THE EFFECT OF A MAGNETIC FIELD ON THE NEMATIC STATE.

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Received in German 21st February, 1933, translated by H. D. Megaw.

Two fundamentally different hypotheses have hitherto been used to account for the changes in nematic systems in a magnetic field; these are the Swarm Theory and the Distortion Theory (*Verbiegungstheorie*). It is extremely important to decide which is the correct one, not only for the particular problem dealt with in this paper, but for the whole general question of the structure of these phases.

The experimental evidence for the swarm theory depends essentially on the changes of dielectric constant in magnetic fields, to which Ornstein [1] applies Langevin's theory of ferromagnetism, while Fréedericksz [2] uses Gans's theory of diamagnetism. A quantitative comparison with the distortion theory has not hitherto been possible, as the necessary mathematical treatment was not available. This is given in what follows.

A theory of distortion in a magnetic field was given some years ago by the author.[3] In that a case was considered which involved no changes in the dielectric constant. We shall consider it briefly. The following assumptions are made. (1) The whole substance tends to take up a position such that the axial direction at every point is the same. (2) Any force acting so as to disturb this state where the directions are uniform causes a distortion in which the direction changes continuously until a restoring force of an elastic nature holds the applied force in equilibrium. (3) At surfaces of solid bodies (*e.g.*, glass or metal) the positions at first assumed are almost unchangeable.

Let us now consider a case in which the substance is placed between a fixed plate and one which can be rotated; and assume that at both plates it orientates itself with the principal axes parallel. Then when no forces act, the movable plate sets with its direction of axis parallel to that of the fixed plate. A torque D acting on the movable plate causes a rotation which increases with the turning-moment. For small distortions, the angle ϕ between the azimuths at the upper and lower plates will be proportional to the turning-moment, *i.e.*, it will obey Hooke's Law. The elastic resistance is directly proportional to the area q of the layer, and inversely proportional to its thickness z. This gives the relation

$$D = q\frac{\phi}{z}k_t. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The quantity k_t corresponds to a kind of torsion modulus, and has the dimensions of a force; hence it is expressed in dynes. It can be seen that there is an analogy with the deformation of ordinary solid bodies,

[1] L. S. Ornstein, *Ann. Physik*, **74**, 445, 1924.
[2] V. Fréedericksz and A. Repiewa, *Z. Physik*, **42**, 532, 1927.
[3] H. Zocher, *Physik. Z.*, **28**, 790, 1927.

though the deformation is actually of a different nature. It consists of a pure torsion without sheer, which in a solid cylinder only occurs in a line along the axis.

If a magnetic field is now allowed to act on an undeformed layer perpendicular to the axial direction, a state will be arrived at in which the elastic forces are in equilibrium with the magnetic forces. The energy of a layer of thickness dx in a field H is given by

$$dE = q\frac{H^2}{2}(\kappa_1 \cos^2\phi + \kappa_2 \sin^2\phi)dx,$$

where κ_1 and κ_2 are the susceptibilities parallel and perpendicular respectively to the axis of the molecule, and ϕ the angle between the axis and the direction of the field. The increase in the turning-moment in a direction from the movable to the fixed plate is, for each layer,

$$dD = q\frac{H^2}{2}(\kappa_1 - \kappa_2) \sin 2\phi dx.$$

But, from equation (1),

$$D = qk_t\frac{d\phi}{dx}, \text{ and } \frac{dD}{dx} = qk_t\frac{d^2\phi}{dx^2},$$

hence

$$k_t\frac{d^2\phi}{dx^2} = \frac{H^2}{2}(\kappa_1 - \kappa_2) \sin 2\phi,$$

$$\therefore \quad \frac{d\phi}{dx} = H\sqrt{\frac{\kappa_1 - \kappa_2}{k_t}}\sqrt{\sin^2\phi - \sin^2\phi_0}, \qquad . \quad . \quad (2)$$

where ϕ_0 is the angle between the direction of the field and the axis at the movable surface. For large thicknesses, $\phi_0 = 0$, and therefore

$$\frac{d\phi}{dx} = H\sqrt{\frac{\kappa_1 - \kappa_2}{k_t}} \sin\phi.$$

By integrating (2), a relation can be obtained connecting x, the distance from the movable plate, with the axial azimuth :

$$xH\sqrt{\frac{\kappa_1 - \kappa_2}{k_t}} = \int_{\phi_0}^{\phi} \frac{d\phi}{\sqrt{\sin^2\phi - \sin^2\phi_0}} \qquad . \quad . \quad (3)$$

This integral can easily be brought to Legendre's normal form of an elliptic integral of the first kind :

$$xH\sqrt{\frac{\kappa_1 - \kappa_2}{k_t}} = \int_{\psi}^{\frac{\pi}{2}} \frac{d\psi}{\sqrt{1 - \cos^2\phi_0 \sin^2\psi}},$$

where

$$\sin\psi = \frac{\cos\phi}{\cos\phi_0}.$$

We can now imagine a second layer with a second fixed plate so placed above the movable plate that it is a mirror image of the first ; it must then necessarily be in equilibrium. Finally, if we make the movable plate infinitely thin, we obtain the case of a layer between two fixed plates. If z is now the total thickness of the layer,

$$\frac{z}{2}H\sqrt{\frac{\kappa_1 - \kappa_2}{k_t}} = \int_{0}^{\frac{\pi}{2}} \frac{d\psi}{\sqrt{1 - \cos^2\phi_0 \sin^2\psi}} \qquad . \quad . \quad (4)$$

for the case, that $\phi = \pi/2$ at the plates.

