D through twice the angle external to ADC. The combination is therefore equivalent to a birefringent plate of retardation 2δ whose fast axis is inclined at c_1 to that of the first plate—where $\delta = \pi - \mathrm{ADC}$, and $2c_1 = \text{arc AD}$.

The expressions which we shall derive for δ and c_1 do not depend on assuming that D lies within AB.

From the triangle ADC, denoting arc CD by d

$$\cos \delta_1 = \cos \phi \cos \delta + \sin \phi \sin \delta \cos d \tag{1}$$

From the triangle DBC

$$\cos \delta_2 = \cos 2\phi \cos \delta + \sin 2\phi \sin \delta \cos d \tag{2}$$

Eliminating d by multiplying (1) by $2 \cos \phi$ and subtracting from (2), we obtain:

$$\cos \delta = 2 \cos \phi \cos \delta_1 - \cos \delta_2$$

The value of $\cos\phi$ to be substituted is obtained from the triangle ABC.

$$\cos \phi = \cos \delta_1 \cos \delta_2 - \sin \delta_1 \sin \delta_2 \cos 2c$$

Hence

$$\cos \delta = \cos 2\delta_1 \cos \delta_2 - \sin 2\delta_1 \sin \delta_2 \cos 2c$$

which is the required expression (a).

To get an expression for c_1, we use a well-known trigonometrical theorem, which gives from triangle ABC, on denoting are AC by b

$$\cot 2c \sin b = \cot \mathrm{ACB} \sin \delta_1 + \cos b \cos \delta_1$$

and from triangle ACD

$$\cot 2c_1 \sin b = \cot \mathrm{ACD} \sin \delta_1 + \cos b \cos \delta_1$$

or

$$\sin b\,(\cot 2c_1 - \cot 2c) = 2 \sin \delta_1 \cot \phi$$

Substituting

$$\sin b = \sin \delta_2 \cdot \frac{\sin 2c}{\sin \phi}$$

we obtain,

$$\sin 2c\,(\cot 2c_1 - \cot 2c) = \frac{2 \sin \delta_1}{\sin \delta_2} \cos \phi$$

i.e.,

$$\sin 2c \cot 2c_1 - \cos 2c = \frac{2 \sin \delta_1}{\sin \delta_2} (\cos \delta_1 \cos \delta_2 - \sin \delta_1 \sin \delta_2 \cos 2c)$$

or

$$\sin 2c \cot 2c_1 = \sin 2\delta_1 \cot \delta_2 + \cos 2\delta_1 \cos 2c$$

which is the required expression (*b*).

4. CONDITIONS FOR ACHROMATISM

To make a combination of the type described above achromatic in the immediate neighbourhood of the wave-length λ we may differentiate the expressions on the right-hand side of the equations (*a*) and (*b*), and equate to zero. Since however our object is to attain achromatism over a finite range of wave-lengths we proceed in a different manner.

Let λ' and λ'' be two wave-lengths on either side of λ for which the retardations of each individual plate are multiplied by a factor $(1-f)$ and $(1+f)$ respectively. Values corresponding to these two wave-lengths will be denoted by corresponding single- and double-primed symbols.

We impose the conditions that the retardation $2\delta'$ and $2\delta''$ of the combination for these two wave-lengths be equal to one another and to 2Δ, the required retardation of the achromatic combination; also that the orientations of the fast axes of the combination for these two wave-lengths should be the same, *i.e.*, $c_1' = c_1''$. We then get three equations involving the three unknowns δ_1, δ_2 and c:

$$\cos \Delta = \cos 2\delta_1' \cos \delta_2' - \sin 2\delta'_1 \sin \delta_2' \cos 2c \qquad (1)$$

$$\cos \Delta = \cos 2\delta_1'' \cos \delta_2'' - \sin 2\delta_1'' \sin \delta_2'' \cos 2c \qquad (2)$$

$$\sin 2\delta_1' \cot \delta_2' + \cos 2\delta_1' \cos 2c = \sin 2\delta_1'' \cot \delta_2'' + \cos 2\delta_1'' \cos 2c \qquad (3)$$

From these three relations we may get two relations involving only the unknowns δ_1 and δ_2.

Thus eliminating $\cos 2c$ from (1) and (2)

$$\frac{\cos \delta_2' \cos 2\delta_1' - \cos \Delta}{\sin 2\delta_1' \sin \delta_2'} = \frac{\cos \delta_2'' \cos 2\delta_1'' - \cos \Delta}{\sin 2\delta_1'' \sin \delta_2''} \qquad (4)$$

For the second equation, we eliminate $\cos 2c$ as well as $\cos \Delta$ between the three equations. Thus equating the right-hand expression of (1) and (2), and then substituting the value of $\cos 2c$ from (3) we get:

$$\frac{\cos 2\delta_1' \cos \delta_2' - \cos 2\delta_1'' \cos \delta_2''}{\sin 2\delta_1' \sin \delta_2' - \sin 2\delta_1'' \sin \delta_2''} = \frac{\sin 2\delta_1' \cot \delta_2' - \sin 2\delta_1'' \cot \delta_2''}{\cos 2\delta_1'' - \cos 2\delta_1'}$$

which on simplification yields,

$$(1 - \cos 2\delta_1' \cos 2\delta_1'')\ (\cos \delta_2' + \cos \delta_2'')$$

$$= \sin 2\delta_1' \sin 2\delta_1'' \ \frac{\sin \delta_2' \cos \delta_2'' + \cos \delta_2' \sin \delta_2''}{\sin \delta_2' \sin \delta_2''}$$

Substituting

$$\delta_2' = (1 - f)\,\delta_2 \text{ and } \delta_2'' = (1 + f)\,\delta_2,$$

we get

$$(1 - \cos 2\delta_1' \cos 2\delta_1'')\, 2 \cos \delta_2 \cos f\,\delta_2 = \frac{\sin 2\delta_1' \sin \delta_1'' \cdot \sin 2\delta_2}{\frac{1}{2}(\cos f\,\delta_2 - \cos \delta_2)} \tag{5}$$

We have to find values of δ_1 and δ_2 which simultaneously satisfy (4) and (5). The task is considerably simplified when we note that equation (5) is identically satisfied for $\delta_2 = \pi/2$. The corresponding value of δ_1 may be found from (4), which now becomes:

$$\sin f \frac{\pi}{2} \cdot \sin 2\,(\delta_1' + \delta_1'') = \cos \varDelta\,(\sin 2\delta_1'' - \sin 2\delta_1')$$

Substituting

$$\delta_1' = (1 - f)\,\delta_1 \text{ and } \delta_1'' = (1 + f)\,\delta_1,$$

this gives

$$\sin f\,.\,2\delta_1 = \frac{\sin f \cdot \frac{\pi}{2}}{\cos \varDelta} \cdot \sin 2\delta_1 \tag{I}$$

An expression for $\cos 2c$ is got by eliminating $\varDelta$ from (1) and (2).

$$\cos 2c = \frac{\sin f \frac{\pi}{2}}{\cos f \frac{\pi}{2}} \cdot \frac{\cos 2\delta_1' + \cos 2\delta_1''}{\sin 2\delta_1' - \sin 2\delta_1''}$$

or

$$\cos 2c = -\frac{\tan f \frac{\pi}{2}}{\tan f \cdot 2\delta_1} \tag{II}$$

For any required retardation $2\varDelta$ and for any choice of the arbitrary parameter f which determines the range of achromatism, the retardation $2\delta_1$ of the first and last plates of the achromatic combination may be found from I; since this is a transcendental equation it has to be solved by an iteration procedure. The orientation c of the central plate, which should be a half-wave plate, may then be obtained from II. The orientation c_1' of the principal planes of the combination may, if required, be calculated from

$$\sin 2c \cot 2c_1' = \sin (1 - f)\, 2\delta_1 \tan f \frac{\pi}{2} + \cos (1 - f)\, 2\delta_1 \cos 2c \tag{III}$$

The retardation and the orientation of the principal planes of the achromatic retardation plate, taken as a whole, will disperse slightly with wave-length. The combination will possess exactly the same retardation 2Δ and the same orientation c_1' of its fast vibration direction, for two wave-lengths; these wave-lengths, if we neglect the dispersion of birefringence, will be $(1+f)\,\lambda$ and $(1-f)\lambda$; and we may, somewhat arbitrarily, consider the range of achromatism as extending from $(1+\sqrt{2}f)\lambda$ to $(1-\sqrt{2}f)\lambda$.

We shall present the numerical solutions only for the case of an achromatic quarter-wave plate—*for which we must substitute* $2\Delta = 90°$. If we choose $f = \cdot 18$ the solution of I can be shown to be $2\delta_1 = 115° \, 42'$; so that from II, $\cos 2c = -\cdot 7639$ or $2c = 139° \, 48'$. The corresponding value of c_1' is got from III, which yields $\cot 2c_1' = \cdot 5489$ or $2c_1' = 61° \, 14'$.

On the other hand if $f = \cdot 1414$ we get

$$2\delta_1 = 115° \, 30', \; 2c = 140° \, 26', \; 2c_1' = 61° \, 30'$$

Thus an achromatic quarter-wave plate is obtained by superposing three plates of the same birefringent material (the dispersion of the birefringence of which need not be negligible). The central plate should be a half-wave plate for the wave-length λ in the middle of the spectral range to be covered. The first and last plates should have their principal planes in parallel orientation and their retardations of the same magnitude—equal to, say, $2\delta_1$ for the wave-length λ. With respect to the common fast vibration direction of the first and last plates, let the inclinations of the fast vibration direction of the central plate, and of the combination taken as a whole, be c and c_1' respectively. Then for covering the range of wave-lengths from about $1 \cdot 25\,\lambda$ to $\cdot 75\,\lambda$ the set of values, $2\delta_1 = 115° \, 42'$, $c = 69° \, 54'$ may be used—for which $c_1' = 30° \, 37'$. The achromatism is not high but can be increased by restricting the range to be covered. Thus for covering the region from $1 \cdot 2\,\lambda$ to $\cdot 8\,\lambda$ the values suitable are:

$$2\delta_1 = 115° \, 30', \; c = 70° \, 13',$$

for which

$$c_1' = 30° \, 45'$$

We may mention that the range over which these combinations may be considered achromatic would have to be altered if the dispersion of the birefringence is appreciable, but their essentially achromatic nature would not be changed. For retardation plates of mica, the dispersion of birefringence is negligible.[2]

EXPERIMENTAL VERIFICATION

Two plates of mica were cleaved, whose thicknesses were in the ratio of 180: 115·75, the former being nearly a half-wave plate for the D lines of sodium. The second plate was cut into two portions which were then superposed and cemented together at a corner—the principal planes of the two portions being made exactly coincident while the cement was still wet. After the cement was dry, the half-wave plate—with a drop of copal varnish on either side—was inserted *between* the other two plates at roughly the calculated angle. The combination was placed on a mirror and, with the aid of another mirror, white light from a point source was made to pass normally through a polaroid and the combination of plates and then back again—after which it reached the eye. The orientation of the central plate was then gradually altered while the varnish was still wet—and a position was found where the image of the point source could be almost completely extinguished by rotating the polaroid. It was also verified that the combination thus prepared showed two practically black extinction positions when rotated between crossed polaroids.

The author's thanks are due to Prof. Sir C. V. Raman for his kind interest in this work.

SUMMARY

An achromatic quarter-wave plate is obtained by superposing three birefringent plates of the same material; the first and last should have the same retardation $2\delta_1$, their fast vibration directions being parallel to one another but inclined at a specific angle c to that of the central plate—of retardation π. The desired range of achromatism determines the optimum values of $2\delta_1$ and c (which, in turn, will determine the orientation of the effective principal planes of the combination). As an example, using mica retardation plates prepared for Hg 5461, the range from 4100 Å to 6800 Å is covered with $2\delta_1 = 115° 42'$ and $c = 69° 54'$.

Further, for a particular wave-length, a birefringent compensator of variable retardation (0 to 2π) is obtained by interposing a half-wave plate that can be rotated in its own plane, between two quarter-wave plates that have their fast vibration directions parallel.

The results follow from the Poincaré sphere by geometrically compounding successive rotations.

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THE ELASTIC BEHAVIOUR OF ISOTROPIC SOLIDS

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1. Introduction

It is a classic result in the phenomenological theory of elasticity that *two* independent constants suffice to describe the stress-strain relationships for an isotropic solid. If, for example, the bulk modulus and the shear modulus of the material are known, Young's modulus and Poisson's ratio may be calculated therefrom. In the present paper, the ideas regarding the nature of the strains and stresses in solids on which the derivation of this result is based are critically examined and it is shown that they are untenable. A re-formulation of the phenomenological theory of elasticity not open to the same objections is then presented and its consequences are developed. It emerges that *three* independent constants are needed to describe the stress-strain relationships of an isotropic body; in particular, it is shown that the bulk modulus of the material cannot be evaluated from the experimental data for the velocities of propagation of longitudinal and transverse waves respectively in the solid and its density.

2. Some General Considerations

As is well known, the elastic constants of solids can be determined independently by static and dynamic methods. The latter are based on measurements of the velocity of propagation of waves of different types in the material. In all studies of this nature we are clearly concerned with *heterogeneous* strains, in other words with strains which are not of the same magnitude throughout the solid at any given instant; clearly, there could be no wave-propagation if the strains were the same everywhere. On the other hand, in the static methods of measuring elastic constants the strains may be homogeneous or heterogeneous according to the nature of the experiment. The change in volume of a solid under hydrostatic pressure is a case of the first kind, while the twisting of a rod by couples applied at its two ends is clearly a case of heterogeneous strain. The examples cited are sufficient to show that any theory of elastic behaviour has necessarily to concern itself with *heterogeneous* strains; a theory which restricts itself to the consideration of homogeneous strains would be fundamentally incomplete.

The twisting of a rod by couples applied at its two ends also serves to illustrate certain fundamental aspects of the theory of elasticity. As just mentioned, it is an example of heterogeneous strain, and indicates that the movements of the parts of the solid in such strains may be angular movements or rotations, the magnitude of which varies through the volume of the solid. Thus, we are forced to recognize that the strains in a solid cannot, in general, be described solely as *elongations* but may also include *twists.* Further, in the case referred to, the external stresses applied to the body are *couples.* It follows that the internal stresses may also be of the same nature. In other words, the stresses in an elastic solid cannot be assumed to be exclusively in the nature of *tractive forces* but may also include *torques.*

The arguments in the classical theory of elasticity by which the familiar result quoted in the opening sentence of the paper are derived may be summed up briefly as follows: that it is sufficient to consider the case of homogeneous strains; that any homogeneous strain may be analysed into a "pure strain" and a rotation and that the latter should be ignored in formulating the stress-strain relationships; and finally that the tractive forces assumed to act on elements of area in the solid are so related that no torques tending to rotate the volume-elements of the solid are present. Everyone of these statements is at variance with the considerations set forth above. It follows that the argument with all its consequences is unacceptable.

3. FORMULATION OF THE THEORY

If now we denote by u_x, u_y, u_z the three components of the displacements of a point (x, y, z) of the material and by $u_x + u_x'$, $u_y + u_y'$, $u_z + u_z'$ the corresponding displacements of a neighbouring point situated at $(x + x', y + y', z + z')$, then it is a well-known result that the strains in the neighbourhood of the point (x, y, z) can be represented by the scheme of equations

$$\begin{aligned} u_x' &= u_{xx}x' + u_{xy}y' + u_{xz}z' \\ u_y' &= u_{yx}x' + u_{yy}y' + u_{yz}z' \\ u_z' &= u_{zx}x' + u_{zy}y' + u_{zz}z' \end{aligned} \tag{1}$$

where u_{xy} stands, for brevity, for the differential coefficient $\frac{\partial u_x}{\partial y}$

In view of what has been said in the previous section, all the nine components of strain figuring in the equations (1) are required for a complete specification of the deformations in which rotations are not ignored. Then the changes in the state of a volume element contemplated in (1) can be analysed into (i) changes of volume, (ii) changes in shape not involving rotations or alterations of volume, and (iii) rotations.

Likewise, the stresses in the interior of the solid require nine components for their full specification. Denoting by $T_{x\nu}$, $T_{y\nu}$ and $T_{z\nu}$ the components of the tractive forces parallel to the three axes of co-ordinates on any elementary area whose normal has a specified direction ν, these tractions are related to the stresses acting on the three co-ordinate planes by means of the relations

$$\begin{aligned} T_{x\nu} &= T_{xx}\cos(x,\nu) + T_{xy}\cos(y,\nu) + T_{xz}\cos(z,\nu) \\ T_{y\nu} &= T_{yx}\cos(x,\nu) + T_{yy}\cos(y,\nu) + T_{yz}\cos(z,\nu) \\ T_{z\nu} &= T_{zx}\cos(x,\nu) + T_{zy}\cos(y,\nu) + T_{zz}\cos(z,\nu) \end{aligned} \tag{2}$$

As mentioned earlier, the three components of the angular momenta of any volume element will not vanish in dynamic experiments or for heterogeneous strains involving rotations and which accordingly involve torques. We therefore retain all the nine stress components in our formulation and do not make the usual reduction in their number from nine to six.

At this stage, we introduce a slight change in notation which enables us to pass on from symbols with double subscripts to symbols involving a single suffix only. We use for the stress components

$T_{xx}\ T_{yy}\ T_{zz}\ T_{yz}\ T_{zy}\ T_{zx}\ T_{xz}\ T_{xy}\ T_{yx}$ the symbols

$T_1\ T_2\ T_3\ T_4\ T_5\ T_6\ T_7\ T_8\ T_9$ respectively and similarly write the strain variables

$u_{xx}\ u_{yy}\ u_{zz}\ u_{yz}\ u_{zy}\ u_{zx}\ u_{xz}\ u_{xy}\ u_{yx}$ as

$u_1\ u_2\ u_3\ u_4\ u_5\ u_6\ u_7\ u_8\ u_9$ respectively.

With this notation the stress-strain relations take a neat form. Since the stresses in the solid are dependent on the strain produced in the solid, the stress components can be expanded as a power series in the strain variables. If we measure the stresses from an initial state corresponding to the undeformed condition of the solid and consider infinitesimal strains only, so that squares and higher powers of the strain variables can be neglected in comparison with first order terms, the stresses at any point of the solid are linear functions of the strain components at that point. The stress-strain relations can then be expressed as

$$T_m = \sum_{n=1}^{9} d_{mn}\, u_n \quad (m = 1, 2, \ldots 9) \tag{3}$$

and these involve 81 constants. Here the constant d_{mn} relates the stress T_m to the strain u_n and is the ratio of the two for a deformation in which all strain components other than u_n vanish.

The 81 constants figuring in (3) are not all independent, but reduce in the first instance to forty-five for all solids in view of the relations

$$d_{mn} = d_{nm} \; (m, n = 1, 2 \ldots .9) \tag{4}$$

These relations follow from the well-known theorem of reciprocity relating forces and the corresponding displacements in dynamical systems.[4] The reciprocity relations further enable us to write down the expression for the deformation energy per unit volume in the neighbourhood of any point and this is given by

$$U = \tfrac{1}{2} \sum_{m=1}^{9} T_m u_m$$

or

$$2U = \sum_m \sum_n d_{mn} u_m u_n \tag{5}$$

4. THE THREE ELASTIC CONSTANTS OF ISOTROPIC SOLIDS

The isotropic nature of a body results in a great reduction of the number of independent constants occurring in the stress-strain relationships. Most of these constants in fact are zero and the others become equal to each other in sets for isotropic materials. Some of these relations can be deduced easily from simple symmetry considerations, without going into the full details of the analytic apparatus needed to derive them. For example, the cubic symmetry possessed by the material endows it with the same property for all the three directions of the axes of co-ordinates and therefore the stress-relationships should remain invariant under any permutation of the symbols x, y, z in both the strain variables (u_{xy}) as well as in the stress components T_{xy}. We thus get

$$\begin{aligned} d_{11} &= d_{22} = d_{33}; \\ d_{12} &= d_{23} = d_{31}; \\ d_{45} &= d_{67} = d_{89}; \\ d_{44} &= d_{55} = d_{66} = d_{77} = d_{88} = d_{99} \end{aligned} \tag{6}$$

Again, the operations of reflection about any plane in space do not produce observable changes in the properties of isotropic bodies. In the simple case of a reflection about the xy plane, the z co-ordinate of any point changes its sign while its x and y co-ordinates are unaffected. Hence all the strain components like u_{yz} (u_4), u_{zy} (u_5), u_{zx} (u_6), u_{xz} (u_7) in which z

occurs *once* only as a suffix change their sign whereas the other strain variables are unaltered. If therefore we substitute these new values of the strain variables in the energy expression and equate it to the original one, we get

$$\begin{aligned} d_{14} = d_{15} = d_{16} = d_{17} = d_{24} = d_{25} = d_{26} = d_{27} = d_{34} = d_{35} \\ = d_{36} = d_{37} = d_{48} = d_{49} = d_{58} = d_{59} = d_{68} = d_{69} = d_{78} = d_{79} = 0 \end{aligned} \tag{7}$$

Similarly by considering reflections about the planes $x = 0$, and $y = 0$, we could show that

$$d_{18} = d_{19} = d_{28} = d_{29} = d_{38} = d_{39} = d_{46} = d_{47} = d_{56} = d_{57} = 0 \tag{8}$$

Simple symmetry considerations thus reduce the number of non-zero and independent constants to four. Even these constants (*i.e.*) d_{11}, d_{12}, d_{44} and d_{45} however are not independent but are connected to each other by means of a linear relation. To obtain this, we use the special symmetry property possessed by isotropic solids alone, namely invariance in behaviour under all rotations in space. Considering a rotation about the z-axis through an angle θ, this operation changes the strain variables into a new set of quantities u_1', u_2'.....u_9' related to the original ones in accordance with the following scheme:

$$\begin{aligned} u_1' &= u_1 \cos^2\theta + (u_8 + u_9) \sin\theta \cos\theta + u_2 \sin^2\theta; \\ u_2' &= u_1 \sin^2\theta - (u_8 + u_9) \sin\theta \cos\theta + u_2 \cos^2\theta; \\ u_3' &= u_3; \\ u_4' &= u_4 \cos\theta - u_7 \sin\theta; \\ u_5' &= u_5 \cos\theta - u_6 \sin\theta; \\ u_6' &= u_5 \sin\theta + u_6 \cos\theta; \\ u_7' &= u_4 \sin\theta + u_7 \cos\theta; \\ u_8' &= (u_2 - u_1) \sin\theta \cos\theta + (u_8 \cos^2\theta - u_9 \sin^2\theta); \\ u_9' &= (u_2 - u_1) \sin\theta \cos\theta + (u_9 \cos^2\theta - u_8 \sin^2\theta). \end{aligned} \tag{9}$$

Hence under the operation of a rotation about the z-axis by an amount θ, the energy expression (5) changes into

$$\begin{aligned} 2U = d_{11}u_3^2 &+ d_{11}\{u_1 \cos^2\theta + (u_8 + u_9) \sin\theta \cos\theta + u_2 \sin^2\theta\}^2 \\ &+ d_{11}\{u_1 \sin^2\theta - (u_8 + u_9) \sin\theta \cos\theta + u_2 \cos^2\theta\}^2 \\ &+ 2d_{12}(u_1 + u_2)\, u_3 \end{aligned}$$

$$
\begin{aligned}
&+ 2d_{12}\{u_1\cos^2\theta + (u_8+u_9)\sin\theta\cos\theta + u_2\sin^2\theta\}\\
&\qquad \times\{u_1\sin^2\theta - (u_8+u_9)\sin\theta\cos\theta + u_2\cos^2\theta\}\\
&+ d_{44}\{(u_2-u_1)\sin\theta\cos\theta + u_8\cos^2\theta - u_9\sin^2\theta\}^2\\
&+ d_{44}\{(u_2-u_1)\sin\theta\cos\theta + u_9\cos^2\theta - u_8\sin^2\theta\}^2\\
&+ d_{44}(u_4^2+u_5^2+u_6^2+u_7^2) + 2d_{45}(u_4u_5+u_6u_7)\\
&+ 2d_{45}\{(u_2-u_1)\sin\theta\cos\theta + u_8\cos^2\theta - u_9\sin^2\theta\}\\
&\qquad \times\{(u_2-u_1)\sin\theta\cos\theta + u_9\cos^2\theta - u_8\sin^2\theta\} \qquad (10)
\end{aligned}
$$

Comparing this with the expression

$$
\begin{aligned}
2U = {} & d_{11}(u_1^2+u_2^2+u_3^2) + 2d_{12}(u_2u_3+u_3u_1+u_1u_2)\\
&+ d_{44}(u_4^2+u_5^2+u_6^2+u_7^2+u_8^2+u_9^2)\\
&\qquad + 2d_{45}(u_4u_5+u_6u_7+u_8u_9) \qquad (11)
\end{aligned}
$$

we get

$$d_{11} = d_{12} + d_{44} + d_{45} \qquad (12)$$

Rotations about the x- and y-axes through any angle should also necessarily lead to the same equation (12). A general rotation about any axis can be effected by a superposition of rotations through different angles about the x, y and z axes. We have thus exhausted all the symmetry operations permissible for isotropic solids. It follows therefore that *the elastic behaviour of isotropic solids requires three independent constants for its description, which may be denoted by* d_{11}, d_{12} *and* d_{44}.

5. RELATIONS BETWEEN THE VARIOUS CONSTANTS

With the aid of the relations (6), (7), (8) and (12), the stress-strain relationships described by (12) can be rewritten. The expressions for the three stretches T_1, T_2 and T_3 become

$$
\begin{aligned}
T_1 &= d_{11}u_1 + d_{12}(u_2+u_3)\\
T_2 &= d_{11}u_2 + d_{12}(u_3+u_1) \qquad (13)\\
T_3 &= d_{11}u_3 + d_{12}(u_1+u_2)
\end{aligned}
$$

whereas the shearing stresses are given by

$$
\begin{aligned}
T_4 &= d_{44}u_4 + (d_{11}-d_{12}-d_{44})\,u_5\\
T_5 &= d_{44}u_5 + (d_{11}-d_{12}-d_{44})u_4 \qquad (14)
\end{aligned}
$$

and four similar equations.

We shall now evaluate some of the important elastic constants, *viz.*, the compressibility or bulk modulus, Young's modulus and Poisson's ratio in terms of these new constants. Consider first the case of a uniform hydrostatic pressure acting at all points on the surface of the body. The state of stress produced by such a compression of the solid is described by $T_1 = T_2 = T_3 = -p$; $T_4 = T_5 = \ldots = T_9 = 0$. Hence adding all the three equations in (13), we get

$$p = \tfrac{1}{3}(d_{11} + 2d_{12})\Delta \tag{15}$$

where Δ denotes the cubical compression $-(u_1 + u_2 + u_3)$. The bulk modulus therefore is given by

$$k = \tfrac{1}{3}(d_{11} + 2d_{12}) \tag{16}$$

Similarly by considering the case of an isotropic body in the form of a cylindrical rod subjected to a tension T which is uniform over its plane ends, we could show that the Young's modulus E and Poisson's ratio σ are related to d_{11} and d_{12} in accordance with the equations

$$E = \frac{(d_{11} + 2d_{12})\,(d_{11} - d_{12})}{(d_{11} + d_{12})} \tag{17}$$

$$\sigma = \frac{d_{12}}{(d_{11} + d_{12})} \tag{18}$$

These expressions are in the same form as the corresponding ones for k, E and σ of the classical theory expressed in terms of the well-known constants c_{11} and c_{12}. The relations among the Young's modulus, bulk modulus, and Poisson's ratio are therefore the same both in the two-constant as well as in the three-constant theories. We emphasize the fact that all the three equations (16), (17) and (18) contain the constants d_{11} and d_{12} only, and none of them involves d_{44} explicitly. This is because all these modulii are determinable from static homogeneous strains alone, whereas d_{44}, being a constant involving rotations of the volume elements requires experiments involving twists for its evaluation.

It may be pointed out here that the relation (12) may be derived directly from very simple considerations. A cube which is subject to normal tractions on a pair of opposing faces and normal pressures of equal magnitude on an adjacent pair of faces would suffer no change of volume, but would expand and contract respectively in the direction of the two normals to the faces by an amount of which $(d_{11} - d_{12})$ is a measure. Likewise, if a pair of opposing faces of a cube are subject to tangential tractions forming a couple and an adjacent pair also subject to tangential tractions which form a balancing couple, the cube would suffer no change of volume but would undergo a change of shape without rotation of which $(d_{44} + d_{45})$ is readily seen to be a measure. The two systems of stresses and the resulting strains can readily be shown to be equivalent and it follows that $(d_{11} - d_{12}) = (d_{44} + d_{45})$.

6. VELOCITY OF PROPAGATION OF WAVES IN THE SOLID

In the absence of body forces, the general equations of motion of an elastic body are given by

$$\rho \frac{\partial^2 u_x}{\partial t^2} = \frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \frac{\partial T_{xz}}{\partial z} ;$$

$$\rho \frac{\partial^2 u_y}{\partial t^2} = \frac{\partial T_{yx}}{\partial x} + \frac{\partial T_{yy}}{\partial y} + \frac{\partial T_{yz}}{\partial z}$$

$$\rho \frac{\partial^2 u_z}{\partial t^2} = \frac{\partial T_{zx}}{\partial x} + \frac{\partial T_{zy}}{\partial y} + \frac{\partial T_{zz}}{\partial z} \tag{19}$$

where ρ is the density of the material. For an isotropic solid, the stress-strain relations are given by equations (13) and (14). Adopting once again the primitive notation of writing differential coefficients $\partial u_x/\partial x, \ldots \partial u_y/\partial z \ldots$ for the strain components $u_1, \ldots u_4 \ldots$ etc., we get on substituting (13) and (14) in (19) that

$$\rho \frac{\partial^2 u_x}{dt^2} = (d_{11} - d_{12}) \nabla^2 u_x + d_{12} \frac{\partial \varDelta}{dx}$$
$$+ (d_{11} - d_{12} - d_{44}) \left\{ \frac{\partial}{\partial z}\left(\frac{\partial u_z}{\partial x} - \frac{\partial u_x}{\partial z}\right) - \frac{\partial}{\partial y}\left(\frac{\partial u_x}{\partial y} - \frac{\partial u_y}{\partial x}\right) \right\} \tag{20}$$

and two similar equations for the displacements in the y and z directions. In the above, $\varDelta$ denotes the dilatation

$$\left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z}\right)$$

or simply divergence **u** where **u** is the vector whose components parallel to the axes are u_x, u_y and u_z respectively. The three equations in (20) can be combined together and written as a single equation in the form

$$\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = (d_{11} - d_{12}) \nabla^2 \mathbf{u} + d_{12} \operatorname{grad} \operatorname{div} \mathbf{u}$$
$$+ (d_{11} - d_{12} - d_{44}) \operatorname{curl} \operatorname{curl} \mathbf{u} \tag{21}$$

Since curl curl $\mathbf{u} = \operatorname{grad} \operatorname{div} \mathbf{u} - \nabla^2 \mathbf{u}$, (21) alternatively becomes

$$\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = d_{44} \nabla^2 \mathbf{u} + (d_{11} - d_{44}) \operatorname{grad} \operatorname{div} \mathbf{u} \tag{22}$$

We shall now take the *divergence* of both sides of (22). This gives us

$$\rho \frac{\partial^2 \Delta}{\partial t^2} = d_{11} \nabla^2 \Delta \tag{23}$$

The above is in fact the equation of wave propagation in the medium. *Compressional waves are therefore propagated in the solid with the velocity* $\sqrt{d_{11}/\rho}$.

Performing next the operation of *curl* on both sides of (22), and writing ω for curl **u**, one gets

$$\rho \frac{\partial^2 \omega}{\partial t^2} = d_{44} \nabla^2 \omega \tag{24}$$

equation (24) therefore shows *that equivoluminal or distortional waves are propagated in the medium with the velocity* $\sqrt{d_{44}/\rho}$.

It will be noticed that the velocities of propagation of both the longitudinal and transverse waves determine the constants d_{11} and d_{44} only, and do not involve the constant d_{12} at all. On the other hand, d_{44} does not make its appearance in the modulii determinable by static homogeneous strains.

7. SUMMARY

The notions regarding stresses and strains adopted in the classical theory of elasticity are critically examined. The neglect of rotations in the analysis of strain and of torques in the analysis of stress characteristic of that theory is shown to be unjustifiable. A reformulation of the stress-strain relationships taking account of these factors leads to the result that an isotropic solid has *three* independent elastic constants and not *two* as hitherto supposed. Two of these three constants determine the velocities of propagation respectively of longitudinal and transverse waves in the solid. The latter of them does not make its appearance in any observations involving only homogeneous strains nor does it appear in the formulae for the bulk modulus, Young's modulus and Poisson's ratio obtained in the present paper.

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ON THE THEORY OF THE ELASTICITY OF CRYSTALS

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1. INTRODUCTION

THE branch of mathematical physics known as the theory of the elasticity of solids is based on certain notions regarding elastic stresses and strains which have been accepted doctrine for many years. It is therefore rather surprising to find that those notions are not sustainable and that the theory based on them has to be laid aside in favour of a stricter formulation. The need for such revision was broadly indicated in a recent publication in these *Proceedings* by the present authors (1955); but in view of the importance of the matter, the present paper is prefaced by a clearer and more precise exposition of the necessity for a revision of the classical theory.

Our recent paper dealt with the case of isotropic solids in a formal manner, considering them as homogeneous substances exhibiting the highest possible symmetry in their elastic properties. Usually, however, the so-called isotropic solids are merely polycrystalline aggregates, and a discussion of their elastic behaviour should therefore properly be based on a consideration of the nature and properties of such aggregates. This is a task which we hope to be able to address ourselves in the not-too-distant future. In the present paper we shall consider the case of truly homogeneous but anisotropic solids, in other words, crystals. The subject will be dealt with from the phenomenological standpoint since this proves to be entirely adequate. We may remark, however, that the conclusions reached are in complete accord with the results of the atomistic approach to the theory of elasticity as developed both from the static and dynamic standpoints in a paper by one of us (Viswanathan, 1954) and illustrated by a detailed discussion of a particular case of great interest, *viz.*, diamond.

2. THE PHYSICAL CHARACTERS OF ELASTIC STRESS AND STRAIN

A solid body may be defined as a material in which the volume elements retain their relative positions and orientations alike when the solid is at rest and when it is in a state of movement, translatory or rotatory, as the case may be. Elastic stresses and strains arise when the situation thus described is departed from to ever so small an extent. Hence, it is evident that the theory of elasticity is concerned with changes in the relative positions and/or the relative orientations of the volume elements of the solid, in other words, with linear displacements and/or angular movements of the volume elements with respect to their neighbours. This is illustrated by the familiar examples of a straight bar which is stretched or bent or twisted by the application of appropriate external stresses. From the general considerations indicated above as well as from the particular examples mentioned, it is clear that only in very special cases would elastic strains be such that a straight line drawn through the solid in any direction in the unstrained condition remains straight in the strained state, suffering only elongations or contractions. In the general case, and inevitably so when the strains involve differential rotations, a straight line in the unstrained condition would be curved in the strained state, and such curvature cannot possibly be ignored in the theory. Hence, it is clear that we have, in general, to consider strains and stresses which are heterogeneous, in other words, strains and stresses whose specifications vary from point to point within the solid. These variations necessarily enter into the equations of equilibrium in the static state and into the equations of motion in dynamic behaviour.

