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The detection of rotatory polarization in an orthorhombic crystal exhibiting crossed axial dispersion.

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THE existence of rotatory polarization is comparatively easy to detect in isotropic crystals and in uniaxial crystals in the direction of the optic axis; but in a biaxial crystal the problem presents far greater difficulties, since in general the rotatory polarization is obscured by the double refraction. The possibility of its existence in a biaxial crystal was denied by É. Mallard (Traité de Cristallographie, 1884, vol. 2, p. 318). However, the persistence of rotatory polarization in a quartz crystal, made biaxial by pressure, brought this conclusion into doubt. Later work, both experimental and theoretical, by H. C. Pocklington (Phil. Mag., 1901, ser. 6, vol. 2, p. 361) established its presence in certain biaxial crystals. Other similar cases have since been investigated by H. Dufet (Bull. Soc. Franç. Min., 1904, vol. 27, p. 156), V. V. Karandyeev (Bull. Acad. Sci. Petrograd, 1915, vol. 9 (part 2), p. 1285), and L. Longchambon (Compt. Rend. Acad. Sci. Paris, 1921, vol. 172, p. 1187; 1921, vol. 173, p. 89). It appeared to me probable that circular polarization might be detected more easily in a biaxial crystal in which the axial planes are crossed, i. e. one which is uniaxial for a certain wave-length of light.

In the examination of orthorhombic crystals of triphenylbismuthine dichloride, $(C_6H_5)_3BiCl_2$, which were kindly supplied by Mr. J. F. Wilkinson, I found that they showed crossed axial dispersion. Further, a plate perpendicular to the acute bisectrix, when arranged so that its axial planes coincided with the polarizing planes of the crossed nicols of a microscope, does not extinguish in parallel white light, but transmits light of a bright-green colour. These facts led to the idea that the crystal possesses the property of circular polarization, which becomes evident for the green rays travelling along their optic axis, when the others are extinguished.

Crystallographic Description.

System.—Orthorhombic; holoaxial (bisphenoidal) class.

Axial Ratio.—$a:b:c = 0{\cdot}774:1:0{\cdot}409$.

Crystallographic Angles.—

Angle.	No.	Limits.	Mean Obs.	Calc.
$(010):(110)$	42	51° 48′–52° 52′	52° 16′	*
$(1\bar{1}0):(1\bar{1}1)$	16	55 39–56 40	56 14	*
$(011):(0\bar{1}1)$	9	44 23–44 57	44 43	44° 30′
$(010):(111)$	9	69 53–70 34	70 11	70 7
$(010):(120)$	7	32 42–33 41	33 15	32 52
$(110):(011)$	10	76 11–77 15	76 33	76 36
$(0\bar{1}1):(1\bar{1}1)$	11	25 40–26 34	26 4	26 4

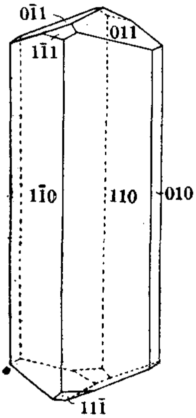

FIG. 1.

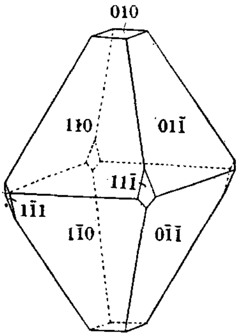

FIG. 2.

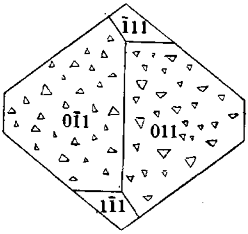

FIG. 3.

Crystals of Triphenylbismuthine dichloride.

Forms and Habit.—Two types of crystals were obtained. The most usual habit is a prismatic one (fig. 1), consisting of the forms $\{110\}$, $\{010\}$, $\{011\}$, $\{1\bar{1}1\}$, and fairly frequently $\{100\}$ and $\{120\}$. Crystals of a pyramidal habit were sometimes found; these consist of the forms $\{110\}$ and $\{011\}$ about equally developed, $\{010\}$ as a square face, and $\{1\bar{1}1\}$ as little facets. If they are placed with the *b* axis vertical, they closely resemble tetragonal bipyramids terminated by basal planes, as represented in fig. 2. The faces of the crystals are often not very smooth. Cleavage parallel to (100) and (001).