The experiment considered here, which we shall call Case III, had not previously been performed, but it will be dealt with in the experimental part of the work. The other two possibilities for the position of the layer in a magnetic field, which will next be discussed, were first investigated in detail by Mauguin,[4] who described qualitatively the optical effect. More recently, van Wyk [5] and Fréedericksz [6] have made optical measurements, Jezewski [7] and Kast [8] dielectric measurements. The first possibility is that the position of the substance at the surface is the same as in Case III, but that the field is applied perpendicular to the plate (Case I). The second is that the substance has its axes perpendicular to the plate (so-called uniaxial orientation), and that the field is applied parallel to the plate at any arbitrary azimuth (Case II). In both these cases, distortion must occur, such that the axis of rotation of the distortion no longer coincides with the x-axis but is perpendicular to it. The angle made by the axis of the molecules in each layer with the axis of x, at a distance $x = 0$ (*i.e.*, in the middle of the layer), approaches 0° in Case I, 90° in Case II, as the field strength increases. The axial lines, *i.e.*, the lines which give the direction of the axis at any point, will be as shown in Figs. 1*a* and *b*. The configuration will always be given by plane curves if the setting assumed to occur at the surface is homogeneous.

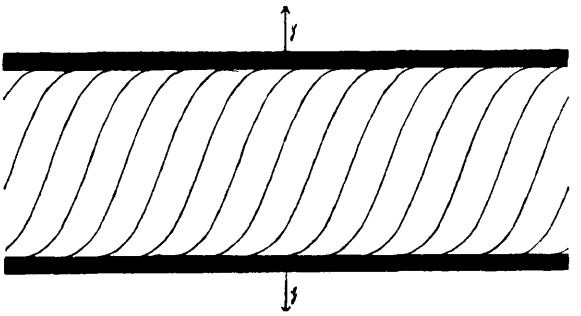

FIG. 1*a*.—Case I. Axial lines in a magnetic field. $\phi_0 = 20°$.

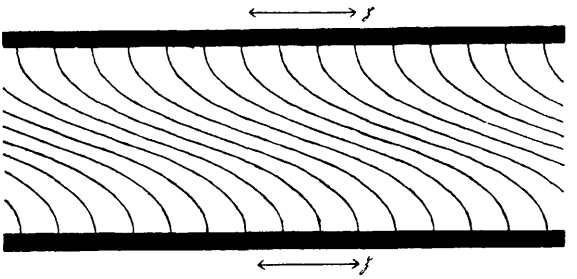

FIG. 1*b*.—Case II. Axial lines in a magnetic field. $\phi_0 = 20°$.

Both these cases are complicated by the fact that the angle made by the axial direction with the x-direction varies, so that even for constant $\frac{d\phi}{dx}$ it is not certain whether the torque producing the distortions is the same. The case when the principal axis coincides with the x-direction was previously called by the author "lengthwise distortion" (*Längsbiegung*), that in which the two directions are at right angles, "fan formation" (*Auffächerung*) or "cross distortion" (*Querbiegung*). The

[4] Ch. Mauguin, *Comptes Rendus*, **152**, 1680, 1911.
[5] A. van Wyk, *Ann. Physik*, **3**, 879, 1929.
[6] V. Fréedericksz and V. Zolina, *Z. Krist.*, **79**, 255, 1931.
[7] M. Jezewski, *Z. Physik*, **40**, 153, 1926.
[8] W. Kast, *Z. Krist.*, **79**, 146, 1931.

moduli k_1 and k_2 corresponding to these may be very different, the behaviour of smectic substances results from this. In these, k_1 is so much greater that the lengthwise distortion never occurs, and the axial lines are always straight lines. Hence follows the principle of the deformation of the smectic state, *i.e.*, the conical structures which have been established by the beautiful work of G. Friedel. The law is obeyed perfectly by this whole range of complicated and remarkably interesting phenomena.

In nematic substances, on the other hand, the two moduli may be very nearly equal. Experiment shows that this may be true to a first approximation. Van Wyk [5] has worked out a theory for Case I that is almost identical with equation (2) given above. In his optical experiments, the great thickness of the layer used enabled him to put $\phi_0 = 0$. The observations are in good agreement with the theory. Further, Fréedericksz [6] has shown that his optical observations agree very well, both for Case I and Case II, with the theory which he adopted from van Wyk. In this, he does not assume that $\phi_0 = 0$, but applies the calculation to thin layers by the introduction of the elliptic function.