3. ANALYTICAL SPECIFICATION OF STRESSES AND STRAINS

The mathematical theory of elasticity proceeds on the basis that the strains and stresses in the interior of the solid can be expressed in terms of the movements of the smallest possible elements of volume into which it can be imagined to be subdivided and of the forces acting on them. If the volume elements be small enough, their movements can be described completely in terms of the three positional co-ordinates of each element and their variations. Likewise, when the elements of volume are small enough, the interactions between each element and its neighbours can be expressed in terms of tractive forces alone, it being then clearly unnecessary to introduce anything in the nature of couples or torques. On the basis of these ideas, the state of strain in the solid at any given point can be expressed by resolving the displacement of the elementary volume originally located at such point along three mutually perpendicular directions and differentiating these three components of displacement again along each of the three axes in turn. We thus obtain the nine components of the strain tensor. Likewise, for specifying the state of stress to which the volume element is subject, we consider the tractive forces acting on an infinitesimal area drawn respectively normal to the three co-ordinate planes in turn at the position of the element and then again resolve these tractive forces along each of the three co-ordinate axes. We thus obtain the nine components of the stress tensor.

It is evident that this method of representation of the stresses and strains uniquely defines the state of the solid at any point and also enables us to determine whether the element of volume would or would not remain in equilibrium. If the components of stress do not vary along any of the three axes, the element would necessarily remain at rest. If, on the other hand, the stress components vary, their differential coefficients along the normals to the planes on which they act gives us a measure of the forces on the volume element in their respective directions. Adding up the three forces along each axis thus evaluated and putting their sums separately equal to zero, we obtain the conditions of equilibrium.

The well-known and familiar treatments given in the standard treatises proceed on the basis that the components of the strain and stress tensors are both reducible in number from nine to six. The arguments on which the reduction in number from nine to six of the components of strain is based may be summarised by the statement that the elastic strains can be separated into what are called " pure strains " and " rotations," and that the latter can be ignored. That this argument is unsustainable will be evident at once from the remarks made in the foregoing section regarding the physical nature of elastic strains. We have, in general, to take account of both differential displacements and differential rotations and it is therefore not permissible to eliminate the rotational parts of the strain, these being physically quite as real as the irrotational parts.

The arguments justifying the reduction in the number of the independent components of stress from nine to six are based upon the idea that equilibrium would be possible only if the angular momenta of the tractions taken about each of the three co-ordinate axes in turn cancel each other out. That this idea is misconceived will be evident from the remarks already made earlier regarding the conditions necessary for equilibrium. In the case of homogeneous strains, the tractive forces acting on each volume element necessarily balance each other. In the case of heterogeneous strains, the conditions of equilibrium can be expressed in terms of the differential coefficients of the stress components along the normals to the planes on which they act, as already explained. In either case, if the equilibrium conditions for each volume element of the solid are satisfied, then the solid as a whole necessarily remains in equilibrium; *vice versa*, if the external stresses acting on the solid are such that it remains as a whole in equilibrium, the elastic stresses would everywhere necessarily be such as to ensure equilibrium of the individual volume elements. It follows that no general relations connecting the magnitude of the tensor components and enabling their number to be reduced from nine to six can be derived from considerations based on the conditions for equilibrium.

We may summarise our conclusions by stating that neither the reduction of the strain components nor the reduction of the stress components in number from nine to six has any theoretical justification; a correct and complete theory of elasticity has necessarily to take all the nine components of the stress and strain tensors into consideration.

4. THE STRESS-STRAIN RELATIONSHIPS

Writing the nine components of the strain tensor as

$$\begin{matrix} u_{xx} & u_{yy} & u_{zz} & u_{yz} & u_{zy} & u_{zx} & u_{xz} & u_{xy} & u_{yx} \\ u_1 & u_2 & u_3 & u_4 & u_5 & u_6 & u_7 & u_8 & u_9 \end{matrix}$$

and likewise the nine components of the stress tensor as

$$\begin{matrix} \mathrm{T}_{xx} & \mathrm{T}_{yy} & \mathrm{T}_{zz} & \mathrm{T}_{yz} & \mathrm{T}_{zy} & \mathrm{T}_{zx} & \mathrm{T}_{xz} & \mathrm{T}_{xy} & \mathrm{T}_{yx} \\ \mathrm{T}_1 & \mathrm{T}_2 & \mathrm{T}_3 & \mathrm{T}_4 & \mathrm{T}_5 & \mathrm{T}_6 & \mathrm{T}_7 & \mathrm{T}_8 & \mathrm{T}_9 \end{matrix}$$

the stress-strain relations can be expressed in the general form

$$\mathrm{T}_m = \sum_{n=1}^{9} d_{mn} u_n \qquad (m = 1, 2, \ldots 9) \qquad (1)$$

and involve *81* constants. Here the constant d_{mn} relates the stress T_m to the strain u_n and is the ratio of the two for a deformation in which all components other than u_n vanish.

The *81* constants figuring in (1) are not all independent, but reduce in the first instance to forty-five for all solids in view of the relations

$$d_{mn} = d_{nm} \qquad (m, n = 1, 2 \ldots 9) \qquad (2)$$

The above relations follow from the well-known theorem of reciprocity relating forces and the corresponding displacements of dynamical systems. The reciprocity relations further enable us to write down the expression for the deformation energy per unit volume in the neighbourhood of any point and this is given by

$$\mathrm{U} = \tfrac{1}{2} \sum_{m=1}^{9} \mathrm{T}_m u_m$$

or

$$2\mathrm{U} = \sum_{m} \sum_{n} d_{mn} u_m u_n \qquad (3)$$

Thus in the general case of a completely anisotropic solid, we have forty-five elastic constants instead of the *21* contemplated by the classical theory.

TABLE I

Crystal System	Point Group	No. of Elastic Constants	
		I	II
Triclinic	All	21	45
Monoclinic	All	13	25
Orthorhombic	All	9	15
Tetragonal	C_4 (4) S_4 ($\bar{4}$) C_{4h}($4/m$)	7	13
	D_4 (422) C_{4v}($4mm$) $S_{4v}=D_{2d}$ ($\bar{4}2m$) D_{4h} ($4/m2/m2/m$)	6	9
Trigonal	C_3 (3) S_6 ($\bar{3}$)	7	15
	D_3 (32) C_{3v} ($3m$) D_{3d} ($\bar{3}2/m$)	6	10
Hexagonal	C_6 (6) C_{3h} ($\bar{6}$) C_{6h} ($6/m$)	5	11
	D_6 (622) C_{6v} ($6mm$) D_{3h} ($\bar{6}m2$) D_{6h} ($6/m2/m2/m$)	5	8
Cubic	T (23) T_h ($2/m\bar{3}$)	3	5
	O (432) T_d ($\bar{4}3m$) O_h ($4/m\bar{3}2/m$)	3	4

The number of independent elastic constants which is forty-five for a completely anisotropic solid diminishes in the case of solids possessing the various elements of symmetry characteristic of the different crystal classes, coming down to four for crystals of the classes T_d, O and O_h. The *number* of surviving constants in each symmetry class can be computed in an elegant fashion by adopting the group-theoretical method developed by Bhagavantam (1949). One is concerned in the present case with a linear relationship between nine stress components and nine strain components, the constants of proportionality being the elastic constants (matrix d_{mn}). Further, the elements of the " elastic constants 9 by 9 matrix " satisfy the relation $d_{mn} = d_{nm}$. With these restrictions, the transformation matrix for the elastic constants can be written out and the corresponding character can be deduced. This comes out as

$$\chi_j' (\mathrm{R}) = 16c^4 \pm 16c^3 + 8c^2 \pm 4c + 1 \tag{4}$$

where $c = \cos \phi$, R is a symmetry operation and ϕ, the rotation. The *plus* sign is used for proper rotations, and *minus* for an improper one. The corresponding character for the 21-constant theory is

$$\chi_j' (\mathrm{R}) = 16c^4 \pm 8c^3 - 4c^2 + 1 \tag{5}$$

Table I gives the number of independent constants according to the two formulæ for each symmetry class, while the constants that survive and those that vanish are exhibited in detail for the various cases in Tables II to XII. A comparison of these tables amongst themselves will enable the reader to realise how the existence of common symmetry elements results in the appearance of common features in the Tables of elastic constants. For example, all the twenty constants that vanish for monoclinic crystals also

TABLE II

Triclinic (C_1, C_i)

d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}	d_{17}	d_{18}	d_{19}
	d_{22}	d_{23}	d_{24}	d_{25}	d_{26}	d_{27}	d_{28}	d_{29}
		d_{33}	d_{34}	d_{35}	d_{36}	d_{37}	d_{38}	d_{39}
			d_{44}	d_{45}	d_{46}	d_{47}	d_{48}	d_{49}
				d_{55}	d_{56}	d_{57}	d_{58}	d_{59}
					d_{66}	d_{67}	d_{68}	d_{69}
45 constants						d_{77}	d_{78}	d_{79}
							d_{88}	d_{89}
								d_{99}

TABLE III

Monoclinic (C_s, C_2, C_{2h})—diad axis $\parallel z$, plane of reflection $\perp$ to z

d_{11}	d_{12}	d_{13}	0	0	0	0	d_{18}	d_{19}
	d_{22}	d_{23}	0	0	0	0	d_{28}	d_{29}
		d_{33}	0	0	0	0	d_{38}	d_{39}
			d_{44}	d_{45}	d_{46}	d_{47}	0	0
				d_{55}	d_{56}	d_{57}	0	0
					d_{66}	d_{67}	0	0
						d_{77}	0	0
							d_{88}	d_{89}
								d_{99}

25 constants

TABLE IV

Orthorhombic (C_{2v}, D_2, D_{2h})

d_{11}	d_{12}	d_{13}	0	0	0	0	0	0
	d_{22}	d_{23}	0	0	0	0	0	0
		d_{33}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{55}	0	0	0	0
					d_{66}	d_{67}	0	0
						d_{77}	0	0
							d_{88}	d_{89}
								d_{99}

15 constants

TABLE V

Tetragonal (C_4, S_4, C_{4h})—tetrad axis $\parallel z$

d_{11}	d_{12}	d_{13}	0	0	0	0	d_{18}	d_{19}
	d_{11}	d_{13}	0	0	0	0	$-d_{19}$	$-d_{18}$
		d_{33}	0	0	0	0	d_{38}	$-d_{38}$
			d_{44}	d_{45}	d_{46}	0	0	0
				d_{55}	0	$-d_{46}$	0	0
					d_{55}	d_{45}	0	0
						d_{44}	0	0
							d_{88}	d_{89}
								d_{88}

13 constants

TABLE VI

Tetragonal (C_{4v}, S_{4v}, D_4, D_{4h})—tetrad axis || z

d_{11}	d_{12}	d_{13}	0	0	0	0	0	0
	d_{11}	d_{13}	0	0	0	0	0	0
		d_{33}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{55}	0	0	0	0
					d_{55}	d_{45}	0	0
						d_{44}	0	0
							d_{88}	d_{89}
								d_{88}

9 constants

TABLE VII

Trigonal (C_3, S_6)—triad axis || z

d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}	d_{17}	d_{18}	$-d_{18}$
	d_{11}	d_{13}	$-d_{14}$	$-d_{15}$	$-d_{16}$	$-d_{17}$	d_{18}	$-d_{18}$
		d_{33}	0	0	0	0	d_{38}	$-d_{38}$
			d_{44}	d_{45}	d_{46}	0	d_{17}	$-d_{17}$
				d_{55}	0	$-d_{46}$	$-d_{16}$	$-d_{16}$
					d_{44}	d_{45}	d_{15}	d_{15}
						d_{55}	d_{14}	d_{14}
							d_{88}	d_{89}
								d_{88}

$d_{88}=d_{11}-d_{12}-d_{89}$

15 constants

TABLE VIII

Trigonal (D_3, D_{3d}, C_{3v})—triad axis || z

d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	0	0	0	0
	d_{11}	d_{13}	$-d_{14}$	$-d_{15}$	0	0	0	0
		d_{33}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{55}	0	0	0	0
					d_{44}	d_{45}	d_{15}	d_{15}
						d_{55}	d_{14}	d_{14}
							d_{88}	d_{89}
								d_{88}

$d_{88}=d_{11}-d_{12}-d_{89}$

10 constants

TABLE IX

Hexagonal (C_{3h}, C_6, C_{6h})—hexad axis $\parallel z$

d_{11}	d_{12}	d_{13}	0	0	0	0	d_{18}	$-d_{18}$
	d_{11}	d_{13}	0	0	0	0	d_{18}	$-d_{18}$
		d_{33}	0	0	0	0	d_{38}	$-d_{38}$
			d_{44}	d_{45}	d_{46}	0	0	0
				d_{55}	0	$-d_{46}$	0	0
					d_{44}	d_{45}	0	0
						d_{55}	0	0
							d_{88}	d_{89}
								d_{88}

$d_{88}=d_{11}-d_{12}-d_{89}$

11 constants

TABLE X

Hexagonal (D_{3h}, C_{6v}, D_6, D_{6h})—hexad axis $\parallel z$

d_{11}	d_{12}	d_{13}	0	0	0	0	0	0
	d_{11}	d_{13}	0	0	0	0	0	0
		d_{33}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{55}	0	0	0	0
					d_{44}	d_{45}	0	0
						d_{55}	0	0
							d_{88}	d_{89}
								d_{88}

$d_{88}=d_{11}-d_{12}-d_{89}$

8 constants

TABLE XI

Cubic (T, T_h)

d_{11}	d_{12}	d_{12}	0	0	0	0	0	0
	d_{11}	d_{12}	0	0	0	0	0	0
		d_{11}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{55}	0	0	0	0
					d_{44}	d_{45}	0	0
						d_{55}	0	0
							d_{44}	d_{45}
								d_{55}

5 constants

TABLE XII

Cubic (T_d, O, O_h)								
d_{11}	d_{12}	d_{12}	0	0	0	0	0	0
	d_{11}	d_{12}	0	0	0	0	0	0
		d_{11}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{44}	0	0	0	0
					d_{44}	d_{45}	0	0
4 constants						d_{44}	0	0
							d_{44}	d_{45}
								d_{44}

disappear in the orthorhombic, tetragonal and cubic systems. Likewise, all the thirty constants that vanish for orthorhombic crystals vanish also for those tetragonal crystals which possess three mutually perpendicular diad axes and for all cubic crystals. A noteworthy feature is that the cubic crystals which exhibit a four-fold axis of symmetry have only four different elastic constants, whereas those cubic crystals that do not exhibit this feature have five constants different from each other.

5. WAVE-PROPAGATION IN CRYSTALS

The general equations of motion of an elastic solid are given by

$$\begin{aligned}
\rho\frac{\partial^2 u_x}{\partial t^2} &= \frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \frac{\partial T_{xz}}{\partial z} \\
\rho\frac{\partial^2 u_y}{\partial t^2} &= \frac{\partial T_{yx}}{\partial x} + \frac{\partial T_{yy}}{\partial y} + \frac{\partial T_{yz}}{\partial z} \\
\rho\frac{\partial^2 u_z}{\partial t^2} &= \frac{\partial T_{zx}}{\partial x} + \frac{\partial T_{zy}}{\partial y} + \frac{\partial T_{zz}}{\partial z}
\end{aligned} \tag{6}$$

where ρ is the density of the medium and $T_{xx}, \ldots$ are the stress components. If the solid is in equilibrium, the quantities on the left-hand side of these equations, representing the acceleration of an unit volume element, will vanish and we get the conditions of equilibrium of the solid.

To evaluate the velocity of propagation of waves in the solid in any given direction, we first seek solutions of the above equations which are in the form of plane waves of the type

$$\mathbf{u} = A \exp i\,\frac{2\pi}{\lambda}(\nu t - \mathbf{e}\cdot\mathbf{r}) \tag{7}$$

Denoting the components of A in the directions of the co-ordinate axes by A^x, A^y, A^z and using once again the four-suffixed symbols for the elastic constants, we now get on substitution of (7) in (6) that

$$\rho v^2 A^x = \sum_{\bar{x}} \sum_{y\bar{y}} d_{x\bar{x},\, y\bar{y}}\, e_{\bar{x}}\, e_{\bar{y}}\, A^y \tag{8}$$

and two similar equations for the y and z components.

For a wave progressing in the direction (lmn) equations (8) can alternatively be written as

$$\begin{aligned} (\lambda_{xx} - \rho v^2)\, A^x + \lambda_{xy}\, A^y + \lambda_{xz}\, A^z &= 0 \\ \lambda_{xy}\, A^x + (\lambda_{yy} - \rho v^2)\, A^y + \lambda_{yz}\, A^z &= 0 \\ \lambda_{xz}\, A^x + \lambda_{yz}\, A^y + \lambda_{zz}\, A^z &= 0 \end{aligned} \tag{9}$$

where λ_{xx}, λ_{xy}.... are given by the scheme

$$\begin{pmatrix} \lambda_{xx} \\ \lambda_{yy} \\ \lambda_{zz} \\ \lambda_{yz} \\ \lambda_{zx} \\ \lambda_{xy} \end{pmatrix} = \begin{pmatrix} d_{11} & d_{88} & d_{77} & 2d_{78} & 2d_{17} & 2d_{18} \\ d_{99} & d_{22} & d_{44} & 2d_{24} & 2d_{49} & 2d_{29} \\ d_{66} & d_{55} & d_{33} & 2d_{35} & 2d_{36} & 2d_{56} \\ d_{69} & d_{25} & d_{34} & (d_{23} + d_{45}) & (d_{39} + d_{46}) & (d_{59} + d_{26}) \\ d_{16} & d_{58} & d_{37} & (d_{57} + d_{38}) & (d_{67} + d_{13}) & (d_{15} + d_{68}) \\ d_{19} & d_{28} & d_{47} & (d_{27} + d_{48}) & (d_{14} + d_{79}) & (d_{12} + d_{89}) \end{pmatrix} \begin{pmatrix} l^2 \\ m^2 \\ n^2 \\ mn \\ nl \\ lm \end{pmatrix}$$

Equations (9) determine the velocities of propagation of the three types of waves in any direction for crystals of the triclinic system which possess no symmetry of structure at all. The number of constants figuring in the wave equations will diminish rapidly as we pass on to crystals of higher symmetry, and become only three for crystals of the T_d, O and O_h classes. We tabulate below the wave equations for the different classes of crystals taking into account of their symmetry.

I. *Monoclinic system* (C_s, C_2, C_{2h})—*diad axis parallel to the z-axis*

$$\begin{aligned} &(d_{11}l^2 + d_{88}\, m^2 + d_{77}n^2 + 2d_{18}\, lm - \rho v^2)\, A^x + \{d_{19}l^2 + d_{28}m^2 + d_{47}n^2 \\ &\qquad + (d_{12} + d_{89})\, lm\}\, A^y + \{(d_{38} + d_{57})\; mn + (d_{13} + d_{67})\, nl\}\, A^z = 0. \\ &\{d_{19}l^2 + d_{28}m^2 + d_{47}n^2 + (d_{12} + d_{89})\, lm\}\, A^x + (d_{99}l^2 + d_{22}m^2 + d_{44}n^2 \\ &\qquad + 2d_{29}lm - \rho v^2\}\, A^y + \{(d_{23} + d_{45})\, mn + (d_{39} + d_{46})\, nl\}\, A^z = 0. \\ &\{(d_{38} + d_{57})\, mn + (d_{13} + d_{67})\, nl\}\, A^x + \{(d_{23} + d_{45})\, mn + (d_{39} + d_{46}) nl\} \\ &\qquad A^y + (d_{66}l^2 + d_{55}m^2 + d_{33}\, n^2 + 2d_{56}lm - \rho v^2)\, A^z = 0. \end{aligned}$$

The wave equation contains *twenty* independent constants.

II. *Orthorhombic system* (C_{2v}, D_2, D_{2h}).

$$\begin{aligned}
&(d_{11}l^2 + d_{88}m^2 + d_{77}n^2 - \rho v^2)\,A^x + (d_{12} + d_{89})\,lm\,A^y \\
&\qquad + (d_{13} + d_{67})\,nl\,A^z = 0, \\
&(d_{12} + d_{89})\,lm\,A^x + (d_{99}\,l^2 + d_{22}m^2 + d_{44}n^2 - \rho v^2)\,A^y \\
&\qquad + (d_{23} + d_{45})\,mn\,A^z = 0. \\
&(d_{13} + d_{67})\,nl\,A^x + (d_{23} + d_{45})\,mn\,A^y + (d_{66}l^2 + d_{55}m^2 \\
&\qquad + d_{33}n^2 - \rho v^2)\,A^z = 0.
\end{aligned}$$

The wave-equations involve *twelve* distinct constants.

III. *Tetragonal* (C_4, S_4, C_{4h})—*tetrad axis parallel to the z-axis.*

$$\begin{aligned}
&\{d_{11}l^2 + d_{88}m^2 + d_{44}n^2 + 2d_{18}\,lm - \rho v^2\}\,A^x + \{d_{19}\,(l^2 - m^2) \\
&\qquad + (d_{12} + d_{89})\,lm\}\,A^y + \{(d_{38} - d_{46})\,mn + (d_{13} + d_{45})\,nl\}\,A^z = 0 \\
&\{d_{19}\,(l^2 - m^2) + (d_{12} + d_{89})\,lm\}\,A^x + \{d_{88}\,l^2 + d_{11}m^2 + d_{44}n^2 - 2d_{18}lm \\
&\qquad - \rho v^2\}\,A^y + \{(d_{13} + d_{45})\,mn + (d_{46} - d_{38})\,nl\}\,A^x = 0. \\
&\{(d_{38} - d_{46})\,mn + (d_{13} + d_{45})\,nl\}\,A^x + \{(d_{13} + d_{45})\,mn + (d_{46} - d_{38})\,nl\} \\
&\qquad A^y + \{d_{55}\,(l^2 + m^2) + d_{33}n^2 - \rho v^2\}\,A^z = 0.
\end{aligned}$$

The number of independent constants contained in the wave equation is *ten.*

IV. *Tetragonal* (C_{4v}, S_{4v}, D_4, D_{4h})—*tetrad axis parallel to the z-axis.*

$$\begin{aligned}
&(d_{11}\,l^2 + d_{88}m^2 + d_{44}n^2 - \rho v^2)\,A^x + (d_{12} + d_{89})\,lm\,A^y + (d_{13} \\
&\qquad + d_{45})\,nl\,A^z = 0. \\
&(d_{12} + d_{89})\,lm\,A^x + (d_{88}\,l^2 + d_{11}m^2 + d_{44}n^2 - \rho v^2)\,A^y + (d_{13} \\
&\qquad + d_{45})\,mn\,A^z = 0. \\
&(d_{13} + d_{45})\,nl\,A^x + (d_{13} + d_{45})\,mn\,A^y + \{d_{55}\,(l^2 + m^2) + d_{33}\,n^2 \\
&\qquad - \rho v^2\}\,A^z = 0.
\end{aligned}$$

The number of independent constants contained in the wave-equation is *seven.*

V. *Trigonal system* (C_3, S_6)—*triad axis parallel to the z-axis.*

$$\begin{aligned}
&\{d_{11}l^2 + d_{88}m^2 + d_{55}\,n^2 + 2d_{14}mn + 2d_{17}nl + 2d_{18}lm - \rho v^2\}\,A^x \\
&\qquad + \{d_{18}\,(m^2 - l^2) - 2d_{17}\,mn + 2d_{14}nl + (d_{12} + d_{89})\,lm\}\,A^y \\
&\qquad + \{d_{16}\,(l^2 - m^2) + (d_{38} - d_{46})\,mn + (d_{13}+d_{45})\,nl + 2d_{15}lm\}A^z=0,
\end{aligned}$$

$$\begin{aligned}&\{d_{18}(m^2 - l^2) - 2d_{17}\,mn + 2d_{14}nl + (d_{12} + d_{89})\,lm\}\,\mathrm{A}^x\\ &\quad + \{d_{88}\,l^2 + d_{11}m^2 + d_{44}n^2 - 2d_{14}mn - 2d_{17}\,nl - 2d_{18}lm - \rho v^2\}\,\mathrm{A}^y\\ &\quad + \{d_{15}(l^2 - m^2) + (d_{13} + d_{45})\,mn + (d_{46} - d_{38})\,nl\\ &\qquad\qquad - 2d_{16}\,lm\}\,\mathrm{A}^z = 0.\end{aligned}$$

$$\begin{aligned}&\{d_{16}(l^2 - m^2) + (d_{38} - d_{46})\,mn + (d_{13} + d_{45})\,nl + 2d_{15}\,lm\}\,\mathrm{A}^x\\ &\quad + \{d_{15}(l^2 - m^2) + (d_{13} + d_{45})\,mn + (d_{46} - d_{38})\,nl - 2d_{16}lm\}\,\mathrm{A}^y\\ &\quad + \{d_{44}l^2 + d_{55}m^2 + d_{33}n^2 - \rho v^2\}\,\mathrm{A}^z = 0\end{aligned}$$

where

$$d_{88} = (d_{11} - d_{12} - d_{89})$$

The number of independent constants contained in the wave equations is *twelve.*

VI. *Trigonal* (D_3, D_{3d}, C_{3v})—*triad axis parallel to the z-axis.*

$$\begin{aligned}&\{d_{11}l^2 + d_{88}\,m^2 + d_{55}\,n^2 + 2d_{14}mn - \rho v^2\}\,\mathrm{A}^x + \{2d_{14}nl\\ &\quad + (d_{12} + d_{89})\,lm\}\,\mathrm{A}^y + \{(d_{13} + d_{45})\,nl + 2d_{15}\,lm\}\,\mathrm{A}^z = 0.\end{aligned}$$

$$\begin{aligned}&\{2d_{14}nl + (d_{12} + d_{89})\,lm\}\,\mathrm{A}^x + \{d_{88}l^2 + d_{11}m^2 + d_{44}n^2\\ &\qquad - 2d_{14}mn - \rho v^2\}\,\mathrm{A}^y + \{d_{15}(l^2 - m^2)\\ &\qquad\qquad + (d_{13} + d_{45})\,mn + d_{46}nl\}\,\mathrm{A}^z = 0.\end{aligned}$$

$$\begin{aligned}&\{(d_{13} + d_{45})\,nl + 2d_{15}\,lm\}\,\mathrm{A}^x + \{d_{15}(l^2 - m^2)\\ &\quad + (d_{13} + d_{45})\,mn + d_{46}\,nl\}\,\mathrm{A}^y + \{d_{44}l^2 + d_{55}m^2 + d_{33}n^2\\ &\qquad - \rho v^2\}\,\mathrm{A}^z = 0.\end{aligned}$$

where

$$d_{88} = (d_{11} - d_{12} - d_{89})$$

The number of independent constants contained in the wave equations is *eight.*

VII. *Hexagonal* (C_{3h}, C_6, C_{6h})—*hexad axis parallel to the z-axis.*

$$\begin{aligned}&\{d_{11}l^2 + d_{88}\,m^2 + d_{55}\,n^2 + 2d_{18}\,lm - \rho v^2\}\,\mathrm{A}^x + \{d_{18}(m^2 - l^2)\\ &\quad + (d_{12} + d_{89})\,lm\}\,\mathrm{A}^y + \{(d_{38} - d_{46})\,mn + (d_{13} + d_{45})\,nl\}\,\mathrm{A}^z = 0.\end{aligned}$$

$$\begin{aligned}&\{d_{18}(m^2 - l^2) + (d_{12} + d_{89})\,lm\}\,\mathrm{A}^x + \{d_{88}\,l^2 + d_{11}m^2 + d_{44}n^2\\ &\quad - 2d_{18}\,lm - \rho v^2\}\,\mathrm{A}^y + \{(d_{13} + d_{45})\,mn + (d_{46} - d_{38})\,nl\}\,\mathrm{A}^z = 0.\end{aligned}$$

$$\begin{aligned}&\{(d_{38} - d_{46})\,mn + (d_{13} + d_{45})\,nl\}\,\mathrm{A}^x + \{(d_{13} + d_{45})\,mn\\ &\quad + (d_{46} - d_{38})\,nl\}\,\mathrm{A}^y + \{d_{44}l^2 + d_{55}\,m^2 + d_{33}\,n^2 - \rho v^2\}\,\mathrm{A}^z = 0.\end{aligned}$$

where

$$d_{88} = (d_{11} - d_{12} - d_{89})$$

The number of independent constants contained in the wave equations is *eight*.

VIII. *Hexagonal* (D_{3h}, C_{6v}, D_6, D_{6h})—*hexad axis parallel to the z-axis.*

$$(d_{11}l^2 + d_{88}m^2 + d_{55}n^2 - \rho v^2)\, A^x + (d_{12} + d_{89})\, lm\, A^y + (d_{13} + d_{45})\, nl\, A^z = 0.$$

$$(d_{12} + d_{89})\, lm\, A^x + (d_{88}l^2 + d_{11}m^2 + d_{44}n^2 - \rho v^2)\, A^y + (d_{13} + d_{45})\, mn\, A^z = 0.$$

$$(d_{13} + d_{45})\, (nl\, A^x + mn\, A^y) + (d_{44}l^2 + d_{55}m^2 + d_{33}n^2 - \rho v^2)\, A^z = 0.$$

Here again the relation

$$d_{88} = d_{11} - d_{12} - d_{89}$$

characteristic of crystals of the trigonal systems subsists, and number of independent constants appearing in the wave equations is *six*.

IX. *Cubic* (T *and* T_h).

$$(d_{11}l^2 + d_{44}m^2 + d_{55}n^2 - \rho v^2)\, A^x + (d_{12} + d_{45})\, (lm\, A^y + nl\, A^z) = 0.$$

$$(d_{12} + d_{45})\, lm\, A^x + (d_{11}m^2 + d_{44}n^2 + d_{55}l^2 - \rho v^2)\, A^y + (d_{12} + d_{45})\, mn\, A^z = 0.$$

$$(d_{12} + d_{45})\, (nl\, A^x + mn\, A^y) + (d_{11}n^2 + d_{44}l^2 + d_{55}m^2 - \rho v^2)\, A^z = 0.$$

The number of independent elastic constants appearing in the wave equations is *four*.

X. *Cubic* (T_d, O *and* D_h).

$$\{d_{11}l^2 + d_{44}(m^2 + n^2) - \rho v^2\}\, A^x + (d_{12} + d_{45})\, \{lm\, A^y + nl\, A^z) = 0\}.$$

$$(d_{12} + d_{45})\, lm\, A^x + \{d_{11}m^2 + d_{44}(l^2 + m^2) - \rho v^2\}\, A^y + (d_{12} + d_{45})\, mn\, A^z = 0.$$

$$(d_{12} + d_{45})\, \{nl\, A^x + mn\, A^y\} + \{d_{11}l^2 + d_{44}(l^2 + m^2) - \rho v^2\}\, A^z = 0.$$

The number of independent constants appearing in the wave equations is *three*.

6. STATIC DEFORMATION PROBLEMS

Equations (1) express the nine stress components in terms of the nine strain coefficients. One can work out the inverse transformation of (1) and express instead the strain coefficients as linear functions of the stress variables. The strain-stress relations can therefore alternatively be written also as

$$u_m = \sum_{n=1}^{9} D_{mn}\, T_n \qquad (m = 1, 2, \ldots 9) \qquad (10)$$

If Δ_{mn} denotes the co-factor of the element d_{mn} in the determinant of the transformation (1) and $\Delta =$ determinant $|d_{mn}|$, then $D_{mn} = (\Delta_{mn}/\Delta)$.

The strain-energy can be expressed purely as a function of the stress coefficients and we have another expression

$$2U = \sum_m \sum_n D_{mn} T_m T_n \tag{11}$$

for the deformation energy which is equivalent to (3).

In the classical theory the nine stress variables are reduced to six by means of the relations $T_{yz} = T_{zy}$; $T_{zx} = T_{xz}$; $T_{xy} = T_{yx}$. The deformation energy of the solid is thus a function of the six stress variables only. Adopting the usual convention of writing T_1', T_2', T_3', T_4', T_5', T_6' for T_{xx}, T_{yy}, T_{zz}, T_{yz} or T_{zy}, T_{zx} or T_{xz}, T_{xy} or T_{yx} respectively, the classical expression (4) for the strain-energy becomes

$$2U_1 = \sum \sum_{m,\, n=1}^{6} s_{mn} T_m' \, T_n' \tag{12}$$

The coefficients s_{mn} occurring in the above expression are the well-known *elastic moduli* of the classical theory. One can obtain formulæ for these moduli in terms of our constants D_{mn} by considering cases of homogeneous stresses for which the relations $T_{yz} = T_{zy}$; $T_{zx} = T_{xz}$; $T_{xy} = T_{yx}$ hold good. Making these substitutions in (11) and comparing the resulting expression with (2), we get $s_{mn} = D_{mn}$ when both m and n are 1, 2, or 3 and relations of the type

$$\begin{aligned} s_{14} &= (D_{14} + D_{15}); \\ s_{44} &= (D_{44} + 2D_{45} + D_{55}); \\ s_{45} &= (D_{46} + D_{47} + D_{56} + D_{57}); \end{aligned} \tag{13}$$

for the other coefficients.

We can now write down the expressions for the compressibility, Young's modulus, and the Poisson's ratio for any crystal in simple terms. In view of the fact that all these moduli are determinable from experiments dealing with purely homogeneous strains, the formulæ for them are not essentially different from the corresponding ones of the classical theory. By following the same methods as those adopted in the latter,[3] we give below the formulæ for these moduli in our present notation.

