

LIGHT PROPAGATION IN ABSORBING CRYSTALS POSSESSING OPTICAL ACTIVITY

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§ 1. INTRODUCTION

AN excellent though unsuspected example of a biaxial crystal possessing both optical activity and pronounced pleochroism was brought to light—in the shape of certain intensely coloured sectors of amethyst—during certain optical studies on this material. Interference figures of a remarkable nature—to be illustrated and discussed in a later paper—were exhibited by these areas. Indeed, it was the peculiarity of the optical phenomena displayed, which first invited the present investigation on the theory of light propagation in such media—a theory which provides, as we shall see, a simple basis for their explanation. Such a theory has also a more general interest: for instance, the measurement of the rotatory power of a biaxial crystal along an optic axial direction cannot be pursued into the absorbing regions of the spectrum without taking cognizance of its results (§§ 8 and 9c).

It has been established that the behaviour of both transparent active crystals (Pockels, 1906; Bruhat, 1930) and inactive absorbing crystals (Pancharatnam, 1955 *a*, *b*; Jones, 1942) may be physically pictured and quantitatively explained by a principle of the superposition of the 'elementary properties' associated with the medium. Thus linear birefringence has to be blended either with optical rotation (circular birefringence) or with linear dichroism—according as we are dealing with the former or latter class of crystals. Following the same geometrical method as was adopted for non-active absorbing crystals (Pancharatnam, 1955 *a*; hereafter referred to as *P-a*) we shall discuss the propagation in an active absorbing crystal as due to the superposed effects of linear birefringence, linear dichroism and optical rotation. For any particular direction of propagation, the last-mentioned properties are to be determined respectively, in the usual manner from the corresponding surfaces which characterise the optical properties of the medium; *viz.*, the index- and absorption-ellipsoids (*see P-a*, § 2 *a* and § 4 *d*), and the surface of optical rotation. Were this not the case, the method of superposition would have little practical value since the directional variation

of the properties of the medium—as revealed for example in convergent light phenomena—is naturally the most interesting part of the optics of anisotropic media.

It turns out that the two waves that can be propagated along any direction not only possess different velocities and coefficients of absorption, but are in different states of elliptical polarisation, the geometrical forms of which bear no simple relation to one another (§ 4)—except in certain special cases (§§ 7 and 8). The practical advantage of the method of superposition in such a complex case can be properly appreciated only in a later paper, where the principal results are experimentally confirmed. Sections 2–8 deal with media possessing no circular dichroism—the latter being a property which need not be exhibited in all the absorption bands (Lowry, 1935). The results may, however, be expected to apply fairly accurately for all crystals where linear dichroism is visible to the eye—since circular dichroism, even when present, is usually an extremely feeble effect. In § 9 we shall formally include the effects of circular dichroism, using again the principle of superposition.

For the case of absorbing crystals, the method of superposition was first introduced by Jones (1942, 1948) while developing a comprehensive matrix calculus treatment for general optical systems. Jones did not then pursue the method in sufficient detail as to give an overall picture of the optical properties of anisotropic absorbing media. He has, however, recently (Jones, 1956) attempted to correlate his method with the results of the electromagnetic theory; it will be pointed out in a later paper that this portion of his discussion contains an error as far as its applicability to optically active media is concerned.

Pending a more direct theoretical explanation (*see* § 6) as to why the method of superposition works even under the most diverse conditions (Ramachandran and Ramaseshan, 1952; Ramachandran and Chandrasekharan, 1951), its justification in the present instance has to be based on the equivalence of its results with those of the electromagnetic theory of light propagation in active absorbing crystals. The electromagnetic theory will be discussed in a later paper. We may mention that the theory has thus far been solved only for uniaxial crystals (Forsterling, 1912, quoted in Szivessy, 1928).

§ 2. PHYSICAL DESCRIPTION OF THE METHOD OF ANALYSIS

Consider a crystal plate cut perpendicular to an arbitrary direction of propagation Oz , which direction we may with advantage take as being normal to the plane of the paper (*see* Fig. 1 *a*). We first wish to find the states of polarisation of the two plane waves that can be propagated along this direction

(with specific velocities and coefficients of absorption). The principle of the method adopted may be described as follows. Suppose we are given the state of polarisation P , and the phase, of the elliptic vibration incident on the plane z in the medium. Then if the crystal possessed no linear dichroism, the state of polarisation P' and the phase of the elliptic vibration emerging at the plane $(z + dz)$ could be completely determined from the theory of

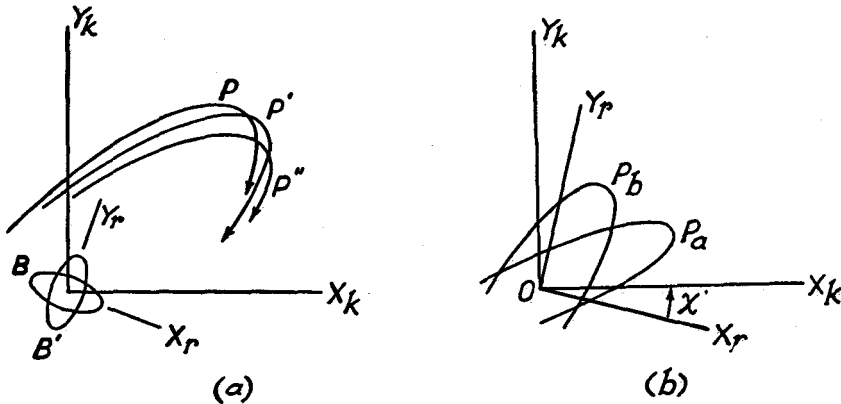


FIG. 1. P —State of polarisation at plane z . P' —State of polarisation at $(z + dz)$ if crystal were transparent. P'' —State of polarisation at $(z + dz)$ with linear dichroism also present. P_a, P_b —States propagated unchanged in absorbing active crystal (*i.e.*, states for which $P = P''$). B, B' —States propagated unchanged in transparent active crystal (*i.e.*, for which $P = P'$). OX_k, OY_k —States propagated unchanged with linear dichroism alone present.

propagation in *transparent* active crystals. Since the crystal possesses linear dichroism, we regard the actual vibration emerging at the plane $(z + dz)$ as obtained by further subjecting the vibration P' to the following operation of linear dichroism: the vibration P' is first resolved into its components along the *principal planes of linear dichroism* OX_k and OY_k ; the amplitudes of these components are then multiplied by the reducing factors $(1 - k_1 dz)$ and $(1 - k_2 dz)$ respectively, where k_1 and k_2 are the principal absorption coefficients if only dichroism were present. (OX_k and OY_k are parallel to the major and minor axes of the elliptic section of the absorption ellipsoid made by the xy plane.) The operation of dichroism not only causes a diminution in the intensity; because of the differential absorption of the two components the vibration at the plane $(z + dz)$ is now altered to the state of polarisation P'' .

In general, however, we shall show that there will be two particular forms of the initial elliptic vibration P for which the vibration P'' at the plane $(z + dz)$ will be in the *same* state of polarisation as the vibration at the plane

z , being therefore altered only in intensity and phase.* These will therefore be the required states of polarisation P_a and P_b of the two waves that can be propagated along the z direction with specific velocities and coefficients of absorption (Fig. 1 *b*).