The difference between van Wyk's treatment and that given above will not be considered here. A practical application of Fréedericksz's measurements will, however, be made. It appears that for any given field strength there is a certain thickness of layer above which distortion first occurs. For less than this thickness, the distortion is zero, that is, any distortion would require a bigger expenditure of mechanical energy than would be available from the magnetic energy released by orientation in the field. The phenomenon is closely analogous to the behaviour of a loaded column, which only bends sideways at a fixed "breaking stress."

In equation (4) this implies that $\phi_0 = \frac{\pi}{2}$, and hence

$$\frac{z}{2}H\sqrt{\frac{\kappa_1 - \kappa_2}{k}} = \int_0^{\frac{\pi}{2}} d\psi = \frac{\pi}{2}.$$

Fréedericksz showed that the product of z_0 and H_0 as given by this relation is constant; for *p*-azoxyanisole below 120° it has the value 8·4. From this,

$$z_0 H_0 = \frac{\pi}{\sqrt{\frac{\kappa_1 - \kappa_2}{k}}} = 8{\cdot}4,$$

and therefore

$$\sqrt{\frac{\kappa_1 - \kappa_2}{k}} = {\cdot}37.$$

From the measurements of Foex and Royer, $\kappa_1 - \kappa_2$ is about $0{\cdot}15 \times 10^{-6}$. Thus k must be $1{\cdot}0 \times 10^{-6}$ dynes.

For these very small magnitudes of the elasticity, it is obvious that, as Mauguin [4] has observed, it is not possible to obtain thicker layers in an unbent state without magnetic field. It is only possible to do so up to a thickness of 0·2 mm. Then, according to the above, a turning-moment of 10^{-4} ergs per cm.^{2} suffices to give the middle of the layer an angular distortion of unity. A torque of this magnitude might easily be introduced by differences in density caused by small temperature changes. Since the friction depends on the direction, heat convection can give distortions. The thicker the layer, the greater the difficulty with which a homogeneous orientation is achieved.

It is of interest to consider the highest torque per unit area of surface that can be achieved with the strongest available fields. This, of course, occurs at the outside of a thick layer, where it has the value

$$k\frac{d\phi}{dx} = H\sqrt{k(\kappa_1 - \kappa_2)}.$$

For 25,000 Gauss it gives, in the example just mentioned, 0·0094 ergs per cm.^{2} The dimensions are those of a surface tension, the magnitude with which it competes. The orientation of the phase at the fixed plate is determined by the difference of surface tensions in the different positions. When the axes are parallel to the wall, the surface tension (σ_1) may be quite different from that when they are perpendicular (σ_2), since the two surfaces actually possess quite different structures. The difference may be of the order of magnitude of 10 ergs per cm.^{2}, which is 1000 times greater than the greatest attainable torque. This explains the fact observed by van Wyk and by Fréedericksz, that the angle at the surface against glass is independent of the field strength. If the surface tension is given by the relation

$$\sigma = \sigma_1 \sin^2\phi + \sigma_2 \cos^2\phi,$$

where ϕ is the angle between the axis and the normal to the plate, then for $\sigma_1 - \sigma_2 = 10$ ergs per cm.^{2}, the change of angle would only be about two minutes.

The effect of the field on the capacity of a condenser filled with a nematic substance will next be considered. It will be assumed that we are dealing with Case I, and that the normal to the condenser plates makes an angle α with the lines of magnetic force. The axial lines will then only lie in a plane if the direction of the axes at the surface lies in the same plane as the lines of electric and magnetic force. This case will be dealt with first in what follows. Let the angle between the direction of the axes and the magnetic field be ϕ, that between the axes and the lines of electric force $\chi = \phi + \alpha$. The equation is the same as before (equation 4), except that ϕ at the solid boundary has the value $\frac{\pi}{2} - \alpha$ instead of $\frac{\pi}{2}$. Then

$$\begin{aligned}\frac{z}{2}H\sqrt{\frac{\kappa_1 - \kappa_2}{k}} &= \int_{\phi_0}^{\frac{\pi}{2}-\alpha} \frac{d\phi}{\sqrt{\sin^2\phi - \sin^2\phi_0}} \\ &= \int_{\psi_0}^{\frac{\pi}{2}} \frac{d\psi}{\sqrt{1 - \cos^2\phi_0 \sin^2\psi}} \\ &= F(\cos\phi_0, \pi/2) - F(\cos\phi_0, \psi),\end{aligned}$$

where $$\sin\psi_0 = \frac{\sin\alpha}{\cos\phi_0}.$$

The numerical values of the two elliptic integrals of the first class, F, may be found from the tables.[9] The dielectric constant ϵ of the nematic layer in the field varies continuously from place to place in the condenser along the x-direction :

$$\epsilon = \epsilon_1 \cos^2\chi + \epsilon_2 \sin^2\chi,$$

[9] *E.g.* E. Jahnke and F. Emde, *Funktionstafeln*, Teubner, Berlin, 1928; L. Kiepert, *Integralrechnung*, Hanover, 1910.