When the crystal is subjected to a uniform hydrostatic pressure P, we have from the first three of the equations (10)

$$\begin{aligned} u_1 &= (D_{11} + D_{12} + D_{13})\,P \\ &= (s_{11} + s_{12} + s_{13})\,P \text{ from (13)} \\ u_2 &= (s_{21} + s_{22} + s_{23})\,P \\ u_3 &= (s_{31} + s_{32} + s_{33})\,P \end{aligned}$$

The linear compressibility modulus in the direction of the x-axis is therefore given by

$$k_x = (P/u_1) = 1/(s_{11} + s_{12} + s_{13}) \tag{14}$$

and the bulk modulus is expressed by the formula

$$k = P/(u_1 + u_2 + u_3) = 1/(s_{11} + s_{22} + s_{33} + 2s_{23} + 2s_{31} + 2s_{12}) \tag{15}$$

If the solid is subjected to a uniform tension T in the direction of the x-axis, obviously $T_1 = T$; $T_2 = T_3 = \,..T_9 = 0$. Hence it follows from (10) that the Young's modulus in the direction of the x-axis is given by

$$E = T/u_1 = (1/D_{11}) = (1/s_{11}) \tag{16}$$

Similarly the Poisson's ratio in the direction of the y-axis is given by

$$\sigma = -\,(s_{12}/s_{11}) \tag{17}$$

To write down the expressions for the Young's modulus and Poisson's ratio in any general direction (l, m, n), we require the law of transformation of the strain as well as the stress components when one passes over from one co-ordinate system to another. If the direction cosines of the axes Ox', Oy' Oz' of a new co-ordinate system referred to the original one are $(l_1\ m_1\ n_1)$, $(l_2\ m_2\ n_2)$ and $(l_3\ m_3\ n_3)$ respectively, we have

$$\begin{aligned} T_{x'x'} &= l_1^2\,T_{xx} + m_1^2\,T_{yy} + n_1^2\,T_{zz} + m_1n_1\,(T_{yz} + T_{zy}) \\ &\qquad + n_1l_1\,(T_{zx} + T_{xz}) + l_1m_1\,(T_{xy} + T_{yx}) \\ T_{x'y'} &= l_1l_2\,T_{xx} + m_1m_2\,T_{yy} + n_1n_2\,T_{zz} + (m_1n_2\,T_{yz} + m_2n_1\,T_{zy}) \\ &\qquad + (n_1l_2\,T_{zx} + n_2l_1\,T_{xz}) + (l_1m_2\,T_{xy} + l_2m_1\,T_{yx}) \qquad (18) \\ T_{y'x'} &= l_1l_2T_{xx} + m_1m_2\,T_{yy} + n_1n_2\,T_{zz} + (m_2n_1\,T_{yz} + m_1n_2\,T_{zy}) \\ &\qquad + (n_2l_1\,T_{zx} + n_1l_2\,T_{xz}) + (l_2m_1\,T_{xy} + l_1m_2\,T_{yx} \end{aligned}$$

$$\begin{aligned} u_{x'x'} &= l_1^2u_{xx} + m_1^2u_{yy} + n_1^2u_{zz} + m_1n_1\,(u_{yz} + u_{zy}) \\ &\qquad + n_1l_1\,(u_{zx} + u_{xz}) + l_1m_1\,(u_{xy} + u_{yx}) \qquad (19) \\ u_{x'y'} &= l_1l_2\,u_{xx} + m_1m_2\,u_{yy} + n_1n_2\,u_{zz} + (m_1n_2\,u_{yz} + m_2n_1\,u_{zy}) \\ &\qquad + (n_1l_2\,u_{zx} + n_2l_1u_{xz}) + (l_1m_2\,u_{xy} + l_2m_1\,u_{yx}) \\ u_{y'x'} &= l_1l_2\,u_{xx} + m_1m_2\,u_{yy} + n_1n_2\,u_{zz} + (m_2n_1\,u_{yz} + m_1n_2\,u_{zy}) \\ &\qquad + (n_2l_1\,u_{zx} + n_1l_2u_{xz}) + (l_2m_1u_{xy} + l_1m_2u_{yx}) \end{aligned}$$

Now, if the solid is subjected to a uniform tension T over the planes $x' = \text{const.}$ of which the normal has direction cosines $(l_1\, m_1\, n_1)$, we get from the transformation rules

$$T_{xx} = l_1^2 T;\ T_{yy} = m_1^2 T;\ T_{zz} = n_1^2 T;\ T_{yz} = T_{zy} = m_1 n_1 T;$$

$$T_{zx} = T_{xz} = n_1 l_1 T;\ T_{xy} = T_{yx} = l_1 m_1 T$$

Further, $u_{x'x'}$ is given by (19). Hence denoting by $\mathbf{q}_{x'}$ the row vector $(l_1^2\ m_1^2\ n_1^2\ m_1 n_1\ n_1 l_1\ l_1 m_1)$ with six components, we find the expression for the Young's modulus in the direction of the vector $(l_1\, m_1\, n_1)$ as

$$E_{x'} = 1/\mathbf{q}_{x'}\, S\, \tilde{\mathbf{q}}_{x'} \tag{20}$$

where S denotes the matrix (s_{mn}). Similarly the Poisson's ratio in the direction of the y'-axis which has direction cosines $(l_2\, m_2\, n_2)$ with respect to O_x, O_y and O_z is given by

$$\sigma_{y'} = -\frac{1}{2\phi}\left[l_2^2 \frac{\partial\phi}{\partial l_1^2} + m_2^2 \frac{\partial\phi}{\partial m_1^2} + n_2^2 \frac{\partial\phi}{\partial n_1^2} + m_2 n_2 \frac{\partial\phi}{\partial (m_1 n_1)} + n_2 l_2 \frac{\partial\phi}{\partial (n_1 l_1)} + l_2 m_2 \frac{\partial\phi}{\partial (l_1 m_1)}\right] \tag{21}$$

where $\phi = \mathbf{q}_{x'} S \tilde{\mathbf{q}}_{x'}$ and the differential coefficients are formed as if these arguments are independent.

It is interesting to note that only twenty-one of the forty-five constants figuring in (10) appear in the above formulæ. As mentioned earlier, this is a consequence of the homogeneity of the strains applied to evaluate these static moduli.

The stresses and strains which appear when elastic materials are subject to torsion or flexure are essentially heterogeneous, and hence in dealing with them, our elastic moduli D_{mn} will appear in combinations other than those which figure in homogeneous deformations. The present theory is quite competent to handle such problems, but to deal with them in detail would carry us far beyond the scope of this paper.

7. SOME CONCLUDING REMARKS

The main purpose of the present paper has been to establish the necessity for an amendment of the phenomenological theory of elasticity as universally accepted hitherto. Any theory to be acceptable should include in its scope elastic stresses and strains of the most general type and specify them in an analytical form from which the equations of equilibrium in static problems and the equations of motion in wave-propagation can be written down immediately. These requirements are not met by the present form of the theory but are completely satisfied if all the nine components of stress and strain in the usual tensor formulation are retained. When thus amended, the phenomenological theory is capable of handling all the problems of the subject, including those which arise in its practical applications. The more important of these are considered in detail in the course of the paper and the results are set out explicitly for the different crystal classes so that they could be readily made use of.

As already remarked in the introduction, the phenomenological theory as amended gives results in complete accord with these derived from the atomistic approach to the theory of elasticity of crystals based on the most general scheme of interatomic forces. To discuss the latter further or to give an account of the somewhat confused history of the subject would lie outside the scope of the present paper. A few remarks regarding these matters will however be found in the attached appendix.

SUMMARY

The fundamental aspects of the phenomenological theory of elasticity are critically examined and it is shown that the tensor representation of the elastic strains and stresses in the general case should be in the unsymmetrical form. On this basis, the stress-strain relationships are deduced and tabulated for the different crystal classes. The equations determining the velocities of wave-propagation in different directions are also obtained and tabulated. Static deformation problems are then discussed and it is shown that in the particular case of homogeneous strains, the elastic constants group themselves in linear combinations which are equivalent to the elastic modulii of the theory in its familiar form. In wave-propagation, however, the strains and stresses are heterogeneous and hence all the elastic constants are involved and appear in linear combinations which are different and also larger in number than those which figure in the formulæ for homogeneous deformations. These results are completely in accord with the consequences of the atomistic theory based on interatomic forces of the most general type.

APPENDIX

As is well known, the theory of the elasticity of solids in its present form was initiated by Cauchy who put forth the fundamental idea of expressing elastic stresses and strains in the manner adopted in the phenomenological theory, and also developed the theory on an atomistic basis. Later theorists, notably Green, Stokes and Kelvin retained Cauchy's method of specifying elastic stresses and strains but adopted a purely phenomenological approach. The view advocated by them that a completely ælotropic body would have twenty-one elastic constants and not fifteen as derived by Cauchy received general acceptance.

In a paper published in these *Proceedings* some years ago by one of us (Raman, 1943), a theory of the dynamic behaviour of crystal lattices was developed based on the assumption of interatomic forces of the most general type. In subsequent years, the consequences of that theory was worked out in detail for the case of diamond and confirmed by a series of spectroscopic investigations on the scattering of light, the luminescence and infra-red absorption by that crystal. The high values of the interatomic force-constants disclosed by the spectroscopic behaviour of diamond were evidently related to its exceptional elastic behaviour. In the endeavour to place this relationship on a quantitative basis, a fresh approach was made by one of us (Viswanathan, 1954) to the atomistic theory of the elasticity of crystals, both from the static and dynamic points of view, and some surprising results emerged. Contrary to the assertion made in the papers of Max Born and his collaborators which also finds a place in their recent book (Born and Kun Huang, 1954), no difficulty was encountered in expressing the energy of static deformations in terms of interatomic forces of the most general type. It was found that this expression contained forty-five independent constants, but for homogeneous or irrotational strains they appeared in twenty-one distinct linear combinations. The dynamics of wave-propagation in crystals was also investigated and it was shown that the expressions for the wave-velocity contained the same forty-five constants but in different linear combinations. The work of Born and his school on the dynamic problem was critically examined and it was shown that the assumptions made by them in the attempt to reduce the forty-five constants which appeared in their theory to twenty-one had no theoretical justification.

The results of Born and his school were also contradicted by Laval in some recent publications (1951). More recently still, a series of papers have been published by Le Corre in which Laval's ideas have been further developed. On reading those papers, one obtains the impression that their author believes the results of the atomistic and phenomenological approaches to differ essentially. For example, in order to account for the non-symmetric character of the stress tensor, internal couples are postulated to balance the differences in the angular momenta. We may remark that there is no room for such a postulate, since the analytical specification of the stresses in terms of the tensor components should itself suffice to describe the state of the solid completely. In the last paper of the series, a statement also appears that an atomistic approach is essential to solve such familiar problems in elasticity as torsion and flexure.

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CORRIGENDA

The following corrections should be made in a recent paper published in these *Proceedings*, Section A, 1955, Vol. **42**, page 51.

In all the four tables appearing in pages 58 and 59 which give the number of distinct constants for crystals of the trigonal and hexagonal classes, the constants d_{44} and d_{55} occurring in the sixth and seventh rows respectively should be interchanged. Similarly in all the wave-equations pertaining to these four crystal classes, the terms $d_{55}n^2$ appearing in the matrix element λ_{xx} and $d_{44}l^2$ appearing in the element λ_{zz} should be changed respectively into $d_{44}n^2$ and $d_{55}l^2$.

In *page* 61, *line* 10 read $(\lambda_{zz} - \rho v^2)\, A^z$ instead of $\lambda_{zz}\, A^z$.

In *page* 64, *line* 20 read (T_d, O and O_h) instead of T_d, O and D_h).

In *page* 65, *line* 19 read " with (12) " for " with (2) ".

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RAMAN SPECTRA OF NICKEL SULPHATE CRYSTALS

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(*Memoir No. 74 from the Raman Research Institute, Bangalore 6*)

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1. INTRODUCTION

NICKEL sulphate crystallizes from solution at room temperature (30° C.) as $NiSO_4.7H_2O$ in the orthorhombic system. At about 35° C it crystallizes as $NiSO_4 \cdot 6H_2O$ in the tetragonal system, while at about 60° C. it crystallizes as $NiSO_4 \cdot 6H_2O$ but in the monoclinic system. The complete Raman spectrum of crystalline nickel sulphate has not so far been reported since the λ 4358 and λ 4046 radiations of the mercury arc ordinarily employed are absorbed. Nisi (1930) using the group of lines at λ 3126 in the mercury arc spectrum has reported in the case of $NiSO_4 \cdot 7H_2O$ the principal sulphate frequency of shift 985 cm.$^{-1}$ and two water bands at 3209 and 3432 cm.$^{-1}$

The absorption in the near ultraviolet for nickel sulphate lies at λ 3850 and the crystals are transparent to radiations of shorter wavelengths over a wide range in the ultraviolet. The present paper reports the results of an investigation with the orthorhombic and tetragonal crystals using the resonance radiation λ 2536·5 of the mercury arc for exciting the Raman effect.

2. EXPERIMENTAL DETAILS

The crystals of $NiSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ were grown by the method of slow evaporation, the latter at a temperature of 35° C. in a thermostat. The crystals of $NiSO_4 \cdot 6H_2O$ were of a deeper green in colour than those of $NiSO_4 \cdot 7H_2O$. The biaxial nature of the interference figures in the case of $NiSO_4 \cdot 7H_2O$ and the uniaxial nature of the figures of $NiSO_4 \cdot 6H_2O$ observed under the polarising microscope confirmed their respective identification from depth of colour and external form. The crystals of $NiSO_4 \cdot 7H_2O$ were in the form of rectangular tablets of size 20 mm. × 10 mm. × 2 mm. The crystals of $NiSO_4 \cdot 6H_2O$ which were pyramidal in form were rather small. Since both the crystals were efflorescent, a thin film of glycerine was put over them to reduce the rate of efflorescence. However, the crystals of $NiSO_4 \cdot 7H_2O$ deteriorated rapidly and fresh crystals had to be used frequently.

The Raman spectra were recorded with a Hilger medium quartz spectrograph having a dispersion of 140 cm.$^{-1}$ per mm. in the λ2536·5 region. A water-cooled magnet controlled quartz mercury arc served as an intense source of λ 2536·5. The crystals were placed near the arc and the scattered radiations were focussed on the slit of the spectrograph with a quartz condenser. The scattered resonance radiation was filtered out by the mercury vapour inside the spectrograph. With a slit width of 0·04–0·05 mm., exposures of the order of ten hours were given to obtain reasonably intense spectrograms.

3. RESULTS

Figs. (1) and (2) in the accompanying Plate reproduce the spectra obtained with $NiSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ respectively. The lowermost part of the spectrum in Fig. 2 which is very intense due to parasitic light helps to identify the lines of the mercury arc.

An examination of the spectra of the two crystals reveals the following features: (1) The low frequency spectra of these crystals are faint and

TABLE I

Frequency Shifts in cm.$^{-1}$

	$NiSO_4 \cdot 7H_2O$	$NiSO_4 \cdot 6H_2O$
Lattice Oscillations	~ 75 v.w. ~ 110 v.w. ~ 156 w. 210 m. 255 b.m.	210 m. 236–69 b.m.
ν_2	400 w. 444 s. 465 s.	440 s. 469 s.
ν_3	620 ?	620 ?
ν_1	986 v.s.	988 v.s.
ν_4	1060 b.s. 1098 b.m. 1138 b.s. ~1165 v.w.	1092 b.s. 1133 b.s.
Water Bands	~3282 v.s. ~3438 v.s.	~3257 v.s. ~3439 v.s.

s., Strong; w., weak; v.s., very strong; v.w., very weak; m., medium; b., broad.

~ value of the frequency shift estimated from the relative position of the line with respect to the neighbouring iron arc lines.

diffuse. (2) The frequency shifts due to the oscillations of the sulphate ions in the two crystals are different in the two cases. It may be noticed that the splitting of the doubly degenerate oscillation at 450 cm.$^{-1}$ is larger in the case of $NiSO_4 \cdot 6H_2O$ than in the case of $NiSO_4 \cdot 7H_2O$. Measurements indicate that the non-degenerate oscillation has a frequency shift of 986 cm.$^{-1}$ in the case of $NiSO_4 \cdot 7H_2O$, while in the case of $NiSO_4 \cdot 6H_2O$ it has a shift of 988 cm.$^{-1}$ It will also be noticed that the triply degenerate oscillation at 1100 cm.$^{-1}$ has split into more components in the case of $NiSO_4 \cdot 7H_2O$ which is of lower symmetry than $NiSO_4 \cdot 6H_2O$. The water bands also show differences in their structure in the two cases.

Table I gives the frequency shifts observed in the two cases. The frequency shifts of some of the lines which were faint and diffuse could only be approximately estimated. The sulphate ion frequency of shift about 620 cm.$^{-1}$ could not be unambiguously observed owing to the proximity of the intense mercury line at λ 2576.

4. DISCUSSION

$NiSO_4 \cdot 7H_2O$ has been assigned to the space group $P\,2_1 2_1 2_1\,(D_2^4)$ of the enantiomorphous hemihedral class of the orthorhombic system, whereas $NiSO_4 \cdot 6H_2O$ has been assigned to the space group $P\,4_1 2_1 2\,(D_4^4)$ of the enantiomorphous hemihedral class of the tetragonal system. (Beevers and Schwartz, 1935; Beevers and Lipson, 1932). In the case of $NiSO_4 \cdot 6H_2O$ the nickel and sulphur atoms occupy the special positions with the symmetry of the two-fold axis of rotation. The six water molecules are said to be approximately octahedrally co-ordinated around the nickel ions. On the other hand, in $NiSO_4 \cdot 7H_2O$ the nickel and sulphur ions do not occupy any such symmetric special positions. Six of the seven water molecules are approximately octahedrally co-ordinated around the nickel ions in this case as well. In the case of $NiSO_4 \cdot 7H_2O$ as well as in $NiSO_4 \cdot 6H_2O$ there are four molecules per unit cell.

The degradation of the symmetry of the sulphate ion in the crystalline state and the consequent removal of the degeneracy of the oscillations results in the splitting of the degenerate oscillations, and hence all the nine frequencies of the SO_4 ion should appear. The coupling between the four molecules in the unit cell further increases the number of these internal oscillations. Thus, in the case of $NiSO_4 \cdot 7H_2O$ thirty-six components should appear whereas in the case of $NiSO_4 \cdot 6H_2O$ this number is only twenty-four owing to the higher symmetry of the crystal. Though the theoretically expected multiplicity of lines is not fully manifested in the spectra, the differences in the nature of the spectra due to the difference in the crystal symmetry and structure are evident. The breadth of some of the lines (*e.g.*, the group near 1100 cm.$^{-1}$) might be attributed to the overlapping of several of the components and their inadequate resolution.

The Raman spectrum of $NiSO_4 \cdot 7H_2O$ exhibits a close correspondence with the spectrum of $MgSO_4 \cdot 7H_2O$ (Shantakumari, 1953) the crystal structure of which is isomorphous with that of $NiSO_4 \cdot 7H_2O$. The following frequencies have been reported by her. 56, 75, 97, 118, 150, 252, 303, 445, 461, 609, 620, 986, 1059, 1064, 1076, 1098, 1134, 1148, 3185, 3228, 3338, 3406, 3446 and 3485 cm.$^{-1}$

Schaefer and Schubert (1916) report from their studies on the infra-red reflection spectrum of $NiSO_4 \cdot 6H_2O$, frequencies at 635, 1111, 1116, 2940, 3030 and 3125 cm.$^{-1}$ No infrared absorption studies appear to have been made with crystalline nickel sulphate.

In conclusion, the author wishes to express his sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for the kind interest that he took during the course of this investigation.

5. SUMMARY

The Raman spectra of orthorhombic $NiSO_4 \cdot 7H_2O$ and the tetragonal $NiSO_4 \cdot 6H_2O$ have been investigated using the resonance radiation of mercury for excitation. Readily observable differences are exhibited by the spectra in the two cases which may be ascribed to the differences in crystal structure and symmetry.

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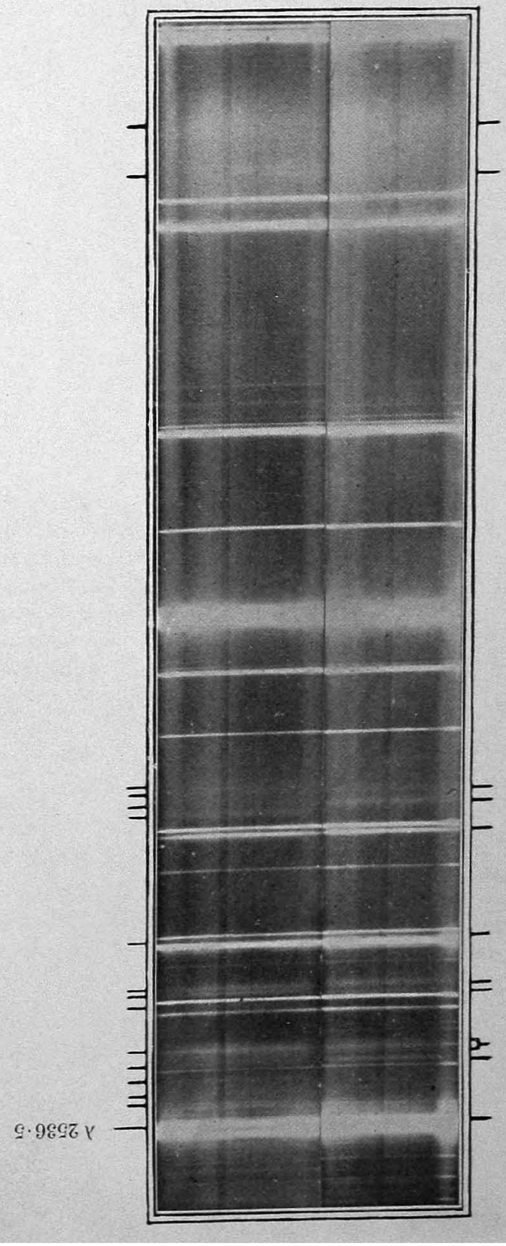
FIG. 1 FIG. 2



Raman Spectra of (1) $NiSO_4 \cdot 7H_2O$ and (2) $NiSO_4 \cdot 6H_2O$.

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THE PROPAGATION OF LIGHT IN ABSORBING BIAXIAL CRYSTALS—I. THEORETICAL

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1. INTRODUCTION

ABSORBING biaxial crystals in general display a variety of remarkable optical phenomena in the vicinity of both the optic axes. For example, if an extended source of unpolarised light is viewed through a plate of highly pleochroic material cut normal to an optic axis, two dark brushes—the Brewster's brushes—are generally seen in the field of view; while if a polariser be inserted in front of the plate, the so-called idiophanic rings are observed—similar to the interference rings that can appear in the case of a transparent crystal *if an analyser be also present.*

The theoretical investigations of Waldemar Voigt focussed attention on the fact that certain of the features relating to the propagation of light in the vicinity of an optic axis differ radically from those obtaining in transparent media. Thus, whereas along any general direction in a transparent crystal there are two particular linearly polarised vibrations that can be propagated without change of form, this is no longer the case in absorbing crystals. As a matter of fact, close to an optic axis and on either side of it, there even exist two directions—the singular axes—with the following remarkable properties: *only* a right-circular vibration can be propagated without change of form along one of these axes, and *only* a left-circular vibration along the other.* In this paper it will be shown that the various features of the propagation of light in absorbing media may also be conveniently regarded as due to the superposed effects of birefringence and dichroism. Because of the simplicity of the method, it has also been possible to make a more detailed investigation of the following interesting question: what will happen when, for example, a right-circular vibration is incident in the direction of a singular axis where only a left-circular vibration can be propagated without change of form ? The results obtained in this connection are at variance with those expected by Voigt (Section 6).

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* A non-mathematical summary, in English, of the main results of Voigt's investigations may be found in Reference 1.

The analysis of the propagation of light in absorbing biaxial media from the standpoint of the electromagnetic theory has been discussed by several authors. The comparatively simple case of orthorhombic crystals (where the principal axes of the dielectric tensor and the complex conductivity tensor necessarily coincide) is discussed in Drude's treatise.[2] But the somewhat oversimplified presentation there given omits entirely those theoretical and experimental features with which we shall be particularly concerned. These may be found described in more detailed treatments,[3-5] particularly those of Voigt and Pockels. In view of the complexity of the phenomena involved, it would appear that a consideration of the problem from a simpler though less rigorous standpoint would certainly be useful. Such an approach is provided in the present paper, and, as we shall show, the method adopted leads to results that are practically identical with those of the electromagnetic theory.

2. GENERAL FEATURES OF LIGHT PROPAGATION IN ABSORBING MEDIA

(*a*) *The Index and Absorption Ellipsoids*

In an absorbing biaxial medium not possessing optical activity, the two waves propagated along any direction appreciably inclined to both the optic axes may be regarded as practically plane polarised (though not rigorously so, as in the transparent crystal). And as in a transparent crystal their ‘ vibration-directions ’ may then be considered to lie on the principal planes, their velocities being determined by their vibration-directions thus: the reciprocal of any radius of a so-called *index ellipsoid* gives the velocity for vibrations parallel to that radius. In addition, the two waves have different coefficients of extinction κ_1 and κ_2, these being determined again by their vibration-directions thus: the reciprocal of any radius of a so-called *absorption ellipsoid* gives the value of $\sqrt{(2\kappa v^3/c)}$ for vibrations parallel to that radius, v being the velocity for that vibration-direction.

By assuming that the above statements hold good even for directions in the vicinity of an optic axis, it is indeed possible to explain *some* of the phenomena observed there—and such a procedure is in fact followed in Drude's treatise. For example, the occurrence of Brewster's brushes can be explained along the following lines. In the neighbourhood of an optic axis, a comparatively small change in the direction of propagation will in general cause an appreciable change in the inclinations of the two principal planes to the axial plane; this in turn will lead to a large variation in the total absorption, since the absorption coefficients of the two waves will be determined by the orientation of their vibration-directions.

(*b*) *The Elliptical Polarisation of the Waves*

The appearance of idiophanic interference rings with a polarizer *alone* cannot however be explained on the assumption that the light incident along any direction is split up into two linearly polarized beams with their vibrations at right angles to one another; their states of polarization being *orthogonal*, two such beams will be incapable of interference with one another (unless brought to the same plane of vibration by an analyser).

The fact is that when we turn to directions of propagation in the vicinity of an optic axis, we are no longer justified in neglecting a remarkable and important consequence of the phenomenological theory: namely, that the two waves propagated in any general direction in an absorbing biaxial medium are in reality, *elliptically polarized.* Though the two elliptic vibrations have their axes *majores* at right angles, and their ellipticities equal, they are rendered *non-orthogonal* by the fact that they are of the *same* handedness; and this last mentioned feature (together with the fact that the major axes do not in general coincide with the principal planes) distinguishes the situation sharply from that obtaining in optically active (transparent) crystals.

In the context of the elliptical polarisation of the waves, the index and absorption ellipsoids—strictly speaking—retain significance only in terms of the dielectric and conductivity-like tensors by means of which they are *defined.* Nevertheless, as we shall show, the existence of the two non-orthogonal elliptically polarised waves may be conveniently treated as due to the superposed effects of birefringence and dichroism—just as the propagation of two orthogonal elliptically polarised waves near to an optic axis in an optically active transparent medium, may (by Gouy's hypothesis[4,6]) be conveniently treated as due to the superposed effects of birefringence and rotation.

3. THE SUPERPOSITION OF BIREFRINGENCE AND DICHROISM

Consider a plate cut perpendicular to an arbitrary direction z which is also taken as being normal to the plane of the paper. Let OX_r and OY_r (Fig. 1) be the trace of the principal planes of refraction—defined as usual, either in terms of the index ellipsoid or the optic binormals. Similarly let OX_k and OY_k be the trace of the *principal planes of absorption*—which we shall define analogously, *either* as containing the major and minor diameters of the elliptical section of the absorption ellipsoid made by the plane of the paper, *or* as the internal and external bisectors of the angle subtended on the z-direction by the two absorption-binormals (normals to the circular sections of the absorption ellipsoid).

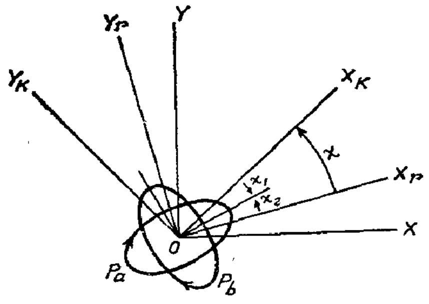

FIG. 1

P_a and P_b—States of polarisation propagated unchanged.
OX_k and OY_k—Trace of the principal planes of absorption.
OX_r and OY_r—Trace of the principal planes of refraction.

Consider an arbitrary elliptic vibration P (which, for the sake of concreteness, may be temporarily identified with the one marked P_a in the figure). In the absence of absorption the arbitrary elliptic vibration P will be resolved into two vibrations (along the principal planes of refraction, OX_r and OY_r) between which an infinitesimal phase difference δdz will be introduced corresponding to a passage dz. Since, however, anisotropic absorption is also present, we perform, in addition, the infinitesimal operation of linear dichroism; the elliptic vibration—as modified by the infinitesimal operation of birefringence—is resolved into two linear vibrations (this time, along the principal planes of absorption, OX_k and OY_k), the amplitudes of which are then reduced by the multiplying factors $(1 - k_1dz)$ and $(1 - k_2dz)$ respectively. The differential absorption of the two components will cause the state of the elliptic vibration to ' move towards ' the state of polarisation of the less absorbed component OX_k (a phrase which acquires a more vivid meaning in the Poincaré sphere representation). Those states of polarisation alone can be propagated without change of form, which under the successive infinitesimal operations of birefringence and dichroism (applied in either order) remain unaltered in form and orientation—and to these states of polarisation alone can definite velocities of propagation and coefficients of absorption be assigned.

Several particular cases may first be noted. Along the optic axial directions where the birefringence vanishes, the two waves (propagated with different coefficients of absorption) are linearly polarised along the principal planes of absorption. Similarly, the waves propagated along directions appreciably inclined to the optic axes will be practically plane polarised along the principal planes of refraction, since the absolute values of the dichroism (k_2-k_1) is usually such that it is very small compared with the birefringence $(\delta_1-\delta_2)$ along such directions. Also, where the principal planes of absorption and refraction coincide (as for example along the axial plane in orthorhombic crystals) the waves will be rigorously linearly polarised along the common principal planes.

The more general case, where the solution is not so apparent, is discussed analytically in Section 7, but the main results will first be proved more briefly and elegantly by the use of the Poincaré sphere. For this purpose, the form of the arbitrary elliptic vibration P—as distinct from its intensity and absolute phase—must first be specified by means of certain parameters. The principal planes of absorption and refraction form the two natural co-ordinate systems to which the vibration P may be referred. The ratio tan ϕ of the amplitudes of the components of the vibration P along OY_r and OX_r does not by itself completely specify the form of the elliptic vibration (since the phase difference θ_r between these components has also to be given). Similarly the ratio tan ψ of the amplitudes of the components of P along OY_k and OX_k does not by itself completely specify the form of P (since the phase difference θ_k between these components has also to be given). But ϕ and ψ together form two convenient symmetrical parameters completely specifying the form of the elliptic vibration P (ϕ, ψ)—provided we separately give the sense of description of the ellipse. It may also be noted that apart from an intensity factor, cos 2ϕ and cos 2ψ are the two values of the second Stokes parameter M of the vibration P (ϕ, ψ) when it is referred successively to co-ordinate systems along the principal planes of refraction and absorption respectively.

As indicated in the figure, it turns out that there are two particular elliptic vibrations described in the same sense, P_a (ϕ_a, ψ_a) and P_b (ϕ_b, ψ_b), that can be propagated without change of form under the superposed effects of birefringence and dichroism. The form of the vibration P_b can be obtained from that of P_a merely by rotating the latter by 90° in its own plane—which means that ϕ_b and ψ_b are complementary to ϕ_a and ψ_a respectively.

4. USE OF THE POINCARÉ SPHERE FOR SUPERPOSITION

(a) *The General Method*

The Poincaré sphere,[4,7] which has proved very useful for the analysis of the propagation of polarised light in *transparent* media, turns out also to be of great use in our present discussion on absorbing crystals.

As is well known, a one-to-one correspondence can be set up between all the points on the surface of a sphere (the Poincaré sphere) and all the possible forms of elliptic vibrations that can be conceived (circular and linear vibrations being regarded as particular cases of elliptic vibrations). In particular the arbitrary elliptic vibration P referred to in the previous section is represented by a corresponding point P on the Poincaré sphere, while a linear vibration along OX_k will be represented by some other point X_k. The infinitesimal operation of anisotropic absorption described in the last section will obviously alter the form of the elliptic vibration P in such a manner that one may say it gets more polarised in the direction of OX_k, since this is the less absorbed component. This infinitesimal alteration in the state of the elliptic vibration P corresponds (on the Poincaré sphere) to an infinitesimal movement of the point P directly towards X_k, *i.e.*, along the direction of the shortest arc joining them.

Similarly the infinitesimal alteration in the state of the (initial) elliptic vibration P due to the operation of birefringence alone, corresponds to an infinitesimal movement ds_r of the representative point P. If the elliptic vibration is to be propagated without change of form, this movement ds_r should be equal and opposite to the displacement of P due to dichroism alone; and the problem of finding the states of polarisation that can be propagated without change of form is therefore reduced to the simple geometrical problem of finding the points P on the Poincaré sphere which satisfy the above requirement.

(*b*) *The Operations of Dichroism and Birefringence*

Referring to Fig. 2, let X_k and Y_k give the orientations of the principal planes of absorption. (The arbitrary elliptic vibration P has not been indicated on the sphere, but for the sake of concreteness, may be temporarily identified with the particular state P_a in the figure.) If the elliptic vibration P is resolved into two orthogonal linear vibrations in the states X_k and Y_k, then the amplitudes F_k and G_k of these components will be proportional to $\cos\psi$ and $\sin\psi$, where 2ψ is the angular distance of the point P from X_k on the Poincaré sphere. (For a proof of this statement, see reference 7.) Hence $G_k/F_k = \tan\psi$. If the amplitudes of these components are reduced by the multiplying factors $e^{-k_1 z}$ and $e^{-k_2 z}$, the angular distance of P from X_k will change from 2ψ to $2\psi'$ where:

$$\tan\psi' = \frac{G_k\, e^{-k_2 z}}{F_k\, e^{-k_1 z}} = \tan\psi\, e^{-(k_2-k_1)z} \qquad (1)$$

Since the phases of the X_k and Y_k components of P are to be left unaltered in this operation, the movement of P will be entirely on the meridional arc

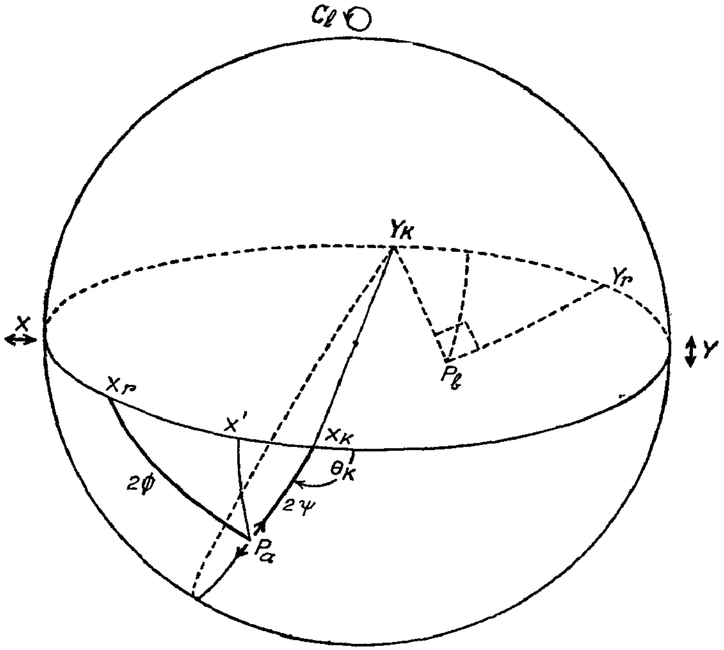

FIG. 2

(X_k, Y_k) and (X_r, Y_r)—Principal planes of absorption and refraction, respectively.

P_a and P_b —States of polarisation propagated unchanged.

$X_rX_k = 2\chi$; $X_kX' = 2\chi_1$; $X_rX' = 2\chi_2$; $P_aX' = 2\theta$.

Y_kPX_k. This follows from the fact that *the X_k and Y_k components of all elliptic vibrations on this arc have the same phase difference* θ_k (where θ_k is the angle indicated in Fig. 2); for, if an additional phase difference $-\theta_k$ be introduced between these components, any such elliptic vibration will be reduced to a linear vibration on the equatorial arc $X_kY_rY_k$ (by a well known property of the Poincaré sphere).

The infinitesimal operation of linear dichroism (corresponding to a passage dz) will, apart from reducing the intensity, cause the initial state of polarisation P to move along the arc PX_k towards the state X_k (the less absorbed component), through an arc $ds_k = -2d\psi$. From (1) we have

$$\tan\psi + d(\tan\psi) = [1 - (k_2 - k_1)\,dz]\tan\psi$$

or

$$2\sec^2\psi d\psi = -2(k_2 - k_1)\,dz\cdot\tan\psi$$

which leads to the simple relation

$$ds_k = (k \sin 2\psi)\, dz \tag{2}$$

where

$$k \text{ denotes } (k_2 - k_1)$$

Let X_r and Y_r represent the orientations of the principal planes of refraction, the former corresponding to the slower wave in the absence of absorption; let δ denote the phase difference $(\delta_1 - \delta_2)$ introduced per unit distance (in the absence of dichroism). The infinitesimal operation of birefringence (corresponding to a passage dz) consists in rotating the sphere clockwise about the equatorial diameter $X_r Y_r$ through the infinitesimal angle δdz. This operation will cause the initial state of polarization P to move along the arc of a small circle with X_r as pole through an arc ds_r, where

$$ds_r = (\delta \sin 2\phi)\, dz \tag{3}$$

(*c*) *The States of Polarisation Propagated Unchanged*

In order that the simultaneous superposition of linear dichroism and birefringence should cause no change in the state of P, the movements ds_k and ds_r must be equal in magnitude and opposite in direction. Since arc ds_k is along PX_k while arc ds_r is perpendicular to PX_r we must have firstly, $X_r PX_k = \pi/2$, or

$$\cos 2X = \cos 2\phi \cos 2\psi \tag{4}$$

and secondly

$$\delta \sin 2\phi = k \sin 2\psi \tag{5}$$

together with the condition that P will be a right- or left-elliptic vibration according as χ (the angle between the X_k and X_r axes) is positive (0 to $\pi/2$) or negative (0 to $-\pi/2$).