§ 3. GEOMETRICAL FORMULATION OF THE PROBLEM

(a) *The Poincaré sphere.*—The problem of finding these states of polarisation P_a and P_b permits of an elegant solution if we take recourse to the Poincaré sphere (see Fig. 2)—as was done for inactive absorbing crystals (*P-a*). The state of polarisation of any particular elliptic vibration described in the xy plane is represented by a specific point on the surface of this sphere.

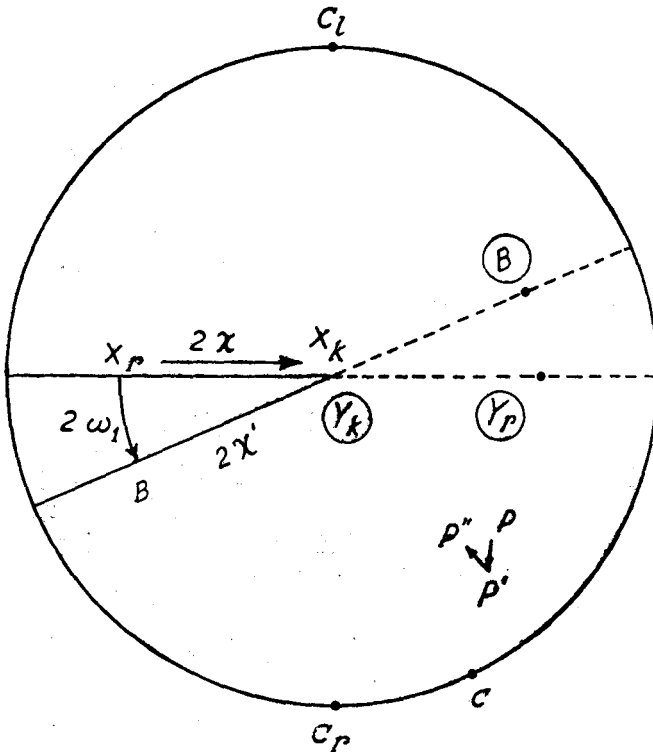


FIG. 2. Representation on the Poincaré sphere of the states described under Fig. 1 *a*. State P' is obtained from P by a clockwise rotation Δdz of the sphere about BB . State P'' is obtained by displacing P' towards the less absorbed component X_k through a distance $k dz \sin PX_k$.

* The sequence in which the two infinitesimal operations are applied is immaterial (if we neglect second order quantities). To prove this, consider the passage of light through a packet made up of infinitesimal lamellæ of two types, the odd members being transparent and the even members absorbing; the effect will not be modified (except to an infinitesimal extent) if the first transparent lamella is removed and placed last.

The definition of the mapping allows the form of the ellipse represented by any point to be directly visualised in terms of the longitude 2λ and the latitude 2ω of the point; for λ is the azimuth of the major axis and ω the angle of ellipticity.

Thus two linear vibrations along OX_k and OY_k will be represented respectively by two diametrically opposite points X_k and Y_k on the equator of the sphere, Fig. 2 being drawn such that the diameter X_kY_k is normal to the plane of the paper. The states of elliptic polarisation of the slower and faster waves that can be propagated in the Oz direction in the absence of linear dichroism will be respectively represented by two diametrically opposite points B and B' . From the theory for transparent active crystals we may regard the oppositely polarised states B and B' as known, as also the 'elliptic birefringence' Δ in the absence of linear dichroism, *i.e.*, the phase retardation which the slower wave B suffers *relative* to the other per unit distance traversed.

The relevant results from the theory of propagation in *transparent active crystals* may be briefly recalled. The states B and B' have respectively the same longitudes as the opposite points X_r and Y_r on the equator which represent the principal planes of linear birefringence OX_r and OY_r (drawn in Fig. 1). Denoting by $2\omega_1$ and $(-2\omega_1)$ the latitudes of B and B' we have

$$\left. \begin{aligned} \tan 2\omega_1 &= -\frac{2\rho}{\delta} \\ \Delta^2 &= \delta^2 + (2\rho)^2 \end{aligned} \right\} \quad (1)$$

where ρ is the optical rotatory power for the direction of propagation considered, and δ the linear birefringence, as determined from the index-ellipsoid. The mean of the refractive indices of the waves is the same as in the absence of optical activity (Szivessy, 1928; *see also* § 9 *b* below); *i.e.*, if Δ_1 and Δ_2 be the absolute phase retardations suffered per unit distance by the slower and faster waves, δ_1 and δ_2 being the corresponding values in the absence of optical activity, then

$$\Delta_1 + \Delta_2 = \delta_1 + \delta_2 \quad (2)$$

(*b*) *Choice of co-ordinate axes in the Poincaré sphere.*—The state of polarisation of the arbitrary elliptic vibration at the plane z (referred to in the previous section) will be represented by a general point P on the Poincaré sphere. We wish to find the condition that the state P should be propagated unchanged. Hence the point P may be most conveniently specified by giving the cosines of the respective angular distances 2ψ , 2ϕ , 2ξ , which it makes with the reference points X_k , B , and a third point C

on the sphere: these points form a right-handed system, the point C being at an angular distance of $\frac{1}{2}\pi$ from X_k and B. (Since the squares of three direction cosines are not independent it is sufficient to specify $\cos 2\psi$ and $\cos 2\phi$ and give merely the sign of $\cos 2\xi$.) The specification of the state of polarisation P by 'direction cosines' is closely analogous to its specification by Stokes' parameters (Fano, 1949; Ramachandran, 1952; Pancharatnam, 1956 *b*). It must, however, be noted that our reference system does not form a rectangular co-ordinate system; the angular distance $2\chi'$ of X_k from B is in general different from $\frac{1}{2}\pi$, and we have

$$\cos 2\chi' = \cos 2\omega_1 \cos 2\chi = (\delta/\Delta) \cos 2\chi \quad (2)$$

where 2χ is the acute angle between OX_r and OX_k , and ω_1 the ellipticity of the slower vibration B in the absence of dichroism, as given by (1).

(c) *Operations of elliptic birefringence and linear dichroism.*—The state of polarisation P'—which would be described at the plane ($z + dz$) if the crystal were a transparent active one—is obtained from P by an infinitesimal rotation of the sphere about the diameter BB' through a clockwise angle Δdz

(Pockels, *loc. cit.*). The infinitesimal movement \vec{PP}' is therefore perpendicular to the arc BP and has a magnitude ds_R which is equal to $\Delta dz \sin 2\phi$ (see Fig. 2). To obtain the actual state of polarisation P'' at the plane ($z + dz$), we subject the vibration in the state P' to the infinitesimal operation of linear dichroism—whereupon we may expect it to move directly towards the state of polarisation X_k of the less absorbed component, and away from Y_k . It has been proved in a previous paper (Pancharatnam, 1955 *a*, § 4 *b*) that the infinitesimal movement $\vec{P'P''}$ is actually directed along the arc PX_k and has a magnitude ds_k equal to $k dz \sin 2\psi$, where k denotes the 'linear dichroism' ($k_2 - k_1$).