where ϵ_1 and ϵ_2 are the dielectric constants parallel and perpendicular to the axis respectively. If the change of capacity with field strength is attributed to an alteration of " the " dielectric constant, the quantity so obtained is an average value ϵ'. This can be calculated from the " air distance " of the condenser plates, *i.e.*, the distance between the plates for which the capacity in air (or more accurately in vacuo) would be the same. The " air thickness " of the nematic layer is

$$\frac{z}{\epsilon'} = 2\int_0^{\frac{z}{2}} \frac{dx}{\epsilon_1 \cos^2\chi + \epsilon_2 \sin^2\chi}.$$

Let $\epsilon_2 - \epsilon_1 = \Delta$.

Then for zero field strength, the " air distance " is z/ϵ_2, and for infinite field strength, $\dfrac{z}{\epsilon_2 - \Delta\cos^2\alpha}$. The difference

$$\frac{z}{\epsilon_2 - \Delta\cos^2\alpha} - \frac{z}{\epsilon'}$$

can be put equal to

$$(\epsilon_2 - \epsilon' - \Delta\cos^2\alpha)z/\epsilon^2$$

if Δ is small compared with ϵ_1 and ϵ_2. From the measurements of Jezewski [7] in the example taken above, $\epsilon_2 = 5{\cdot}31$, $\epsilon_1 = 5{\cdot}15$, so that the above gives a good approximation. Hence

$$\epsilon' - \epsilon_2 + \Delta\cos^2\alpha = \frac{2\epsilon^2}{z}\int_0^{\frac{z}{2}}\left(\frac{1}{\epsilon_2 - \Delta\cos^2\alpha} - \frac{1}{\epsilon_2 - \Delta\cos^2\chi}\right)dx$$

$$= \frac{2\Delta}{z}\int_0^{\frac{z}{2}}(\cos^2\alpha - \cos^2\chi)dx.$$

Putting (eq. 2)

$$dx = \frac{d\phi}{H\sqrt{\frac{\kappa_1 - \kappa_2}{k}}(\sin^2\phi - \sin^2\phi_0)},$$

and $\chi = \phi + \alpha$,

we obtain finally

$$\epsilon_2 - \epsilon' = \Delta\left[\cos^2\alpha - \frac{\{E(\cos\phi_0, \pi/2) - E(\cos\phi_0, \psi_0)\}\cos 2\alpha + \cos\phi_0\cos\psi_0\sin 2\alpha}{F(\cos\phi_0, \pi/2) - F(\cos\phi_0, \psi_0)}\right] \quad (5)$$

Here E is the elliptic integral of the second kind,

$$E(\cos\phi_0, \pi/2) - E(\cos\phi_0, \psi_0) = \int_{\psi_0}^{\frac{\pi}{2}} \sqrt{1 - \cos^2\phi_0\sin^2\psi}\, d\psi.$$

It may be found in the tables.

This equation will be briefly discussed. Fig. 2 represents graphically the relation between $\dfrac{\epsilon_2 - \epsilon'}{\Delta}$ and $\dfrac{2}{zH\sqrt{\frac{\kappa_1 - \kappa_2}{k}}}$ for several values of α.

When $\alpha = 0$, the quotient in the bracket becomes $\dfrac{E}{K}$; this expression was derived by Fréedericksz for the double refraction in Case I, and $1 - \dfrac{E}{K}$

in Case II. This can easily be understood, because the double refraction, like the difference of the dielectric constants, is proportional to $\sin^2 \chi$. The axial lines in Figs. 1*a* and 1*b* have been drawn for Case I and Case II when $\alpha = 0$ and $\phi = 20°$. It is interesting in this formula that for $\alpha \neq 0$ the discontinuous character of the function disappears; ϕ_0 reaches the value $\frac{\pi}{2} - \alpha$ at $z = 0$. Even the thinnest layer has a distortion, which, however, is very small for values of z below z_0. The effect is therefore not essentially different for values of α of a few degrees; the function here shows a strong curvature. (See the curve for $\alpha = 5°$ in Fig. 2.) For large values of H the equation becomes