In general there are two positions P which simultaneously satisfy these conditions—the relations (4) and (5) being unchanged when we alter 2ϕ and 2ψ to $\pi - 2\phi$ and $\pi - 2\psi$ respectively. Thus in the figure the state P_b whose distances from the points Y_k and Y_r are 2ψ and 2ϕ, is also propagated unchanged. The states P_a and P_b have the same latitudes, their longitudes differing by π.

Hence we arrive at the result, also obtained from the electromagnetic theory, that the states of polarisation propagated unchanged along any general direction are two similarly rotating elliptic vibrations which have their major axes crossed and their ellipticities equal.

In order to construct these two elliptic vibrations (see Fig. 1) we must first determine the orientations of one of the principal diameters—for example the orientation of OX′ which is the major axis of P_a and also the minor axis of P_b. Let the inclination of OX′ be χ_2 (anti-clockwise) with respect to OX_r and χ_1 (clockwise) with respect to OX_k. The direction of OX′ may be determined by the relation

$$\frac{\sin 4\chi_1}{\sin 4\chi_2} = \frac{\delta^2}{k^2} \tag{6}$$

Next the ratio $\tan\theta$ of the minor to the major axis of the elliptic vibrations may be obtained from

$$\sin^2 2\theta = \tan 2\chi_1 \tan 2\chi_2 \tag{7}$$

—a relation which gives the ellipticity ($\tan\theta = \operatorname{cosec}^2 2\theta + \sqrt{\operatorname{cosec}^2 2\theta - 1}$) in terms of the orientation of the axes of the elliptic vibrations. It may be noted that equations (6) and (7) remain unaltered when we change χ_1 and χ_2 to $(\pi/2+\chi_1)$ and $(\pi/2+\chi_2)$ respectively.

The relations stated in the previous paragraph will now be proved with the aid of the Poincaré sphere (Fig. 2). The direction OX′ is given by the point X′ on the equator having the same longitude as P. Then since the triangles X_rPX' and X_kPX' are both right-angled, we have

$$\left.\begin{aligned}\cos 2\phi &= \cos 2\chi_2 \cos 2\theta\\ \cos 2\psi &= \cos 2\chi_1 \cos 2\theta\end{aligned}\right\} \tag{8}$$

Multiplying these equations and comparing with (4),

$$\cos(2\chi_1 + 2\chi_2) = \cos 2\chi_1 \cos 2\chi_2 \cos^2 2\theta$$

which on simplification gives the relation (7).

To prove (6) we consider the right-angled triangles X_kPX_r and X_kPX':

$$\cos\hat{X}_k = \frac{\tan 2\psi}{\tan 2\chi} = \frac{\tan 2\chi_1}{\tan 2\psi}$$

Hence

$$\tan^2 2\psi = \tan 2\chi_1 \tan 2\chi$$

$$\tan^2 2\phi = \tan 2\chi_2 \tan 2\chi$$

or,

$$\frac{\tan^2 2\psi}{\tan^2 2\phi} = \frac{\tan 2\chi_1}{\tan 2\chi_2} \tag{9}$$

From relations (8) we also have

$$\frac{\cos^2 2\psi}{\cos^2 2\phi} = \frac{\cos^2 2\chi_1}{\cos^2 2\chi_2} \tag{10}$$

Multiplying (9) and (10) and comparing with (5) we get the required relation (6).

(*d*) *Comparison with the Electromagnetic Theory*

The relation (7) giving the ellipticity in terms of the orientation of the axes of the elliptic vibration, is identical with that deduced from the electromagnetic theory (Pockels, *loc. cit.*, p. 399, eq. 54); while the relation (6) giving the orientation of the axes of the elliptic vibrations has to be compared with the following similar relation (Pockels, *loc. cit.*, p. 397, eq. 53):

$$\frac{\sin 4\chi_1}{\sin 4\chi_2} = \frac{\rho^2}{\sigma^2} \tag{6'}$$

where

$$\rho = \tfrac{1}{2}(a_2 - a_1) \text{ and } \sigma = \tfrac{1}{2}(b_2 - b_1)$$

The tensor components a_1, a_2, etc., may be easily shown to have the following geometrical meanings. The major and minor semi-axes of the elliptical section of the index ellipsoid made by the plane of the paper have lengths $1/\sqrt{a_1}$ and $1/\sqrt{a_2}$ respectively, while the major and minor semi-axes of the elliptical section of the absorption ellipsoid have lengths $1/\sqrt{b_1}$ and $1/\sqrt{b_2}$ respectively. Relations (6) and (6′) will be identical if

$$\delta^2/k^2 = \rho^2/\sigma^2 \tag{11}$$

As pointed out in Section 2, the waves propagated along directions appreciably inclined to the optic axes may be considered as linearly polarised; and for such directions of propagation, if $1/\sqrt{b}$ be the length of any radius of the absorption ellipsoid, then $b = 2\kappa v^3/c$, where κ is the extinction coefficient and v the velocity for that vibration-direction. In consonance with this it would be natural to use the following relation for the hypothetical extinction coefficients κ_1 and κ_2 in the absence of birefringence:

$$\frac{2\kappa_1 v_m{}^3}{c} = b_1\,; \quad \frac{2\kappa_2 v_m{}^3}{c} = b_2 \tag{12}$$

where v_m is a mean velocity. We then have

$$k = \frac{2\pi}{\lambda_0}(\kappa_2 - \kappa_1) = \frac{2\pi c}{\lambda_0}\,\frac{\sigma}{v_m{}^3}$$

Relation (11) will be obviously satisfied if we analogously set

$$\delta = \frac{2\pi c}{\lambda_0} \cdot \frac{\rho}{v_m{}^3} = \frac{2\pi c}{\lambda_0} \cdot \frac{a_2 - a_1}{2v_m{}^3} \tag{13}$$

Since the velocoties v_1 and v_2 in the absence of absorption are equal to $\sqrt{a_1}$ and $\sqrt{a_2}$ respectively, relation (13) will be *exactly* satisfied if we define the mean velocity v_m by

$$v_m{}^3 = \tfrac{1}{2}(v_1 + v_2) \cdot v_1 v_2 \tag{14}$$

5. THE ABSORPTION COEFFICIENTS AND REFRACTIVE INDICES OF THE WAVES

It is well known that in the case of a transparent crystal, it is simpler to specify the velocities of the waves as functions of the vibration directions than as functions of the directions of propagation: the former leads to the simple index-ellipsoid representation, the latter to the comparatively more complex wave surface of two sheets. We shall show that for absorbing crystals too, if we choose to express the velocities and absorption coefficients as functions of the states of polarisation (ϕ, ψ) of the waves, the resulting expressions (as deduced both by the method of superposition and by the electromagnetic theory) may be put in a very simple form.

When an elliptic vibration of unit intensity in any state of polarisation travels a distance *dz*, the diminution in its intensity may be calculated directly from the reduction of intensity involved in the infinitesimal operation of dichroism corresponding to the passage *dz*—since the operation of birefringence produces no reduction in intensity. If, in addition, the elliptic vibration be in a state of polarisation P_a that can be propagated without change of form, this reduction in intensity may be equated to $2k_a\,dz$ where k_a is the coefficient of absorption for that wave. The amplitudes of the X_k and Y_k components of the elliptic vibration P_a will be $\cos\psi_a$ and $\sin\psi_a$ respectively; hence the reduction in intensity of these components will obviously be $2k_1\cos^2\psi_a\,dz$ and $2k_2\sin^2\psi_a\,dz$ respectively. Therefore,

$$\left.\begin{aligned} & k_a = k_1\cos^2\psi_a + k_2\sin^2\psi_a \\ \text{Similarly} \quad & \\ & k_b = k_1\sin^2\psi_a + k_2\cos^2\psi_a \\ \text{So that} \quad & \\ & (k_a - k_b) = (k_1 - k_2)\cos 2\psi_a \end{aligned}\right\} \tag{15}$$

Here 2ψ being the arc PX_k on the Poincare sphere may be evaluated by the relations (4) and (5) of Section 4*c*, which determine the states of polarisation of the waves.

Expressions for the refractive indices of the waves (in terms of the state of polarisation of one of them) are equally simple, being given by:

$$\left.\begin{aligned} n_a &= n_1 \cos^2 \phi_a + n_2 \sin^2 \phi_a \\ n_b &= n_1 \sin^2 \phi_a + n_2 \cos^2 \phi_a \\ (n_a - n_b) &= (n_1 - n_2) \cos 2\phi_a \end{aligned}\right\} \tag{16}$$

The proofs of these relations do not have the same simplicity as those of (15), and will be given only at the end of Section 7, since recourse must be taken to the analytically derived equations obtained there.

(6) THE PROPAGATION OF LIGHT ALONG THE AXES OF CIRCULAR POLARISATION

(*a*) *The Singular Axes*

The electromagnetic theory predicts that close to an optic axis and on either side of it, there exist two directions along each of which only *one* state of polarisation (and not two) can be propagated unchanged: only a right-circularly polarised wave can be propagated along one of these axes, and only a left-circularly polarised wave along the other. These directions have been termed the *Windungsachsen*; Voigt has also referred to them as *singular axes* and we shall follow this simpler nomenclature. At these two axes of circular polarisation the inclinations of the principal planes of absorption with respect to the *corresponding* principal planes of refraction are +45° and −45° respectively. Further, along these two directions the pure birefringence term δ is equal to the dichroic term k.

The remarkable property of these axes follows very simply from the standpoint of the method of superposition by the use of the Poincaré sphere. Let us suppose for example that the principal plane of absorption OX_k makes an angle of −45° with respect to the corresponding principal plane of refraction OX_r. In Fig. 3, the diameter X_kY_k will then be at right angles to X_rY_r as shown. If we consider a state of polarisation initially coincident with the pole C_l, it can be seen that its movement ds_r (due to an infinitesimal clockwise rotation δdz, about X_rY_r) will be oppositely directed to the movement ds_k towards the less absorbed component X_k; and the movements will be equal in magnitude if $\delta = k$. Thus a left-circular vibration can be propagated unchanged along such a direction. Further, there can be no other state which can also be propagated unchanged, since the 2 elliptic vibrations propagated unchanged along any direction must have the same sense of description and the same ellipticity. Similarly, where OX_k makes an angle

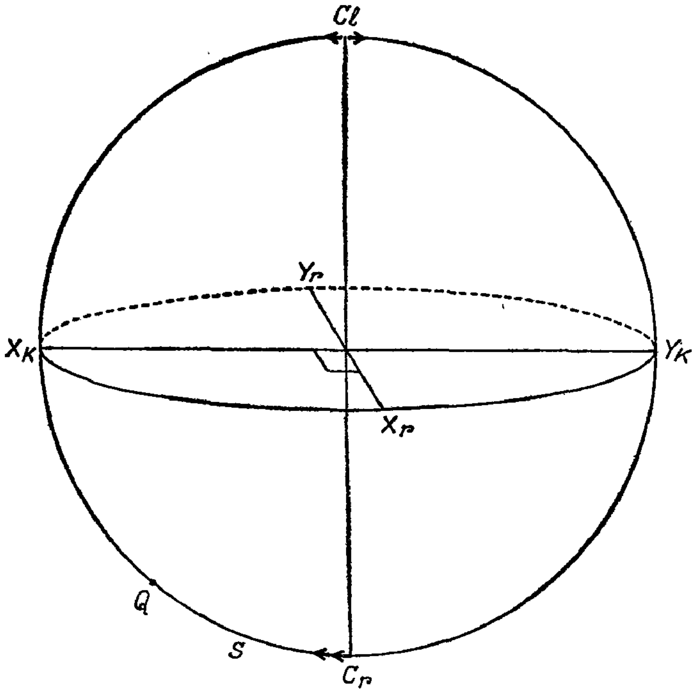

FIG. 3

C_r—Right circular vibration incident in the direction of a singular axis (where only the left-circular vibration C_l can be propagated unchanged).

Q—The state of vibration at a depth z (specified by the arc s).

of + 45° with respect to OX_r, and where in addition $\delta = k$, only a right-circular vibration can be propagated unchanged. The refractive index of the circularly polarised wave that can be propagated unchanged along a singular axis is $\frac{1}{2}(n_1 + n_2)$ and its absorption coefficient $\frac{1}{2}(k_1 + k_2)$ as may be seen by setting $\phi = \psi = \pi/4$ in relation (18) and (19).

Before proceeding to discuss in more detail the propagation of light along the singular axes, we consider it relevant to point out that the functions with which we are concerned show no discontinuity at the singular axes. Thus both the elliptic vibrations propagated without change of form along any general direction, gradually degenerate into two (identical) circular vibrations as we approach a singular axis from any side whatsoever. [This can be seen by making $\chi \rightarrow 45$ and $\delta \rightarrow k$ in relations (4) and (5) of Section 4 *c*.] The refractive indices and absorption coefficients of these two waves, being determined by their states of polarisation (by relations 15 and

16 of Section 5) tend towards the common values $\frac{1}{2}(n_1 + n_2)$ and $\frac{1}{2}(k_1 + k_2)$ respectively, as we approach a singular axis. (See also reference 8.)

(*b*) *Effects with Incident Circularly Polarised Light*

In this section we shall inquire as to what will happen when, for example right circularly polarised light C_r is incident in the direction of a singular axis where only a left circular vibration C_l can be propagated unchanged (Fig. 3). Our results in this connection are at variance with those expected by Voigt. It was supposed by Voigt[3, 4] that if a plate cut normal to an optic axis is viewed in convergent circularly polarised light, then along the singular axis where the incident vibration can be propagated unchanged, more light would get through than in the neighbourhood of the other singular axis where only the oppositely directed circular vibration can be propagated unchanged; and that the latter direction should in consequence appear darker than the former.* On performing an actual experiment, he observed a dark and a bright spot in the field of view, one on either side of the optic axis and this was considered by him as confirming his view. According to our analysis, however, it is the singular axis where the incident vibration can be propagated unchanged that should appear *darker* than the other singular axis (where only the oppositely directed circular vibration can be propagated *unchanged*).

We shall apply *directly* the method of superposition, according to which, given the state of vibration at a particular plane in the medium, the state of the vibration at a further distance *dz* is obtained by superposing the effects of pure birefringence and pure dichroism corresponding to that passage. The state of vibration should then get progressively altered as we proceed into the medium.

Referring to Fig. 3, if the state of polarisation be initially coincident with the pole C_r, its movement ds_r (due to a clockwise rotation δdz about X_rY_r) is in the *same* direction as its movement ds_k towards the less absorbed component X_k; and the sum of these movements will give the alteration in the state of vibration corresponding to a passage *dz*. Continuing this procedure, it can be seen that as we proceed into the medium, the state of polarisation progressively moves along the arc $C_rX_kC_l$. At a particular depth the vibration would be linearly polarised along the principal plane

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* In a later paper [8], Voigt has suggested that if we could get a plate exactly normal to a singular axis, and have circularly polarised light of the proper sense incident precisely along this normal, the light would be *totally* reflected—the reflection being partial in practical cases. This idea receives no support from the results of the present investigation.

of absorption OX_k. After this stage the movement ds_k due to dichroism opposes the movement ds_r due to birefringence; but the latter being greater in magnitude, the state of polarisation continues to alter as we proceed further into the medium, tending towards the state C_l that can be propagated without change of form.

Thus if we consider the state of polarisation at successive depths within the medium, we see that the incident right-circular vibration will first get modified to an elliptic vibration (with major axis always at 45° to the principal planes of refraction), which in turn gets reduced to a linear vibration; as we proceed further the linear vibration opens out into a *left-handed* elliptic vibration, which gradually tends towards the state of a left-circular vibration that can be propagated unchanged. Nevertheless, as may be seen physically, this last state is never attained at any finite depth; for as the state of polarisation comes close to that of a left-circular vibration, the modification of the state corresponding to an additional passage dz becomes correspondingly reduced.

It is easy to deduce an explicit expression for the state of polarisation P that should be expected (according to the above line of argument) at any depth z inside the medium. The state P may be specified by giving the length s of the arc C_rP. Then the state $s + ds$ at the depth $z + dz$ will be given by

$$ds = (\delta + k \cos s)\, dz \tag{17}$$

according to relations (2) and (3) of Section 4 *b*. Since $\delta = k$, we have on integration,

$$\tan \tfrac{1}{2}s = kz \tag{18}$$

This relation shows that the transformation from a right-circular vibration ($s = 0$), to a linear vibration at 45° to the principal planes of refraction ($s = \pi/2$), occurs within a smaller depth than if the crystal had been transparent; whereas the corresponding alteration from the linear vibration to a left circular vibration (which for a transparent crystal would have occurred at a finite depth) requires here an infinite passage, due to the 'retarding' effect of the dichroism.

We shall next calculate the intensity I_z of the vibration P at a distance z inside the medium. The diminution of intensity $-dI_z$ corresponding to an additional passage dz is given by

$$-dI_z/I_z = 2k_z dz \tag{19}$$

where, it must be noted k_z is not a constant but a function of the state of polarisation and hence also of the depth z. We will have for k_z an expression analogous to (15), Section 5:

$$k_z = k_1 \cos^2 \psi + k_2 \sin^2 \psi$$
$$= \tfrac{1}{2}(k_1 + k_2) - \tfrac{1}{2}k \cos 2\psi \qquad (20)$$

Thus k_z is always less than the coefficient of absorption $\frac{1}{2}(k_1 + k_2)$ of the left-circularly polarised wave that can be propagated without change of form along the same direction. (This is more directly seen by the fact that the state of polarisation is always nearer to the less absorbed component X_k than is a left-circular vibration.) Hence *when the sense of description of a circular vibration incident in the direction of a singular axis is* opposed *to that which can be propagated unchanged along that direction, the emergent intensity should in fact be* greater *than when the sense of description of the incident vibration is reversed.* An expression for the ratio of the emergent intensities in the two cases will now be deduced. Since, from our point of view, the incident disturbance can propagate into the medium in both cases (though in one case with a progressive change in the state of polarisation) we have no particular reason to assume that the reflection losses would be different in the two cases.

Substituting the value of k_z given by (20) in (19) we get

$$-\,dI_z/I_z = (k_1 + k_2)\,dz - k \sin\, s\, dz$$

Expressing sin s in terms of z by using relation (18), and integrating, we have —if I_1 be the emergent intensity and I_0 the intensity entering the medium,

$$\log (I_0/I_1) = (k_1 + k_2)\,z - \log(1 + k^2z^2) \qquad (21)$$

On the other hand if I_2 be the emergent intensity when the incident circular vibration is of the sense which can be propagated unchanged,

$$\log (I_0/I_2) = (k_1 + k_2)\,z \qquad (22)$$

From (21) and (22) we have the following simple relation for the ratio of the intensities emerging in the two cases:

$$I_1/I_2 = 1 + k^2z^2$$

a ratio which is always greater than unity.

Though our results regarding the properties of the singular axes are at variance with those expected by Voigt, it must not therefore be concluded that the method of superposition leads to results differing from the electromagnetic theory—since it is possible to regard the former merely as a mathematical artifice: for (as has been pointed out in Section 8), by reversing the entire scheme of arguments, the propagation of two elliptically polarised waves with different absorption coefficients and velocities (*as given by the electromagnetic theory*) may for mathematical convenience be rigorously treated by the method of superposition; the convenience of this artifice being particularly manifest when we wish to find the limiting effects as the two elliptically polarised waves gradually tend towards the state of two (identical) circularly polarised waves with equal velocities and absorption coefficients.

7. ANALYTICAL DISCUSSION OF SUPERPOSITION

Referring to Fig. 1, let us suppose that we are given the equation of the elliptic vibration described at any particular plane z in the medium. If the initial state of polarisation is to be propagated without change of form, then the equation of the vibration at the plane $z + dz$ can be obtained not only by the method of superposition but also from the usual equation for the propagation of a damped wave. By equating these two expressions we can determine not only the states of polarisation that can be propagated without change of form but also their velocities and extinction coefficients.

Let OX and OY be two arbitrary rectangular axes taken in the plane of the figure, the inclinations of OX_k and OX_r with respect to the positive x-axis being α_1 and α_2 respectively. Let the components of the arbitrary elliptic vibration P along the axes OX, OY, have the following equations (using complex notation and indicating the complex quantities by bars):

$$\left.\begin{aligned} x &= \mathrm{F}e^{i(\omega t-\theta_1)} = \bar{f}e^{i\omega t} \\ y &= \mathrm{G}e^{i(\omega t-\theta_2)} = \bar{g}e^{i\omega t} \end{aligned}\right\} \tag{23}$$

so that

$$\frac{\bar{g}}{\bar{f}} = \frac{\mathrm{G}}{\mathrm{F}}\,e^{i\theta}$$

where $\bar{g}/\bar{f}$ is the ratio of the complex amplitudes, G/F the ratio of the real amplitudes and θ the difference of phase $(\theta_1 - \theta_2)$ between the x and y components. (It may be noted that G/F and θ will have—on the Poincaré sphere—geometrical interpretations essentially similar to those that have been described in Section 4 c for $\mathrm{G}_k/\mathrm{F}_k$ and θ_k.)

Let the complex amplitudes become $\bar{f}'$, $\bar{g}'$, after the infinitesimal operation of dichroism alone, and $\bar{f}''$, $\bar{g}''$, after both the infinitesimal operations of dichroism and birefringence corresponding to a passage dz. But if the initial state of polarisation $(\bar{f}, \bar{g})$ is to be propagated without change of form, and with a specific extinction coefficient κ and refractive index n, then its state $(\bar{f}'', \bar{g}'')$ after propagating a distance dz should also be given by:

$$\bar{f}'' e^{i\omega t} = \bar{f} e^{i\left(\omega t - \frac{2\pi}{\lambda_0} \bar{n}\, dz\right)}$$

or

and

$$\left.\begin{aligned} \bar{f}'' &= \bar{f}\left(1 - i\frac{2\pi}{\lambda_0}\bar{n}\, dz\right) \\ \bar{g}'' &= \bar{g}\left(1 - i\frac{2\pi}{\lambda_0}\bar{n}\, dz\right) \end{aligned}\right\} \qquad (24)$$

where $\bar{n}$ is the complex refractive index $(n - i\kappa)$ of the elliptically polarised wave. We shall now, by the method of superposition, proceed to determine expressions for the final state $(\bar{f}'', \bar{g}'')$ in terms of the initial state $(\bar{f}, \bar{g})$, and then substitute these expressions in (24).

The Operation of Dichroism.—The elliptic vibration P, given by (23), is first referred to the axes OX_k, OY_k along the principal planes of absorption; the complex amplitudes $(\bar{f}_k, \bar{g}_k)$ of the components along these directions can be obtained from the amplitudes $(\bar{f}, \bar{g})$ by the usual transformation scheme for the rotation of co-ordinate axes through an angle α_1. These amplitudes $\bar{f}_k$, $\bar{g}_k$ are then multiplied by $(1 - 2\pi/\lambda_0 . \kappa_1 dz)$ and $(1 - 2\pi/\lambda_0 . \kappa_2 dz)$ respectively, to give the amplitudes $\bar{f}_k'$, $\bar{g}_k'$ of the x_k, y_k components after the operation of dichroism. Finally the elliptic vibration $\bar{f}_k'$, $\bar{g}_k'$ thus obtained is referred back to the axes OX, OY; the complex amplitudes $\bar{f}'$, $\bar{g}'$ of the components along these directions are obtained from the amplitudes $\bar{f}_k'$, $\bar{g}_k'$ by the usual transformation scheme for the rotation of the co-ordinate axes through an angle $-\alpha_1$.

If we go through the straightforward but lengthy algebraic substitutions involved in the procedure described in the last paragraph, it can be shown that the amplitudes $\bar{f}'$, $\bar{g}'$ of the x, y components after the operation of dichroism are related to the corresponding initial amplitudes $\bar{f}$, $\bar{g}$ by relations which may be put in a form analogous to (24):

$$\left.\begin{aligned} \bar{f}' &= \bar{f}\left[1 - \frac{2\pi}{\lambda_0}\left(\kappa_{11} + \frac{\bar{g}}{\bar{f}} \cdot \kappa_{12}\right) dz\right] \\ \bar{g}' &= \bar{g}\left[1 - \frac{2\pi}{\lambda_0}\left(\kappa_{22} + \frac{\bar{f}}{\bar{g}} \cdot \kappa_{12}\right) dz\right] \end{aligned}\right\} \qquad (25)$$

where, if α_1 be the orientation of the positive OX_k axis,

$$\left.\begin{aligned} \kappa_{11} &= \kappa_1 \cos^2\alpha_1 + \kappa_2 \sin^2\alpha_1 \\ \kappa_{22} &= \kappa_1 \sin^2\alpha_1 + \kappa_2 \cos^2\alpha_1 \\ \kappa_{12} &= \tfrac{1}{2}(\kappa_1 - \kappa_2)\sin 2\alpha_1 \end{aligned}\right\} \qquad (26)$$

If an ellipse be drawn with its principal semi-axes of lengths $1/\sqrt{\kappa_1}$ and $1/\sqrt{\kappa_2}$ lying along OX_k and OY_k, then $1/\sqrt{\kappa_{11}}$ and $1/\sqrt{\kappa_{22}}$ are the lengths of the radii vectors intercepted by the OX and OY directions, the equation of the ellipse being

$$\kappa_{11}\, x^2 + \kappa_{22}\, y^2 + 2\kappa_{12}\, xy = 1$$

The Operation of Birefringence.—The mathematical procedure involved in the infinitesimal operation of birefringence is essentially the same as in the operation of dichroism. The elliptic vibration $\bar{f}', \bar{g}'$ obtained after the operation of dichroism is first referred to the axes OX_r, OY_r along the principal planes of refraction; the complex amplitudes $\bar{f}_r'\, \bar{g}_r'$ of the components along these directions are then multiplied by $\exp\,(-\, i\, 2\pi/\lambda_0 . n_1 dz)$ and $\exp\,(-\, i\, 2\pi/\lambda_0 . n_2 dz)$ respectively—where n_1 and n_2 are the refractive indices in the absence of absorption. On referring the final vibration $(\bar{f}_r'', \bar{g}_r'')$ back to the axes OX, OY we will have the complex amplitudes $(\bar{f}'', \bar{g}'')$ of the x, y components, related to the corresponding amplitudes $\bar{f}', \bar{g}'$ (before the birefringence operation) by equations essentially similar to (25), though put in the form of (24):

$$\left.\begin{aligned} \bar{f}'' &= \bar{f}'\left[1 - i\frac{2\pi}{\lambda_0}\left(n_{11} + \frac{\bar{g}'}{\bar{f}'}\cdot n_{12}\right)dz\right] \\ \bar{g}'' &= \bar{g}'\left[1 - i\frac{2\pi}{\lambda_0}\left(n_{22} + \frac{\bar{f}'}{\bar{g}'}\cdot n_{12}\right)dz\right] \end{aligned}\right\} \qquad (27)$$

Here n_{11}, n_{22} and n_{12} are to be regarded as *defined* by the relations (analogous to (26):

$$\left.\begin{aligned} n_{11} &= n_1 \cos^2 a_2 + n_2 \sin^2 a_2 \\ n_{22} &= n_1 \sin^2 a_2 + n_2 \cos^2 a_2 \\ n_{12} &= \tfrac{1}{2}(n_1 - n_2) \sin 2a_2 \end{aligned}\right\} \qquad (28)$$

where a_2 gives the angle made by the positive OX_r axis with the x-axis.

Since we shall omit terms involving dz^2, the value of $(\bar{g}'/\bar{f}')$ to be substituted in (27) need not include even the terms of the first order in dz, *i.e.*, we may write $(\bar{g}/\bar{f})$ for $(\bar{g}'/\bar{f}')$ in (27). We then obtain as the equation connecting the final state of polarisation $\bar{f}'', \bar{g}''$ (after both the infinitesimal operation of birefringence and dichroism corresponding to a passage dz), with the initial state $\bar{f}, \bar{g}$:

$$\left.\begin{aligned} \bar{f}'' &= \bar{f}\left\{1 - i\frac{2\pi}{\lambda_0}\left[\overline{n_{11} - i\kappa_{11}} + \frac{\bar{g}}{\bar{f}}\cdot\overline{n_{12} - i\kappa_{12}}\right]dz\right\} \\ \bar{g}'' &= \bar{g}\left\{1 - i\frac{2\pi}{\lambda_0}\left[\overline{n_{22} - i\kappa_{22}} + \frac{\bar{f}}{\bar{g}}\cdot\overline{n_{12} - i\kappa_{12}}\right]dz\right\} \end{aligned}\right\} \qquad (29)$$

The Final Equations for Wave Propagation.—We now introduce the values of $\bar{f}''$, $\bar{g}''$ given by (29), into equation (7). Conciseness will obviously be attained if we first introduce the complex quantities:

$$\bar{n}_{11} = n_{11} - i\kappa_{11}$$
$$\bar{n}_{22} = n_{22} - i\kappa_{22}$$
$$\bar{n}_{12} = n_{12} - i\kappa_{12}$$

where the n_{hk} and κ_{hk} have already been defined in relations (26) and (28). We then obtain as our final equations:

$$\left.\begin{aligned} \bar{n} - \bar{n}_{11} &= \frac{\bar{g}}{\bar{f}} \cdot \bar{n}_{12} \\ \bar{n} - \bar{n}_{22} &= \frac{\bar{f}}{\bar{g}} \cdot \bar{n}_{12} \end{aligned}\right\} \tag{30}$$

There will be two pairs of values $(\bar{n}_a, \bar{g}_a/\bar{f}_a)$ and $(\bar{n}_b, \bar{g}_b/\bar{f}_b)$ which simultaneously satisfy (30); and—since $\bar{g}/\bar{f}$ and $\bar{n}$ are both in general complex—this means that there should be two elliptically polarized waves that can be propagated, each with a specific velocity and coefficient of extinction. Eliminating $\bar{n}$ between the two equations of (30) by subtracting, we get the following quadratic in $\bar{g}/\bar{f}$ determining the states of polarisation propagated without change of form:

$$\frac{\bar{f}}{\bar{g}} - \frac{\bar{g}}{\bar{f}} = \frac{\bar{n}_{11} - \bar{n}_{22}}{\bar{n}_{12}} \tag{31}$$

The two roots of this equation are obviously connected by the relation $(\bar{g}_a/\bar{f}_a) = -(\bar{f}_b/\bar{g}_b)$, from which it follows that the two elliptically polarised vibrations have their major axes at right angles and their ellipticities equal, but are described in the same sense (see, *e.g.*, McLaurin[9]).

Eliminating $\bar{g}/\bar{f}$ between the two equations (30) by multiplying the two, we get the following quadratic in $\bar{n}$ determining the complex refractive indices of the waves:

$$(\bar{n} - \bar{n}_{11})(\bar{n} - \bar{n}_{22}) = \bar{n}_{12}^2 \tag{32}$$

From this we get the expressions for the sum and difference of the complex refractive indices:

$$(\bar{n}_a - \bar{n}_b)^2 = (\bar{n}_{11} - \bar{n}_{22})^2 + 4\bar{n}_{12}^2 \tag{33}$$

and

$$(\bar{n}_a + \bar{n}_b) = \bar{n}_{11} + \bar{n}_{22} \tag{34}$$

Velocities and Absorption Coefficients of the Waves.—The expressions for the velocities and absorption coefficients given in Section 4 may be derived from the equations (30) which give the complex refractive $\bar{n}$ in terms of the corresponding state of polarisation $\bar{g}/\bar{f}$. If we choose axes of co-ordinates along OX_r, OY_r then $n_{12} = 0$, $a_2 = 0$ and $a_1 = 2X$. The first of the two relations in (30) gives:

$$(n - i\kappa) = (n_1 - i\kappa_{11}) + \frac{G_r}{F_r} e^{i\theta_r} \cdot (-i\kappa_{12})$$

Equating real parts

$$n = n_1 + (G_r/F_r)\,\kappa_{12} \sin \theta_r$$
$$= n_1 + (G_r/F_r) \cdot \tfrac{1}{2}(\kappa_1 - \kappa_2) \sin 2X \sin \theta_r$$

Referring to Fig. 2, since $\theta_r = PX_r X_k$ we have

$$\sin 2X \sin \theta_r = \sin 2\psi$$

Hence on using eq. (5), Section 4 *c*, we have

$$n = n_1 - (G_r/F_r) \cdot \tfrac{1}{2}(n_1 - n_2) \sin 2\phi$$

Since $(G_r/F_r) = \tan \phi$, we get as our final expression for the refractive index,

$$n = n_1 \cos^2 \phi + n_2 \sin^2 \phi$$

Similarly we will have for the extinction coefficient,

$$\kappa = \kappa_1 \cos^2 \psi + \kappa_2 \sin^2 \psi$$

8. COMPARISON WITH THE ELECTROMAGNETIC THEORY

Let the sections of the index and absorption ellipsoids made by the *xy* plane be given by the respective equations:

$$\left.\begin{aligned} a_{11}x^2 + a_{22}y^2 + 2a_{12}xy = 1 \\ b_{11}x^2 + b_{22}y^2 + 2b_{12}\,xy = 1 \end{aligned}\right\} \tag{35}$$

Let us introduce the quantities

$$\bar{c}_{hk} = a_{hk} + ib_{hk} \tag{36}$$

Then the equations (30) giving the states of polarisation and the complex refractive indices of the two waves propagated along any direction have to be compared with the following similar relations obtained from the electromagnetic theory:

$$\left.\begin{aligned}(\bar{v}^2 - \bar{c}_{11}) &= \frac{\bar{g}}{\bar{f}} \cdot \bar{c}_{12} \\ (\bar{v}^2 - \bar{c}_{22}) &= \frac{\bar{f}}{\bar{g}} \cdot \bar{c}_{12}\end{aligned}\right\} \quad (37)$$

where the complex velocity $\bar{v} = v\,(1 + ix')$

We may first remark that it would indeed be possible to *define* the quantities $\bar{n}_{11}$, $\bar{n}_{22}$ and $\bar{n}_{12}$ (in terms of $\bar{c}_{11}$, $\bar{c}_{22}$ and $\bar{c}_{12}$) in such a manner that the results obtained by the method of superposition would be identical with the results of the electromagnetic theory. But in order to retain the physical content of the method of superposition it is necessary to regard the velocities v_1 and v_2 in the absence of absorption as being equal to $\sqrt{a_1}$ and $\sqrt{a_2}$ respectively (where $1/\sqrt{a_1}$ and $1/\sqrt{a_2}$ are the lengths of the principal radii of the elliptical section of the index ellipsoid). And once this is done, at least some of the results obtained by the method of superposition have necessarily to be regarded as approximations. We shall however show that for directions near an optic axis where the birefringence is necessarily very small and where alone the ellipticity of the waves play an important role, the error involved is negligible. To this end we shall start by assuming the relations (12) and (14) which give a connection between the extinction coefficients κ_1 and κ_2 on the one hand, and the lengths $1/\sqrt{b_1}$ and $1/\sqrt{b_2}$ of the principal radii of the elliptical section of the absorption ellipsoid on the other. The quantities a_{hk} occurring in equation (35) can obviously be expressed in terms of a_1 and a_2 thus:

$$\left.\begin{aligned}a_{11} &= a_1 \cos^2 \alpha_2 + a_2 \sin^2 \alpha_2 \\ a_{22} &= a_1 \sin^2 \alpha_2 + a_2 \cos^2 \alpha_2 \\ a_{12} &= \tfrac{1}{2}(a_1 - a_2) \sin 2\alpha_2\end{aligned}\right\} \quad (38)$$

Similar relations analogous to (26) hold for the b_{hk}.