Crystal Symmetry.—The system is orthorhombic. After many attempts, satisfactory etching figures were obtained. They were produced by etching the dome-faces {011} with petroleum. Fig. 3, reproducing their character, indicates that the crystal has no plane of symmetry and belongs to the holoaxial class. Further, the form {1$\bar{1}$1} appears to be a sphenoid and not a bipyramid, although occasionally faces of the complementary form {111} are present.

Optical Examination.

The acute bisectrix is the crystallographic axis *b*, and the axial planes are crossed: for red to green the plane is (100), whilst for green to violet it is (001). The double refraction is strong and positive.

Refractive Indices.—The high values of the refractive indices made it impossible to use the method of total reflection for their measurement. Minimum deviation experiments could not be carried out with the prisms furnished by the forms {110} and {011}, which would have given refractive indices for the axial directions, since total internal reflection occurred. Measurements were therefore made using the two prisms formed by the faces ($\bar{1}$00), (110) and (0$\bar{1}$0), (110). These gave values for the refractive indices for two definite directions in the crystal, together with two independent values for the direction *c*, which is one of the principal indices required. From the other two indices and the position of the corresponding vibration-directions in the section of the optical ellipsoid by the plane (001), it is very easy to determine the values of the other two principal indices of the crystal. Measurements were made at room temperature (about 17° C.) for three wave-lengths, namely the yellow sodium-light and the green and violet of the mercury spectrum. The following results were obtained, an interchange of α and β taking place between the green and violet mercury lines.

	α.	β.	γ.
Na yellow ...	1·733	1·734	1·795
Hg green ...	1·7445	1·745	1·803
Hg violet ...	1·785	1·7885	1·848

Owing to the strong double refraction, the optic axial angle is comparatively small on either side of the uniaxiality point. The first condition of A. E. H. Tutton (Proc. R. Soc. London, 1908, ser. A, vol. 81, p. 40) for the crossing of axial planes, namely weak double refraction, appears rather to be a condition for a large optic axial angle before and after crossing, than a condition for actual crossing itself. Another example of a substance possessing crossed axial dispersion together with strong double refraction is to be found in brookite; the values quoted by Groth (Chem. Kryst. 1906, vol. 1, p. 90) for the double refraction of the light of the lithium and sodium flames respectively are 0·1036 and 0·1582.

Optic Axial Angles.—A series of measurements of the apparent optic axial angles in air was carried out at the ordinary temperature (about 17° C.) by means of the Hutchinson Universal Apparatus. The wave-length for which the crystal is uniaxial was kindly determined by Mr. T. V. Barker of Oxford, using his monochromatic illuminator, and found to be 0·00051 mm. In determinations of optic axial angles at higher temperatures, difficulties are introduced by heat conduction into the metal of the goniometer. The optic axial angle apparatus was therefore enclosed in an asbestos box; at the front was an opening through which the eyepiece projected, and at the back was another opening for the entrance of the light. The box was heated inside by two carbon filament lamps, and the temperature was read on a thermometer suspended with its bulb near to the crystal. The box was heated up to 35° C., the lamps turned off, and a reading taken before the temperature fell. The following table shows the optic axial angles for various wave-lengths of light at the two temperatures, viz. 17° C. and 35° C.

Source of light.	Wave-length.		2E at 17° C.		2E at 35° C.
Li flame	0·000671 mm.	...	49° 56′	...	47° 29′
Na flame	0·000589	...	36 18	...	32 9
Hg lamp	0·000546	...	19 53	...	6 41
Tl flame	0·000535	...	13 52	...	*14 48*
Hg lamp	0·000436	...	*69 18*	...	*71 53*

The values in italics represent angles in the plane (001). The curves of fig. 4 show the variation of optic axial angle with wave-length of light. They agree in shape and in being more sensitive to change of wave-length near the uniaxiality point with the theoretical deductions of F. Pockels (Lehrb. der Kristalloptik, 1906, p. 71) and S. Kreutz (Sitzungsber. Akad. Wiss. Wien, Math.-naturw. Kl., 1908, Abt. 1, vol. 117, p. 884). It is also of interest to note that the optic axial angle is much more sensitive to change of temperature for wave-lengths near the point of uniaxiality.

Investigation of the green light transmitted in the extinction position.

