Physics. — "*Contribution to the research of liquid crystals.* II. *The influence of the temperature on the extinction; further experiments upon the influence of the magnetic field.*" By Dr. W. J. H. MOLL and Prof. Dr. L. S. ORNSTEIN. (Communicated by Prof. JULIUS).

(Communicated in the meeting of February 24, 1917).

In the further research of the liquid crystals, the results of which we intend to communicate hereafter, the same method as described in a former communication was used again. (These Proc. XIX p. 1315). The method was improved in a few respects only, the principal change being that a copper-disk with a central hole of about three millimeter diameter takes the place of the glass-pieces in the oven. The substance is put between two object-glasses, which lie on the disk. In this way we get the advantage that the matter does not come into contact with the copper, and that it is possible to examine several substances successively with the same oven. Though the narrow hole in the copper diminishes the intensity of the image on the thermo-pile it secures an absolutely homogeneous heating of the very small part of the matter under observation.

§ 1. *The influence of the temperature on the extinction.*

The extinction in its dependence on the temperature was measured in the following way. The matter that has been melted before between two glasses and congealed afterwards, is put on the oven the temperature of which is below the melting-point. Then such a value is given to the heating current, that in the long the melting to isotropic-liquid will be reached. Then if after some time the substance has been molten, the current of heating is put off (or diminished) so that the substance gets liquid crystalline again and congeales afterwards. In the method described before the extinction is registered during this rising and falling of temperature. There were examined p-azoxy-anisol, p-azoxy-phenetol, anisaldazine and p-azoxy-benzoeacid-aethylester. In fig. 1 and 2 the curves of extinction are reproduced of two of these substances [1]).

[1]) p azoxy-phenetol and anisaldazine produced melting curves of the same character as p azoxy-anisol.

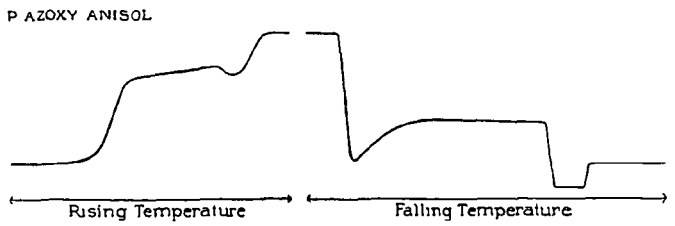

Fig. 1.

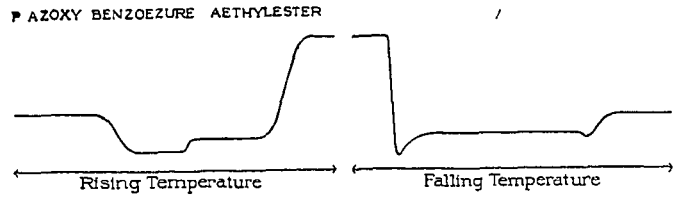

Fig. 2

When we consider these curves of extinction, the fact is obvious that the extinction in the liquid-crystalline condition, proceeding from melting of the solid phase ("ex-solid") is different from the liquid-crystalline condition formed by cooling of the isotropic liquid ("ex-liquid"). This different extinction is accompanied by an absolutely different aspect.

These differences are mostly conspicuous in the case of p-azoxy-benzoe-acid-aethylester. With this substance the ex-solid condition is milky-opalescent, the ex-liquid grainy-opalescent, and when the preparation is heated the first condition always changes into the other at the same temperature. In the curve that transition appears by a leap-wise increase of the extinction. In the cooling-branch of the extinction-curve we only found an indication that at the sudden transition from liquid into liquid-crystal during a short period the ex-solid state might inconstantly have existed as instable, however by cooling very quickly we succeeded in obtaining durably the ex-solid condition from the liquid state.

With the three other substances examined, also a very obvious difference in extinction between the ex-liquid state and the ex-solid state (vid. fig. 1) shows itself, but contrary to p-azoxy-benzoe-acid aethylester, with these three substances of both liquid-crystal conditions the ex-liquid one is the most opaque.