On examining the equations [(30) and 37)] obtained by the method of superposition and by the electromagnetic theory, we notice that the two are entirely similar in form, the only difference being the occurrence of the quantities $\bar{c}_{hk}$ instead of $\bar{n}_{hk}$ and $\bar{v}^2$ instead of $\bar{n}$. Hence it follows that given any equation obtained by the method of superposition, a corresponding exact equation obtainable from the electromagnetic theory can be written down, merely by changing the symbols occurring in the equation according to the following scheme:

n	n_1	n_2	κ	κ_1	κ_2
v^2	a_1	a_2	$-\dfrac{2\kappa v^3}{c}$	$-b_1$	$-b_2$

Thus to obtain the states of polarisation (ϕ, ψ) that can be propagated without change of form, we have to replace the ratio δ/k in eqn. (5) by the ratio ρ/σ where $\rho = \frac{1}{2}(a_2 - a_1)$ and $\sigma = \frac{1}{2}(b_2 - b_1)$. This replacement will however leave the equation unaltered, as we have already shown in Section 4 (*d*) that $\delta/k = \rho/\sigma$. It is also possible to show that the *sense* of description of the two vibrations as obtained by the method of superposition is the same as that obtained by the electromagnetic theory.

Expressions for the velocities and absorption coefficients according to the electromagnetic theory may be similarly written down from the relations (15) and (16):

$$v^2 = a_1 \cos^2 \phi + a_2 \sin^2 \phi \tag{39}$$

$$\frac{2\kappa v^3}{c} = b_1 \cos^2 \psi + b_2 \sin^2 \psi \tag{40}$$

We hence obtain

$$(v_a{}^2 - v_b{}^2) = (a_1 - a_2) \cos 2\phi_a$$

Or, if v_m be the mean velocity introduced in Section 4 (*d*)

$$\frac{v_b{}^2 - v_a{}^2}{2v_m{}^3} \cdot c = (n_1 - n_2) \cos 2\phi_a$$

On comparing this with the last equation in (16) we see that the approximation involved in using the method of superposition is to regard the expression on the left-hand side of the above equation as being practically equal to the difference in refractive indices $(n_a - n_b)$. This is justifiable along directions where the birefringence is low, and in fact this same approximation is also made when the propagation in transparent optically active crystals is regarded from the standpoint of superposition (Pockels, *loc. cit.*, p. 312).

From Eqn. (40) we get

$$2\kappa_a v_a{}^3 - 2\kappa_b v_b{}^3 = (b_1 - b_2) \cos 2\psi_a$$

Or, using (12)

$$\frac{\kappa_a v_a{}^3 - \kappa_b v_b{}^3}{v_m{}^3} = (\kappa_1 - \kappa_2) \cos 2\psi_a$$

On comparing this with the last equation in (15), we see that the approximation we have to make is to regard the expression on the left as being prac-

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EVALUATION OF THE FOUR ELASTIC CONSTANTS OF SOME CUBIC CRYSTALS

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1. Introduction

The mathematical theory of elasticity in its generally accepted form derives from a memoir by A. L. Cauchy presented to the Academy of Sciences at Paris in 1822. The analytical specification of the strains and stresses in elastic solids adopted in that theory expresses the strains in terms of the differential displacements of neighbouring points in the solid and the stresses in terms of the tractive forces on infinitesimal areas in the same location. The theory, however, does not make use of these representations with complete generality, but following Cauchy, adopts them in modified forms on the basis of arguments put forward by him and considered as authoritative ever since. But when one examines those arguments critically, they are found to be indefensible. This is particularly clear in regard to the representation of strains. In the most general case, we have nine components of strain, but Cauchy reduced their number to six by eliminating movements which he identified with rigid body rotations. Actually, however, the components thus eliminated are not rigid body rotations, but differential rotations which are of the same nature as those appearing in the deformation of solids by torsion or flexure and hence, their elimination is not justified. Then again, Cauchy's reduction in the number of the stress components from nine to six is based on the idea that the angular momenta of the tractions taken about each of the co-ordinate axes and summed up should cancel out. But since the stresses are assumed to be in the nature of tractive forces and defined in terms of their magnitudes over infinitesimal areas, they have to be considered as acting on volume elements which are small enough to be regarded as particles and hence no consideration of angular momenta is called for. The reduction in number of the components of stress from nine to six has therefore no justification. Indeed, when once it is admitted that we have to retain all the nine components of strain, a similar step in regard to the components of stress follows inevitably.

In a recent paper (Raman and Viswanathan, 1955) the consequences of adopting the representations of stress and strain in elastic solids in their most general form have been discussed in detail. It has been shown in that paper that Cauchy's assumptions result in restricting the cases which fall within its scope to homogeneous strains properly-so-called. The more general case of heterogeneous strains, including especially all cases of wave-propagation and static deformations in the nature of torsion and flexure, lie outside its scope. Nevertheless, the mathematical theory of elasticity has actually been applied to these cases and formulæ have been obtained and the constants appearing in them have been evaluated experimentally. For example, the results of experimental studies with cubic crystals have been expressed in terms of three constants usually designated as C_{11}, C_{12} and C_{44} respectively. On the other hand, the more general theory shows that four constants designated as d_{11}, d_{12}, d_{44} and d_{45} are needed for the classes O*h* and T*d* of the cubic system. Hence, by an examination of the experimental data for those cubic crystals of the O*h* and T*d* classes which have been investigated with adequate precision by different methods, it should be possible to decide whether those data are expressible in terms of three constants only, or whether four constants are actually needed. It is the object of the present paper to present the results of such an examination.

2. SOME GENERAL REMARKS

The determination of elastic constants of crystals can be made independently by static and dynamic methods. In the former case we naturally deal with the elastic constants under isothermal conditions and in the latter case under adiabatic conditions. The dynamic methods depend upon the determination of velocity of propagation of high-frequency waves of different types in the solid. Many of the recent determinations of the elastic constants of crystals have been made by these methods and it would seem that a high degree of precision has been attained in the resulting data. We shall accordingly make use of them in the evaluation of the elastic constants of the respective materials.

The classical expression for the velocity of propagation in a cubic crystal in the older theory is given by equations of the type

$$\rho v^2 A^x = A^x \{C_{11} l^2 + C_{44}(m^2 + n^2)\} + (C_{12} + C_{44})(A^y lm + A^z ln)$$

while in the corrected theory it is given by equations of the type

$$\rho v^2 A^x = A^x \{d_{11} l^2 + d_{44}(m^2 + n^2)\} + (d_{12} + d_{45})(A^y lm + A^z ln)$$

Thus in reducing the experimental data we make the following identifications:

$$d_{11} = C_{11};\ d_{44} = C_{44} \text{ and } (d_{12} + d_{45}) = (C_{12} + C_{44}).$$

It will be seen at once that if $d_{44} = d_{45}$, then the two theories lead to identical results.

Whereas in the older theory, if the wave-velocities had been measured for a sufficient number of directions the data resulting would suffice to determine the constants C_{11}, C_{12} and C_{44}, in the present theory it only enables us to evaluate the three quantities d_{11}, d_{44} and $(d_{12}+ d_{45})$. Thus, at least one additional determination is needed by static methods yielding values for a different linear combination of the four constants. The most appropriate determination appears to be the bulk modulus the expression for which under the older theory is $(C_{11}+ 2C_{12})/3$, whereas in the new theory it is $(d_{11}+2d_{12})/3$. While determinations of the bulk modulus are not easy, there is reason to believe that a degree of precision adequate for our present purpose has been reached in the measurements made and reported from Bridgman's laboratory at Harvard. It is obvious that to utilize these data in conjunction with the determinations by the dynamic methods, it is necessary to assume that we are dealing in both cases with the same material and under the same physical conditions. Such an assumption would appear *prima facie* justifiable in the cases considered in the present paper, *viz.*, crystallised solids of very simple chemical composition. The correctness of the assumption is reinforced by an intercomparison of the elastic constants determined by dynamic methods and reported by different authors from different laboratories. In general, these values do not differ more than can reasonably be ascribed to inevitable uncertainties in the experimental determinations.

Some further remarks are also necessary in this connection. Since the experimental values for the compressibility refer to isothermal conditions it is necessary to correct them to obtain its value under adiabatic conditions in order that a comparison might be possible with the adiabatic constants determined by dynamic methods. This correction is effected making use of the well-known formula

$$\chi_{iso}- \chi_{adia}= \frac{9a^2T}{\rho C_p}$$

where χ represents the compressibility, a the coefficient of linear expansion of the substance, T the absolute temperature, ρ the specific gravity of the solid and C_p the specific heat of the solid in ergs per gram. The numerical values of the constants used in the calculation of this correction term have been taken from the *Landolt-Bornstein Tables* and the *International Critical Tables*.

The compressibility determinations made in Bridgman's laboratory usually extended upto very high pressures. We naturally make use of the compressibility value for zero pressures computed by the investigators themselves from the experimental data. The values reported by Bridgman and Slater prior to 1946 are subject to correction by a constant term $-0 \cdot 033 \times 10^{-7}\, kg^{-1} \cdot \mathrm{cm.}^{2}$ in the light of Bridgman's latest determination of the linear compressibility of iron. Since the compressibility as well as the other elastic constants are functions of temperature, it is necessary that the comparison should be made for their values at the same temperature, either as reported by the authors themselves or as reduced to the same temperature from a knowledge of the variation of the elastic constants with temperature.

In selecting the substances the data for which are discussed in the present paper, the choice has naturally fallen on those substances which have been frequently the subject of experimental study. It so happens that these substances also fall into well-defined groups being very similar in chemical composition and their crystal structure, *e.g.*, NaCl, KCl, KBr, NaBr, LiF, MgO and AgCl, all of which have the rock-salt structure; diamond, silicon, germanium, zinc blende and fluorspar all of which again have closely similar structures and finally the metallic elements aluminium, copper, nickel and silver which have the face-centred cubic structure. In tabulating our final results we have arranged the substances in the order stated, in order to facilitate intercomposition of their elastic behaviour.

3. CRYSTALS WITH THE ROCK-SALT STRUCTURE

(*a*) *Rock-salt.*—The elastic constants of NaCl were determined by Voigt first in 1888 by the methods of torsion and flexure. Bridgman has also in 1929 determined the constants by the same methods. With the development of techniques based on ultrasonic wave-propagation, several determinations have been made recently by numerous investigators namely, Bergmann, Rose, Durand, Hunter and Siegel, Huntington, Galt, Lazarus and Bhagavantam. The values reported by these investigators and the methods used by them are given in Table I.

The values for C_{12} reported by the investigators who have used the static methods are distinctly higher than the values for the same constant obtained using dynamic methods, and this difference appears to be larger than can be reasonably ascribed to experimental errors. On the other hand, the values for C_{11} and C_{44} do not exhibit such a difference. The close agreement between the results reported by the three investigators who have used the pulse technique indicate that this method yields precise results. Hence, the mean of the values reported by these three workers have been adopted here as the best values.

TABLE I

Author	Method	C_{11}	C_{12}	C_{44}
Voigt	*Static*	4·77	1·32	1·29
Bridgman	,,	4·94	1·37	1·28
Bergmann	Diffraction patterns	4·77	1·25	1·21
Rose (270° K.)	Composite oscillator	5·06	1·30	1·278
Durand (300° K.)	,,	4·96	1·31	1·268
Hunter and Siegel	,,	4·86	1·194	1·281
Huntington (25° C.)	Pulse	4·85	1·23	1·265
Galt (298° K.)	,,	4·87	1·24	1·260
Lazarus (298° K.)	,,	4·911	1·225	1·284
Bhagavantam (R. T.)	Ultrasonic	4·97	1·27	1·27

The isothermal compressibility had been determined by static methods by a series of investigators, *viz.*, Rontgen and Schneider, Madelung and Fuchs, Richards and Jones, Adams, Williamson and Johnston, Slater and Bridgman. Table II shows the values reported by the various authors. Of these, the

TABLE II

Author	Temp.	χ in 10^{-7} kg.$^{-1}$ cm.^{2}
Rontgen and Schneider	R.T.	50
Madelung and Fuchs	0° C.	40·5
Richards and Jones	20° C.	44·0
Adams, Williamson and Johnston	R.T.	40·4
Slater	30° C.	41·8
Bridgman	30° C.	41·82
	75° C.	43·44

most accurate are evidently those reported by Slater and Bridgman, and they have accordingly been adopted as correct. The values reported by Madelung and Fuchs refer to the pressure range 50–200 kg./cm.^{2}, those of Richards and Jones to the range 100–510 kg./cm.^{2} The values of Slater and Bridgman quoted are for zero-pressure always.

These values are however subject to correction by a constant term $-0\cdot033 \times 10^{-7}$ kg.$^{-1}$ cm.^{2} in the light of Bridgman's latest determination of the linear compressibility of iron. After making this correction and using the known value of g at Harvard, the isothermal compressibility of rock-salt comes out as $42\cdot62\times10^{-13}$ cm.^{2}/dyne at 30° C. The value of the compressibility at 25° C. is found by linear interpolation from the values reported by him at 30° C. and 75° C. This correction when effected leads to a value of χ (isothermal) $= 42\cdot44$. The difference between the isothermal and adiabatic compressibilities can be calculated from the formula given earlier. For rock-salt, the numerical values used in the formula are: $\alpha = 44\times10^{-6}$; $\rho = 2\cdot168$; $C_p = 0\cdot2078$ cal./gm. The value of the adiabatic compressibility at 25° C. is found to be $39\cdot68\times10^{-13}$ cm.^{2}/dyne. Hence the bulk modulus comes out as $2\cdot52\times10^{11}$ dynes/cm.^{2} On the other hand, the value for the bulk modulus calculated from the formula $(C_{11} + 2C_{12})/3$ comes out as $2\cdot45\times10^{11}$ dynes/cm.^{2} the difference clearly being greater than can be explained in terms of experimental errors. The average values of the dynamically determined constants used in the calculation are: $C_{11} = 4\cdot877$; $C_{12} = 1\cdot232$; $C_{44} = 1\cdot269\times10^{11}$ dynes/cm.^{2}, while the four constants evaluated in the manner already explained come out as $d_{11} = 4\cdot88$; $d_{12} = 1\cdot34$; $d_{44} = 1\cdot27$; and $d_{45} = 1\cdot16\times10^{11}$ dynes/cm.^{2}

(*b*) *Potassium Chloride.*—The elastic constants of KCl have been determined by static methods by Voigt, Forsterling and Bridgman. The later workers who have determined the elastic constants by the dynamic methods of ultrasonics are Durand, Galt and recently Lazarus. Their values appear in Table III.

It will be noticed from Table III that the values reported by the different authors are in much less satisfactory agreement amongst themselves than in the case of rock-salt. The values for C_{12} in particular appear rather erratic and this is probably due to the fact that measurements usually involve the determination of linear combinations of C_{11} and C_{12} and since C_{12} is much smaller of the two, errors of measurement would influence its determined value very noticeably. Voigt gives C_{12} to three significant figures but his value is undoubtably an error. As in the case of rock-salt we shall

TABLE III

Author		Method	C_{11}	C_{12}	C_{44}
Voigt	R.T.	Static	3·75	0·198	0·655
Forsterling	R.T.	,,	3·88	0·640	0·65
Bridgman	30° C.	,,	3·70	0·81	0·79
Durand	R.T.	Composite oscillator	4·00	0·6	0·625
Galt	25° C.	Pulse	3·98	0·625	0·62
Lazarus	25° C.	,,	4·095	0·705	0·630

assume as a definitive value the mean of the measurements by the pulse method at 25° C.

The static measurements of compressibilities by different authors shown in Table IV agree remarkably well amongst themselves. We shall here accept the measurement by Slater as corrected by Bridgman to be the most reliable. This comes out as $56 \cdot 27 \times 10^{-13}$ dynes^{-1} cm.^{2} at 30° C. and after correction using the temperature coefficient given by Slater, the value at 25° C. is found as $56 \cdot 14 \times 10^{-13}$ cm.^{2}/dyne. From this the adiabatic compressibility at 25° C. is calculated using the following values for KCl in the correction formula.

TABLE IV

Author	Temp.	χ in 10^{-7} kg.$^{-1}$ cm.^{2}
Rontgen and Schneider	..	56
Madelung and Fuchs	0° C.	55·1
Richards and Jones	20° C.	53·0
Slater	30° C.	55·2

$\alpha = 36 \times 10^{-6}$; $\rho = 1 \cdot 992$; and $C_p = 0 \cdot 1661$ cal./gm. The adiabatic compressibility is found to have a value $53 \cdot 62 \times 10^{-13}$. Hence the bulk modulus at 25° C. comes out as $1 \cdot 865 \times 10^{11}$ dynes/cm.^{2}

The mean values for C_{11}, C_{12} and C_{44} adopted are $4 \cdot 038$, $0 \cdot 663$ and $0 \cdot 628 \times 10^{11}$ respectively. The bulk-modulus calculated using the classical expression $(C_{11} + 2C_{12})/3$ comes out as $1 \cdot 788 \times 10^{11}$ dynes/cm.², which is definitely smaller than the experimentally determined value. The values found for the four elastic constants of the new theory are respectively: $d_{11} = 4 \cdot 038$; $d_{12} = 0 \cdot 779$; $d_{44} = 0 \cdot 628$; $d_{45} = 0 \cdot 512 \times 10^{11}$ dynes/cm.²

(*c*) *Potassium Bromide.*—Static measurements of the elastic constants have been reported by Bridgman. Using the pulse technique Huntington and Galt have independently determined the constants at room temperature. The values are given in Table V.

TABLE V

Author		Method	C_{11}	C_{12} $\times 10^{11}$ dynes/cm.²	C_{44}
Bridgman	30° C. ..	Static	3·33	0·58	0·62
Huntington	25° C. ..	Pulse	3·45	0·54	0·508
Galt	25° C. ..	,,	3·46	0·58	0·505

The compressibility measurements have been made by Richards and Jones, and Slater independently and the values reported are $6 \cdot 5 \times 10^{-6}$ kg.$^{-1}$cm.² at 20° C. and $6 \cdot 57 \times 10^{-6}$ kg.$^{-1}$ cm.² at 30° C. respectively, being in good agreement with each other. Using the temperature coefficient given by Slater, the isothermal compressibility at 25° C. on calculation is found to be $66 \cdot 78 \times 10^{-13}$ cm.² dyne^{-1}. The adiabatic compressibility is found using the correction formula given earlier. The values adopted for KBr are: $\alpha = 41 \times 10^{-6}$; $\rho = 2 \cdot 756$; $C_p = 0 \cdot 1033$ cal./gm. $\chi_{(\text{adiabatic})}$ comes out as $62 \cdot 99 \times 10^{-13}$ cm.²/dyne and hence the bulk modulus is $1 \cdot 588 \times 10^{11}$ dynes/cm.² at 25° C.

Adopting the mean of the values given by Galt and Huntington the bulk modulus in terms of the classical formula $(C_{11} + 2C_{12})/3$ is found to be $1 \cdot 525 \times 10^{11}$ dynes/cm.², thus differing from the actually observed value corrected for the adiabatic nature of deformation.

The values adopted for the elastic constants are $C_{11} = 3 \cdot 455$, $C_{12} = 0 \cdot 56$, $C_{44} = 0 \cdot 507$, while the four constants evaluated in the manner explained are $d_{11} = 3 \cdot 455$; $d_{12} = 0 \cdot 655$; $d_{44} = 0 \cdot 507$; $d_{45} = 0 \cdot 412 \times 10^{11}$ dynes/cm.²

(*d*) *Sodium Bromide.*—The static measurements of the elastic constants are due to Bridgman, while they have been determined by Bhagavantam using ultrasonic methods.

TABLE VI

Author	Temp.	C_{11}	C_{12}	C_{44}
Bridgman ..	30° C.	3·30	1·31	1·33
Bhagavantam ..	R.T.	3·87	0·97	0·97

The values reported by Bhagavantam differ appreciably from those of Bridgman. However, we shall take for our calculations the values determined by dynamic methods as usual, since the identification of the constants of the new theory with that of the older theory is by identifying the two wave-equations.

The compressibility determinations in the case of NaBr have been made by Richards and Saerens at 20° C., the value being $5{\cdot}4\times10^{-6}$ kg.$^{-1}$ cm.^{2} in the pressure range 100–510 kg/cm.^{2}, and by Slater at 30° C. who reports a zero pressure value of $4{\cdot}98\times10^{-6}$ kg.$^{-1}$ cm.^{2} The isothermal compressibility at 30° C. is found to be $50{\cdot}762\times10^{-13}$ cm.^{2}/dyne. Correcting this to the adiabatic value we get $\chi_{(\text{adiabatic})}$ as 47·576. The values used in the calculation of the correction term are: $\alpha = 43\times10^{-6}$; $\rho = 3{\cdot}213$; $C_p = 0{\cdot}1178$ cal./gm. The bulk modulus value hence comes out as $2{\cdot}102\times10^{11}$ dynes/cm.^{2} whereas according to the classical theory this value should be $1{\cdot}936\times10^{11}$ dynes/cm.^{2}

The values of the elastic constants according to the new theory are: $d_{11} = 3{\cdot}87$; $d_{12} = 1{\cdot}22$; $d_{44} = 0{\cdot}97$; $d_{45} = 0{\cdot}72\times10^{11}$ dynes/cm.^{2}

(*e*) *Lithium Fluoride.*—The elastic constants of LiF have been determined by dynamic methods by Bergmann, Huntington, Sundara Rao and Seshagiri Rao and their values are shown in Table VII.

It will be noticed that there are notable divergences between the values reported by different investigators though they all use ultrasonic methods. A clue to the origin of these differences is to be found in the differences in density reported by the different investigators in their respective papers. The density of LiF calculated from the lattice spacing and known atomic weights is 2·627, while Huntington, Seshagiri Rao and Sundara Rao give the density as 2·295, 2·635 and 2·601 respectively. The value found in Landolt Bornstein Table is 2·640. As the value reported by Seshagiri Rao corresponds to this, we use his data in our calculations.

TABLE VII

Author		Method	C_{11}	C_{12}	C_{44}
Bergman	R.T. ..	Diffraction patterns	12·0	4·41	6·4
Huntington	25° C. ..	Pulse	9·74	4·04	5·54
Sundara Rao	R.T. ..	Ultrasonic	11·9	4·58	5·42
Seshagiri Rao	R.T. ..	,,	11·9	5·38	5·34

The compressibility of LiF has been determined by Slater as $15\cdot3 \times 10^{-7}$ kg.$^{-1}$ cm.^{2} at 30° C. and in a redetermination Bridgman has corrected this value and gives it as $14\cdot95 \times 10^{-7}$ kg.$^{-1}$ cm.^{2} The isothermal compressibility at 30° C. is accordingly $15\cdot215 \times 10^{-13}$ cm.^{2} dyne^{-1}. The following values are used in the correction term for adiabatic compressibility: $\alpha = 36 \times 10^{-6}$; $\rho = 2\cdot64$; and $C_p = 0\cdot373$ cal./gm. The adiabatic compressibility comes out as $14\cdot357 \times 10^{-13}$ and hence the bulk modulus as $6\cdot965 \times 10^{11}$ dynes/cm.^{2}, while the bulk modulus using the data of Seshagiri Rao and the classical formula $(C_{11} + 2C_{12})/3$ is found to be having a different value of $7\cdot55 \times 10^{11}$ dynes/cm.^{2} Using the values of Seshagiri Rao in our calculation we find the following values for the four elastic constants. $d_{11} = 11\cdot9$; $d_{12} = 4\cdot5$; $d_{44} = 5\cdot34$; and $d_{45} = 6\cdot22 \times 10^{11}$ dynes/cm.^{2}

(*f*) *Magnesium Oxide.*—The elastic constants of MgO have been determined dynamically by Durand and by Bhagavantam and their values are shown below:—

TABLE VIII

Author		C_{11}	C_{12}	C_{44}
Durand	30° C. ..	28·92	8·77	15·47
Bhagavantam	R.T. ..	28·6	8·7	14·8

Their values agree fairly well and the slight difference in the value of C_{44} might be due to experimental errors. No static determinations of the elastic constants appear to have been made.

The compressibility of MgO has been determined by Madelung and Fuchs and by Bridgman. The former investigators report varying values with the different specimens they used, while Bridgman using a clear single crystal has reported the value of $5 \cdot 904 \times 10^{-7}$ kg.$^{-1}$ cm.^{2} at 30° C. The isothermal compressibility at 30° C. is hence $5 \cdot 988 \times 10^{-13}$ cm.^{2}/dyne. The values of the constants appearing in the correction term are: $\alpha = 13 \cdot 3 \times 10^{-6}$; $\rho = 3 \cdot 576$; $C_p = 0 \cdot 2297$ cal./gm. The adiabatic compressibility comes out as $5 \cdot 847 \times 10^{-13}$ and hence the bulk modulus as $17 \cdot 10 \times 10^{11}$ dynes/cm.^{2}

We shall make use of the mean of the two dynamic determinations for the purposes of our calculation, *i.e.*, $C_{11} = 28 \cdot 76$; $C_{12} = 8 \cdot 74$ and $C_{44} = 15 \cdot 14$. The compressibility calculated using the formula $(C_{11} + 2C_{12})/3$ is found to be equal to $15 \cdot 41 \times 10^{11}$ dynes/cm.^{2}, being distinctly different from the observed and corrected value of $17 \cdot 10 \times 10^{11}$. The elastic constants according to the new theory are as follows: $d_{11} = 28 \cdot 76$; $d_{12} = 11 \cdot 27$; $d_{44} = 15 \cdot 14$; $d_{45} = 12 \cdot 61 \times 10^{11}$ dynes/cm.^{2}

(*g*) *Silver Chloride*.—The elastic constants of AgCl have been recently determined using the pulse method by Arenberg (1950). The values have been reported for two different specimens and show good agreement between themselves. However, it is stated by him that the values from one of the specimens are to be preferred and they are given as $C_{11} = 6 \cdot 05$; $C_{12} = 3 \cdot 64$. $C_{44} = 0 \cdot 624 \times 10^{11}$ dynes/cm.^{2} The compressibility of fused and solidified AgCl has been determined by Richards and Jones, while Bridgman has studied the case of AgCl with compressed powder. The isothermal bulk-modulus value of $4 \cdot 12 \times 10^{11}$ obtained by extrapolating Bridgman's data to zero pressure agrees well with the value of $4 \cdot 17 \times 10^{11}$ dynes/cm.^{2} reported by Richards and Jones. Adopting the value due to Bridgman and using the values $\alpha = 30 \times 10^{-6}$; $\rho = 5 \cdot 5$; and $C_p = 0 \cdot 0875$ cal./gm. for AgCl, the adiabatic bulk modulus is found to be $4 \cdot 338 \times 10^{11}$ dynes/cm.^{2} According to the classical formula $(C_{11} + 2C_{12})/3$ this value comes out as $4 \cdot 444 \times 10^{11}$ dynes/cm.^{2}, being different from the value given above. The four elastic constants according to the new theory are: $d_{11} = 6 \cdot 05$; $d_{12} = 3 \cdot 482$; $d_{44} = 0 \cdot 624$; $d_{45} = 0 \cdot 782 \times 10^{11}$ dynes/cm.^{2}

4. CRYSTALS WITH THE DIAMOND-LIKE STRUCTURE

(*a*) *Diamond*.—The elastic constants of diamond have been determined by the ultrasonic wedge method by Bhagavantam and Bhimasenachar (1946). The following are the values reported by them. $C_{11} = 9 \cdot 5 \times 10^{12}$; $C_{12} = 3 \cdot 9 \times 10^{12}$ and $C_{44} = 4 \cdot 3 \times 10^{12}$ dynes/cm.^{2} The compressibility has been determined first by Adams and again by Williamson in the same laboratory, the values being $0 \cdot 16 \times 10^{-12}$ and $0 \cdot 18 \times 10^{-12}$ cm.^{2}/dyne respectively.

The latter value is reported to be preferred since better material was used in the determination by Williamson. This gives a value of $5 \cdot 56 \times 10^{12}$ dynes/cm.^{2} for the isothermal bulk modulus. The correction for the adiabatic bulk modulus is negligible. Using this value of $5 \cdot 56 \times 10^{12}$ and the reported values for the elastic constants the values of the four elastic constants are calculated. They are: $d_{11} = 9 \cdot 5$; $d_{12} = 3 \cdot 59$; $d_{44} = 4 \cdot 30$; and $d_{45} = 4 \cdot 61 \times 10^{12}$ dynes/cm.^{2}

(*b*) *Germanium.*—The elastic constants of Ge have been determined by ultrasonic methods by Bond and others, Fine and McSkimin and their values are shown in Table IX.

TABLE IX

Author	Method	C_{11}	C_{12}	C_{44}
Bond and others 25° C. ..	Pulse	12·90	4·84	6·69
Fine 25° C. ..	Composite Oscillator	13·16	5·09	6·69
McSkimin 30° C. ..	Pulse	12·88	4·825	6·705

All the determinations have been made in the Bell Telephone Laboratories and McSkimin and Fine have studied the variations of the constants with temperature. The values show good agreement between themselves. The values due to McSkimin are taken from the graphs given by him exhibiting the variation of the elastic constants with temperature.

The compressibility of *polycrystalline* germanium has been determined by Bridgman at 30° C. on two occasions with different specimens and the values are $13 \cdot 78 \times 10^{-7}$ kg.$^{-1}$ cm.^{2} and $14 \cdot 11 \times 10^{-7}$ kg.$^{-1}$ cm.^{2} and the latter value is said to be more reliable. The isothermal compressibility at 30° C. is hence $14 \cdot 358 \times 10^{-13}$ cm.^{2}/dyne. The constants used in the correction term to find the adiabatic compressibility are: $\alpha = 5 \cdot 5 \times 10^{-6}$; $\rho = 5 \cdot 323$; $C_p = 22 \cdot 3$ Joules/gm. atom. The corrected value of the adiabatic compressibility is $14 \cdot 308 \times 10^{-13}$ cm.^{2}/dyne and hence the bulk modulus value is $6 \cdot 989 \times 10^{11}$ dynes/cm.^{2}

The elastic constants for 30° C. could be more accurately and directly obtained from McSkimin's detailed data. Using his values we find that the bulk modulus value according to the classical formula should be $7 \cdot 51 \times 10^{11}$ dynes/cm.^{2} The four elastic constants are found to be $d_{11} = 12 \cdot 88$; $d_{12} = 4 \cdot 04$; $d_{44} = 6 \cdot 705$; and $d_{45} = 7 \cdot 49 \times 10^{11}$ dynes/cm.^{2}

(*c*) *Silicon.*—The elastic constants of crystalline silicon have been determined by McSkimin and others and subsequently in detail by McSkimin over a wide range of temperatures. The following values for the constants at 30° C. are found from the graphs given by him. $C_{11} = 16 \cdot 56$; $C_{12} = 6 \cdot 386$; $C_{44} = 7 \cdot 953 \times 10^{11}$ dynes/cm.^{2} The compressibility of *polycrystalline* silicon has been determined over a wide range of pressures by Bridgman at 30° C. and on extrapolating his values to zero pressure, the isothermal compressibility is found to be $9 \cdot 92 \times 10^{-7}$ kg.$^{-1}$ cm.^{2}, *i.e.*, $10 \cdot 118 \times 10^{-13}$ dynes^{-1} cm.^{2} The following values are used in the correction term for adiabatic compressibility. $\alpha = 2 \cdot 25 \times 10^{-6}$; $\rho = 2 \cdot 331$; $C_p = 0 \cdot 1712$ cal./gm. On correction the adiabatic compressibility is found to be $10 \cdot 11 \times 10^{-13}$ dynes^{-1} cm.^{2} and hence the bulk modulus as $9 \cdot 89 \times 10^{11}$ dynes/cm.^{2} The value calculated using the formula $(C_{11} + 2C_{12})/3$ is found to be $9 \cdot 78 \times 10^{11}$ dynes/cm.^{2} The four elastic constants calculated are: $d_{11} = 16 \cdot 56$; $d_{12} = 6 \cdot 56$; $d_{44} = 7 \cdot 953$; and $d_{45} = 7 \cdot 78 \times 10^{11}$ dynes/cm.^{2}

(*d*) *Zinc blende.*—The elastic constants of zinc blende have been reported by Bhagavantam and Suryanarayana using ultrasonic methods. The constant C_{44} has however been obtained by them from static torsion experiments. The crystalline material used by them contained only 94% of zinc sulphide. The following values are reported by them. $C_{11} = 10 \cdot 79 \times 10^{11}$; $C_{12} = 7 \cdot 22 \times 10^{11}$; $C_{44} = 4 \cdot 12 \times 10^{11}$. These values are in disagreement with the values reported by Voigt from static methods, which are: $C_{11} = 9 \cdot 43 \times 10^{11}$; $C_{12} = 5 \cdot 68 \times 10^{11}$; $C_{44} = 4 \cdot 37 \times 10^{11}$.

The compressibility of a single crystal of zinc blende has been determined by Bridgman as $12 \cdot 81 \times 10^{-7}$ kg.$^{-1}$ cm.^{2} at 30° C. This gives a value of $13 \cdot 032 \times 10^{-13}$ dynes^{-1} cm.^{2} at 30° C. for the isothermal compressibility. The constants used in the correction term for adiabatic compressibility are: $\alpha = 6 \cdot 7 \times 10^{-6}$; $\rho = 4 \cdot 102$; and $C_p = 0 \cdot 1146$ cal./gm. The corrected value of the adiabatic compressibility is found to be $12 \cdot 97 \times 10^{-13}$ dynes^{-1} cm.^{2}, and hence the bulk modulus is $7 \cdot 71 \times 10^{11}$ dynes/cm.^{2} The bulk-modulus calculated from the formula $(C_{11} + 2C_{12})/3$ using Bhagavantam and Suryanarayana's values is $8 \cdot 41 \times 10^{11}$ whereas Voigt's values give $6 \cdot 93 \times 10^{11}$ dynes/cm.^{2}

In the calculation of the four elastic constants, we make use of Bhagavantam and Suryanarayana's values since they are for the major part obtained from dynamic methods. We obtain the following values for the constants. $d_{11} = 10 \cdot 79$; $d_{12} = 6 \cdot 17$; $d_{44} = 4 \cdot 12$; and $d_{45} = 5 \cdot 17 \times 10^{11}$ dynes/cm.^{2}

(*e*) *Fluorspar*.—The elastic constants of fluorspar have been determined using static methods by Voigt, and by Bergmann and Bhagavantam using dynamic methods. Their values are shown in Table X.

TABLE X

Author	Method	C_{11}	C_{12}	C_{44}
Voigt ..	Static	16·4	4·47	3·38
Bergmann ..	Diffraction patterns	16·76	4·72	3·69
Bhagavantam ..	Ultrasonic	16·44	5·02	3·47

For our calculations we take here the mean of the values of Bergmann and Bhagavantam, *i.e.*, $C_{11} = 16 \cdot 6$; $C_{12} = 4 \cdot 87$; and $C_{44} = 3 \cdot 58 \times 10^{11}$ dynes/cm.^{2}

The compressibility of CaF_2 has been determined by Madelung and Fuchs at 0° C. and in the pressure range 50–200 kg./cm.^{2} and the value reported by them is $12 \cdot 2 \times 10^{-7}$ kg.$^{-1}$ cm.^{2} Bridgman has also determined the compressibility at 30° C. and reports a zero pressure value of $12 \cdot 06 \times 10^{-7}$ kg.$^{-1}$ cm.^{2}, *i.e.*, $12 \cdot 267 \times 10^{-13}$ cm.^{2}/dyne. The values used in the correction term are: $\alpha = 19 \cdot 11 \times 10^{-6}$; $\rho = 3 \cdot 18$; $C_p = 0 \cdot 887$ Joules/gm. The adiabatic compressibility value is found to be $11 \cdot 914 \times 10^{-13}$ cm.^{2}/dyne and hence the bulk modulus is $8 \cdot 39 \times 10^{11}$ dynes/cm.^{2} The bulk modulus value using the formula $(C_{11} + 2C_{12})/3$ is found to be $8 \cdot 78 \times 10^{11}$ dynes/cm.^{2}

The four elastic constants calculated are: $d_{11} = 16 \cdot 6$; $d_{12} = 4 \cdot 29$; $d_{44} = 3 \cdot 58$; and $d_{45} = 4 \cdot 16 \times 10^{11}$ dynes/cm.^{2}

5. METALS CRYSTALLIZING IN THE CUBIC SYSTEM

(*a*) *Aluminium*.—The elastic constants of single crystals of aluminium have been determined using static methods by Goens. Recently Lazarus and Sutton have independently measured the elastic constants by ultrasonic methods. The values reported by all these investigators are shown in Table XI.