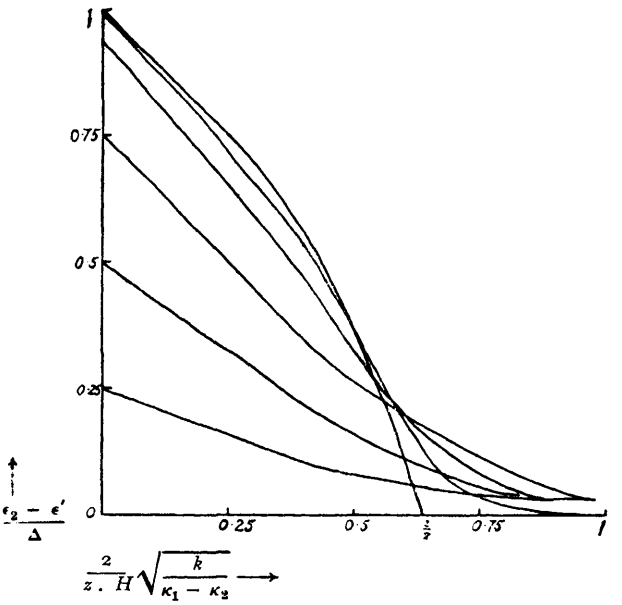

FIG. 2.—Graphs of $\frac{\epsilon_2 - \epsilon'}{\Delta}$ plotted against $\frac{2}{zH}\sqrt{\frac{k}{\kappa_1 - \kappa_2}}$ for $\alpha = 0°$, 5°, arc sin $\frac{1}{4}$, 30°, 45° and 60°.

$$\epsilon_2 - \epsilon' = \Delta\left(\cos^2 \alpha - 2\,\frac{\cos 2\alpha + \sin \alpha}{zH\sqrt{\frac{\kappa_1 - \kappa_2}{k}}}\right).$$

If the values of $\epsilon_2 - \epsilon'$ are plotted against the reciprocal of the field strength, then at high field strengths straight lines are obtained which cut off an intercept on the y-axis proportional to $\cos^2 \alpha$. Their slope is proportional to $(\cos 2\alpha + \sin \alpha)$, which has a maximum at $\sin \alpha = 0{\cdot}25$ ($\alpha = 14° 29'$ approx.). For $\alpha = 30°$ the line is parallel to that for $\alpha = 0$, and becomes continuously less steep as α increases. The curve for $\alpha = 0$ is everywhere concave to the x-axis, but the other curves for small field strengths show a convex curvature towards it which is predominant above $\alpha = 30°$. It is also of interest that the effect of the field strength in the neighbourhood of

$$H_0 = \frac{\pi}{z\sqrt{\frac{\kappa_1 - \kappa_2}{k}}}.$$

at first increases with increasing α, and later decreases.

The measurements of Kast [10] and Jezewski (*loc. cit.*) may be adduced in support of the theory. In Fig. 3, curve (1) shows Kast's measurements I on *p*-azoxyanisole at 119° C. plotted against $\frac{I}{H}$, and curves (2) and (3) similar measurements for *p*-azoxyphenetole at 138° C. and 153° C. respectively. For large field strengths they are very nearly straight lines. It is not possible to calculate the curve *a priori*, as the thickness of the layer in the condenser is not given. But we can assume the value of $\sqrt{\frac{\kappa_1 - \kappa_2}{k}}$ from the measurements of Fréedericksz,[6] and calculate the thickness from this :

$$z = \frac{2}{H\sqrt{\frac{\kappa_1 - \kappa_2}{k}}\left(1 - \frac{\epsilon_2 - \epsilon'}{\Delta}\right)}.$$

From the value for *p*-azoxyanisole at 119° C., for which

$$\sqrt{\frac{\kappa_1 - \kappa_2}{k}} = \frac{\pi}{8{\cdot}4},$$

z is found to be approximately 0·05 mm.; from *p*-azoxyphenetole at 153° C.,

$$\sqrt{\frac{\kappa_1 - \kappa_2}{k}} = \frac{\pi}{8{\cdot}06},$$

and hence z is 0·03 mm. Curves (4) and (5) give the measurements of Jezewski for *p*-azoxyphenetole at 143° C. and *p*-azoxyanisole at 122° C. The curves appear to be irregular. The thickness z being given as 0·07 cm., the value of $\sqrt{\frac{\kappa_1 - \kappa_2}{k}}$ calculated from the approximate course of curve (4) is about half as big as that found from Fréedericksz's values of $z_0 H_0$, while from curve (5) it is about equal to it.

For small field strengths, however, Kast's measurements deviate considerably from the theoretical curve. His curves are convex instead of concave to the axis. Apart from the fact that the theory involves several doubtful assumptions, this discrepancy is not surprising. In the first place, the measurements are made with a condenser surrounded with nickel wire, so that the field strength, and field direction, must differ appreciably from that in the absence of nickel. Secondly, the theory only refers to that part of the condenser where the axis of the nematic substance is parallel to the condenser plate. But near the edge this is certainly not true. Further, dust particles (particles of the mica used for insulation) may cause deformation in the absence of a field. It has been shown that the effect is greatest when the angle between the axis and the magnetic field has an intermediate value, and the field strength is small.