§ 4. STATES OF POLARISATION OF THE WAVES

We wish to find those states P ($2\psi, 2\phi, 2\xi$) for which the state of polarisation P'' obtained after passage through a thickness dz is identical with P. The condition for this is obviously $\vec{PP}' = -\vec{P'P''}$, and this is equivalent to three conditions: (a) the magnitudes of the infinitesimal displacements due to elliptic birefringence and linear dichroism should be equal, *i.e.*, $ds_R = ds_k$; (b) the displacements \vec{PP}' and $\vec{P'P''}$ should be collinear, *i.e.*, from what has been said above, $\angle X_kPB = \frac{1}{2}\pi$; (c) the displacements should be oppositely directed—which means that P is restricted to the hemisphere for which 2ξ lies between 0 and $\frac{1}{2}\pi$. Expressed mathematically the states P

which are propagated unchanged are those for which 2ψ and 2ϕ satisfy the relations:

$$\Delta \sin 2\phi = k \sin 2\psi \quad (4)$$

$$\cos 2\phi \cos 2\psi = \cos 2\chi' \quad (5)$$

together with the condition that $\cos 2\xi$ should be positive.

Let P_a ($2\psi_a$, $2\phi_a$) represent a state for which 2ϕ is less than $\frac{1}{2}\pi$, and which remains invariant under the operations of elliptic birefringence and linear dichroism (see Fig. 3). It is then geometrically evident that the state P_b which makes the same angular distances with the opposite points Y_k and B' , will also remain invariant under these operations; this may also be seen from the fact that equations (4) and (5) are unaltered when 2ϕ and 2ψ are changed to their supplements. These states are consequently propagated without change of form. It can be shown that in general there are only two such states, and no more [see equations (6) and (7) below]. From the figure it is seen that these states P_a and P_b are represented by two general points on the Poincaré sphere whose longitudes do not in general differ by π and whose latitudes are unequal. We thus arrive at the result that in a medium possessing optical activity, linear birefringence and linear dichroism, *the two polarised waves that can be propagated without change of form along any direction are in elliptical states of polarisation whose geometrical forms bear no simple relation to one another—i.e., the major axes of the elliptic vibrations are in general not crossed, their ellipticities are not numerically equal, and they may or may not be described in the same sense. Two polarised states such as P_a and P_b —not being represented by opposite points on the Poincaré sphere—are non-orthogonally polarised, and are capable of mutual interference (when coherent) to an extent determined by their 'similarity factor' $\cos^2 \frac{1}{2} P_a P_b$ (Pancharatnam, 1956 a). It is seen from the figure that the great circular arc $P_a P_b$ is bisected by C, and hence the (common) third 'direction cosine' $\cos 2\xi$, of the two states acquires an importance as the factor expressing the degree of non-orthogonality of the two states of polarisation.*

For the sake of completeness we shall give explicit expressions for the 'direction cosines' of the points P_a and P_b representing the states of polarisation of the two waves. By introducing in (5) the value of $\cos^2 2\psi$ obtained from (4) we obtain a quadratic in $k^2 \cos^2 2\psi$; the positive root of this quadratic (which alone will give a real solution for $\cos 2\psi$) is then found to be given by

$$k^2 \cos^2 2\psi = \frac{1}{2} \{ (k^2 - \Delta^2) + \sqrt{(k^2 - \Delta^2)^2 + 4\Delta^2 k^2 \cos^2 2\chi'} \} \quad (6)$$

Similarly, eliminating $\cos^2 2\phi$ between (4) and (5)

$$\Delta^2 \cos^2 2\phi = \frac{1}{2} \{ (\Delta^2 - k^2) + \sqrt{(\Delta^2 - k^2)^2 + 4 \Delta^2 k^2 \cos^2 2\chi'} \} \quad (7)$$

It may be recalled that in these equations $\cos 2\chi'$ is given by (3).

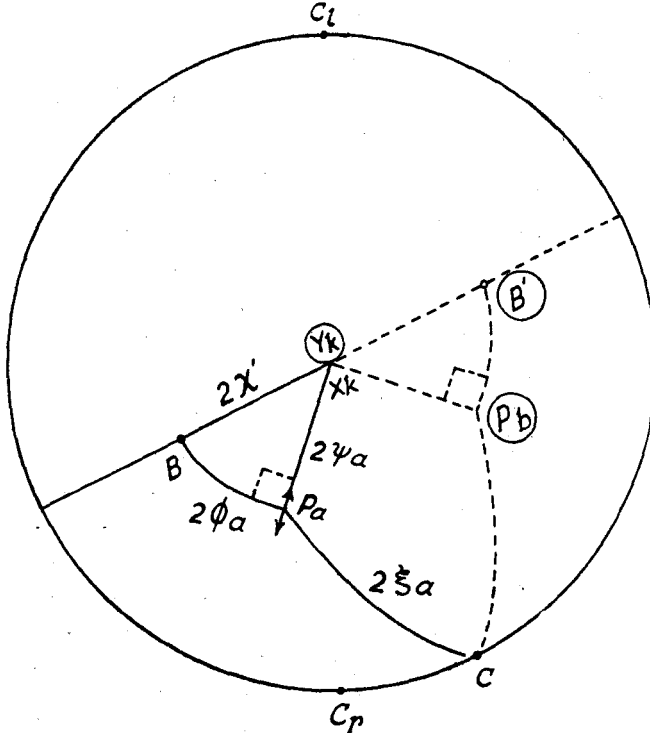


FIG. 3. P_a and P_b represent the states which remain invariant under the operations of elliptic birefringence and linear dichroism described under Fig. 2. The angular distances $2\psi_a$ and $2\phi_a$ of the slower state P_a from X_k and B , are also the angular distances of the faster state P_b from Y_k and B' .

Equation (6) gives two values of $\cos 2\psi$ which differ only in sign, while equation (7) gives two values of $\cos 2\phi$ which again differ only in sign. The corresponding pairs $(2\psi_a, 2\phi_a)$ and $(2\psi_b, 2\phi_b)$ are identified without ambiguity from the condition given by (5) that $\cos 2\phi$ and $\cos 2\psi$ have the same sign if $2\chi'$ lies between 0 and $\pi/2$, while they have opposite signs if $2\chi'$ lies between $\frac{1}{2}\pi$ and π .

The third 'direction cosine' $\cos 2\xi$ is always positive and is the same for both the states P_a and P_b ; it is obtained from the first two by the following relation which we shall not prove here.

$$\cos 2\xi = \frac{\sin 2\phi \sin 2\psi}{\sin 2\chi'} \quad (8)$$

§ 5. ABSORPTION COEFFICIENTS OF THE WAVES

The absorption coefficients, k_a and k_b , of the waves in states P_a and P_b may be evaluated exactly as in the case of non-active crystals (Pancharatnam, 1955 *a*). The diminution of intensity $2 k_a dz$ which a vibration of unit intensity in the state P_a suffers on travelling a distance dz arises entirely from the operation of dichroism; this operation diminishes the intensities of the X_k and Y_k components of the original vibration by $2 k_1 dz \cos^2 \psi_a$ and $2 k_2 dz \sin^2 \psi_a$. Hence we obtain, on addition,

$$\left. \begin{aligned} k_a &= \frac{1}{2}(k_1 + k_2) - \frac{1}{2}k \cos 2\psi_a \\ k_b &= \frac{1}{2}(k_1 + k_2) + \frac{1}{2}k \cos 2\psi_a \end{aligned} \right\} \quad (9)$$

so that

$$k_b - k_a = k \cos 2\psi_a \quad (10)$$

The absorption coefficients have thus been conveniently expressed as functions of the states of polarisation; they may also be otherwise expressed by using the explicit value of $k \cos 2\psi_a$ as obtained from (6). It may be recalled (P-*a*, equation 12) that for any one direction of propagation, k_1 and k_2 are proportional to b_1 and b_2 —where $1/\sqrt{b_1}$ and $1/\sqrt{b_2}$ are the lengths of the corresponding principal radii of the absorption ellipsoid.