The accuracy in the measurements of Lazarus is greater than that of Sutton as is evidenced by the comments made by them in their respective papers. Moreover the purity of the specimens used by Lazarus and Sutton is given as 99·99% and 99·93% respectively. In view of these facts we take Lazarus's values for the purposes of our calculation.

TABLE XI

Author		Method	C_{11}	C_{12}	C_{44}
Goens	R.T. ..	Static	10·82	6·22	2·84
Lazarus	25° C. ..	Pulse	10·56	6·39	2·853
Sutton	20° C. ..	Composite oscillator	11·29	6·65	2·783

The isothermal compressibility of aluminium single crystals has been determined by Bridgman as $13 \cdot 38 \times 10^{-7}$ kg.$^{-1}$ cm.^{2} at 30° C. and as $13 \cdot 76 \times 10^{-7}$ kg.$^{-1}$ cm.^{2} at 75° C. The value at 25° C. on linear extrapolation comes out as $13 \cdot 338 \times 10^{-7}$ kg.$^{-1}$ cm.^{2}, *i.e.*, $13 \cdot 57 \times 10^{-13}$ dynes^{-1} cm.^{2} The following values for the constants are used in the correction term for adiabatic compressibility: $\alpha = 23 \cdot 06 \times 10^{-6}$; $\rho = 2 \cdot 702$; $C_p = 0 \cdot 2129$ cal./gm. The adiabatic compressibility is found to be $12 \cdot 97 \times 10^{-13}$ dynes^{-1} cm.^{2} and hence the bulk modulus is $7 \cdot 71 \times 10^{11}$ dynes/cm.^{2} The bulk modulus obtained from the values of Lazarus is $7 \cdot 78 \times 10^{11}$. The values of the four elastic constants calculated are: $d_{11} = 10 \cdot 56$; $d_{12} = 6 \cdot 29$; $d_{44} = 2 \cdot 853$; $d_{45} = 2 \cdot 953 \times 10^{11}$ dynes/cm.^{2}

(*b*) *Copper.*—The elastic constants of copper single crystals have been determined using the composite oscillator method by Goens and Weerts. Recently Lazarus, Long, and Overton and Gaffney have determined the constants using pulse methods. The values are shown in Table XII.

TABLE XII

Author		Method	C_{11}	C_{12}	C_{44}
Goens and Weerts	R.T. ..	Composite oscillator	16·98	12·26	7·53
Lazarus	25° C. ..	Pulse	17·1	12·39	7·56
Long	300° K. ..	,,	16·83	12·21	7·54
Overton and Gaffney	300° K. ..	,,	16·84	12·14	7·54

There is very good agreement between the three sets of values determined by the pulse method and hence for the purposes of our calculation we shall make use of the mean of these values.

The compressibility of polycrystalline copper of high purity has been determined by Bridgman as $7\cdot 19\times 10^{-7}$ kg.$^{-1}$ cm.^{2} at 30° C. and $7\cdot 34\times 10^{-7}$ at 75° C. Hence the value at 300° K. is found to be $7\cdot 173\times 10^{-7}$ kg.$^{-1}$ cm.^{2}, *i.e.*, $7\cdot 283\times 10^{-13}$ dynes^{-1} cm.^{2} The following values are used in the correction term for the adiabatic compressibility: $\alpha = 17\cdot 09\times 10^{-6}$; $\rho = 8\cdot 92$; $C_p = 0\cdot 0919$ cal./gm. The corrected value of adiabatic compressibility is $7\cdot 05\times 10^{-13}$ dynes^{-1} cm.^{2} and hence the bulk modulus is $14\cdot 18\times 10^{11}$ dynes/cm.^{2} The average values of the elastic constants from pulse method are: $C_{11} = 16\cdot 92$; $C_{12} = 12\cdot 25$; and $C_{44} = 7\cdot 55\times 10^{11}$ dynes/cm.^{2} The bulk modulus using the formula $(C_{11} + 2C_{12})/3$ is found to be $13\cdot 81\times 10^{11}$ dynes/cm.^{2} The four elastic constants calculated are: $d_{11} = 16\cdot 92$; $d_{12} = 12\cdot 81$; $d_{44} = 7\cdot 55$; and $d_{45} = 6\cdot 99\times 10^{11}$ dynes/cm.^{2}

(*c*) *Nickel.*—The elastic constants of single crystals of nickel have been determined recently using the ultrasonic pulse method by Bozorth and others and also by Neighbours and others. Their values are given in Table XIII.

TABLE XIII

Author	C_{11}	C_{12} in 10^{12} dynes/cm.^{2}	C_{44}
Bozorth and others ..	2·53	1·58	1·22
,, ..	2·524	1·538	1·23
,, ..	2·523	1·566	1·23
Neighbours and others ..	2·528	1·52	1·238

The average value of these at 25° C. are: $C_{11} = 2\cdot 526$; $C_{12} = 1\cdot 551$; and $C_{44} = 1\cdot 23\times 10^{12}$ dynes/cm.^{2}

The compressibility of pure nickel has been determined by Bridgman at 30° C. as $5\cdot 29\times 10^{-7}$ kg.$^{-1}$ cm.^{2} and at 75° C. as $5\cdot 35\times 10^{-7}$. The value at 25° C. is hence $5\cdot 283\times 10^{-7}$ kg.$^{-1}$ cm.^{2} The isothermal compressibility is hence $5\cdot 355\times 10^{-13}$ dynes^{-1} cm.^{2} The values used in the correction term for adiabatic compressibility are: $\alpha = 13\cdot 15\times 10^{-6}$; $\rho = 8\cdot 9$; and $C_p = 0\cdot 107$ cal./gm. The adiabatic compressibility is found to be $5\cdot 239\times 10^{-13}$ dynes^{-1} cm.^{2} and hence the bulk modulus is $19\cdot 09\times 10^{11}$ dynes/cm.^{2} The bulk modulus using the classical formula is found to be $18\cdot 76\times 10^{11}$ dynes/cm.^{2} The four elastic constants calculated are: $d_{11} = 25\cdot 26$; $d_{12} = 16\cdot 01$; $d_{44} = 12\cdot 3$; and $d_{45} = 11\cdot 8\times 10^{11}$ dynes/cm.^{2}

(*d*) *Silver.*—The elastic constants of single crystals of silver have been determined by Rohl using the classical static and dynamic methods. The constants have been recently determined by Bacon and Smith using the ultrasonic pulse method. The values are shown below:—

TABLE XIV

Author	Method	C_{11}	C_{12}	C_{44}
Rohl R.T. ..	Static, etc.	11·9	8·94	4·37
Bacon and Smith R.T. ..	Pulse	12·4	9·34	4·61

The compressibility of pure silver has been determined by Bridgman at 30° C. as $9 \cdot 87 \times 10^{-7}$ kg.$^{-1}$ cm.^{2}, *i.e.*, $10 \cdot 034 \times 10^{-13}$ dynes^{-1} cm.^{2} The constants used in the correction term are: $\alpha = 18 \cdot 9 \times 10^{-6}$; $\rho = 10 \cdot 5$; $C_p = 25 \cdot 2$ Joules/gm. atom. The adiabatic compressibility is found to be $9 \cdot 939 \times 10^{-13}$ dynes^{-1} cm.^{2} and hence the bulk modulus is $10 \cdot 06 \times 10^{11}$ dynes/cm.^{2} The value calculated using the formula $(C_{11} + 2C_{12})/3$ is found to be $10 \cdot 36 \times 10^{11}$ dynes/cm.^{2} The four constants calculated are: $d_{11} = 12 \cdot 4$; $d_{12} = 8 \cdot 89$; $d_{44} = 4 \cdot 61$; and $d_{45} = 5 \cdot 06 \times 10^{11}$ dynes/cm.^{2}

6. SOME FINAL REMARKS

In Table XV the results for the individual cases given in the foregoing pages have been collected together. The columns C_{11}, C_{12} and C_{44} show the results of the ultrasonic measurements, while the columns d_{11}, d_{12}, d_{44} and d_{45} represents the constants as evaluated from the ultrasonic data in conjunction with the bulk modulus as determined by Bridgman and his collaborators after making *all* necessary corrections. The values of C_{11} and d_{11} are in each case identical; likewise those of C_{44} and d_{44}. But C_{12} and d_{12} are different and such difference is a measure of the failure of the three constant-theory to represent the actual elastic behaviour of the crystal. The difference between d_{44} and d_{45} also expresses the same situation in another way.

Certain general features emerge from the table. For all the four alkali halides which are soluble in water, C_{12} is less than d_{12} and likewise d_{45} is less than d_{44}. This regularity of behaviour taken in conjunction with the reliability of the data in these cases makes it clear that these differences are real and justify us in concluding that the elastic behaviour of cubic crystals cannot be expressed in terms of three constants, but needs four. Diamond, germanium, zinc blende and fluorspar also exhibit a parallel behaviour which is the reverse of that shown by the four water-soluble alkali halides. In their cases, C_{12} is decidedly greater than d_{12}, while *per contra* d_{44} is less than d_{45} and these differences are numerically more striking than in the case of the alkali halides. Magnesium oxide for which the data are reliable exhibits a noteworthy behaviour; the differences between C_{12} and d_{12} and likewise between d_{44} and d_{45} are in the same sense as in the alkali halides but proportionately much larger. Differences of the same order of magnitude but in the opposite sense are shown by lithium fluoride. In the case of the metals crystallising in the face-centred cubic system, we also find differences between C_{12} and d_{12} and between d_{44} and d_{45}, but they are not always in the same sense. This is a feature which need not surpirse us in view of the very great differences exhibited by these metals in other respects.

TABLE XV

Elastic Constants in 10^{11} *dynes/cm.*^{2}

Substance	C_{11}	C_{12}	C_{44}	d_{11}	d_{12}	d_{44}	d_{45}
NaCl ..	4·877	1·232	1·269	4·877	1·34	1·269	1·16
KCl ..	4·038	0·663	0·628	4·038	0·779	0·628	0·512
KBr ..	3·455	0·56	0·507	3·455	0·655	0·507	0·412
NaBr ..	3·87	0·97	0·97	3·87	1·22	0·97	0·72
LiF ..	11·9	5·38	5·34	11·9	4·5	5·34	6·22
MgO ..	28·76	8·74	15·14	28·76	11·27	15·14	12·61
AgCl ..	6·05	3·64	0·624	6·05	3·482	0·624	0·782
Diamond ..	95	39	43	95	35·9	43·0	46·1
Ge ..	12·88	4·825	6·705	12·88	4·04	6·705	7·49
Si ..	16·56	6·386	7·953	16·56	6·56	7·953	7·78
ZnS ..	10·79	7·22	4·12	10·79	6·17	4·12	5·17
CaF_2 ..	16·6	4·87	3·58	16·6	4·29	3·58	4·16
Al ..	10·56	6·39	2·853	10·56	6·29	2·853	2·953
Cu ..	16·92	12·25	7·55	16·92	12·81	7·55	6·99
Ni ..	25·26	15·51	12·3	25·26	16·01	12·3	11·8
Ag ..	12·4	9·34	4·61	12·4	8·89	4·61	5·06

7. SUMMARY

The belief that the elastic behaviour of cubic crystals can be described in terms of three constants rests on theoretical considerations which are examined in the paper and shown to be indefensible. The correct theory demands four constants for cubic crystals belonging to the O_h and T_d classes.

The experimental results for sixteen different crystals belonging to these classes for which the most precise data are available are critically examined and it is shown that the adiabatic bulk modulus as computed respectively from the observed velocities of ultrasonic wave propagation and from the static determinations of compressibility made at Harvard are in systematic disagreement. The data show very clearly that the elastic behaviour of these crystals cannot be expressed in terms of three constants, but needs four. The latter have been computed and tabulated.

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THE NATURE OF THE THERMAL AGITATION IN CRYSTALS

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1. Introduction

The present memoir concerns itself with a problem of fundamental importance in the physics of the solid state, namely the determination of the nature of the atomic movements which constitute the thermal agitation in a crystal. It would be no exaggeration to say that on our taking the correct view of the nature of these movements depends the possibility of our understanding the physical behaviour of crystals aright, not only in the thermal field but also in diverse other fields, as for example their spectroscopic behaviour and the phenomena of X-ray diffraction in crystals. The problem is considered in this paper from two distinct points of view. The first method of approach is to examine the basic experimental facts in the light of fundamental physical principles and to draw the inferences following logically therefrom. The second method of approach is the analytical investigation of the problem on the basis of classical mechanics and the general principles of thermodynamics and the quantum theory. The result in either case is to show that the ideas underlying the well-known specific heat theory of Debye and the lattice dynamics of Born and his collaborators are untenable. The picture of the thermal agitation in a crystal which emerges from the present investigation is fundamentally different from that postulated in the theories of Debye and Born.

2. Some General Considerations

The identification on a quantitative basis of the thermal energy of a crystal with the energy of atomic oscillations rests on two fundamental ideas; (*a*) that the oscillators can be enumerated, their total number being three times the number of atoms comprised in the crystal; (*b*) that the energy of the oscillators is quantized and for any particular frequency has an average value which can be calculated with the aid of Boltzmann's theorem. We proceed to examine these ideas critically with a view to determine their precise significance as well as their implications.

The first of the two ideas referred to above is based on the fundamental theorem in classical mechanics which states that all the possible modes of small vibration of a system of connected particles are superpositions of a set of normal modes, the number of such modes being the same as the number of degrees of dynamic freedom of the system, and further that in each such normal mode all the particles of the system have the same frequency of vibration and oscillate in the same or opposite phases. In the present context, therefore, the term oscillator must be considered as referring to a set of atoms vibrating in a normal mode, all of them having the same frequency and the same or opposite phases of vibration.

The second idea, namely that of averaging the energy of an oscillator, arises because of the chaotic nature of thermal agitation which involves energy fluctuations whose magnitude is determined by the frequency of the vibration. The theorem of Boltzmann which enables the average to be calculated is a description in statistical form of the behaviour of the individual units in an assembly consisting of an immense number of such units which are physically identical but differ in their energy states and being in a position to exchange energy with each other form a system in thermodynamic equilibrium. In the present context, the units are the oscillators defined in the preceding paragraph. Hence, if the application of Boltzmann's theorem is to be legitimate, it is necessary to postulate that in the crystal is present an assembly of this nature, *viz.*, a great number of individual oscillators all of which vibrate with the same frequency but are in the different energy states permitted by the quantum theory. For each separate frequency of oscillation, a fresh assembly of that nature is needed to enable the energy for each individual frequency to be separately averaged.

The foregoing theoretical picture of the thermal agitation agrees completely with the actual physical picture in the case under consideration. For, every crystal is itself an assembly of an immense number of similar and similarly situated groups of atoms, the internal vibrations of which can occur with one or another of the characteristic frequencies of the group. The energy of vibration of a group with any one of these frequencies may have any of the series of values allowed by the quantum theory and hence would vary from group to group in an entirely unpredictable manner within the crystal. Such a picture would be in perfect harmony with the basic notions of thermodynamics, but would be wholly irreconcilable with any theory which seeks to identify the energy of thermal agitation with the energy of regular wave propagation in the crystal. But this latter idea is precisely what forms the basis of the specific heat theories of Debye and Max Born. It follows that these theories are fundamentally misconceived and must therefore fail, together with all their consequences.

3. THE NORMAL MODES OF VIBRATION

The normal modes of vibration of the atomic groupings in the crystal referred to above may be determined and enumerated without any difficulty. It is obviously not permissible in this connection to regard the unit cell in the crystal structure as isolated from the rest of the crystal. For, any oscillation which occurs in a particular cell will necessarily communicate itself immediately to the surrounding cells and set the latter in vibration with the same frequency. Hence, to ascertain the normal modes of vibration, we have to consider vibrations extending over domains whose dimensions are at least as large as the range of the inter-atomic forces. Further, to ensure that the oscillations persist unchanged in character, it is necessary to assume that the oscillation in each of the unit cells included within such a domain is similar and similarly related to the oscillations in the cells surrounding it.

Remembering that in a normal mode the oscillations of all the particles have the same frequency and the same or opposite phase, the foregoing requirements lead us to the following description of the normal modes of vibration: In any normal mode, the oscillations of equivalent atoms in adjoining cells have the same amplitude of vibration but their phases are either the same or the opposite in the cells adjacent to one another along one, two or all three of the axes of the lattice structure. Thus there are $2 \times 2 \times 2$ or 8 possible situations. As a consequence of the identity of the amplitudes of vibration of equivalent atoms in all the cells which need to be considered, the $3p$ equations of motion of the p atoms in any particular cell contain only $3p$ unknowns. Accordingly, it becomes possible to solve the equations completely and determine the $3p$ normal modes and the corresponding frequencies of vibration. As there are eight different situations in respect of the phases of vibration, the equations of motion would necessarily be different in each of them. Accordingly we have $3p \times 8$ or $24p$ normal modes and frequencies of vibration.

An alternative and convenient way of describing the normal modes is to consider a supercell of the lattice whose dimensions are twice as large in each direction as the unit cell. Such a supercell would contain $8p$ atoms and the total number of degrees of freedom associated therewith would be $24p$, and this is the same as the number of normal modes permissible. We may therefore describe these modes as the vibrations of the atoms comprised in the supercell. When this description is adopted, it becomes immediately evident that three of these modes would represent simple translations of the supercell and would therefore have to be excluded in enumerating the internal vibrations of the supercell. We have then left only $(24p - 3)$ normal modes of vibration properly so-called.

4. WAVE PROPAGATION IN CRYSTAL LATTICES

As is well known, the classical theory of elasticity leads to the conclusion that three types of waves can be propagated in any given direction within crystal with the velocities determined by the density of the material and certain linear combinations of its elastic constants. The analysis which leads to this result regards the volume elements of the crystal as simple mass particles whose equations of motion can be written down in terms of the tractive forces arising from the elastic strains. Hence the theory and its consequences would cease to be applicable when these assumptions are invalid and the position would then have to be considered afresh from the atomistic standpoint. A formal investigation on the latter basis shows that only in the limiting case of very low frequencies and of correspondingly long waves are the results of the classical theory of elasticity valid. When we enter the region of the higher frequencies, the phase velocity and the group velocity diverge from each other and the very significant result emerges that the group velocity vanishes for $(24p - 3)$ modes of vibration of the lattice. These modes are found to be identical with the $(24p - 3)$ normal modes referred to in the foregoing section.

To avoid breaking the thread of the argument, the detailed dynamical investigation which has been worked out by Dr. K. S. Viswanathan is printed as an appendix to this memoir. It will therefore suffice here to comment on the significance of the results there derived by him. As is very well understood, it is the group velocity which is physically significant in all considerations regarding wave-propagation, since it is a measure of the rate of energy transport in the medium. The vanishing of the group velocity for the whole series of characteristic frequencies of atomic vibration *signifies that there is no wave propagation in the real or physical sense of the term when we are considering oscillations in which the interatomic displacements play a significant role*. It follows that considerations of the kind used in the classical theory of elasticity to ascertain the normal modes of vibration of a solid body of finite extension are entirely out of place in the atomistic problem. But it is precisely such considerations that are employed in the theories of Debye and Born to describe and enumerate the movements which they identify with the thermal agitation. Thus, even on the basis of the classical mechanics, the ideas underlying those theories are unsustainable and they have therefore to be laid aside as being completely unreal.

5. THE FREQUENCY SPECTRUM OF THE THERMAL AGITATION

We may sum up what has been said in the foregoing pages by the statement that the energy of the thermal agitation in a crystal may be identified with the energy of an immense number of atomic oscillators which together fill up the volume of the crystal, the individual oscillators being in the various states of excitation corresponding to each of the $(24p-3)$ frequencies common to them all, supplemented by the energy of the low frequency oscillations which the three omitted degrees of freedom represent. These $(24p-3)$ frequencies correspond to modes of vibration which are related to the structure of the crystal in precisely definable terms. It will be seen that this description of the thermal agitation bears no resemblance whatever to that envisaged in the theories of Debye and Born; these authors identify the energy of the thermal agitation with the energy of waves in immense numbers traversing the crystal in all directions and having frequencies which are all different from one another, the energy of the wave of any particular frequency as well as the sum total of the energy of all the waves taken together being distributed uniformly over the volume of the crystal.

It is noteworthy that in his fundamental paper of 1907 introducing the quantum theory of specific heats, Einstein derived his expression for the average energy of an oscillator of given frequency assuming, as is indeed necessary for applying Boltzmann's theorem, that the crystal is an assembly of an immense number of oscillators all having the same frequency but in different energy states and in thermodynamic equilibrium with each other. The theories of Debye and Born make use of Einstein's expression for the average energy of an oscillator, while on the other hand the frequencies of the waves with which they identify the thermal agitation are all different from each other. Thus it will be seen that there is no logical consistency in their approach to the specific heat problem. Further, the uniform distribution of the thermal energy through the whole volume of the crystal which such identification demands is irreconcilable with the fundamental ideas regarding the nature of the thermal energy of material bodies inherent in the Second Law of Thermodynamics, namely, that the distribution of the energy over the volume of the crystal should exhibit fluctuations which are the more violent the higher the frequency of vibration.

The foregoing comments do not by any means traverse all the arguments and assumptions on which the theories of Debye and Born are based. One of the basic objections to their method of approaching the specific heat problem is that since wave motions involve progressive changes of phase along the direction of propagation and may have any frequency assigned to them, they can neither be treated as normal modes nor enumerated. The theories of Debye and Born seek to escape this difficulty by postulating that the number of wave motions is identical with the number of degrees of freedom of the system, while the choice of wavelengths is determined by still another postulate, *e.g.*, the so-called postulate of the cyclic lattice which is claimed to represent the effect of the external boundary of the crystal. Since it is obviously impossible to formulate any boundary conditions for the atomic movements at the external surface of a crystal, the procedure is clearly artificial. But that it is also fallacious becomes evident when we remark that the characteristic modes and frequencies of the atoms in the interior of the crystal are determined exclusively by the structure of the crystal and by the interatomic forces whose range is exceedingly small and hence there exists no justification whatever for the assumption which is inherent in the postulate that these modes and frequencies are influenced by the presence of an external boundary.

6. THE SPECTROSCOPIC BEHAVIOUR OF CRYSTALS

It is not proposed in this memoir to discuss how the ideas set forth in it impinge on various aspects of crystal physics. We shall however make a brief reference to those cases in which facts already well established illustrate the validity of the conclusions reached in it.

As Einstein emphasized in his fundamental paper of 1907, the theory of the specific heats of crystals stands in the closest relation to their spectroscopic behaviour. In seeking to explain the data then available for the case of diamond, he made the simplifying assumption that all the oscillators in that crystal have a single common frequency. He recognized however, that in general a crystal would possess several characteristic frequencies and that the expression for its specific heat would involve a summation over them all. In the particular case of diamond, the $(24p-3)$ frequencies indicated by the present theory are reduced from 45 to 9 in number by reason of the cubic symmetry of the crystal. One of these 9 frequencies represents the triply degenerate oscillation of the two lattices of carbon atoms against each other, while the other eight represent either the longitudinal or the transverse oscillations of the layers of carbon atoms in the cubic and octahedral planes of the crystal. In numerous papers published in these *Proceedings* in recent years, it has been shown that all these nine frequencies can be ascertained by spectroscopic observation and that the specific heat of diamond can be successfully evaluated with the aid of the data thus obtained.

But the case of diamond does not stand alone in this respect. In recent years, the spectroscopic behaviour of numerous crystals have been studied by diverse methods, *e.g.*, the scattering of light, absorption in the visible, ultra-violet and infra-red regions of the spectrum, and in particular cases, also their luminescence. The whole of the evidence which has thus come to hand indicates that the vibration spectrum of a crystal consists of a discrete set of monochromatic frequencies and that where there is any departure from this state of affairs, an adequate explanation is forthcoming.

7. X-RAY DIFFRACTION IN CRYSTALS

That the atomic vibrations in crystals appear with precisely defined frequencies and with modes bearing a precise geometric relationship to the architecture of the crystal has a most important bearing on the subject of the diffraction of X-rays by crystals. Here again, a particularly striking illustration is furnished by the case of diamond. When a plate of this crystal is traversed by a narrow pencil of X-rays and the resulting Laue pattern is recorded on a photographic plate, it is found that in addition to the usual Laue spots, other sets of sharply defined spots appear on the plate, corresponding to each of the monochromatic components in the incident X-radiation. This phenomenon which was discovered in the year 1940 by Dr. Nilakantan and the present writer using octahedral cleavage plates of diamond has since been thoroughly re-investigated at this Institute by Mr. Jayaraman and the writer. The results are found to be in complete accord with the hypothesis that the incident X-radiation excites the triply degenerate oscillation of the two lattices of carbon atoms in the crystal against each other. These movements occur along the directions of the three cubic axes and as a consequence, all the lattice planes of the crystal are disturbed, giving rise to dynamic X-ray reflections by them. *Three* sharply-defined spots corresponding to each monochromatic component in the incident X-ray beam are demanded by the theory for the dynamic reflections by each of the (111) planes of the crystal, since these planes are equally inclined to the cubic axes. These reflections are actually observed in the directions indicated by the theory with suitable settings of the crystal. Other sets of lattice planes in the crystal also give dynamic reflections in the directions demanded by the theory, but since such planes are unequally inclined to the three cubic axes which are the directions of movement of the atoms in the excited oscillations, they are not all equally conspicuous.

Here again the case of diamond does not stand by itself, since analogous phenomena are also exhibited by other crystals. But it is not necessary here to enter into the details of these cases.

8. SUMMARY

The principles of thermodynamics and of the quantum theory indicate that the thermal energy in a crystal is identifiable with the energy of an immense number of atomic oscillators which have their frequencies of vibration in common but are in different states of excitation. Dynamical investigation of the problem shows that if the crystal contains p interpenetrating Bravais lattices of atoms, there are $(24p-3)$ frequencies of vibration common to all the oscillators. An investigation of the propagation of waves in crystal lattices shows that the results of the classical theory of elasticity are valid only in the limiting case of very low frequencies and proves further that the group velocity of the waves vanishes for $(24p-3)$ frequencies which may accordingly be identified as the characteristic frequencies of atomic vibration in the crystal. Since there is no wave-propagation in the real or physical sense except in the very lowest range of frequencies, the identification of the thermal energy with the energy of waves traversing the crystal in all directions and having frequencies all different from one another which forms the basis of the specific heat theory of Debye and of Born's lattice dynamics ceases to be justifiable. Other aspects of these latter theories are also examined and it is shown that the assumptions which they involve are untenable and that in consequence the theories have no claim to validity. The experimental results which confirm that the atomic oscillators have specific frequencies in common and modes of vibration specifically related to the crystal structure are briefly set out.

APPENDIX

We shall consider the most general case of a crystal whose structure includes p interpenetrating Bravais lattices, all of which are geometrically similar and similarly situated in the crystal arrangement. An unit cell of the crystal will therefore contain p atoms whose masses we shall denote by $m_1, m_2, \ldots m_p$.

Since a crystal is triply periodic in space, any unit cell can be reached from any other cell of the crystal by the application of three primitive translations or integral multiples of them. We denote the three primitive translations by the three vectors $\mathbf{d}_1$, $\mathbf{d}_2$ and $\mathbf{d}_3$. In the same way, we denote the three primitive vectors of the reciprocal lattice by $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$. In what follows, the symbols $\mathbf{s}$ and σ will be used to denote particular cells in the crystal structure while r and ρ will indicate particular atoms in the unit cell; X, Y, Z are three mutually perpendicular directions chosen as the co-ordinate axes along which the displacements of the atoms from their equilibrium positions are resolved. We represent the displacement-components of any atom, say the rth atom in the sth cell, by means of the symbols $q_{xrs}, q_{yrs}, q_{zrs}$. We can now write the equations of motion of the atoms in the sth cell and they take the form

$$-m_r\ddot{q}_{xrs} = \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\, q_{y\rho\sigma} \quad \begin{pmatrix} x = \mathrm{X, Y, Z} \\ r = 1, 2, \ldots p \end{pmatrix} \tag{1}$$

The force constant $k^{y\rho\sigma}_{xrs}$ occurring in (1) expresses the proportionality existing between the x-component of the force acting on the atom (r, s) to the displacement in the y-direction of the atom (ρ, σ) which gives rise to this force.

Since the crystal is composed of p different Bravais lattices of atoms, we can reasonably expect a wave of a given wavelength and frequency to be propagated with different amplitudes inside the p different lattices. To solve the set of equations (1), we therefore assume solutions of the form

$$\begin{aligned} q_{xrs} &= \mathrm{A}_{xr}\, e^{i(\omega t - a.s)} \\ &= \mathrm{A}_{xr}\, e^{\frac{2\pi i}{\lambda}(\nu t - e.s)} \end{aligned} \quad \begin{pmatrix} x = \mathrm{X, Y, Z} \\ r = 1, 2, \ldots p \end{pmatrix} \tag{2}$$

which are plane waves of wavelength λ and circular frequency ω propagating in the direction of the vector $\mathbf{e}$ of the crystal. If we resolve the wave-vector $\mathbf{a}$ along the three axes of the reciprocal lattice and write $\mathbf{a} = \theta_1\mathbf{b}_1 + \theta_2\mathbf{b}_2 + \theta_3\mathbf{b}_3$ then the equations (2) can alternatively be written as

$$q_{xrs} = \mathrm{A}_{xr}\, e^{i(\omega t - s_1\theta_1 - s_2\theta_2 - s_3\theta_3)} \tag{2'}$$

where s_1, s_2 and s_3 are the components of s along the three Bravais axes of the crystal. Substituting the equations (2) in (1), we obtain

$$m_r \omega^2 \mathrm{A}_{xr} = \sum_{y\rho} \mathrm{A}_{y\rho} \left(\sum_{\sigma} k_{y\rho\sigma}^{xrs} e^{ia.\sigma - s}\right) \quad \begin{pmatrix} x = \mathrm{X, Y, Z} \\ r = 1, 2, \ldots . p \end{pmatrix} \tag{3}$$

Equations (3) are a set of $3p$ equations in the $3p$ amplitudes A_{x1}, A_{y1}, A_{z1}, $\mathrm{A}_{x2}, \ldots . \mathrm{A}_{zn}$ of the waves. By eliminating the amplitudes from these homogeneous equations, we can obtain a determinental equation containing $3p$ rows and $3p$ columns whose elements are the coefficients of the various $\mathrm{A}_{y\rho}$'s in the equations (3). By expanding this determinant, we can rewrite this equation in the form

$$s_0 \omega^{6p} + s_1 \omega^{6p-2} + \ldots\ldots + s_{3p} = 0 \tag{4}$$

in which s_0, s_1, $\ldots . s_{3p}$ are functions of the coefficients of the amplitudes in the equations (3), and hence are also functions of the wave-vector of the waves. The roots of the equations (4) are consequently functions of the wavelengths of the waves, in other words, the waves are dispersive. Since an algebraic equation of degree $3p$ has $3p$ roots, for each value of a we obtain $3p$ permissible values for ω which are the roots of (4). Thus there are $3p$ waves of a given wavelength moving in any direction of the crystal.

We shall now consider any one of the $3p$ roots of the equation (4). If this is denoted by $\omega_k{}^2$, then $\omega_k{}^2$ expressed as a function of the wave-vector **a** has the following properties:

(i) $\omega_k{}^2$ is a periodic function of θ_1, θ_2 and θ_3 with periods 2π for each one of these variables;

(ii) $\omega_k{}^2$ is a real function of θ_1, θ_2 and θ_3;

(iii) $\omega_k{}^2$ is an even function of the wave-vector **a** (*i.e.*), $\omega_k{}^2(\mathbf{a}) = \omega_k{}^2(-\mathbf{a})$.

Condition (i) follows from the fact that the coefficients of the amplitudes in (3) are of the form

$$\sum_{\sigma} k_{xrs}^{y\rho\sigma} \exp.\, i\mathbf{a} \cdot (\sigma - \mathbf{s}) \text{ or}$$

$$\sum_{\sigma} k_{xrs}^{y\rho\sigma} \exp.\, i\,(\overline{\sigma_1 - s_1}\theta_1 + \overline{\sigma_2 - s_2}\theta_2 + \overline{\sigma_3 - s_3}\theta_3$$

and hence are periodic functions of θ_1, θ_2 and θ_3 with periods 2π for each of them. The frequencies of the waves which are functions only of these coefficients are therefore also periodic functions of θ_1, θ_2 and θ_3.

Condition (ii) can easily be understood from physical considerations. Condition (iii) follows from the fact that the frequency of a wave of given wavelength and amplitude should be the same both for waves travelling in one and the opposite directions. Alternatively, these two conditions are consequences of the hermitian property of the coefficients of the amplitudes of the waves in the right-hand side of the equations (3).

Since $\omega_k{}^2$ is a periodic function of θ_1, θ_2 and θ_3 we can express it as a three-dimensional Fourier-series in the form

$$\omega_k{}^2 = \sum_{n_1,} \sum_{n_2,} \sum_{n_3 = -\infty}^{+\infty} A_{n_1 n_2 n_3} \, e^{i(n_1\theta_1 + n_2\theta_2 + n_3\theta_3)} \tag{5}$$

where the summation extends over all integral values of n_1, n_2 and n_3 from $-\infty$ to $+\infty$.

If we use a single symbol $\mathbf{n}$ to denote the triplet $(n_1 \cdot n_2 \; n_3)$ we can rewrite (5) also in the form

$$\omega_k{}^2 = \sum_{\mathbf{n}} A_n \, e^{ia.n} \tag{6}$$

Since $\omega_k{}^2$ is real, the coefficients of $e^{i(n_1\theta_1+n_2\theta_2+n_3\theta_3)}$ and $e^{-i(n_1\theta_1+n_2\theta_2+n_3\theta_3)}$ in (5) should be complex conjugates. Hence we have

$$A_n = \bar{A}_{-n} \tag{7}$$

Now by writing $-\mathbf{a}$ for $\mathbf{a}$ in (6), we get

$$\omega_k{}^2 (-\mathbf{a}) = \sum_{\mathbf{n}} A_n \; e^{-ia.n} \tag{8}$$

Since from condition (iii), $\omega_k{}^2 (-\mathbf{a}) = \omega_k{}^2 (\mathbf{a})$ we see by a comparison of (6) and (8) that

$$A_n = A_{-n} \tag{9}$$

Combining (7) and (9) we get

$$A_n = \bar{A}_{-n} = \bar{A}_n \tag{10}$$

or A_n is real.

We can therefore rewrite (5) as

$$\begin{aligned} \omega_k{}^2 &= A_{000} + 2 \sum A_{n_1 n_2 n_3} \cos (n_1\theta_1 + n_2\theta_2 + n_3\theta_3) \\ &= A_{000} + 2 \sum_{\mathbf{n}} A_n \cos \mathbf{a.n} \end{aligned} \tag{11}$$

where the summation now is over all lattice points on and above any one of the lattice planes $\mathbf{d}_1 = 0$ or $\mathbf{d}_2 = 0$ or $\mathbf{d}_3 = 0$.