It might be thought (and this was the explanation that first suggested itself) that the crystal is only pseudo-orthorhombic, being really monoclinic and having the *b*-axis as the acute bisectrix. Such a crystal would show crossed dispersion of the monoclinic type, in which the axial planes for different coloured lights are a series of planes intersecting in the acute bisectrix. When the polarizing planes of the nicols coincided with one of these axial planes, a certain wave-length would be extinguished, whilst the others would be transmitted and produce a colour complementary to that extinguished. Further observations, however, disprove this view. A slight rotation of the crossed nicols would now extinguish another colour of light, and thus produce some other complementary tint. This, however, is not the case. Again, the axial planes do not intersect at various angles in the acute bisectrix, but coincide strictly with the planes (100) or (001) according as the optic axial angle concerned is produced by light of a greater or smaller wave-length than the green: the interference-figure is always symmetrical to the planes (100) and (001), both in white light and monochromatic light.

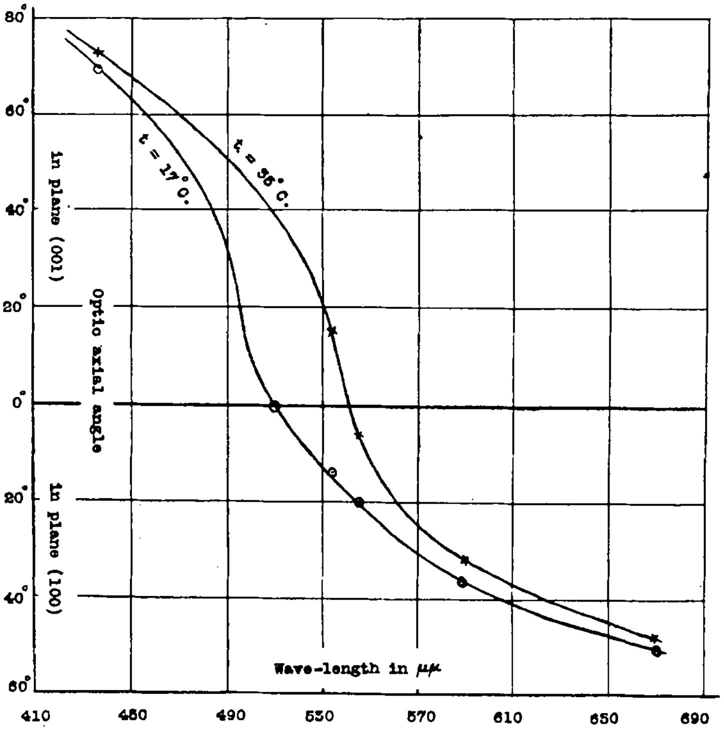

FIG. 4. Curves of the optic axial angle of Triphenylbismuthine dichloride.

The other possible explanation is that the crystal possesses the property of circular polarization. Now for a certain wave-length in the green the crystal is uniaxial: it is thus to be expected that the crystal would behave to green light as a crystal of quartz does to light of all wave-lengths. Under the conditions of the experiment, green light will pass through the crystal along the optic axis and will emerge circularly polarized. Light of other wave-lengths will pass through the crystal in this same direction also circularly polarized, but since this direction is inclined to the optic axes for these rays, they will also experience double refraction. The effect of optical activity is therefore not so apparent, and this effect will be more and more obscured as the angle between the optic axes for the successive wave-lengths and the normal to the crystal section increases. The result of this will be that the green light and also light of nearly the same wave-length for which the circular polarization is still visible, will pass through crossed nicols in the direction of the *b*-axis. As we pass along the spectrum towards each end, two limits will be reached for which the double refraction will be so great as to completely mask the effect of the circular polarization: light of any wave-length beyond these limits will be extinguished. Further, the above arguments hold for any thickness of the crystal section, and consequently the light transmitted will always be green. In this respect the crystal differs from quartz, where the tint of the transmitted light depends on the thickness of the section. Thus according to the first explanation the transmitted light would be of a composite nature, whilst according to the second it would be practically monochromatic green light. This is susceptible to an experimental test by means of spectroscopic analysis, and with this object the following experiment was carried out.