The measurements II of Kast [11] for varying angle α will next be compared with the theory. Unfortunately Kast gives no complete table of his numerical results, so that the points in question have had to be taken from Figs. 3 and 4 of Kast's paper. Table I gives the change of acoustic

[10] L. S. Ornstein, *Ann. Physik*, **74**, 445, 1924.
[11] W. Kast, *Ann. Physik*, **83**, 391, 1927.

interference frequency thus obtained; in this, the values taken from Kast's Fig. 3 for $\alpha = 0$ have been decreased by 1 per cent. to correct for the temperature difference of 0·5° C. All the measurements lie in a range where $\epsilon_2 - \epsilon'$ decreases linearly with the reciprocal of the field strength. In Fig. 4 are shown the corresponding straight lines calculated for the actual distance between the plates of 0·75 mm. It is clear that the measured results agree well with those calculated. This is the more noteworthy, that only one parameter Δ was to be derived from the measurements; and incidentally, the straight lines here obtained could have been arrived at beforehand, using only the optical measurements of Fréedericksz. The swarm theory introduces a second parameter,

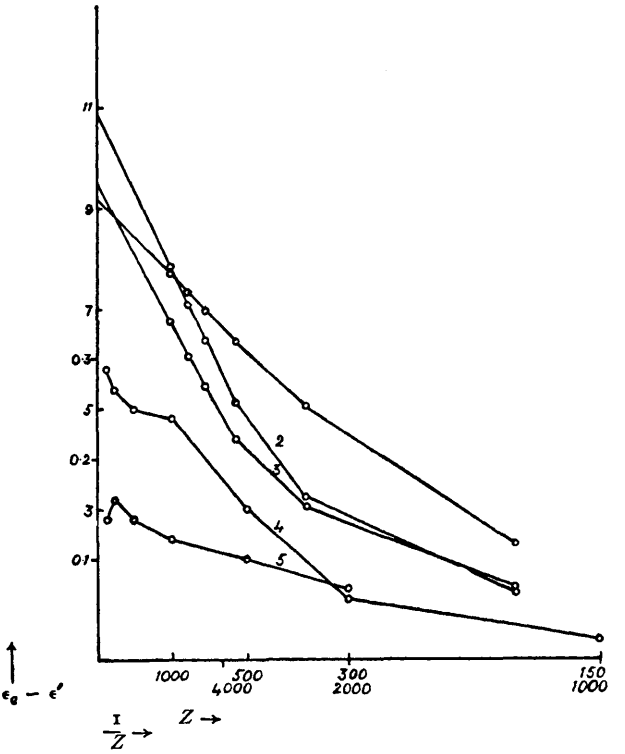

FIG. 3.—1, 2, 3. Measurements I of Kast. $\epsilon_2 - \epsilon'$ in arbitrary units (right-hand numbers along y-axis), H in gauss (upper numbers along x-axis).
4, 5. Measurements of Jezewski. $\epsilon_2 - \epsilon'$ in absolute units (left-hand numbers along y-axis), H in gauss (lower numbers along x-axis).

$$x = \frac{\kappa_1 - \kappa_2}{kT} v,$$

TABLE I.—CHANGE OF ACOUSTIC INTERFERENCE FREQUENCIES ACCORDING TO KAST, II.

α \ H	2900 f. 0° / 2250	725.	375.	225.
0°	537	494	—	377
25°	432	391	357	262
35°	348	318	289	184
45°	276	251	—	—
60°	165	124	—	68
70°	96	—	72	51

besides that mentioned above; it is to be noted that this second parameter is about twenty times bigger when calculated from measurements II than when calculated from measurements I. It is easy to see that this depends on the layer thickness, which is twenty times as great in II. A systematic deviation is only shown by the values for $\alpha = 70°$, which are greater than were to be expected. This is evidently connected with the fact that a change of acoustic frequency is observed even for $\alpha = 90°$, which is not easy to account for. It would seem reasonable to subtract this value for $\alpha = 90°$ from all the other values, when good agreement is obtained even for $\alpha = 70°$. According to Jezewski, the values for the greatest field strengths are represented very accurately by the formula

$$\epsilon = \epsilon_1 \cos^2 \alpha + \epsilon_2 \sin^2 \alpha.$$

The way in which the effect depends on temperature is of particular interest. According to Ornstein, the change in dielectric constant can be written