We shall assume that the series obtained by differentiating term by term the sum on the right-hand side of (11) converges uniformly for all values of θ_1, θ_2 and θ_3 in the interval $(0, 2\pi)$. Then, we have

$$2\omega_k \frac{d\omega_k}{da} = -2 \Sigma A_n \, \mathbf{e.n} \sin \mathbf{a.n} \tag{12}$$

Now, when θ_1, θ_2 and θ_3 each takes one of the values 0 or π, sin **a.n** (*i.e.*) $\sin(n_1\theta_1 + n_2\theta_2 + n_3\theta_3)$ is equal to zero. Hence if

$$\omega_k \neq 0 \tag{13}$$

for these values of θ_1, θ_2 and θ_3, we find from (12) that

$$\frac{d\omega_k}{da} = 0 \quad \text{whenever} \quad \begin{aligned} \theta_1 &= 0 \text{ or } \pi; \\ \theta_2 &= 0 \text{ or } \pi; \\ \theta_3 &= 0 \text{ or } \pi \end{aligned} \tag{14}$$

When $\theta_1 = 0$; $\theta_2 = 0$; $\theta_3 = 0$, it can be proved that three of the roots of (4) will become zero and hence the condition (13) is not satisfied. These are the limiting cases of elastic vibrations of long wavelength in the crystal and for them, since $\omega_k \to 0$ as $a \to 0$

$$\underset{a\to 0}{Lt} \frac{\omega_k}{a} = \frac{d\omega_k}{da} \quad (k = 1, 2, 3),$$

and therefore the group and wave velocities become identical with the velocities of propagation of the elastic vibrations in the crystal lattice.

The eight set of cases considered above now yield a total number of $24p$ frequencies. Leaving out of these the three degrees of freedom pertaining to pure translations and for which, as we have seen, the group velocity is non-zero being equal to its wave velocity, we get $(24p-3)$ frequencies for which the group velocity of the waves vanishes. The modes associated with these frequencies now possess a simple geometric description. By substituting the values of 0 or π for θ_1, θ_2 and θ_3 in (2′), it can easily be seen that in all the $(24p-3)$ cases referred to above, equivalent atoms in adjacent cells vibrate with the same amplitude and with the same or opposite phases along one, two or all three of the Bravais axes of the crystal. Since the group velocity is zero, any disturbance with these frequencies remains centred in the region of its origin. Further, the phase relationships for these $(24p-3)$ modes are exactly the same as those demanded for the normal vibrations of a connected system of particles.

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THE PROPAGATION OF LIGHT IN ABSORBING BIAXIAL CRYSTALS

II. Experimental

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§ 1. INTRODUCTION

THE mineral iolite available in South India shows a very pronounced pleochroism: certain specimens of this material appear practically colourless and transparent in certain orientations, but show an intense blue colour in certain others. Accordingly, a plate cut normal to one of the two optic axes of this orthorhombic mineral was found very suitable for qualitatively verifying some of the rather unexpected results regarding the properties of the singular axes in absorbing crystals that had been derived in the theoretical treatment of Part I. As the plate also exhibited in a striking manner the other well-known phenomena characteristic of absorbing biaxial crystals, it was thought worthwhile to publish illustrations of these phenomena (together with a qualitative verification of some of the more detailed aspects of the theory that had hitherto not been convincingly demonstrated). Broadly speaking, sections 2–4 do not cover original ground, and the phenomena they deal with are also explained, for example, in Pockels' *Lehrbuch*.[1]

In Part I of this paper[2] it was shown that the optical behaviour of absorbing crystals not possessing optical activity could be regarded as due to the effects of linear birefringence and linear dichroism superposed continuously along the depth of the medium.* The peculiar features in biaxial crystals arise because here the principal planes for the usual operation of birefringence do not coincide with those for the operation of dichroism. In spite of the simplification which such a method of consideration represents over the more rigorous electromagnetic theory, the features of propagation in an absorbing biaxial medium are still somewhat complex. Therefore, in explaining the experimental phenomena involved we shall start by assuming the elementary theory of Mallard; and we shall broadly indicate in §§ 2–4, how the experimental results themselves point out the need for a more refined

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* See Note at the end of the paper for references to some earlier work.[3]

theory, as well as to some of the results of such a theory. (The theoretical treatment in many standard texts[4–7] finally amount in practice to the assumptions of Mallard's theory—except for a slight change in the form of the absorption ellipsoid which may be neglected for directions near an optic axis.)

The photographs (Figs. 2–15) illustrated in this paper were all taken with sodium light illumination in convergent light; the simplest method of observing the phenomena which they reproduce is by holding the plate close to the eye and looking towards an extended source of light through the plate —there being arrangements for introducing auxiliary appliances (such as polaroids and quarter-wave plates) both in front of and behind the crystal. Each point in the convergent light figure obviously corresponds to a definite direction of propagation: to visualise this we may represent all directions as passing through the centre of a sphere and defined by their intersection with the spherical surface. The region surrounding an optic axis may then be approximated by a plane (the plane of the paper in Fig. 1), the central point O in the convergent light figure corresponding to the optic axis, and the horizontal line X_k X_k' to the axial plane. (Since the axial angle is not small, the second optic axis does not appear in the figure.)

§ 2. PROPERTY OF THE OPTIC AXES IN ABSORBING CRYSTALS

When a plate of an absorbing biaxial crystal cut normal to an optic axis is examined in convergent light between crossed polaroids, the optic axial direction does not in general appear extinguished (as in transparent crystals) but shows two extinction positions as the crossed polaroids are rotated round together—its behaviour in this respect being similar to that of a *non*-axial direction in a transparent specimen. In the case of an orthorhombic crystal, these extinction positions occur when the vibration-direction of the polariser lies either along or perpendicular to the axial plane; the appearance of the figure which is the same in both cases, is given in Fig. 2, the dark isogyre lying along the axial plane as in transparent crystals. On the other hand Fig. 3 shows that for an intermediate position where the vibration-directions of the crossed polaroids make angles of 45° with the axial plane, the optic axial direction is not extinguished by a vertical isogyre.

Along the optic axis, therefore, two linearly polarised vibrations are propagated. If we take the elliptic section of the absorption ellipsoid normal to the optic axis, these two waves are linearly polarised along the principal radii of this section—which lie parallel to OX_k and OY_k in the case of the orthorhombic crystal iolite. The characteristic feature distinguishing these two waves is not any difference in their refractive indices, but the fact that they have different coefficients of extinction k_1 and k_2, where $1/\sqrt{k_1}$ and

$1/\sqrt{k_2}$ are the principal radii of the absorption ellipsoid lying along OX_k and OY_k respectively; the absorption for the vertical vibration-direction is much greater than that for the horizontal vibration-direction in the case of iolite

The existence of dichroism along the optic axial direction is sometimes[4, 5] expressed by the statement that the absorption of a wave travelling along an optic axis depends on its plane of polarisation. This statement is however somewhat misleading for if a wave incident in the direction of an optic axis has its vibration-direction inclined at an arbitrary angle to the axial plane, the disturbance is not propagated with a single specific coefficient of absorption; on the other hand, it is split up into two waves with different coefficients of absorption polarised along and perpendicular to the axial plane, and the vibration-direction of the wave emerging from the plate will not be the same as that of the incident wave but would have turned towards the less absorbed component—towards the axial plane in the case of iolite. This is the reason why the optic axial direction does not in general appear extinguished between crossed polaroids. According to this explanation the optic axial direction can be extinguished by rotating the analyser away from the crossed position, and this has been done in Fig. 4. The extinction would not have been complete if there had been any (sensible) difference in the refractive indices of the waves.

An estimate of the dichroism along the axial direction will be use fu later, and this can be made if, in Fig. 4, the inclinations ψ and ψ' that thel incident and emergent vibrations, make with the axial plane are known. These angles were estimated to be roughly (90° – 12½°) and 12½° respectively. From equation (1) of Part I we then get $kz = 3$ approximately, where k is the difference in the coefficients of absorption and z the thickness.

[The azimuths of the polariser and analyser had not been directly noted during the experiment. Hence ψ and ψ' were indirectly determined by noting that the two diameters along which the ring system is absent in Fig. 4, are inclined at roughly 25° to the axial plane. We then use the fact that these diameters represent directions where one of the principal planes of refraction coincide with the vibration-direction either of the polariser or of the analyser. (Since the diameters where this occurs are not highly inclined to the axial plane, the waves here may be regarded as linearly polarised.)]

§ 3. BREWSTER'S BRUSHES

With neither polariser or analyser introduced, the convergent light figure reveals the two dark Brewster's absorption brushes which appear in the plane perpendicular to the axial plane (Fig. 5).

The broad features of this phenomena are explicable on Mallard's theory. In Fig. 1 in the text, each double-headed arrow at the border gives the vibration-direction of the faster wave for all points on the corresponding radius of the field of view (assuming Mallard's theory). Now the absorption coefficients for the two vibrations propagated in any direction are determined by the intercepts that these vibrations make on an absorption ellipsoid; and though the orientations of these vibrations remain constant along any one diameter, they turn round rapidly with the diameter—giving rise to the Brewster's brushes.

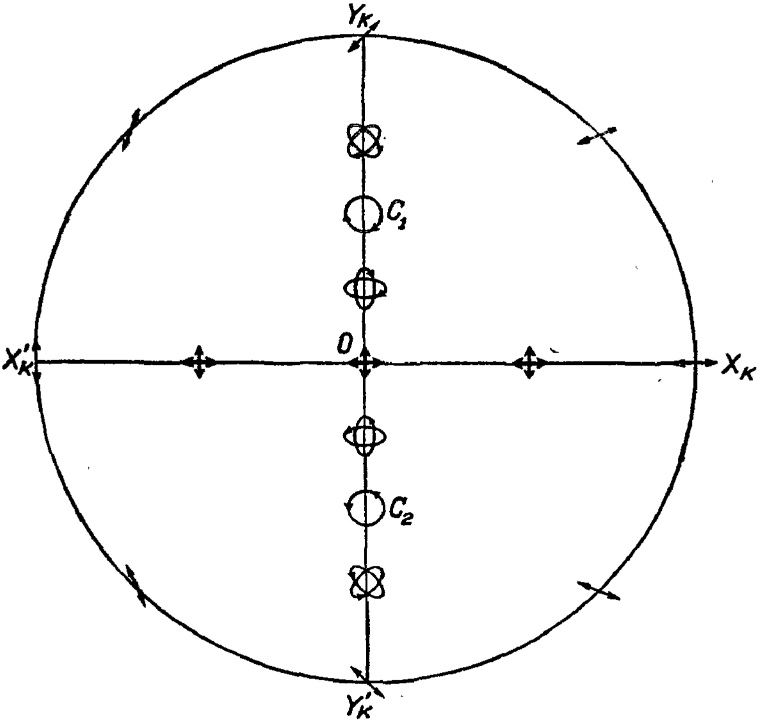

Fig. 1

X_k, X_k' = axial plane; O = optic axis; C_1, C_2 = singular axes.

The elliptical section of the absorption ellipsoid made by the plane of the paper in Fig. 1, may also be taken as the section normal to any direction of propagation in the small angular range covered by the convergent light figure. The mean of the two absorption coefficients may then be considered a constant for all directions in the angular range under consideration.

(On Mallard's theory this follows from a property of any two perpendicular radii of an ellipse, and in the more exact theory by the equations 15 of Part I.) Under this condition it may be easily shown that the sum of the intensities of the two waves emerging from the plate will be *minimum* along those directions where the two waves (into which the incident unpolarised light is split) are absorbed equally strongly; and that the sum of the intensities of these waves will be *maximum* along directions where the two waves differ in their absorption coefficients to the maximum extent.

Now the dichroism will be greatest where the waves are linearly polarised along the principal planes of absorption OX_k and OY_k—a situation which occurs for directions along the axial plane in the case of an orthorhombic crystal like iolite. For directions in the perpendicular plane Y_kY_k' the principal planes of refraction are inclined at 45° to the principal planes of absorption; hence the dichroism should be zero for all points on Y_kY_k' (the optic axial direction O being excepted in the case of Mallard's theory, the small strip C_1C_2 being excepted according to the exact theory). This explains the occurrence of the Brewster's brushes in the plane perpendicular to the axial plane.

§ 4. PHENOMENA NOT EXPLICABLE ON THE ELEMENTARY THEORY

(*a*) *The elliptical polarisation of the waves.*—Referring to Fig. 3, we note that when the plate is viewed between crossed polaroids set in the diagonal position it is not the optic axial direction *alone* that remains unextinguished; the region of non-extinction extends over a finite vertical strip passing through the optic axis, and, in fact, the extinction along the vertical ' isogyre ' becomes perfect only at the boundary of the figure.

An important inference may be drawn from this phenomenon. Along the optic axial direction (where the birefringence is zero) the two waves propagated are linearly polarised along the principal planes of absorption (*i.e.*, along the principal radii of the normal section of the absorption ellipsoid); for directions appreciably inclined to the optic axis (where the birefringence becomes notable) the waves may be regarded as linearly polarised along the principal planes of refraction. But the transition between these two extreme stages (*i.e.*, from waves polarised along the principal planes of absorption to waves polarised along the principal planes of refraction) occurs in some continuous fashion—not discontinuously, as soon as the optic axial direction is departed from, as is required by Mallard's theory. This is also to be expected on the simple ground that the phenomena that are physically observable along the optic axial direction are not really explained by postulating a discontinuous property for the exact axial direction, since we are always concerned with pencils of finite (even if small) convergence. For directions along the axial plane the principal planes of refraction and absorption coincide so that the horizontal isogyre in Fig. 2 is dark and continuous.

Further, those points in the immediate vicinity of the optic axis O, which lie along the vertical line Y_kY_k', cannot be extinguished even on rotating the crossed polaroids together, away from the diagonal setting—which means that the waves here must be *elliptically* polarised. This property resembles that of transparent optically active birefringent crystals where two extinction positions cannot be obtained between crossed polaroids.

(*b*) *Phenomena with polariser or analyser alone.*—For any direction along the axial plane the two waves are polarised along and perpendicular to the axial plane; the two waves have respectively the least and greatest absorption coefficients of all the waves travelling along any direction in the field of view. Hence if a polariser be set with its vibration-direction perpendicular to the axial plane, a dark brush appears along the axial plane, as in Fig. 9; while if it is set along the axial plane, a white brush appears in the same position as in Fig. 6. These two photographs incidentally demonstrate the existence of pleochroism along the axial direction.

The most interesting feature about Figs. 6 and 9, is, however, the occurrence of the idiophanic interference rings, which appear conspicuous in the plane perpendicular to the axial plane. As the polariser is turned from its position along the axial plane in Fig. 6 to that perpendicular to the axial plane in Fig. 9, the figure changes in a manner which appears to depend on the absorption of the specimen. In the present case, the diameter along which the rings are most conspicuous first turns with the polariser (Fig. 7); next a dark brush gets detached from this diameter and turns round towards the axial plane, while the ring system again turns back towards a position perpendicular to the axial plane (Fig. 8).

The occurrence of idiophanic interference rings cannot be expected if the states of polarisation propagated along any general direction are two orthogonal linear vibrations (as assumed in Mallard's theory), or alternatively two orthogonal elliptic vibrations—as occurs in transparent optically active crystals. For even when two such beams are completely coherent (a condition automatically ensured by polarising the incident light), they will be incapable of interference with one another—unless brought to the same state of vibration by the use of a suitable analyser. The two vibrations propagated along any general direction may therefore be assumed to be two *non-orthogonal* elliptic vibrations, propagated with different velocities and absorption coefficients. (Two elliptic vibrations having their major axes crossed and their ellipticities equal, and which are described in opposite senses are said to be orthogonal; any two vibrations not satisfying this condition are non-orthogonal.)

Figure 10 shows the photograph obtained by using an analyser alone, set in the same position as the polariser in Fig. 8, the exposures in the two cases being identical. The two photographs appear identical. It is possible to deduce from this that the non-orthogonal vibrations propagated along any general direction must be of the form of two similarly rotating elliptic vibrations having their major axes crossed and their ellipticities equal. If the non-orthogonal vibrations were of other forms (as for example, two linear vibrations inclined at an angle different from 90°) the observed identity of the effects obtained with a polariser alone and an analyser alone could not, in general, be expected.[†]

Along the axial plane X_kX_k', the principal planes of refraction and absorption are coincident, so that the vibrations for directions of propagation in this plane are linear and orthogonal, as indicated in Fig. 1. This explains the absence of the idiophanic rings along the axial plane in Figs. 6–9.

As we proceed outwards from the optic axis along the radius OY_k, the change in the states of polarisation of the two waves may be easily followed on the Poincaré sphere by applying the principle of superposition developed in Part I. For these directions the principal planes of refraction and absorption have their maximum mutual inclination of 45°, and effects connected with the ellipticity may be expected to be most pronounced. Referring to Fig. 3 in Part I of this paper, as the linear birefringence increases from zero, the two states of polarisation (initially coincident with the principal planes of absorption X_k and Y_k respectively) will move downwards along the arcs X_kC_r and Y_kC_r respectively till both states become coincident with the pole C_r when the linear birefringence δ becomes equal to the linear dichroism k; as the birefringence further increases, the two states again become distinct and move upwards along the meridians of longitude C_rX_r and C_rY_r respectively.

Physically this means that as we proceed outwards along the radius OY_k, the two vibrations (initially polarised along the principal planes of absorption) open out into two right elliptic vibrations which become two identical circular vibrations at C_1; further on these split up into two elliptic vibrations with major axes along the principal planes of refraction, these elliptic vibrations tending to the form of two orthogonal linear vibrations at the

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[†] This will be proved in a later paper dealing with absorbing crystals which are also optically active, where the effects obtained with polariser and analyser are different.

border of the field of view. For directions on the other side of the axial plane the vibrations are left-elliptic. The velocities of the waves are equal for all directions lying within the small vertical strip C_1C_2 (as may be seen by setting $2\phi = \pi/2$ in Equation 14, Part I). But for all other directions in the vertical plane Y_kY_k', the absorption coefficients of the waves are equal, the velocities being, in general, different (as may be seen by setting $2\psi = \pi/2$ in Equation 15, Part I).

For any given angular distance from the axial direction, the ellipticity of the waves (and hence their departure from orthogonality) is maximum for directions lying in the vertical plane Y_kY_k'. Consequently the idiophanic rings may be expected to be most prominently seen, if the polariser is adjusted such that the ring system lies perpendicular to the axial plane as in Figs. 6 and 9. (This effect does not appear to be very pronounced.) The considerations of the previous paragraph show that the rings will appear in the vertical plane when the polariser is set along or perpendicular to the axial plane; for the two waves propagated along any direction in the vertical plane Y_kY_k' (excluding the small strip C_1C_2) will then have equal amplitudes and will consequently be capable of showing the maximum interference effects. (The result of this paragraph has been proved by means of a more exact mathematical treatment in Pockels.)

(*c*) *Interference effects in Brewster's brushes.*—Figure 5 shows distinct traces of periodic maxima and minima in the Brewster's brushes, in the region near the optic axis. The occurrence of such interference effects may be broadly expected on the following grounds. When unpolarised light is split into two orthogonally polarised vibrations, these vibrations will be completely incoherent; but when the incident unpolarised light is being split into two *non-orthogonally* polarised vibrations, as in the present case, the two vibrations must necessarily be considered as partially coherent—for if they were incoherent it can be shown that the resultant beam would be partially polarised and not unpolarised (see *e.g.*, reference 8). Since the beams are partially coherent (to an extent which depends on their departure from orthogonality), they will be capable of restricted interference with one another (to an extent which depends again on their departure from orthogonality). The interference effects are therefore very feeble, being noticeable only in the immediate vicinity of the singular axes—unlike the idiophanic rings which are fairly prominent because complete coherence of the beams is ensured by polarising the incident light. It can be shown‡ that the maxima

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‡ This will be shown incidentally in a later paper dealing with absorbing crystals possessing optical activity.

and minima in the Brewster's brushes must occur in the same position as those in the idiophanic rings obtained by setting the polariser along the axial plane, and this is verified by comparison with Fig. 6.

The explanation of the Brewster's brushes given in §2 is however still applicable. For though the intensity emerging along any direction is not merely equal to the sum of the intensities of the two waves emerging in that direction (because of an additional term expressing their interference), it is this sum that broadly locates the position of the brushes.

From the standpoint of the method of superposition we may also regard the interference effects as arising because the crystal itself acts both as polariser and analyser—and a similar explanation could also be given for the idiophanic rings.

§ 5. THE SINGULAR AXES

(*a*) *Examination between circular polariser and crossed circular analyser.*—The point C_1 represents a direction where only a right-circular vibration can be propagated unchanged; while the point C_2 represents a direction where only a left-circular vibration can be propagated without change of form. These two directions are termed the Windungsachen or singular axes. We shall now give a direct confirmation of the existence of these axes; the only previous experimental work dealing directly with the property of these axes was, as we shall see, not interpreted in a correct manner.

In front of the crystal plate is kept a ' left-circular polariser ' (*i.e.*, an arrangement which transmits left-circularly polarised light when unpolarised light is incident on it). Behind the crystal is kept a ' right-circular analyser ' (*i.e.*, an arrangement which completely cuts off left-circularly polarised light). Under such conditions a transparent crystal will show a system of circular rings with a black spot at the optic axis, where the incident circularly polarised light can be propagated unchanged. In the present case the dark spot occurs slightly to one side of the optic axis (Fig. 11), corresponding to the direction of the lower singular axis C_2. (This is seen better in Fig. 16, which was taken with another plate of iolite having less total absorption.) When the crystal plate is viewed between a right-circular polariser and a crossed circular analyser, the other singular axis C_1 appears extinguished (Fig. 12). The angle between the singular axes is seen to be very small, and has been exaggerated in Fig. 1.

(A quarter-wave plate preceded by a polaroid at 45° to the principal planes, together constitute a convenient circular polariser; a quarter-wave plate followed by a polaroid at 45° to the principal planes, similarly constitute a circular analyser.)

In Part I, Section 4 *c*, it was shown that the vibrations propagated in any direction are right- or left-elliptic according as the principal plane of refraction OX_r (corresponding to the slower wave, in the absence of absorption) makes a negative or positive acute angle with the principal plane of absorption OX_k (corresponding to the less absorbed component in the absence of birefringence). Accordingly in Fig. 1, the sense of description of the elliptic vibrations are correct only if we assume that the arrows at the border give the *faster* vibration-direction (for all points on the corresponding radius) in the absence of absorption. That this assumption was indeed correct, was verified by using the fact that at the border of the field of view the refractive indices and states of polarisation are substantially the same as in the absence of absorption. The polariser and analyser were set along and perpendicular to the axial plane respectively, as in Fig. 2, and a quarter-wave plate was introduced immediately behind the crystal plate with its slow vibration-direction making an angle of + 45° with respect to OX_k. The rings along OY_k moved outwards indicating a diminution of the phase retardation for such directions, while those appearing on the line OY_k' moved towards the centre. This confirmed that the right- and left-circular singular axes occur respectively on the sides of the axial plane that are to be expected according to theory.

§ 6. EFFECTS WITH INCIDENT CIRCULARLY POLARISED LIGHT

When the incident light is circularly polarised it is propagated without change of form along one of the singular axes. In Part I it was shown that for the direction corresponding to the other singular axis, the emergent intensity will not be either zero or negligible (as had been thought by Voigt[1]), but should in fact be greater than the intensity emerging in the direction of the first singular axis. This was confirmed in the following manner. When examined between a left-circular polariser and a crossed circular analyser, we have seen that the singular axis C_2 where the incident vibration is propagated without change of form appears as a dark spot (Fig. 11). If now the circular analyser is removed, the same singular axis appears darker than the other singular axis (which appears within a bright spot), as may be seen in Fig. 13.

Similarly Fig. 14 shows the appearance presented when the incident light is right-circularly polarised. It will be seen by comparison with Fig. 12, that the upper singular axis C_1 where the incident vibration is propagated without change of form appears the darker of the two. Along the other singular axis C_2 the state of vibration alters progressively along the depth of the medium, according to the theoretical analysis of Part I. The emergent vibration in this direction will be elliptically polarised, the major axis of the vibration lying along OX_k (which is the principal plane corresponding to the less absorbed component). Hence if a quarter-wave plate is introduced behind the crystal plate with its principal planes along OX_k and OY_k, the elliptic vibration emerging in the direction of the lower singular axis C_2 will be reduced to a linear vibration at an angle θ to the axial plane—where $\tan \theta$ is the ratio of the minor to the major axis of the elliptic vibration. Thus by introducing a polaroid behind the quarter-wave plate it should be possible to extinguish the singular axis C_2. To verify this, the point C_2 was marked with an ink spot on the ground glass of the camera, after having determined its exact location by the position of the black spot in the arrangement of Fig. 11. By rotating the polaroid it was found that a point of extinction lying on the vertical line Y_kY_k' could be taken continuously *through* the singular axis C_2 (see next paragraph). Figure 15 shows the photograph taken when C_2 has been extinguished in this manner. The angle θ was roughly estimated at 25°; this is roughly the magnitude to be expected since from Equation 18 of Part I we should have: $\tan (\pi/4 + \theta) = kz$, where kz has already been estimated to have a value near 3 (refer § 2).

More generally (with the incident vibration right circularly polarized, as before) the elliptic vibration emerging along any direction on the vertical plane Y_kY_k' will have its principal axes along OX_k and OY_k. This is a consequence of the fact that for any such direction the principal planes of refraction and absorption are inclined at 45° to one another—the corresponding diameters X_rY_r and X_kY_k on the Poincaré sphere being at right angles to one another as in Fig. 3 of Part I; in that figure, if C_r represents the incident vibration, the movements ds_r and ds_k will always lie along the same line-element, so that the emergent vibration will necessarily be represented by some point on the arc $C_rX_kC_lC_r$. Hence if a quarter-wave plate is introduced with its principal planes along OX_k and OY_k (as described in the last paragraph) the vibrations emerging along all the directions in the vertical plane Y_kY_k' will be reduced to linear vibrations (with various azimuths of polarisation). The polaroid behind this quarter-wave plate was set at 45° to the principal planes in such a position that the upper singular axis C_1 where the incident vibration is propagated unchanged appeared extinguished. By rotating the polaroid away from this position in the proper direction, the point of extinction could be moved continuously downwards *through* the lower singular axis C_2.

§ 7. EXTINCTION BETWEEN ELLIPTIC POLARISER AND CROSSED ELLIPTIC ANALYSER

It would be desirable to confirm that the principal axes of the two elliptic vibrations propagated without change of form along any direction, do not (in general) coincide with the principal planes of refraction—for even the behaviour of the idiophanic rings can be sufficiently well explained without taking this factor into account (see Pockels). We shall describe an experiment confirming this for directions represented by the points on C_1C_2, where the principal axes of the elliptic vibrations should lie parallel to OX_k and OY_k whereas the principal planes of refraction are inclined at 45° to these directions.

The arrangement used was that described by Ramachandran and Chandrasekharan[9] in another connection. The crystal was kept between crossed polaroids which could be rotated around together. A quarter-wave plate was set immediately behind the first polaroid, with its principal planes along OX_k and OY_k; another quarter-wave plate was set immediately in front of the second polaroid with its principal planes turned by 90° with respect to the first quarter-wave plate. If the crystal plate were absent, then obviously the elliptically polarised light produced by the arrangement in front would be automatically cut out completely by the arrangement behind, independent of the setting of the ganged polaroids. In the presence of the crystal plate, any direction where the incident elliptic vibration is propagated without change of form will appear extinguished. (The principal axes of the incident elliptic vibration will always lie along OX_k and OY_k.)

Starting with the polariser set along the axial plane, the optic axial direction O appears extinguished as in Fig. 2. As the ganged polaroids are rotated away from this setting in the proper direction, the point of extinction on the line Y_kY_k' moves upwards from O till it reaches the singular axis C_1 (polaroid at 45° to principal planes of $\lambda/4$ plate). As the ganged polaroids are rotated still further the point of extinction retraces its path, moving from C_1 back to O (polariser set perpendicular to axial plane). Further rotation through 90° causes the extinction to move upto C_2 and back to O.

The above experiment provides a direct confirmation of the theoretical result that the two elliptic vibrations propagated along these directions have their major axes crossed, have the same ellipticity and are described in the *same* sense. It also shows that the two elliptic vibrations gradually degenerate into two (identical) circular vibrations as the singular axis is approached.

The author is very grateful to Prof. Sir C. V. Raman for his keen interest in this investigation.

§ 8. SUMMARY

The phenomena shown in convergent light by a section plate of iolite cut normal to an optic axis are discussed and illustrated. Of particular interest among the photographs reproduced are those taken (*a*) between circular polariser and crossed circular analyser, demonstrating the existence of the two singular axes (a right-circular vibration alone being propagated unchanged along one singular axis, and a left-circular vibration alone along the other); (*b*) with a circular polariser alone, confirming the theoretical prediction in Part I that the singular axis where the incident circular vibration can be propagated unchanged should appear darker than the other; the state of the elliptic vibration emerging from the brighter singular axis was also qualitatively in accord with theory. Examination between elliptic polariser and crossed elliptic analyser demonstrated that along any general direction in an (optically inactive) absorbing biaxial crystal, two similarly rotating elliptic vibrations can be propagated unchanged—the major axes being crossed but not coincident with the principal planes of refraction.

§ 9. REFERENCES

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§ 10. DESCRIPTIVE NOTES ON THE PLATES

All photographs were recorded with a plate of iolite cut normal to an optic axis, the plate being held normally with the axial plane horizontal.

Phenomena with polariser and analyser

FIG. 2. Crossed polaroids: vibration directions along and perpendicular to axial plane. (Optic axis extinguished.)

FIG. 3. Crossed polaroids: vibration directions at 45° to axial plane. (Optic axis not extinguished.)

FIG. 4. Non-crossed polaroids: vibration directions equally inclined to axial plane. (Optic axis extinguished.)

Brewster's brushes and idiophanic rings

FIG. 5. Brewster's brushes, with neither polariser nor analyser. (Traces of interference rings seen.)

FIGS. 6, 7, 8 & 9. Idiophanic rings with polariser *alone* at various settings: along the axial plane in Fig. 6, perpendicular to the axial plane in Fig. 9, and at two intermediate orientations in Figs. 7 and 8.

FIG. 10. Idiophanic rings with analyser alone, set in the same position as the polariser in Fig. 8.

Properties of the singular axes

FIG. 11. Left-circular polariser and right-circular analyser. (Lower singular axis extinguished.)

FIG. 13. Left-circular polariser alone. (Lower singular axis appears darker than the other.)

FIG. 12. Right-circular polariser and left-circular analyser. (Upper singular axis extinguished.)

FIG. 14. Right-circular polariser alone. (Upper singular axis appears darker than the other.)

FIG. 15. Right-circular polariser and an elliptic analyser adjusted to cross out the elliptic vibration emerging from lower singular axis.

FIG. 16. Circular polariser and crossed circular analyser. (Photograph taken with a more lightly coloured plate: lower singular axis extinguished.)

NOTE

In Part I of this paper it was shown that the features of wave-propagation in absorbing biaxial crystals may be regarded as due to the effects of linear birefringence and linear dichroism superposed continuously along the depth of the material; this idea was worked out by a simple geometric method using the Poincaré sphere (as also by a more lengthy algebraic method). A series of papers published earlier by Clark Jones[3] dealing with 'A new calculus for the treatment of optical systems' has since then come to the notice of the author; the comprehensive calculus elaborated in the first half of that series uses the representation of any optical device by 2×2 complex matrix (operating on the electric vector of the incident light). In Part IV of that series one of the applications that has been made of the calculus is the derivation of the matrix for a plate of an absorbing crystal by a method which is physically equivalent to the method of superposition; the matrix corresponding to an infinitesimal path has been considered in Part VII.

FIG. 2

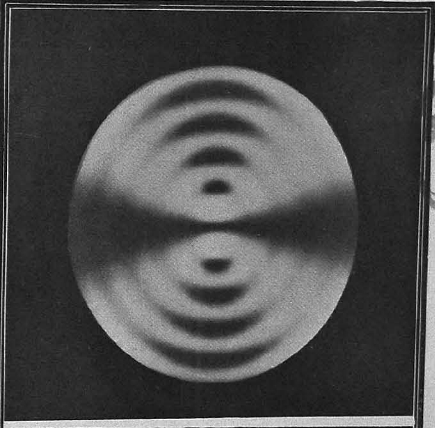


FIG. 3

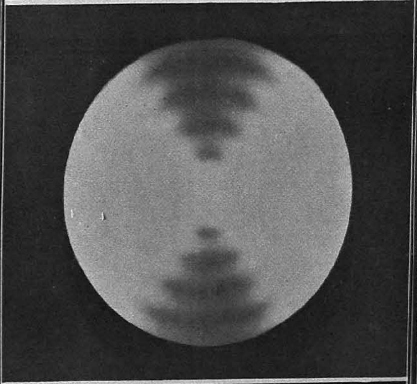
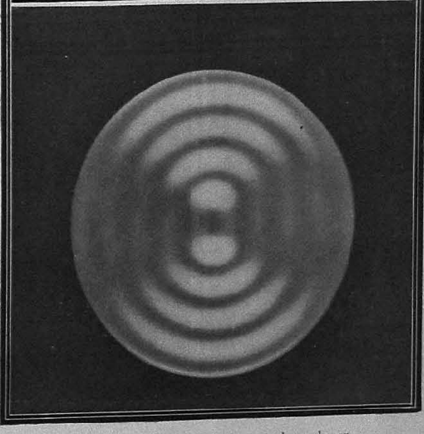


FIG. 4



Phenomena with polariser and analyser

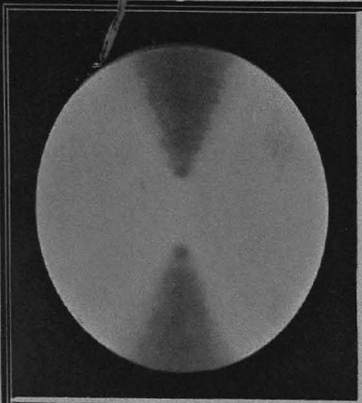


FIG. 5

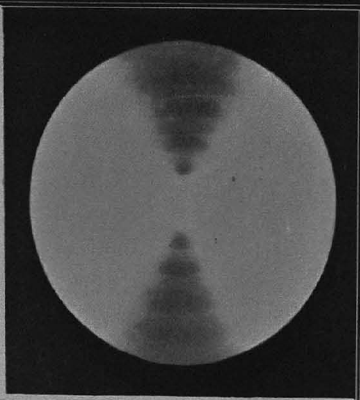


FIG. 6

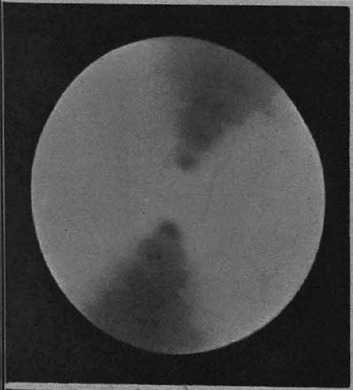


FIG. 7

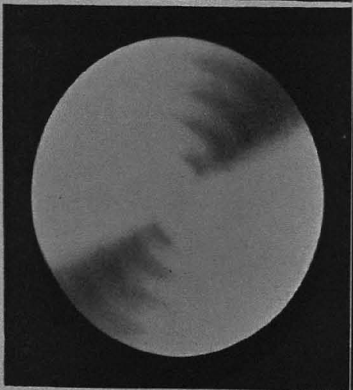


FIG. 8

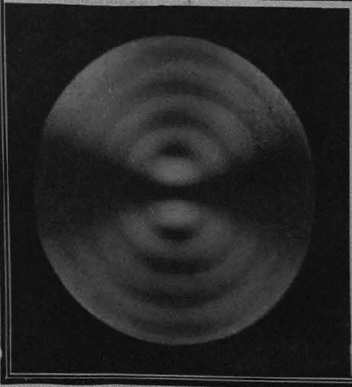


FIG. 9

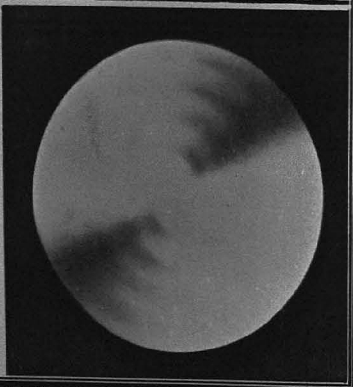


FIG. 10

Brewster's brushes and idiophanic rings

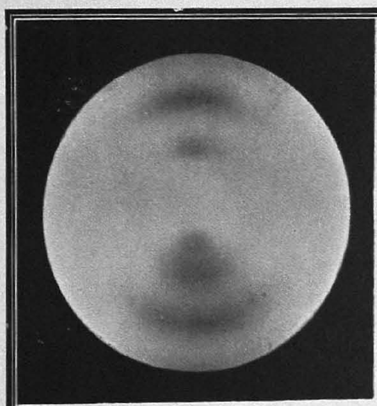


FIG. 11

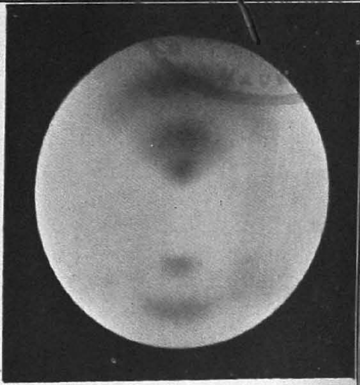


FIG. 12

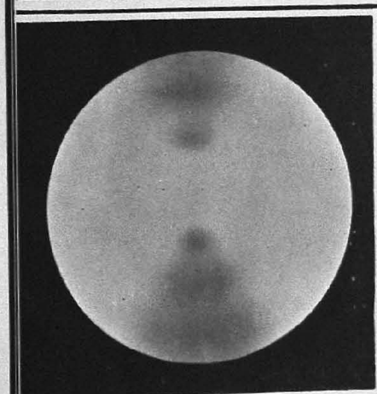


FIG. 13

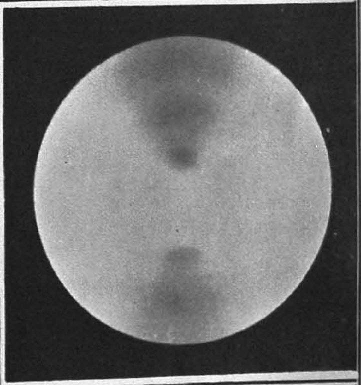


FIG. 14

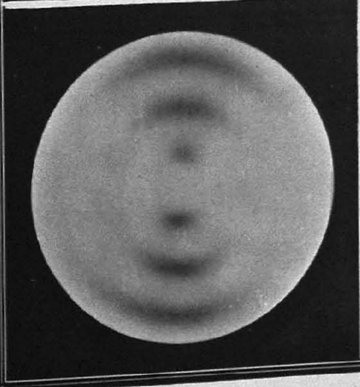


FIG. 15

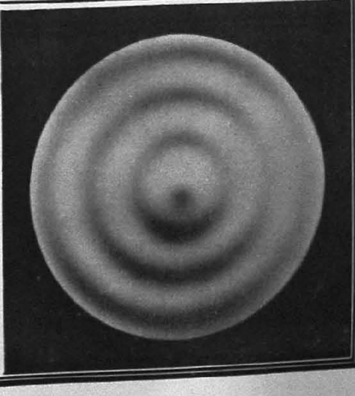


FIG. 16

Properties of the singular axes

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THE ELASTICITY OF CRYSTALS[*]

THE materials used in engineering construction are mostly polycrystalline solids and their elastic behaviour is of the utmost practical importance. It follows that the subject of the elasticity of crystals is of more than merely academic interest. Of recent years the importance of its study has greatly been enhanced by several circumstances. The experimenter today can in many cases work with synthetically prepared crystals of large size and good quality. He has at his disposal several new techniques enabling him to determine their elastic behaviour and obtain precise results. These techniques are mostly based upon the production of waves or standing oscillations in the crystal with the aid of piezoelectric oscillators. These latter oscillators are themselves of importance in technical acoustics and communication engineering. The subject also stands in the closest relation to the structure of crystals as revealed by X-ray diffraction and spectroscopic studies. It is thus an integral part of the rapidly developing physics of the solid state.