Another particularity of the extinction-curves are the different bag-shaped drops.

The drops at the transition from liquid-crystal into isotropic-liquid and the reverse are not real, i.e. they have no meaning for the extinction as such. They are caused by the melting (resp. the getting turbid) not occurring simultaneously in all parts of the substance.

By the great difference in index of refraction of the isotropic and of the crystalline liquid, phenomena of refraction occur at the limit, and therefore the image of the NERNST-burner is broadened, deformed or shifted. A temporary weakening of the thermo-current, therefore a drop of the extinction-curve will be the consequence of this.

In our opinion the slow rise of the extinction-curve when the liquid-crystalline phase has proceeded from the isotropic-liquid phase (the continuation of the bag-shaped drop) can be explained by the fact that at the sudden turbidily a very disorientated state appears, on which only very slowly the directing influence of the glass makes itself felt.

Sometimes the extinction-curve of p-azoxy-anisol showed a peculiar drop at the transition from liquid-crystalline into solid. In fig. 1 this drop is represented. It occurred especially when the preparation had been examined in a very thin layer and was then strongly undercooled. At macroscopic examination it appeared to us that under these conditions greenish-yellow crystals were formed, which we soon could identify with the meta-stable solid phase already described by LEHMANN in 1890. [1])

Finally from our curves the dependence on the temperature of the extinction can be read. If we define ourselves to p-azoxy-anisol (fig. 1) then a strong dependence on the temperature may be stated in the ex-solid condition, in such a way that at rising temperature the extinction decreases. Also the reverse effect, increase of the extinction at falling temperature, could be established with certainty for the ex-solid condition. In the ex-liquid condition the dependence on the temperature is very much less evident, without any doubt it exists however in the same sense as in the case of the ex-solid state. Already in 1902 SCHENCK has performed measurings on this question with the aid of the spectrophotometer of GLAN, and has only reached a negative result. But he examined the extinction for yellow light, whereas our method gives the extinction for a mixture of rays in which ultra-red dominates.

So we thought it useful to examine the dependence on the temperature also in another range of wave-lengths. We chose as such the photographically active rays. The image of the NERNST-burner was for that purpose formed instead of on the vertical slit of the thermopile on the horizontal slit of a photographical registration-

[1]) Perhaps it is well to remark that we succeeded in establishing the reversible melting-point of this greenish-yellow phase at 108°. VORLÄNDER as well as SCHENCK doubt the validity of an analogeous result of LEHMANN.

apparatus. The line thus registrated on the sensitive paper enables us at once to judge by its breadth and blackness of the extinction of the substance.

As well with ex-solid as with ex-liquid the temperature appeared to exercise a plainly perceptible influence on the extinction, but the direction of the effect is for the photographically active rays just the reverse as for the ultra-red rays, i.e. for the short waves at rising temparature the extinction increases. So, as the effect of the temperature in the case of strongly differing wave-lengths has a right to a different sign, the apparent contradiction between the result of SCHENCK and that which follows from our extinction-curves is explained.

§ 2. *The influence of a magnetic field on the extinction.*

The fact that there appeared to exist two liquid-crystalline states, made it desirable to extend our research on the influence of magnetic field to the second states. Besides the magnetic effect on the three remaining substances we disposed of, had to be examined. [1])

With p-benzoë-acid azoxy aethylester no influence could be established, not even with the strongest fields we could excite, (ca. 1100 GAUSS). An examination with still stronger magnetic field is being prepared now. Anisaldazine experiences a strong influence as well in ex-solid as in ex-liquid state. With p-azoxy-phenetol the influence is much weaker, but could still be observed by us with certainty in both states. The character of the effect is for both substances principally the same as for p-azoxy-anisol.