It is advantageous to anticipate here a small correction to the expression (9) and (10) given later by the electromagnetic theory; if the *extinction* coefficients of the waves be denoted by κ_a and κ_b , then the relations (9) derived by the method of superposition have to be replaced by

$$\left. \begin{aligned} 2 \kappa_a v_a^3/c &= \frac{1}{2}(b_1 + b_2) - \frac{1}{2}(b_2 - b_1) \cos 2\psi_a \\ 2 \kappa_b v_b^3/c &= \frac{1}{2}(b_1 + b_2) + \frac{1}{2}(b_2 - b_1) \cos 2\psi_a \end{aligned} \right\} \quad (11)$$

Because the velocities v_a and v_b of the waves have been dragged into these new expressions for the absorption coefficients, an exact application of (11) for directions near an optic axis is fraught with difficulty. Luckily for us, however, the error involved in using (9) will be negligible for such directions, since we may set $v_a \simeq v_b \simeq v_m$, where v_m is a mean velocity (see P-*a*, equation 14).

§ 6. REFRACTIVE INDICES OF THE WAVES

We shall next derive expressions for the refractive indices of the waves or, what is virtually the same thing, the respective phase retardations Δ_a and Δ_b which these waves suffer per unit distance of propagation. Our argument is somewhat involved but at the same time illuminating; for it very clearly indicates that the principle of superposition may be derived by regard-

ing the propagation in the medium as due to the forward scattering from induced doublets (*cf.* Jenkins and White, 1937; Kauzmann, 1957).

Let us consider the propagation through a distance dz of a vibration of unit intensity in the state of polarisation P_a . The effect of dichroism consists in diminishing the X_k and Y_k components (whose respective amplitudes are $\cos \psi_a$ and $\sin \psi_a$) by fractions $k_1 dz$ and $k_2 dz$ respectively. Alternatively the infinitesimal operation of dichroism is equivalent to the operation [which we denote by (a)] of adding to the original vibration the fractions $(-k_1 dz)$ and $(-k_2 dz)$ of its X_k and Y_k components. In the succeeding operation of elliptic birefringence the vibration thus obtained is resolved into its components in states B and B', the phases of these components being then retarded by amounts $\Delta_1 dz$ and $\Delta_2 dz$ respectively (where Δ_1 and Δ_2 are the respective phase retardations per unit distance suffered by the two waves in the absence of dichroism). The operation of elliptic birefringence is therefore similarly equivalent to the operation [which we denote by (b)] of further adding on the fractions $(-i\Delta_1 dz)$ and $(-i\Delta_2 dz)$ of the B and B' components of the original vibration itself (neglecting second order quantities). The occurrence of the imaginary $(-i)$ means that the added vibrations have a phase lag of $\frac{1}{2}\pi$ with respect to the corresponding B and B' components of the original vibration; the 'amplitudes' of the latter components (that is, the square roots of their intensities) are $\cos \phi_a$ and $\sin \phi_a$ respectively.

But the original vibration in the state P_a is propagated without change of polarisation through the thickness dz under the combined effects of dichroism and elliptic birefringence. Hence—insofar as its final contribution is concerned—the effect of dichroism described in (a) becomes equivalent to the addition of two infinitesimal vibrations in the same state of polarisation P_a as the original vibration: these vibrations are really the resolved components in the state P_a of the corresponding vibrations described in (a); they will therefore have amplitudes $k_1 dz \cos^2 \psi_a$ and $k_2 dz \sin^2 \psi_a$; but they will be exactly opposed in phase to the original vibration, since only then will they diminish the intensity by $2k_a dz$ as given by (9). It follows that the operation of elliptic birefringence (b)—Because of its complete formal similarity with (a)—must be effectively equivalent to the addition of two infinitesimal vibrations (whose amplitudes are $\Delta_1 dz \cos^2 \phi_a$ and $\Delta_2 dz \sin^2 \phi_a$) which are in the same state of polarisation as the original vibration, but lag behind in phase by $\frac{1}{2}\pi$. The phase retardation per unit distance Δ_a , suffered by the wave is then equal to $(\Delta_1 \cos^2 \phi_a + \Delta_2 \sin^2 \phi_a)$. Or,

$$\left. \begin{aligned} \Delta_a &= \frac{1}{2}(\delta_1 + \delta_2) + \frac{1}{2}\Delta \cos 2\phi_a \\ \Delta_b &= \frac{1}{2}(\delta_1 + \delta_2) - \frac{1}{2}\Delta \cos 2\phi_a \end{aligned} \right\} \quad (12)$$

where we have used the fact that the mean refractive index in a transparent inactive crystal is the same as when optical activity is also present (Eq. 2). The birefringence is obtained from (12):

$$\Delta_a - \Delta_b = \Delta \cos 2\phi_a \quad (13)$$

When the refractive indices and the birefringence are not required as functions of the states of polarisation, we may introduce in (12) and (13) the explicit value of $\Delta \cos 2\phi_a$ as obtained from (7).

Since the arguments given above are somewhat involved it is worthwhile to indicate how the expression (13) for the birefringence (which alone is of much practical importance) may be *directly* derived. On travelling a distance dz , the alteration of the state of polarisation of any vibration (*e.g.*, from X_k to X_k'), may be evaluated by the method of superposition (as due to linear birefringence alone, in the example quoted). More properly, this alteration is connected with the relative phase retardation $(\Delta_a - \Delta_b) dz$ between the two waves (in states P_a and P_b) into which the original vibration will be decomposed; in fact the relative phase retardation must be equal to the area of the infinitesimal quadrilateral $P_a'X_kP_b'X_k'$ (Pancharatnam, 1956 *a*, equation 5 *b*), where P_a and P_b are points opposite to P_a' and P_b' . The area in question may be shown to be equal to $\Delta dz \cos 2\phi_a$, thus proving (13).

§ 7. CERTAIN SPECIAL CASES

A noteworthy simplification in both uniaxial and biaxial crystals, is that along directions which are nowhere in the vicinity of an optic axis—and where, correspondingly, the linear birefringence δ becomes appreciable—the waves propagated may for most purposes be regarded as linearly polarised along the principal planes of linear birefringence: the reason is that for such directions the ratios (ρ/δ) and (k/Δ) occurring in (1) and (4) usually differ but little from zero. The refractive indices and absorption coefficients of the waves are then obtained from the index and absorption-ellipsoids by the usual constructions (*see P-a*, Eq. 12) since we may set $\Delta \simeq \delta$, $\cos 2\phi_a \simeq 1$ and $\cos 2\psi_a \simeq \cos 2\chi$, in (12) and (11).