$$f(H) \,.\, g(T).$$

This can only be correct to a first approximation; only, in fact, if the variation of Δ with the temperature is appreciable, while that of $\frac{\kappa_1 - \kappa_2}{k}$ is negligible. According to the experimental results of Fréedericksz, $z_0 H_0$ decreases with rise of temperature, and therefore $\frac{\kappa_1 - \kappa_2}{k}$ increases with rise of temperature. This means that for increasing temperature k decreases more rapidly than $\kappa_1 - \kappa_2$. Hence $\frac{\epsilon_2 - \epsilon'}{\Delta}$ is reached with smaller field strengths as the temperature rises. $\kappa_1 - \kappa_2$ should to a first approximation decrease in the same way with rising temperature as do Δ and the double refraction $n_1 - n_2$. Even at the temperature of transition into the amorphous phase, the various kinds of anisotropy possess values different from zero. From the variation of k with temperature follows, according to the Second Heat Theorem, that a change of deformation with change of temperature is connected (cooling associated with deformation, heating with release from deforming forces). The very small size of the effect (order of magnitude $10^{-5°}$) makes proof scarcely possible. Moll and Ornstein [12] observed such an effect, but it was of the opposite sign. For Case III no change of temperature was observed, though the order of magnitude of that expected was the same. The observation that was made must be due to some other effect.

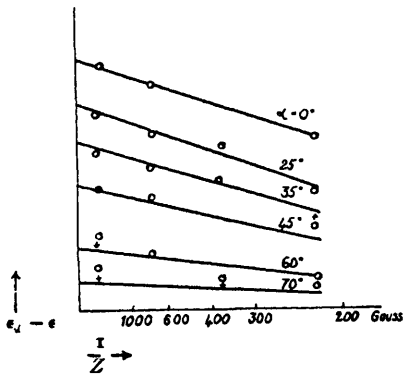

FIG. 4.—Measurements II of Kast. Graph of $\epsilon_3 - \epsilon'$ plotted against $1/\zeta$. The straight lines represent the calculated values.

[12] L. S. Ornstein, *Z. Krist.*, **79**, 90, 1931.

Experimental Section.

Our experiments on the magnetic behaviour of nematic layers relate to two different problems. Till now no exception had been found to the rule that optic axes tend to set parallel to the lines of magnetic force; in other words, that the susceptibility along the axis is greater (the diamagnetism smaller) than at right angles to it:

$$\kappa_1 - \kappa_2 > 0.$$

We now tried to see if substances of quite different constitution from those hitherto examined might not furnish examples of the opposite behaviour. With this in view, we investigated a number of aqueous nematic systems. The experiments showed that nematic concentrated solutions of bromo-phenanthrene sulphonic acid and chlorophenanthrene sulphonic acid, which showed large effects in a magnetic field, both set with their principal axes perpendicular to the lines of force. Since both these systems have negative double refraction, the vibration corresponding to the greater refractive index here lies parallel to the lines of force, just as in the substances previously examined. But the law, even as thus stated, is not generally valid. Thus a concentrated solution of salvarsan is definitely affected by a magnetic field, though to a smaller degree, and sets with the direction of its axis perpendicular to the lines of force. Its double refraction is positive, and hence the vibration direction of greater refractive index is perpendicular to the lines of force. On the other hand, the phase which occurs in a moderately concentrated aqueous solution of potassium laurate seems to show a tendency to set with its axis parallel to the lines of force. Its double refraction is negative, like that of the halogen phenanthrene sulphonic acids, so that in this, as in salvarsan, the vibration direction of greater refractive index is perpendicular to the lines of force.

These experiments show that the rule that the axes tend to set parallel to the lines of force does not always hold.

The rest of our work involves the actual performance of the experiments described as Case III in the theoretical part of the paper. They are purely qualitative, and only give a preliminary account of the orientation. It was necessary for these experiments to obtain preparations with the greatest possible uniformity of orientation of their axes parallel to the surface (which was of glass). For this purpose, we made use of the effect on the orientation of the nematic phase produced by rubbing the glass surface.[13] If a glass plate is rubbed in a given direction, then the nematic phase in contact with it sets with its symmetry axis parallel to the direction of rubbing. The substances to be investigated, *p*-azoxyanisole and anisaldazine, were placed between a plane glass plate and a plano-convex lens, the adjoining surfaces of which were rubbed in the same direction by means of a rotating leather pad. (Layers between a lens and a plate have been used by Lehmann and also by Fréedericksz.) The orientation is almost perfect if the force used in polishing is sufficient. If the direction of rubbing on the plate and the lens are accurately the same, the substance appears dark between crossed nicols when the direction of one nicol is parallel to the direction of rubbing. It is in thicker layers that the well-known self-contained distortions about the lines of discontinuity mostly occur. The preparation was placed in a perforated copper block, electrically heated

[13] H. Zocher and K. Coper, *Z. physik. Chem.*, **132**, 295, 1928.