The magnetic effect of p-azoxy-anisol in the ex-solid condition is represented by the figures 3 and 4. For sake of comparison we

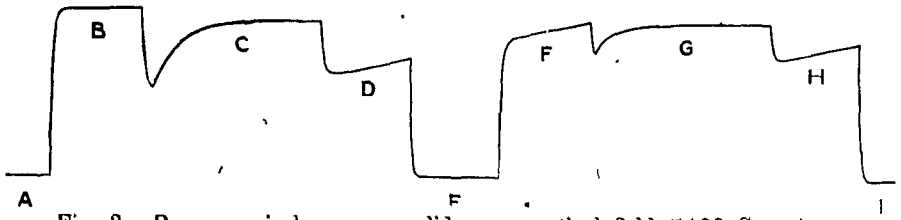

Fig. 3. P-azoxy-anisol ex-solid vertical field (1100 Gauss).

[1]) In our first communication we mentioned the preponderating influence the nature of the adjacent surface has on the magnetic effect. In order to examine this influence more closely we have registered the magnetic effect, for substances of different thickness, put between glass whether or no chemically cleaned, or enclosed between mica. The differences found, however, were only of quantitative character.

reprint from our first communication the figures 5 and 6, which represent the effect of equally strong magnetic fields on the ex-liquid state. [1])

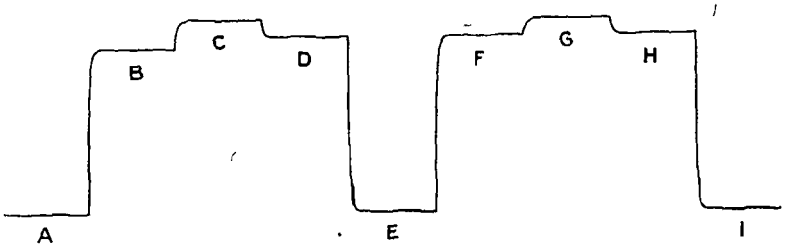

Fig. 4. P-azoxy-anisol ex-solid horizontal field (1100 Gauss).

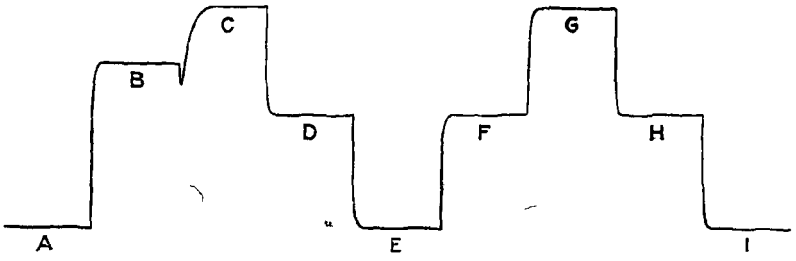

Fig. 5 P-azoxy-anisol ex-liquid vertical field (1100 Gauss)

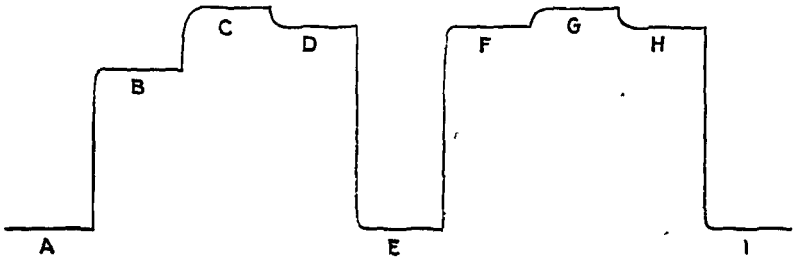

Fig. 6. P-azoxy-anisol ex-liquid horizontal field (1100 Gauss).

A comparison between figures 3 and 5 and also between figures 4 and 6 shows that the magnetic effect for ex-solid indeed differs from that for ex-liquid. That however the difference is greatly quantitative appears when fig. 3 is compared to fig. 7. This figure too is reproduced from our former communication and represents the influence of a *weak* vertical field on the ex-liquid state.

[1]) For the meaning of these figures and the method of registration we refer to our first communication.