(*a*) *Uniaxial crystals*.—In uniaxial crystals both the birefringence δ and the linear dichroism k are determined from *uniaxial* ellipsoids; consequently, the ratio (k/δ) is virtually constant for all directions of propagation, and—in accordance with what has been said in the previous paragraph—this ratio will differ negligibly from zero for *all* directions. The states of polarisation of the two waves are then the same as in a transparent active crystal (Eq. 1), since we may set $\sin \phi \simeq 0$ from (4). The refractive indices of the waves, being functions of the states of polarisation (Eq. 12), are also determined as in a

transparent crystal. The waves, however, possess absorption coefficients which are obtained by setting $\cos 2\psi_a \simeq \pm \cos 2\omega_1$ in (9), or more accurately, in (11)—the upper sign being chosen if both the index and absorption ellipsoids are of the same sign. The last substitution follows from the fact that in a uniaxial crystal the principal planes of linear birefringence and linear dichroism coincide, so that B will have the same longitude either as X_k or Y_k .

(b) *Biaxial crystals: directions not too near an optic axis.*—It is known that in both transparent active crystals as well as inactive absorbing crystals the square of the ellipticity of the waves may be neglected for directions not too near an optic axis. For such directions of propagation in an active absorbing crystal we shall show that the states of polarisation of the waves are related to each other in the following simple manner. *The major axes of the elliptic vibrations may be taken to coincide with the principal planes of linear birefringence; and the respective ellipticities ω_a and ω_b of the slower and faster waves will be given by*

$$\left. \begin{aligned} \omega_a &= \epsilon + \omega_1 \\ \omega_b &= \epsilon - \omega_1 \end{aligned} \right\} \quad (14)$$

Here ω_1 and $(-\omega_1)$ represent as before the ellipticities of the slower and faster waves in the absence of dichroism alone as given by (1); and ϵ is the common ellipticity of the two waves in the absence of optical activity alone. Neglecting their squares in comparison with unity, ω_1 and ϵ will be given by

$$\omega_1 = -\rho/\delta; \quad \epsilon = (k/2\delta) \sin 2\chi \quad (15)$$

where χ is the acute angle that OX_k makes with reference to OX_r (measured with the usual sign convention).

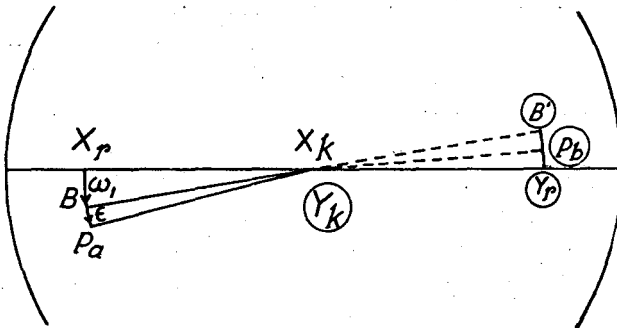


FIG. 4. For directions not in the vicinity of an optic axis each wave has an ellipticity which is the sum of the corresponding ellipticities which would obtain in the transparent active crystal and the inactive absorbing crystal.

For proving these relations we first remark that the directions under consideration are defined by the circumstance that the linear birefringence δ is sufficiently large (compared to both the rotatory power and the linear dichroism) to allow us to neglect the *squares* of (ρ/δ) and k/δ in comparison with unity. We may then also set Δ equal to δ according to (1). It follows that in Figs. 2 and 3, the arcs BX_r and $P_aB (=2\phi_a)$ may both be treated as infinitesimal, since their *squares* may be neglected, according to (1) and (4). The situation is illustrated in Fig. 4 which shows that P_a and P_b have respectively the same longitudes as X_r and Y_r (to our present order of approximation). Also the latitude $2\omega_a$ of P_a is equal to the sum of the *directed* arcs X_rB and BP_a (counted positive if they point to the upper hemisphere). The directed arc X_rB is however equal to $2\omega_1$. Hence for establishing the proposition of the previous paragraph it remains to show that the *directed* arc BP_a must be equal to 2ϵ . This is proved from the following consideration. If in accordance with our approximation we set $2\chi' \simeq 2|\chi|$ and $\Delta \simeq |\delta|$ in (4) and (5), those equations become formally identical with those holding for the case of a *non-active* absorbing crystal (for which case however B coincides with X_r); hence the infinitesimal arc $2\phi_a$ of the present case corresponds to twice the numerical ellipticity of the waves in the non-active absorbing crystal. Moreover, the sign of the directed arc BP_a being opposite to that of 2χ , will be the same as that of ϵ . This proves that first relation in (14) and a similar proof holds for the second relation.

[The approximate expression given in (15) for the ellipticity ϵ of the waves in a non-active absorbing crystal had not been derived in the authors' previous paper on the subject (P-a). It is, however, immediately obtained either from Eq. (4) of the present paper or from the corresponding equation of the previous paper by setting $\sin 2\phi \simeq 2|\epsilon|$ and $\sin 2\psi \simeq \sin 2|\chi|^1$.]

The refractive indices and absorption coefficients of the waves may be determined by the usual index- and absorption-ellipsoid constructions, *as though* the waves were linearly polarised. This is because $\cos 2\phi_a \simeq 1$ and $2\psi_a \simeq |2\chi|$ in (12) and (11).

§8. PROPAGATION ALONG AN OPTIC AXIAL DIRECTION

In a biaxial crystal the linear dichroism does not in general vanish along an optic axial direction, since the circular sections of the index ellipsoid need not coincide with the circular sections of the absorption ellipsoid. In the absence of linear dichroism, however, the waves will be circularly polarised, so that $\Delta = 2|\rho|$, and the state B coincides with C_r if ρ is positive. The arc $2\chi'$ in Fig. 3 is then equal to a right angle, and from the condition that the angle it subtends at P_a should also be a right angle, it may be seen geometri-

cally [or from Eq. (5)] that P_a must lie either on the meridional arc C_rC ($2\psi = \pi/2$) or the equatorial arc CX_k ($2\phi = \frac{1}{2}\pi$)—as illustrated in Figs. 5 and 6 respectively. Two main cases may therefore be distinguished.

(a) *Circular birefringence 2ρ greater than linear dichroism k .*—The situation is illustrated in Fig. 5 for the case when ρ is positive (lævorotation).

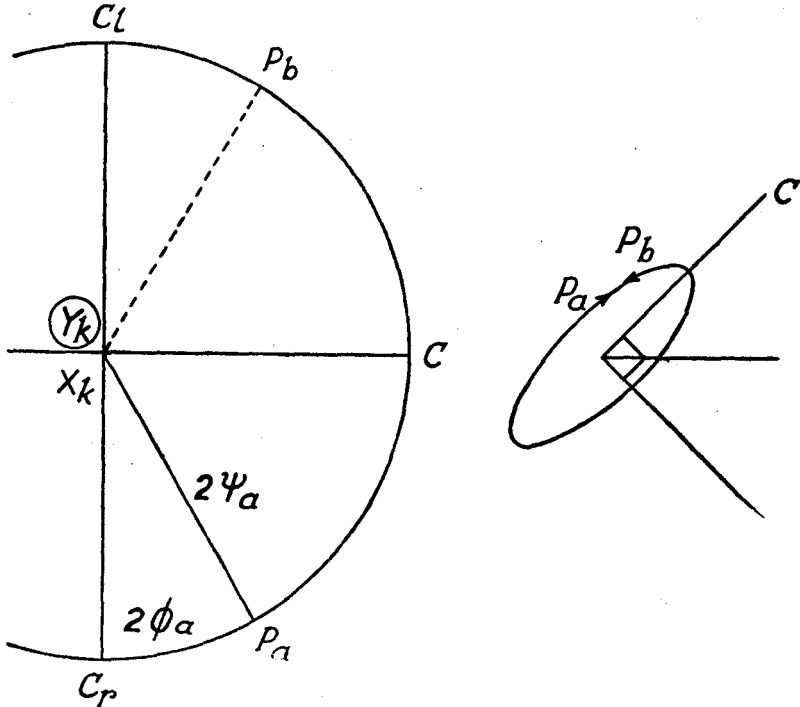


FIG. 5. Discussion of the elliptic states P_a and P_b propagated along an optic axial direction when $2\rho > k$.