2. THE NOTIONS OF STRESS AND STRAIN

The science of elasticity is based on the fundamental notions of stress and strain and —subject to a restriction on their magnitude— on the proportionality between them known as Hooke's law. The precise definition of stress and strain is thus a matter of fundamental importance. Such definitions have necessarily to be comprehensive. They have to cover cases where their magnitudes vary from point to point within the crystal and also cases in which the stresses and strains vary with time as in the theory of wave-propagation. It is essential, further, that they take account of the elastic anisotropy which all crystals exhibit, in other words, the fact that the effect of an impressed force depends on the direction in which it is applied.

An important remark which should be made here is that it is unnecessary to introduce atomistic considerations in defining stress or strain. This is obvious since the phenomena with which we are concerned are open to macroscopic observation. To take account of the variability of stress and strain with the location we define these quantities in relation to a particular point within the solid. The legitimacy of this procedure rests upon the fact that it is possible to imagine the volume of the substance to be divided into elements of such small dimensions that each element can be regarded as a mass particle and yet is large enough to justify its physical properties being assumed to be the same as those of the material in bulk. We are thereby enabled to specify the position of any volume element by its three co-ordinates in space and its state of equilibrium or of motion in terms of simple forces or tractions acting on the volume element.

3. THE ELASTIC CONSTANTS

The foregoing remarks are preliminary to a specification of stress and strain which is logically consistent with the approach made to the subject. We define stress in terms of the tractive force assumed to act on an infinitesimal area drawn through a given point within the solid. Since this area can be set normal to each of the three co-ordinate axes in turn and for each such setting the acting force can be resolved into three components parallel to these axes respectively, we have nine components of stress. Likewise, strain is expressed in terms of the difference in displacements of two neighbouring points within the solid. Since the line joining these two points can be set parallel to each of the three co-ordinate axes in turn and the difference of their displacements in each case can itself be resolved along each of these axes in turn, we have nine components to deal with. The stress-strain relationships of proportionality would in the general case thus involve 9×9 or 81 elastic constants. The well-known law of reciprocity which enables us to interchange the directions of force and displacement without change in the constant of proportionality between them results in the number 81 being reduced to $(9+36)=45$ constants in all. Thus, it requires 45 elastic constants to describe the elastic behaviour of a triclinic crystal. For crystals of other classes, the number of independent constants is diminished by reason of their symmetry properties, the more so the higher the symmetry of the crystal. The number of independent elastic constants in each case can be readily worked out using the formulæ based on group theory given by Bhagavantam. Table I exhibits the

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[*] 1. "On the Theory of the Elasticity of Crystals," by
Sir C. V. Raman and Dr. K. S. Viswanathan ; 2. "Evalua-
tion of the Four Elastic Constants of Some Cubic
Crystals," by Sir C. V. Raman and D. Krishnamurti.
Memoirs Nos. 73 and 76 of the Raman Research Institute, Bangalore, *Proc. Ind. Acad. Sci.*, 1955, **42**, 51 and 111.

situation thus disclosed. The first column shows the symmetry class in the usual language of crystallography, while column II shows the subdivisions of those classes grouped together according to their elastic behaviour. The third column shows the number of independent elastic constants for these sub-classes.

TABLE I

Crystal system	Point Group (Schoenflies notation)	No. of Elastic Constants		
		General	Dynamic	Classical
Triclinic ..	All	45	36	21
Monoclinic ..	All	25	20	13
Orthorhombic	All	15	12	9
Tetragonal	C_4, S_4, C_{4h}	13	10	7
	D_4, C_{4v}, D_{2d}, D_{4h}	9	7	6
Trigonal	C_3, S_6	15	12	7
	D_3, C_{3v}, D_{3d}	10	8	6
Hexagonal	C_6, C_{3h}, C_{6h}	11	8	5
	D_6, C_{6v}, D_{3h}, D_{6h}	8	6	5
Cubic	T, T_h	5	4	3
	O, T_d, O_h	4	3	3

4. WAVE-PROPAGATION IN CRYSTALS

Writing down the equations of motion of the volume of elements of the medium in terms of the space variations of the stress components acting upon them, one can investigate the propagation of waves through the material. It emerges that in any given direction within the solid, three types of waves can be propagated, their velocities being different in each case and also varying with the direction. The wave velocity for each of the three types and for any particular direction of propagation is expressible as a function of the direction and of certain linear combinations of the elastic constants. The number of these combinations is less than the number of general elastic constants in each case. The number can be calculated from formulæ based on group theory and is shown in the fourth column of Table I.

5. REMARKS ON THE CLASSICAL THEORIES

Cauchy, the celebrated French mathematician of the 19th century, in his memoir presented to the Academy of Sciences at Paris in the year 1822 proposed a reduction of the number of components of stress and strain from 9 to 6 in each case. His arguments will be found reproduced in numerous text-books and indeed they form the basis of the mathematical theory of elasticity as hitherto developed. A critical examination shows however that those arguments are not sustainable. In the case of the strain components, the reduction was sought to be justified by eliminating movements which were thought to be rigid body rotations. Actually the quantities eliminated are differential rotations of the same nature as those which appear in the deformation of solids by torsion or flexure and which are quite as much a part of the elastic deformations as extensions and contractions. Hence their elimination is not justified. The argument on which the reduction of the number of stress components from 9 to 6 was based was that the angular momenta of the tractions acting on a volume element taken about each of the co-ordinate axes in turn and summed up should vanish. But since by definition the stresses are assumed to be in the nature of tractive forces acting on volume elements small enough to be regarded as single mass particles, no consideration of angular momenta is called for. Indeed, once we accept the definitions of stress and strain, it becomes logically imperative to take account of all the nine components of each.

On the basis of Cauchy's assumptions the stress-strain relations of proportionality are $6 \times 6 = 36$ in number and these by application of the reciprocity relationship reduce to $(6 + 15) = 21$ in all for a triclinic crystal. Their number is smaller for the crystals of higher symmetry classes and is shown in column 5 of Table I against each of them. The reduction in number of the stress and strain components from 9 to 6 is in effect equivalent to assuming that differential rotations within the solid play no part in the theory of elasticity and to imposing a corresponding restriction on the nature of the acting stresses. As already remarked, differential rotations play a fundamental role both in static deformations, especially in torsion, as also generally in wave propagation. In other words, the classical theory is of restricted validity confined to certain types of static deformation and to particular cases of wave propagation. Since however it has been employed to interpret experimental data in other cases as well, it is useful to express the 21 constants in terms of the more general 45 constants, thereby enabling the latter to be evaluated from the existing data of experiment.

6. THE DATA OF EXPERIMENT

As will be seen from Table I the simplest cases of all are crystals belonging to the Td and the Oh classes of the cubic system. The general theory gives four elastic constants which may be designated as respectively d_{11}, d_{12}, d_{44} and d_{45} while in the classical theory we have only three constants which have been designated as C_{11}, C_{12} and C_{44}. The linear combinations of the elastic constants which determine the velocities of wave propagation are in the former theory d_{11}, d_{44} and $(d_{12}+d_{45})$ while in the classical theory they are C_{11}, C_{44} and $(C_{12}+C_{44})$. Likewise, the expressions for the bulk modulus in the new and the old theory are respectively $(d_{11}+2\,d_{12})/3$ and $(C_{11}+2\,C_{12})/3$. Since the number of elastic constants of these classes is four, while the number of linear combinations that can be determined by dynamic measurements is three, it follows that at least one additional determination by static methods is necessary to enable all the four constants to be evaluated. The most appropriate of such determinations appears to be the bulk-modulus of which very precise measurements have been made by Bridgman and his collaborators at Harvard. It is necessary of course to correct the isothermal static value of the constant to obtain the adiabatic bulk modulus. Many other points have to be borne in mind: the bulk modulus reduced to zero pressures should be used; both the static and dynamic determinations have to be reduced to the same temperature of observation and finally the nature of the material used in the two cases has to be comparable.

In Table II are shown for 16 different crystals of the Td and Oh classes, the values of the four elastic constants calculated in the manner explained. The three constants of the older theory are also shown in the table. The latter are those which appeared to be the most reliable values obtained by ultrasonic techniques, while the former were obtained by combining them with the value for the adiabatic bulk-modulus. The values of C_{11} and d_{11} are in each case identical; likewise those of C_{44} and d_{44}. But C_{12} and d_{12} are different and such difference is a measure of the failure of the three-constant theory to represent the actual elastic behaviour of the crystal. The difference between d_{44} and d_{45} also expresses the same situation in another way.

Certain general features emerge from the Table. For all the four alkali halides which are soluble in water, C_{12} is less than d_{12} and likewise d_{45} is less than d_{44}. This regularity of behaviour taken in conjunction with the reliability of the data in these cases makes it clear that these differences are real and justify us in concluding that the elastic behaviour of cubic crystals cannot be expressed in terms of three constants, but needs four. Diamond, germanium, zinc blende and fluorspar also exhibit a parallel behaviour which is the reverse of that shown by the four water-soluble alkali-halides. In their cases, C_{12} is decidedly greater than d_{12}, while *per contra* d_{44} is less than d_{45} and these differences are numerically more striking than in the case of the alkali-halides. Magnesium oxide for which the data are reliable exhibits a noteworthy behaviour; the differences between C_{12} and d_{12} and likewise between d_{44} and d_{45} are in the same sense as in the alkali halides

TABLE II

Elastic constants in 10^{11} *dynes/cm.*^{2}

Substance	C_{11}	C_{12}	C_{44}	d_{11}	d_{12}	d_{44}	d_{45}
NaCl ..	4·877	1·232	1·269	4·877	1·34	1·269	1·16
KCl ..	4·038	0·663	0·628	4·038	0·779	0·628	0·512
KBr ..	3·455	0·56	0·507	3·455	0·655	0·507	0·412
NaBr ..	3·87	0·97	0·97	3·87	1·22	0·97	0·72
LiF ..	11·9	5·38	5·34	11·9	4·5	5·34	6·22
MgO ..	28·76	8·74	15·14	28·76	11·27	15·14	12·61
AgCl ..	6·05	3·64	0·624	6·05	3·482	0·624	0·782
Diamond ..	95	39	43	95	35·9	43	46·1
Ge .	12·88	4·825	6·705	12·88	4·04	6·705	7·49
Si ..	16·56	6·386	7·953	16·56	6·56	7·953	7·78
ZnS ..	10·79	7·22	4·12	10·79	6·17	4·12	5·17
CaF_2 .	16·6	4·87	3·58	16·6	4·29	3·58	4·16
Al ..	10·56	6·39	2·853	10·56	6·29	2·853	2·953
Cu .	16·92	12·25	7·55	16·92	12·81	7·55	6·99
Ni ..	25·26	15·51	12·3	25·26	16·01	12·3	11·8
Ag ..	12·4	9·34	4·61	12·4	8·89	4·61	5·06

but proportionately much larger. Differences of the same order of magnitude but in the opposite sense is shown by lithium fluoride. In the case of the metals crystallizing in the face-centred cubic system, we also find differences between C_{12} and d_{12} and between d_{44} and d_{45}, but they are not always in the same sense. This is a feature which need not surprise us in view of the very great differences exhibited by these metals in other respects.

C. V. Raman.

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THE THERMAL ENERGY OF CRYSTALS*

BY

SIR C. V. RAMAN

THE determination of the nature of the atomic movements which constitute the thermal agitation in a crystal is a fundamental problem in the physics of the solid state. Its importance will be evident when it is remarked that even the most familiar aspects of the thermal behaviour of solids depend for their explanation on the precise nature of these movements. The subject also stands in the closest relationship with the spectroscopic behaviour of crystals and with X-ray crystallography, to say nothing of various other branches of physics.

Since the atomic movements under consideration are of thermal origin and are presumably in the nature of vibrations about the atomic positions of equilibrium, the subject has to be viewed in the light of the fundamental principles of thermodynamics and the quantum theory. However, as in the parallel problem of the vibration spectra of molecules, we have to seek the aid of classical mechanics for ascertaining the modes and frequencies of vibration with which we are concerned.

2. THERMODYNAMIC CONSIDERATIONS

Every crystal is a three-dimensional grouping in space of atoms held together by their mutual interactions; equivalent atoms in the crystal are located at the points of a Bravais lattice, and if the crystal consists of p interpenetrating Bravais lattices, there would be p atoms in each unit cell of the crystal structure. Since the frequencies of vibration of the atoms are determined by their masses and by the interatomic forces which are of limited range, they would necessarily be the same for the group of atoms contained in every cell of the structure. Hence every crystal may be considered as an assembly of a great number of oscillators physically similar to each other and having a set of vibration frequencies in common, and which since the oscillators can exchange energy with each other, constitute a system in thermodynamic equilibrium. Each oscillator can for any particular frequency of vibration assume any of the energy states permitted by the quantum theory, the probability of its being present in any one state being given by Boltzmann's well-known formula. The energy of the entire assembly of oscillators can therefore be evaluated by multiplying the number of oscillators of any particular frequency by the average energy of an oscillator of that frequency which is calculable from the relative probabilities of its different energy states, and then summing up the results for all the frequencies. The total number of oscillators included in such a reckoning would be three times the number of atoms comprising the crystal. This follows from the theorem in classical mechanics which states that the number of normal modes of vibration of a connected system of particles is the same as the number of degrees of freedom of movement of the entire system.

3. DYNAMICAL THEORY

The dynamics of atomic vibration in a crystal may be dealt with from two different standpoints which may be designated as the "molecular" and "molar" points of view respectively. In the "molecular" approach to the problem, we fix our attention on a particular unit cell of the crystal structure and proceed to write down and solve the $3p$ equations of motion of the p atoms contained in it, with a view to discover and enumerate their normal modes of vibration. In doing this we have necessarily to take

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* "The Nature of the Thermal Agitation in Crystals," by Sir C. V. Raman, Memoir No. 77 from the Raman Research Institute, Bangalore, and *Proc. Ind. Acad. Sci.*, 1955, **42**, 163-74.

account of the forces arising from the movements of the atoms in the surrounding cells which interact with those in the cell under consideration. It is obvious that no mode of vibration of the atoms in the unit cell can persist unchanged unless the atoms in the surrounding cells also vibrate in a similar mode with the same frequency. This would be the case if equivalent atoms in these outer cells also vibrate with the same amplitudes, but as regards their phases of vibration, there are several distinct possibilities. A formal investigation shows that there are $2 \times 2 \times 2$ or eight possibilities in all which can be described as follows : The phases of equivalent atoms are either the same or else opposite in consecutive cells along one, or two, or all the three axes of the Bravais lattice. The identity of the amplitude of vibration of equivalent atoms reduces the number of independent co-ordinates to $3p$ only. Thus. the equations can be solved and result in $3p$ solutions, but as there are eight different situations in respect of the phases, we have $8 \times 3p = 24p$ solutions in all. This is the same as the number of degrees of dynamic freedom of the $8p$ atoms contained in a super-cell having twice the linear dimensions of the unit cell of the crystal structure. Accordingly, we recognize $(24p - 3)$ normal modes of vibration properly so-called, the three omitted degrees of freedom representing the translatory movements of the super-cell.

In the "molar" approach to the problem, we consider the entire crystal as a single physical entity and investigate the propagation of waves through its structure. The wave equations are found to be formally satisfied if it be assumed that the equivalent atoms located at the points of a Bravais lattice have the same amplitude of vibration, this however being different for the different lattices of atoms, while the frequency, wave-length and the direction of the wave-vector are the same for all the interpenetrating lattices. Proceeding to solve the set of $3p$ equations obtained on this basis, an algebraic equation of degree $3p$ for the frequency results, and the solution of this gives us $3p$ different frequencies for a wave of given wave-length travelling in any assigned direction. By considering the functional dependence of these $3p$ frequencies on the wave-length and direction of propagation, it is found that the group-velocity of the waves vanishes for $(24p - 3)$ frequencies associated with eight different wave-vectors in the crystal. The $(24p - 3)$ frequencies thus obtained and the corresponding modes of vibration are found to be the same as the frequencies and normal modes deduced by the "molecular" approach to the problem, namely, those in which equivalent atoms in consecutive cells vibrate with the same amplitude and with phases that are either the same or else opposite along one, two or all three of the Bravais axes of the crystal. They may therefore be identified as the characteristic or normal modes and frequencies of vibration of the crystal structure. The three omitted frequencies represent the limiting case of the three sets of waves of the lowest frequencies and the longest wave-lengths for which the group velocity does not vanish but comes out as equal to the phase-velocity of the waves. These cases are identifiable with the three types of waves whose propagation in any direction in the crystal is shown to be possible by the classical theory of elasticity. The vanishing of the group velocity for all the $(24p - 3)$ frequencies characteristic of the lattice structure is significant. It indicates that no wave-propagation in any real or physical sense is possible in a crystal except in the lowest range of frequencies where alone the ideas and results of the classical theory of elasticity possess any validity.

4. THE SPECTRUM OF THE THERMAL AGITATION

The results of the dynamical theory enable us to complete the thermodynamic picture already indicated above in outline.

The p interpenetrating Bravais lattices of atoms constituting the crystal represent an assembly of atomic oscillators which have a set of $(24p-3)$ vibration frequencies in common. Each of these oscillators can assume one or another of the various energy states for these frequencies permitted by the quantum theory, the relative probabilities of the same being given by the Boltzmann formula. It would not be possible to specify or predict which of the great number of oscillators in the crystal would be in a particular excited state for any of its possible frequencies of vibration at any given instant. In other words, the thermal energy would be distributed through the volume of the crystal in a manner which fluctuates from place to place and from instant to instant in an unpredictable fashion. The fluctuating character of the energy distribution would be the more striking, the higher the frequency under consideration, since the energy jumps indicated by the quantum theory are proportional to the frequency.

Thus, it emerges that $(24p-3)$ out of every $24p$ degrees of freedom of atomic movement in the crystal manifest themselves in the thermal agitation as modes of internal vibration with a precisely defined set of monochromatic frequencies and in modes specifically related to the crystal structure, though they are localised in the crystal in a chaotic and unpredictable fashion. The residual 3 degrees out of every $24p$ degrees of freedom represent, as we have seen, the translatory movements of the super-cells of the crystal lattice. Such movements would disturb the regularity of the crystal structure, in other words, would give rise to stresses and strains of the same general nature as those contemplated in the classical theory of elasticity. Hence, the 3 residual degrees of freedom would also manifest themselves in the thermal agitation as oscillations localised in the crystal in a chaotic and unpredictable fashion, but since the moving masses are now larger, the frequencies would necessarily be lower, being determined by the dimensions of the volume elements which can be regarded as the individual oscillators: the larger these volume elements are, the fewer of them would be needed to fill the crystal and the lower also would be the frequency. Thus, the spectrum of the thermal agitation resulting from movements of the kind under consideration would stretch over a range of frequencies down to low values, but the upper parts of the range would be much more densely populated than the lower.

5. REMARKS ON SOME EARLIER THEORIES

The attentive reader would have noticed that the picture of the thermal agitation in a crystal and its spectroscopic characters which has emerged bears no resemblance whatever to that figuring in the well-known theory of the specific heat of crystals put forward by Debye and in the lattice theory of Max Born and his collaborators. These authors identify the energy of the thermal agitation in a crystal with the energy of an immense number of waves traversing the crystal in all possible directions and of which the frequencies are all different. But nevertheless in evaluating the total energy, these authors make use of the expression for the average energy of an oscillator derived by Einstein for an assembly consisting of an immense number of oscillators having an identical frequency of vibration. In the circumstances, it would not be superfluous to set out briefly the considerations which show that the theories of Debye and Born are fundamentally misconceived and that the conclusions to which they lead are completely unreal.

I. The theory of the specific heat of crystals has necessarily to be based on the theorem in classical mechanics which states that the normal modes of vibration of a connected system of particles form an enumerable set equal in number to the number of degrees of dynamical freedom of the system and that in each such normal mode, all the particles vibrate with the same or opposite phases. Waves are not normal modes, since the phase alters progressively in the direction of the wave-vector, and hence it is an obviously fallacious procedure to seek to found a theory of specific heat on the basis of wave-motions.

II. A dynamical investigation shows that waves of the kind contemplated by the classical theory of elasticity in which the phase-velocity is equal to the group velocity are only possible in the limiting case of very low frequencies and of very great wave-lengths. It also shows that the atoms in a crystal form an assembly of oscillators which have a set of $(24p-3)$ vibration frequencies common to all, and hence form a system to which the principle of Boltzmann can be legitimately applied to determine the average energy of an oscillator of each frequency and thereby to evaluate the total energy of the system.

III. The fundamental principles of thermodynamics and the quantum theory indicate that the thermal agitation in a medium consisting of material particles capable of vibrating about their positions of equilibrium is of a chaotic and unpredictable character, exhibiting fluctuations in the energy of the vibration from place to place and from instant to instant whose magnitude is determined by the frequency of vibration and hence would be different for each different frequency. It would be patently absurd to identify such a disturbance in the crystal with waves of constant amplitude spread over its volume.

IV. The identification of the thermal energy of a crystal with the energy of waves traversing it in all directions and having frequencies all different from each other leads to a totally false picture of the spectroscopic behaviour of crystals, as is shown by several independent methods of experimental investigation. For instance, all crystals usually exhibit at room temperature and always when cooled down to low temperatures the sharply defined *shifts of frequency* in the spectrum of monochromatic light scattered by them, corresponding to each of the $(3p-3)$ frequencies of the structure active in light-scattering. Significantly also, overtones and combinations of these $(3p-3)$ frequencies and of the remaining $21p$ frequencies manifest themselves with observable intensity as sharply defined frequency shifts with many crystals.

V. That the identification of the thermal agitation in a crystal with waves traversing the solid is a misconceived idea is also apparent from the complete dissimilarity between heat energy and sound energy in their observable behaviour. The latter travels through a crystal with a velocity of some thousands of metres per second, while heat energy merely diffuses through it.

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X-RAYS AND CRYSTALS*

By

Sir C. V. Raman

It is familiar knowledge that every crystal is a three-dimensionally periodic grouping in space of atomic nuclei and electrons held together by their mutual interactions so as to form a rigid solid. We recognise in each crystal a unit of its structure containing, say, a group of p atoms, this group repeating itself at regular intervals along three directions which are designated as the axes of the structure. The atoms in the crystal may accordingly be regarded as consisting of p sets, all the atoms of a particular set being equivalent to each other and located at regular intervals in a space lattice whose axes are those of the crystal.

2. Diffraction of X-Rays by Crystals

That the geometric picture of crystal architecture briefly indicated above is not just a mathematical hypothesis but a physical reality was first demonstrated by the famous experiment of Laue and his collaborators. When a narrow pencil of X-rays traverses a crystal and is received on a photographic film held behind it, a pattern of spots surrounding the impress of the incident beam appears on the film when developed. It is well recognised that these Laue spots—as they are called—represent monochromatised reflections of the incident X-ray beam by the stratifications of the electron density parallel to the various crystallographic planes in the structure of the crystal. The intensity of each spot is indicative of the magnitude of the corresponding periodic variations of electron density normal to the planes under consideration. The theory of the Laue experiment can be dealt with in a purely classical manner by attributing a certain scattering power to each volume element in the electron cloud present in the crystal proportional to its local density. This scattering power derives from the fact that the electrons would be set in motion and oscillate with the same frequency as that of the electro-magnetic field which the incident X-ray beam represents. On this basis, the scattered radiations from all the volume elements would have the same frequency as the incident X-rays, as also specific phase relationships determined by their relative positions. The scattered radiations therefore would be capable of reinforcing each other's effects in certain specific directions determined by the wave-length of the X-rays and the spacing of the stratifications, in accordance with recognised optical principles. Concentrations of intensity accordingly appear in the directions representing a highly restricted selection of wave-lengths from the incident white X-radiation.

3. Atomic Nuclei and X-Ray Diffraction

The foregoing picture is obviously however an over-simplification. It implicitly assumes that the electrons which scatter the X-rays remain firmly bound to the structure of the crystal and that the latter also remains otherwise unaffected by the passage of the X-ray beam. The strength of the binding of the electrons to the atomic nucleus or nuclei closest to them necessarily enters into the picture and would influence the intensity and phase of the scattered radiations to an extent determined by the approach of the frequency of the incident X-radiation to the characteristic X-ray absorption frequencies of the electrons. Indeed, recent X-ray researches have shown that these factors have to be taken into account in the theory of X-ray diffraction by crystals.

The foregoing remarks indicate that considerations somewhat analogous to those

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* Presidential Address to the Indian Academy of Sciences at the Hyderabad Meeting on 27th December, 1955.

which enter into the theory of scattering of light in crystals need to be taken into account also in the theory of X-ray diffraction. When a beam of common light traverses a crystal, its wave-length is very great in comparison with the spacing of the electronic stratifications in the crystal and the latter do not therefore reflect the incident radiation but merely transmit it. On the other hand, it is known that the passage of the light excites vibrations of the atomic nuclei with the result that if the incident light be monochromatic, scattered radiations are observed exhibiting sharply defined shifts of frequency corresponding to the characteristic vibration frequencies of the atomic nuclei about their positions of equilibrium. The appearance of such scattered radiations indicates the existence of a coupling between the forced vibrations of the electrons under the influence of the incident electromagnetic field and the natural or free vibrations of the atomic nuclei about their positions of equilibrium. In the language of the quantum theory of dispersion, the appearance of such frequency shifts is described by the statement that the system composed of the nuclei and electrons does not—following the virtual transitions to higher energy states induced by the incident radiation—return to the same level as previously but shifts to a third level in which the atomic nuclei are in a different energy state of vibration.

In the X-ray experiment, the frequency of the incident radiation is usually much higher than the characteristic frequencies of the electrons. Nevertheless, the ideas of the quantum theory of dispersion continue to be applicable and the question therefore arises whether the incident X-radiations can also excite transitions in the energy state of the atomic nuclei by virtue of their mechanical coupling with the electrons and if so, what would be the observable result of such transitions. We shall now proceed to answer these questions.

4. THE CHARACTERISTIC VIBRATIONS OF CRYSTAL LATTICES

As remarked earlier, the fundamental feature of crystal architecture is that it is a repetitive pattern in three-dimensional space of a characteristic unit of the structure containing a finite number of atoms. Each unit of the structure is similar to and similarly situated with respect to the units surrounding it. Hence it follows that in respect of all their physical properties the units of the crystal structure would be similar to each other ; in particular the dynamic behaviour of all the units of the crystal structure would be completely identical. We may put the same situation in slightly different language by saying that every crystal is an assembly of atomic oscillators all of which have identical modes and frequencies of vibration. What these modes and frequencies are is a matter for rigorous mathematical investigation. Such investigations have been carried out and published in recent papers which have appeared in the *Proceedings* of the Indian Academy of Sciences. It emerges that all the atoms in the crystal have $(24p-3)$ modes and frequencies of vibration in common. $(3p-3)$ of these frequencies represent modes in which equivalent atoms in neighbouring cells oscillate with the same amplitudes and in identical phases, while for the remaining $21p$ frequencies, equivalent atoms in adjacent cells oscillate with the same amplitudes but with phases which may be the same or else opposite along one, two or all three axes of the lattice. This picture of the dynamical behaviour of the atoms in a crystal has important consequences for the subject of X-ray diffraction which we shall now proceed to consider.

5. A CLASSICAL ANALOGUE

It is useful in the first instance to consider the position from a purely classical standpoint so that the consequences arising therefrom may be taken over into the quantum-mechanical treatment of the problem.

We shall restrict ourselves here to a consideration of the $(3p-3)$ modes of vibration of the atomic nuclei in which the vibrations in the different cells of the crystal lattice are identical in all respects. In such a vibration it would follow that the stratifications of electron density in the crystal would not remain in fixed positions but would oscillate to and fro with the frequency equal to that of the mode of vibration concerned. An X-ray beam traversing such stratifications would continue to be reflected in the same direction as in the static case. But in consequence of the periodic motion of the stratifications (assumed to be of small amplitude), the reflected X-ray beam would now consist of three spectral components having frequencies respectively ν, $(\nu+\nu^*)$ and $(\nu-\nu^*)$, ν being the incident X-ray frequency and ν^* that of the oscillation of the lattice. The additional components arising by virtue of the oscillations may be regarded as Doppler shifts of frequency resulting from the movement of the stratifications normal to themselves. The amplitudes of the additional components would be determined by the ratio of the amplitude of the oscillations to the wave-length of the X-rays.

The above classical result translated into the language of quantum mechanics would mean that the incident X-radiation traversing the crystal may excite the characteristic vibrations of the lattice, and if such excitation actually occurs, the beam would be reflected in the same direction as in the absence of such excitation but with diminished frequency. If, on the other hand, the characteristic vibration is already present by reason of thermal agitation, the crystal may be de-excited and the incident X-radiation would then be reflected with increased frequency.

6. INFRA-RED ACTIVITY AND X-RAY DIFFRACTION

It will be seen from the foregoing that the mechanism which can give rise to X-ray reflections of altered frequency is altogether different from the mechanism which results in the scattering of light with frequency shifts in crystals. In the latter case it is known that a change in the internuclear distances gives rise to a change in the optical polarisability of the elements of the structure and hence also to secondary radiations with altered frequency; the selection rules which determine whether a particular mode of vibration is or is not active in light-scattering are different from those which determine whether or not the same mode is active in infra-red absorption. In the X-ray problem, the shifts of frequency in the X-ray reflections arise from the periodic movements of the stratifications of the electron density associated with the nuclear oscillation. Hence, it may be expected that the excitation and the de-excitation of the lattice vibrations resulting from the passage of X-rays would appear in circumstances analogous to those in which infra-red absorption manifests itself. In other words, X-rays may be expected to excite or de-excite those oscillations of the lattice which are also infra-red active.

7. THE GEOMETRY OF THE X-RAY REFLECTIONS

In the foregoing we have assumed that the vibrations in the crystal structure appear in all the cells of the crystal lattice not only with the same frequency but also with identical phases. This is evidently a highly idealised situation, which when it actually exists indicates that the X-ray reflection with altered frequency would appear in precisely the same direction as that of unmodified frequency. The modes and frequencies of the lattice vibrations are determined by the interatomic forces which may be assumed to fall off rapidly in magnitude with increasing interatomic distances. Hence, a change of phase of the oscillations occurring progressively as we pass from cell to cell—provided it be small enough—would involve a relatively small change in the actual frequency of vibration. This would give rise to the possibility of observing X-ray reflections with a change of frequency even in settings of the crystal different from those in which the ordinary or unmodified reflections are observed. Such reflections may be regarded as arising from a forced oscillation of the lattice with slightly altered frequency and with the appropriate phases induced by the incidence of the X-radiation. In such circumstances the intensity of the X-ray reflection of altered frequency may be expected to fall off more or less rapidly as the setting of the crystal is altered from the setting needed for an ordinary reflection.

8. THE INFLUENCE OF THERMAL AGITATION

As already indicated, it necessarily follows that if X-rays can excite an infra-red active oscillation of the lattice, they can de-excite such an oscillation if it already exists and thereby give rise to an X-ray reflection of increased frequency. The relative intensities of the X-ray reflections with increased and diminished frequencies respectively would be determined by the Boltzmann factor for the particular frequency of the oscillation of the lattice. The reflections of increased and of diminished frequencies would, of course, appear in the same direction, and it is the summation of their intensities that would determine the observed effects. Accordingly, measurements of the variations in intensity of this observable effect with temperature would enable us to estimate the frequency of the vibrations responsible for them.

9. SUMMARY

The quantum theory of dispersion indicates that the infra-red active vibrations of the atoms in a crystal would be excited by the passage of a beam of X-rays through it. Such excitation would result in the incident beam being reflected by the lattice planes of the crystal with appropriately diminished frequency. Such reflections would also be observable but with diminished intensity when the setting of the crystal is moved away from the position in which X-rays of the given wave-length are selectively reflected by the lattice planes in question with unaltered frequency. The effect of thermal agitation is also considered.

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