An electric arc-lamp was used as the source of light. The light passed through a condensing lens and a water-cell: it then passed through a second lens to render the beam parallel. A microscope arranged horizontally, on which was mounted the crystal section as for an examination in parallel light, was now illuminated by this beam. A diaphragm with a circular opening was introduced into the microscope tube near to the eyepiece, and the nicols were crossed. The light coming out of the microscope was allowed to fall on the slit of a spectrometer arranged to be in line with the microscope. On looking through the eyepiece of the spectrometer there was seen a spectrum crossed by the usual numerous dark bands due to strong double refraction. When the crystal was brought into the extinction position, the two ends of this spectrum disappeared and left only a narrow band of light in the green. This is what would be expected according to the second of the above hypotheses.

A further experiment was made in which the crystal was placed in the extinction position and the analyser was rotated. It was hoped to find a movable band in the green, analogous to that which moves through the spectrum of the light transmitted through a quartz crystal in the direction of the optic axis, when the analyser is rotated. However, as soon as the analyser was moved, light of wave-lengths other than the green interfered with the observations and prevented any satisfactory evidence being obtained.

Another interesting observation, of which the significance is not clear, was made in these experiments. It seems to indicate a peculiarity in the black bands crossing the region of the green, and which may also be an indication of rotatory polarization. When the polarizer and analyser were rotated together from the diagonal to the extinction position, and the spectrum of the transmitted light watched, the following changes were seen to occur. The ends of the spectrum together with their black bands always faded away without any motion of the bands. On the other hand, when the nicols approach the extinction position, the bands in the green patch moved. A band which was originally in the middle of the green patch had just disappeared in the darkness at one side when the extinction position was reached. On further slight rotation, a band moved out of the darkness on the other side and took up its position in the middle of the green patch: the whole spectrum crossed by the usual series of bands was also restored by this rotation. When the next extinction position was reached the same phenomenon was repeated. But if an extinction position was passed through by rotation of the crossed nicols in the reverse direction, the motion of the bands was across the green patch towards the other side.

The effects on the green light of the introduction of a gypsum-plate are what one might expect—no change on introduction along the polarizing directions of the nicols, and behaviour as if the crystal plate were absent on introduction in a diagonal position. In the first case the polarizing planes of the plate and the nicols coincide, and the result is practically an increase in the thickness of the polarizer. In the second case a uniform field (red of the first order) is produced. Now the light of the two ends of the spectrum passes through the crystal as two beams vibrating along the extinction-directions: each of these two beams is split up in the gypsum-plate into beams vibrating along the extinction-directions of the plate, which are at 45° to the polarizing directions of the nicols. Thus the light will pass through the polarizer as two pairs of beams, and between the two members of each pair there is a phase difference which is caused by the passage through the gypsum-plate. In a similar way the beam of green light which emerges from the crystal, polarized in a plane dependent on the amount of rotation that it has undergone, will also be split up by the gypsum-plate into two beams vibrating in the same direction as the light of the other wave-lengths. Further, these two beams of green light will possess a phase difference due to the passage through the plate. The total effect is two beams of white light with a phase difference that produces the characteristic first-order red of the gypsum-plate. Exactly analogous results were obtained by the introduction either of a mica-plate or a quartz-wedge.

A solution of triphenylbismuthine dichloride in acetone does not rotate the plane of polarization. Hence, like sodium chlorate, it is active only in the crystal state.

Detection of similar extinction phenomena in other optically active crystals which show crossed axial dispersion.

A brief examination was made of sections of Seignette salts, which had been prepared in this laboratory for quite another purpose by Mr. H. E. Buckley, and which have their axial planes crossed at right angles. A Seignette salt composed of one part of sodium potassium tartrate and two parts of sodium ammonium tartrate was found to be uniaxial in the green. When brought into the extinction position in parallel polarized light, it transmitted light of a bright-green colour. Another section of Seignette salt of composition one part of sodium potassium tartrate and one part of sodium ammonium tartrate was uniaxial in the blue. When examined in the extinction position, light of a brilliant blue colour was transmitted. When these transmitted lights were examined spectroscopically they were found to be monochromatic, just as the green light transmitted through the triphenylbismuthine dichloride. The peculiar motion of the black bands in the green and blue regions respectively were also observed.

I wish to express my gratitude to Sir Henry A. Miers for his very kind help and encouragement in these experiments: I have also to thank the Scientific and Industrial Research Department for a grant during the tenure of which this investigation was carried out.