Along the optic axis are propagated two elliptic vibrations exactly similar in form and orientation but described in opposite senses ($\omega_a = -\omega_b$). The sense of description of the slower elliptic vibration is the same as that of the slower circular vibration which would be propagated along the optic axis in the absence of linear dichroism; the major axes of the two elliptic vibrations are coincident and make an angle of 45° or -45° with reference to OX_k according as ρ is positive or negative. The numerical value of the ellipticity $|\omega_a|$ of the vibrations may be obtained from (4) since $2\phi_a = \frac{1}{2}\pi - |\omega_a|$, and $2\psi = \frac{1}{2}\pi$.

$$\cos 2\omega_a = k/|2\rho| \quad (16)$$

The two waves have equal absorption coefficients, since $2\psi_a = \frac{1}{2}\pi$ in (10). But they possess different velocities of propagation, the phase retarda-

tion which one wave suffers *relative* to the other per unit distance of propagation being obtained from (13) and (16):

$$\Delta_a - \Delta_b = -2\rho \sin 2\omega_a = +\sqrt{(2\rho)^2 - k^2} \quad (17)$$

(b) *Circular birefringence 2ρ less than the linear dichroism k .*—Figure 6 illustrates this situation for the case when ρ is positive (the point P_a denotes the state of polarisation of the wave with the smaller absorption coefficient, *i.e.*, for which 2ψ is less than $\frac{1}{2}\pi$). The waves propagated along the optic axis are linearly polarised, the angle between the linear vibrations being different from a right angle. The azimuths of the two vibrations with reference to OX_k will be both positive (0 to $\frac{1}{2}\pi$) or both negative (0 to $-\frac{1}{2}\pi$) according as ρ is positive or negative. The numerical value of the azimuths of P_a and P_b (with reference to OX_k) will be ψ_a and $(\frac{1}{2}\pi - \psi_a)$; and if θ be the acute angle between the vibrations, then using (4)

$$\cos \theta = \sin 2\psi_a = |2\rho| / k \quad (18)$$

The two linearly polarised waves have the same velocity since $2\phi = \pi/2$ in (13). They are, however, propagated with different absorption coefficients as given by (10) and (18):

$$k_b - k_a = k \cos 2\psi_a = +\sqrt{k^2 - (2\rho)^2} \quad (19)$$

§9. MEDIA POSSESSING CIRCULAR DICHROISM

(a) *The operation of circular dichroism.*—Turning our attention now to the general example of an optically active absorbing crystal, we have naturally to suppose that even in the absence of optical rotation, linear birefringence and linear dichroism (*i.e.*, if we set $\rho = 0$, $\delta_1 = \delta_2 = \delta_m$ and $k_1 = k_2 = k_m$) the waves propagated in the z -direction will be circularly polarised with a difference σ between their coefficients of absorption (left *minus* right), the mean of their absorption coefficients being k_m . We therefore extend the discussion of §2 in the following manner: the vibration at the plane ($z + dz$) will now be given by further subjecting the vibration P'' (obtained after the operation of elliptic birefringence and linear dichroism) to the infinitesimal operation of circular dichroism; that is, the vibration P'' must be resolved into its right- and left-circular components, and the intensities of these components multiplied by $(1 - \sigma dz)$ and $(1 + \sigma dz)$ respectively (the phases being unaltered). It may be easily shown—using the results of a previous paper (Pancharatnam, 1956 *a*, §6)—that, on the Poincaré sphere, the effect of the infinitesimal operation of circular dichroism will be exactly similar to that of the infinitesimal operation of linear dichroism (considered in P-*a* §4 *b*), since exactly the same argument is applicable to both cases; that is, *the state*

P'' will move directly towards the less absorbed circular state C_r , through an infinitesimal arc $\sigma dz \sin C_r P''$.

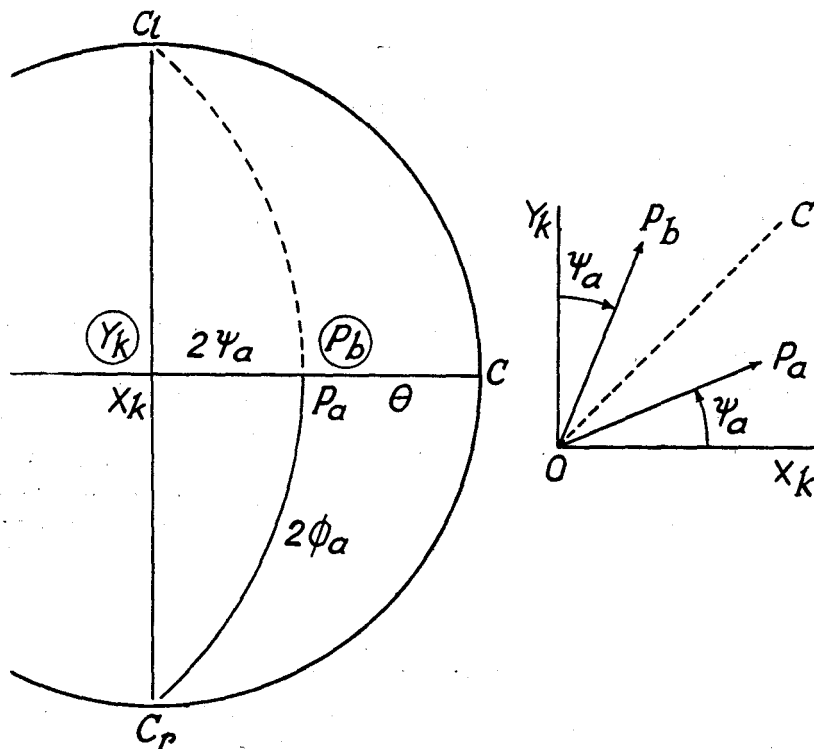


FIG. 6. Discussion of linearly polarised states P_a and P_b propagated along an axial direction when $2\rho < k$.

(b) *The superposition of linear and circular dichroism.*—A notable simplification of the analysis is effected by combining first the effects of the infinitesimal operations of linear and circular dichroism alone. [To fix our ideas we may for example consider the propagation along an optic axial direction for a wave-length where the rotatory power becomes zero, the circular dichroism being however near its maximum (Lowry, 1935)].