above and below the magnetic field, in such a position that the direction of rubbing made only a very small angle with the normal to the lines of force. Observations were made with a polarising microscope. If the polarising prism was set in the extinction position for zero field strength, then when the field was put on the thicker layers became brighter. Near the point of contact of lens and plate, out to a fixed radius from the centre, no effect occurred. (See photograph,* Fig. 5.) This phenomenon is completely analogous to that observed by Fréedericksz for Cases I and II. The values of z_0H_0 are of the same order of magnitude as his, and hence k_t is also of the same order of magnitude as k_1 and k_2. In the part where the effect occurs, the optical behaviour of the layer is of a rather complicated nature. If white light is used, the thicker layers show high order white. The actual tint, however, is not the same as for zero field, but is brownish. This was to be expected. Mauguin [14] showed that for a system in which one surface is rotated relative to the other, a vibration which is initially parallel to the first layer only changes its direction, and emerges parallel to the second layer, so long as the rotation effect is small compared with the double refraction. Hence in the above case, since the first and second layers are parallel, no change would be observed if the ratio of the rotation effect to the double refraction were small. Differences are only observed when this condition is not fulfilled. But for red light the double refraction is very much smaller than for light of shorter wave-length. Therefore the effect must be much more marked in the long-wave part of the spectrum than in the short-wave region, and hence the emergent light must have a brownish tint.

Extinction cannot be obtained by turning the nicols, as in the case of an unrotated layer. If the nicols are respectively parallel and perpendicular to the direction of rubbing, and if a gypsum plate of first order red is introduced between the specimen and the analyser, at 45° to the vibration direction of the nicols, a change appears in the red interference colour which is superimposed on the rather dull high order white. The axial lines of the layer between the two plates must, of course, lie in the same pair of quadrants between the field direction and its normal as does the direction of rubbing. With the gypsum of first order red, a blue addition colour is then obtained if the vibration direction of greater refractive index of the gypsum lies in the other pair of quadrants; if it lies in the same pair of quadrants as the axial lines, a yellow subtraction colour results. The same effect could be brought about without the application of the field, by turning the preparation through a small angle in the pair of quadrants containing the axial lines, and at the same time introducing between the preparation and the gypsum a thin flake of a substance of weak double refraction, with its vibration direction of greater refractive index at about 45° in the second pair of quadrants. The layer rotated in a non-uniform manner by the field therefore produces on the plane-polarised light from the polariser an effect which is to a first approximation the same as that of a layer of high order white on which is superimposed a weakly doubly-refracting layer of constant thickness and different orientation.

The observations in monochromatic light agree with these results. In sodium light, in the absence of a magnetic field, the field of the microscope is dark; but when a magnetic field is applied, it shows a large

[14] Ch. Mauguin, *Bull. Soc. Min.*, **34**, 1911. * Facing page 927.

number of interference rings in the parts where the thickness is great. These cannot be made to disappear by turning the polariser. But if a thin flake of mica (for example, a quarter-wave plate) is introduced between analyser and specimen, then by turning the flake and the analyser a position can always be reached in which the fringes vanish in a region covering a large number of rings (from 5 to 10). In this region there is uniform illumination which varies as the polariser is rotated. The vibration direction of the mica with the greater refractive index is here only turned through a small angle from the direction of rubbing in the quadrants containing the axial lines. The thicker the layer and the stronger the magnetic field, the greater must this angle be. For a given field-strength, the interference fringes in a fixed zone can be made to disappear without turning the analyser, by turning the mica only. Then zones nearer the centre, where the layers are thinner, require the analyser to be turned in the same direction as the mica, those further from the centre in the opposite direction. This shows that for increasing thickness of the layer, as for increasing magnetic field, the double refraction of the imaginary flake of constant thickness must be increased. No appreciable displacement of the interference rings depending on the field strength was observed, which means that the double refraction of the layer of variable thickness (high order white) did not alter appreciably. The azimuth of this can be determined by turning the polariser into the position where the uniform illumination is of minimum intensity. The greater the field strength and the thickness of the layer, the more does it differ from the direction of rubbing. On removal of the mica, the fringes in this position reappear, though they are of small intensity. This implies that the model assumed does not correspond accurately to the properties of the layer.

More accurate observation shows that the position of the axis at the surface is not absolutely independent of the field strength. The difference between the surface tensions when the axes are parallel and perpendicular to the direction of rubbing depends on the anisotropy of the glass surface, and will not necessarily be of the same order of magnitude as the difference previously referred to between σ_1 and σ_2.

Finally, another experimental possibility should be mentioned which does not correspond to any of the three Cases I, II, or III, and which we have been able to realise in practice. In this, the assumption is no longer made that the orientation at the two surfaces is the same. For example, if one of the glass surfaces is treated with acid, *p*-azoxyanisole tends to set with its axis perpendicular to the surface. Hence in this case the axes at one surface are parallel to the direction of rubbing, and at the other they are perpendicular to the surface, and so a distortion occurs when no field is present. This will be constant throughout the layer,

$$\frac{d\phi}{dx} = \frac{\pi/2}{z}.$$

Calculation shows that the phase-difference due to the double refraction is half as great as when the axes at both surfaces are parallel to the direction of rubbing. The experiments confirm this result, at least to a first approximation. A magnetic field acting parallel to the surface then brings about a large decrease in the diameter of the interference rings, that is, an increase in the path difference, which becomes almost double its previous value.