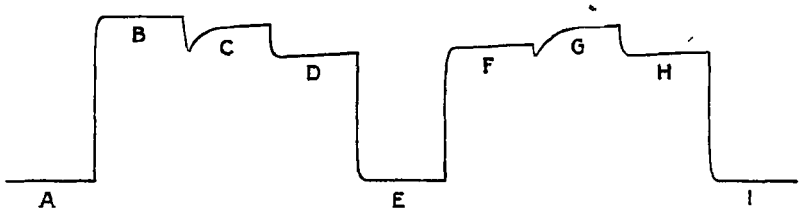

Fig 7. P-azoxy-anisol ex-liquid vertical field (300 Gauss).

The different magnetic effect in the two states consequently can be described as follows: a strong field acts analogeously on ex-solid as a weak field on ex-liquid.

Finally we shall mention a magnetic effect of a particular kind. A horizontal field causes *lasting* clearing up as well in the ex-solid as in the ex-liquid state a. In our former communication we explained this diminishing of the extinction by the fact that the particles are directed to a high degree. Now it seemed to us of importance to examine how a vertical field would *disturb* this order. Figures 8 and 9 show this disorientating influence of a vertical field on ex-liquid and ex-solid, when the substance has first been exposed to the effect of a horizontal field.

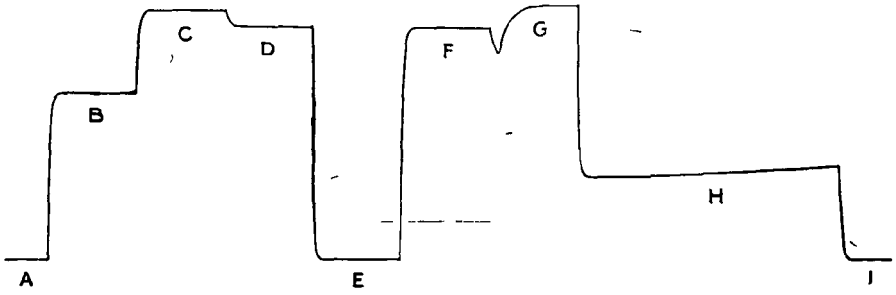

Fig 8. P-azoxy-anisol ex-liquid first horizontal field, then vertical field.

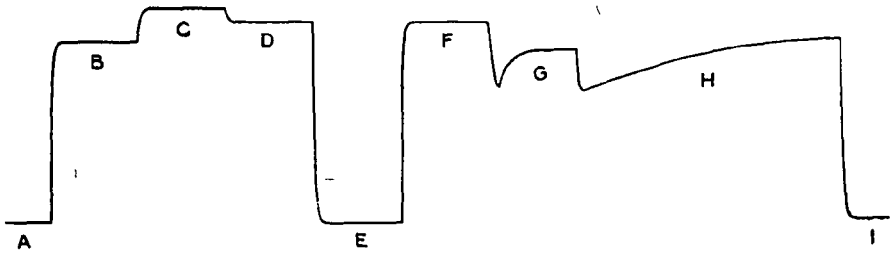

Fig. 7. P-azoxy-anisol ex solid first horizontal, then vertical field.

The explication we gave in our first communication of the magnetic effect, can be transmitted unchanged to the phenomena described above. The different degree of extinction in ex-liquid and ex-solid and the different influence thereupon of a magnetic field, we are inclined to ascribe to the fact that the little parts have a *different directability* in the ex-liquid state and in the ex-solid state.

SUMMARY.

The extinction of p-azoxy-anisol, p-azoxy-phenetal, anisaldazine and p-azoxy-benzoë-acid-aethylester is examined in its dependence on the temperature.

It appears that two different liquid-crystalline states exist ("ex-solid" and "ex-liquid") which possess each a different extinction, and which undergo in a different degree the influence of a magnetic field.

The coefficient of temperature of the extinction appears to be negative for ultra-red and positive for ultra-violet.

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Physical Laboratory
Institute for Theoretical Physics.