Just as the infinitesimal operations of linear birefringence and optical rotation (circular birefringence) may be compounded to yield the infinitesimal operation of elliptic birefringence as given by (1), we shall find that *the superposition of linear and circular dichroism results in elliptic dichroism*. More specifically, we shall show that vibrations in two oppositely polarised elliptic states D and D' (with their major axes along OX_k and OY_k respectively) remain unaltered in form under the combined effects of the infinitesimal operations of linear and circular dichroism (applied in either order); and if

ω_2 be the angle of ellipticity of the less absorbed state D, and K the difference in the absorption coefficients of the vibrations in these two states D' and D, then,

$$\left. \begin{aligned} \tan 2\omega_2 &= -\frac{\sigma}{k} \\ K &= +\sqrt{K^2 + \sigma^2} \end{aligned} \right\} \quad (20)$$

Consider a vibration initially in one of the states of polarisation D or D' (see Fig. 7, where the diameter $X_k Y_k$ is drawn in the plane of the paper). Under the operation of linear dichroism its state will move towards X_k through a distance $k dz \sin |2\omega_2|$. Similarly, under the operation of circular dichroism the state of the vibration will be displaced towards C_r through an infinitesimal distance $\sigma dz \cos 2\omega_2$. These two movements are oppositely directed whatever be the sign of σ (since ω_2 has the opposite sign) and they will exactly cancel each other since $\tan 2\omega_2$ is given by (20). Thus vibrations in the respective states D and D' suffer no alteration in their state of polarisation. The intensities of vibrations in these states will, however, be diminished by specific reduction factors, and correspondingly the absorption coefficients for these two states will have a specific difference K which we proceed to determine.

Consider a linear vibration initially in the state C which lies on the equator at a latitude of -90° with respect to X_k (see Fig. 7). Under the operations of linear and circular dichroism its state suffers the successive displacements of $k dz$ towards X_k and σdz towards C_r ; in other words, it suffers a displacement of $\sqrt{k^2 + \sigma^2} dz$ directly towards the state D. Since however the initial vibration could equally well be considered as the sum of two vibrations (of equal intensity) in states D' and D, it follows that vibrations in these states suffer no relative phase retardation under the combined operations of linear and circular dichroism; and that the difference in the absorption coefficients of these states is given by the relation (20) which we wished to prove (see Pancharatnam, 1956 a, § 6).

Moreover, if the initial vibration in the state C be of unit intensity, the diminution of intensity under the operation of elliptic dichroism will be $(K_1 + K_2) dz$, where $K_1 dz$ and $K_2 dz$ are the diminution in the intensities of the component vibrations (each with an initial intensity of one-half) in the states D and D'. This diminution of intensity may be equated to that occurring under the combined operation of linear and circular dichroism. Following the same argument as given above, it will be seen that the diminution of intensity arising from the operation of linear dichroism will be $(k_1 + k_2) dz$; while the diminution of intensity arising from the operation

of circular dichroism—as described in § 9 *a*—will be zero. Hence, if K_1 and K_2 be the absorption coefficients of the waves which would be propagated in the absence of linear birefringence and optical rotation, then

$$K_1 + K_2 = k_1 + k_2 \quad (21)$$

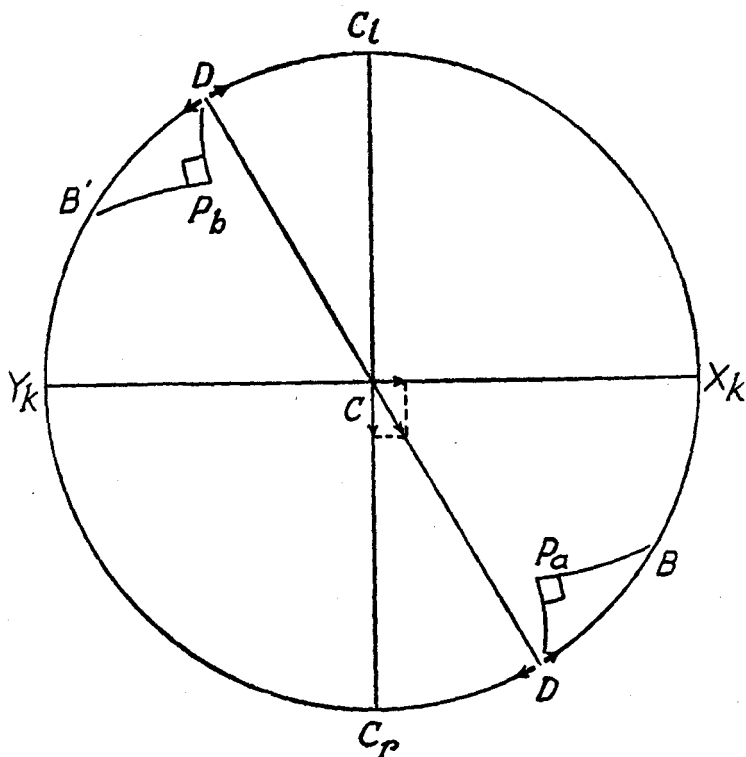


FIG. 7. Illustrating how linear dichroism and circular dichroism may be compounded by a vectorial law to yield elliptic dichroism. P_a and P_b represent the states of the waves propagated along a general direction in a uniaxial crystal possessing circular dichroism.

It has already been shown that the states which remain invariant under the infinitesimal operations of linear and circular dichroism are determined by the same vectorial law which holds for the composition of linear birefringence and optical rotation. Moreover, as in the discussion of § 6, it is easily seen that the infinitesimal operations of linear and circular dichroism are—from the formal mathematical standpoint—completely similar to the corresponding operations of linear birefringence and optical rotation (circular birefringence): the real constants K_1 , K_2 and σ occurring in the former case being replaced by imaginary constants $i\delta_1$, $i\delta_2$ and $i\rho$ in the latter case. As a corollary it follows that since the states which remain invariant under the

successive infinitesimal operations of linear birefringence and optical rotation suffer no *absorption*, the states which remain invariant under the successive infinitesimal operations of linear and circular dichroism can suffer no alteration in *phase*. So also, by proving relation (21) above, we have also established the parallel relation given by Eq. (2).

(c) *The superposition of elliptic birefringence and elliptic dichroism.*—It will now be clear that along any direction in an optically active absorbing crystal, the effect of elliptic birefringence as given by (1) and (2), has to be combined with the effect of elliptic dichroism [which would be present in the absence of optical activity and linear birefringence, and is given by (20) and (21)]. Correspondingly, it becomes more convenient to specify any point on the Poincaré sphere by its 'direction cosines' with respect to the new reference points D, B and C, which form a right-handed set, and in which only the arc BD differs from $\frac{1}{2}\pi$ (see Fig. 8); if we denote arc BD by $2X'$, then we will have instead of (3), the following expression for $\cos 2X'$ obtained from triangle BDC_1 :

$$\cos 2X' = \sin 2\omega_1 \sin 2\omega_2 + \cos 2\omega_1 \cos 2\omega_2 \cos 2X.$$

The problem has now been reduced to a form exactly similar to that considered in the previous sections. Hence the states of polarisation of the waves (*specified with reference to the new co-ordinate system*) and the refractive indices and absorption coefficients of the waves are given again by the relations (4), (5), (9) and (12)—except that *the symbol k representing the linear dichroism has to be replaced by K* (which represents the magnitude of elliptic dichroism). Because of (21), it becomes unnecessary to replace $(k_1 + k_2)$ in (9) by $(K_1 + K_2)$.

We have thus formally obtained the solution for the propagation in media possessing circular dichroism. For any particular direction of propagation the coefficient of circular dichroism σ is to be determined from the surface of circular dichroism. The media which possess circular dichroism to a striking extent and which at first sight would seem best suited for an easy qualitative test of the theory are certain of the so-called liquid crystals (Voigt, 1916); nevertheless in these liquid crystals, the large 'circular dichroism', the enormous rotation of the plane of polarisation and other phenomena indicate that the medium may not be homogeneous and that, on the contrary, it possesses a lamellar structure (Hl. de Vries, 1951). Since a suitable single crystal was not obtained for experimental study we shall not dwell at any length on the specific results of the theory, but content ourselves with mentioning a few of the results.

For directions which are nowhere in the vicinity of an optic axis the ratio k/Δ and ρ/δ will differ very slightly from zero, so that to a good degree of approximation the propagation will be as in non-active absorbing crystals (see § 7). Similarly, if the ratio of the circular to linear dichroism differ very

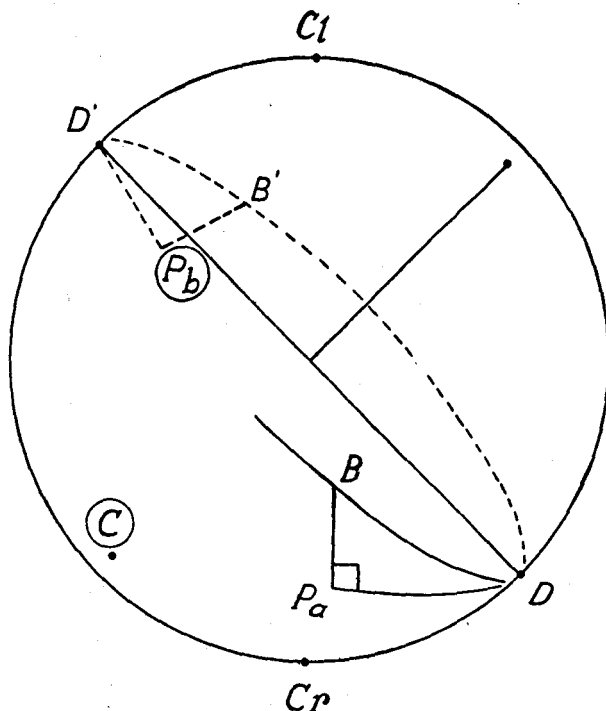


FIG. 8. Propagation in a crystal of the most general class (*i.e.*, possessing circular dichroism also). P_a and P_b represent the states propagated unchanged under the effects of elliptic birefringence Δ (axis BB') and elliptic dichroism K (axis DD').

slightly from zero, as may often be the case in biaxial crystals, we may according to (20) conveniently treat the crystal as though circular dichroism were absent.

For uniaxial crystals, since the principal planes of linear birefringence and dichroism coincide, the points B and D lie on the same great circle passing through the poles. It will then be seen from Fig. 7 that the elliptic states P_a and P_b propagated along any direction bear a simple geometrical relationship to one another; they have the same numerical ellipticity (though they are described in opposite senses); and the orientations of the major axes of the two ellipses are obtained from the principal planes OX_r and OY_r , by turning the latter directions through equal angles in *opposite* directions. This result has been obtained by Forsterling (quoted in Szivessy, 1928) from

the electromagnetic theory of propagation in uniaxial crystals. For directions not too close to the optic axis, the ellipticity of the waves will be the same as in a transparent crystal—since the square of (k/Δ) may be neglected in comparison with unity, so that the arc BP_a is an infinitesimal of the first order and lies along a parallel of latitude.

The states of polarisation of the waves propagated along a general direction in a biaxial crystal will bear no simple relation to one another (*see* Fig. 8); but along the optic axial direction the forms and orientations of the two elliptic vibrations will be simply related to one another—in the same fashion as those propagated along a general direction in a uniaxial crystal (*see* preceding paragraph).

§ 10. CONCLUDING REMARKS

It appears worthwhile to underline the essential difference between our procedure for applying the superposition principle and that customarily followed, *e.g.*, in the case of transparent active crystals by using the Poincaré sphere, or for any crystalline plate by using matrix calculus. The spirit of our method of analysis has *not* been so much to replace the effects produced by an absorbing crystalline plate (on light passing normally through it) by a geometrical or analytical *operation*; it has been to determine the states of polarisation of the two waves that can be propagated along each direction, as well as their velocities and absorption coefficients. This is because the characteristic interference phenomena exhibited by an absorbing crystalline plate, with the incident light partially or completely polarised, is naturally best understood as due to the *interference* and composition of the two non-orthogonally polarised waves emerging from the crystal plate—or their resolved components; in fact this method of analysis is useful for transparent and absorbing crystals alike (*see* Pancharatnam, 1956 *a, b*; 1957 *a, b*). Moreover, the two waves that can be propagated along any general direction have a physical reality that may otherwise be lost sight of. For example, each will in general have a different ray-direction. [The physical reason for this is that the wave-velocities as given by (12) vary with direction, and in any such medium the direction of propagation of an element of the wave-front will not always coincide with the wave-normal, but may be derived from it by a construction from the wave-surface.] One of the chief merits, then, of the use of the Poincaré sphere is that the states of polarisation of the waves, as well as their velocities and absorption coefficients are determined by extremely simple expressions [(4), (5), (9) and (12)] which remain essentially the same whether the crystal is optically active or not.

The peculiar interference figures exhibited by a sector of amethyst will be explained in detail in a later paper by the application of the method of superposition, so that an overall picture of the optics of such media in the vicinity of an optic axis will emerge. The possibility of the existence of *singular axes*, along which only *one* state of polarisation can be propagated without change of form, will also be investigated. That the properties of the singular axes as described by the method of superposition do not really flout the results of the electromagnetic theory (both in the case of active and non-active crystals) will be indicated in a later paper—which will present the electromagnetic theory of light propagation in active absorbing crystals.

The author is highly thankful to Prof. Sir C. V. Raman for his continued interest in the present investigation.

§ 11. SUMMARY

A light beam in an absorbing crystal may be looked upon as travelling under the superposed effects of the various 'elementary properties' associated with the medium, *viz.*, linear birefringence, linear dichroism, optical rotation and circular dichroism. For any general direction of propagation, this postulate yields completely (*a*) the states of polarisation of the two waves (specified conveniently by two corresponding points on the Poincaré sphere), and (*b*) their velocities and absorption coefficients (expressed conveniently as functions of their states of polarisation). The treatment is closely parallel to that for inactive absorbing crystals (Pancharatnam, 1955)—since for each direction, linear and circular birefringence combine to give elliptic birefringence, while linear and circular dichroism similarly combine to yield elliptic dichroism.

The case of biaxial media with negligible or no circular dichroism is dwelt upon at length. The waves along an optic axis are not circularly polarised: they may even be in two non-orthogonal linearly polarised states (if the dichroism exceed twice the rotatory power). For directions in the near vicinity of an optic axis the waves are in two *elliptic* states of unequal ellipticity with their major axes *not* crossed. For other directions, however, the orientations of the major axes—as also the velocities and absorption coefficients of the waves—become substantially the same as for an inactive absorbing crystal; but the ellipticity for each state now approximates to the sum of the corresponding ellipticities obtaining in the inactive absorbing crystal and the active transparent crystal—thus becoming negligible only when the inclination to both the optic axes becomes notable.

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