

*Citation:*

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In this integral the function  $F(r_{hk})$  is zero without the sphere of action, therefore this integral has only to be extended to this region.<sup>1)</sup> Thus the abnormal character, stated by KAMERLINGH ONNES and KEESOM, cannot be explained by a function of disturbance as a consequence of the accidental deviations.

**Physics.** — "*Contributions to the research of liquid crystals.*" By Dr. W. J. H. MOLL and Prof. L. S. ORNSTEIN. (Communicated by Prof. W. H. JULIUS).

(Communicated in the meeting of October 28, 1916).

1. *The extinction of para-azoxyanisol in the magnetic field.*

VOIGT has devoted a circumstantial report to the liquid crystals in the *Physikalische Zeitschrift* XVII 1916. In this report he points specially to the fact that a great uncertainty still exists on the influence exercised by a magnetic field on the extinction. For this reason we further examined the extinction.

We will provisionally explain our method in this communication, and mention some of the results attained, and add a few remarks on a possible explanation of these results.

§ 1. *Method of observation.*

The extinction was measured with the aid of the galvanometer and the thermopile described by one of us formerly.<sup>2)</sup> These sensitive instruments have the great advantage of indicating quickly within two seconds, and so they enable us to follow the changes in the liquid crystals proceeding slowly, but nevertheless so quickly that they must necessarily escape the observer's attention.

These very changes however are of great interest in order to understand the phenomena under consideration.

The substance is heated in a small electric oven, consisting of a strip of copper AA coiled at the two ends with resistance wire. By regulating the current sent through these coils each desired

<sup>1)</sup> According to the explicit calculation of  $g$ , executed by one of us, the solid character is denoted by  $r^{-1} e^{-kr}$ , where  $k = 0$  for the critical point. Comp. ZERNIKE, The clustering tendency of the molecules in the critical state and the extinction of light caused thereby. These Proc. XVIII p. 1520.

<sup>2)</sup> W. J. H. MOLL. Proc. Kon. Acad. v. Wetensch. May and Nov. 1913: Mrs. KIPP and Sons were so kind as to put the apparatus at our disposal.

temperature, up to above the second point of transition may be attained. In the middle of the strip between the coils a circular pole appears, the edge of which carries a round piece of glass, a second piece of glass lying on top of it with a ring of paper between them. The substance is put in the space between the two glasses and the ring.

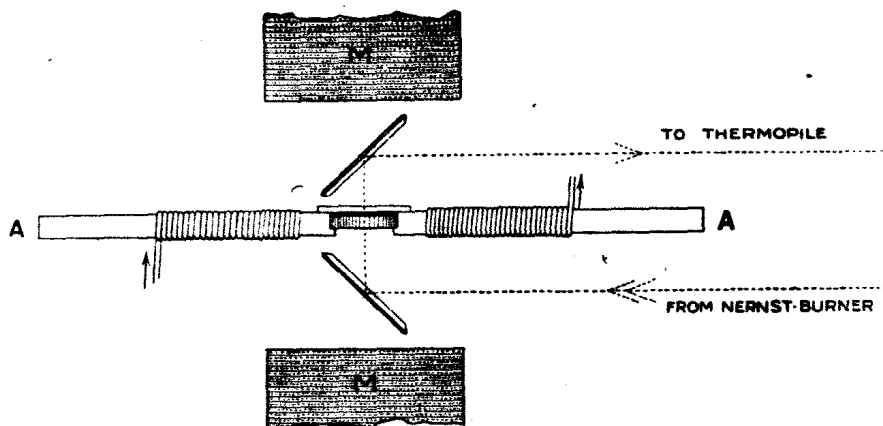


Fig. 1.

By the aid of two small mirrors a beam of light is sent through the substance from aside. During our measurements the small oven was placed horizontally between the poles  $M_1$  and  $M_2$  of a DUBOIS magnet. This magnet is fixed on a stand that allows a rotation round an axis lying in the direction of  $AA$ . Therefore, when the poles are placed as shown in fig. 1, the field of forces will be in a perpendicular position, parallel to the rays of light which penetrate the substance.

When the magnet is rotated  $90^\circ$  the lines of force are horizontal and will cross the rays of light perpendicularly.

A NERNST-burner connected to a battery of accumulators produces the required light. On the thermopile an image of the NERNST-burner is formed by a hollow mirror. The rays of light on this way from the hollow mirror to the thermopile penetrate the substance.

The slit in the thermopile has the same magnitude as the image of the NERNST-burner.

In the liquid-crystalline condition the opalescence of the matter confuses the image proportionally to the opacity. So the intensity of the thermocurrent gives us a measure for the extinction.

The galvanometer records were registered.

## § 2. The measurements.

It had appeared to us that the changes in the extinction caused by the magnetic field often persisted. So it became advisable to

reduce the matter to its original ("virginal") state before the beginning of every series of measurements, which was effected by heating it up to a little above the second point of transition. The current was kept constant during the measurements.

Every series of measurements progressed as follows.

A. The radiation of the NERNST-burner is intercepted and consequently the galvanometer records the zero-condition.

B. The radiation is admitted, the substance being in the virginal condition.

C. The magnetic field is excited.

D. The magnetic field is removed.

E. The radiation is intercepted.

F. The radiation is admitted.

G. The magnetic field is excited.

H. The magnetic field is removed.

I. The radiation is intercepted.

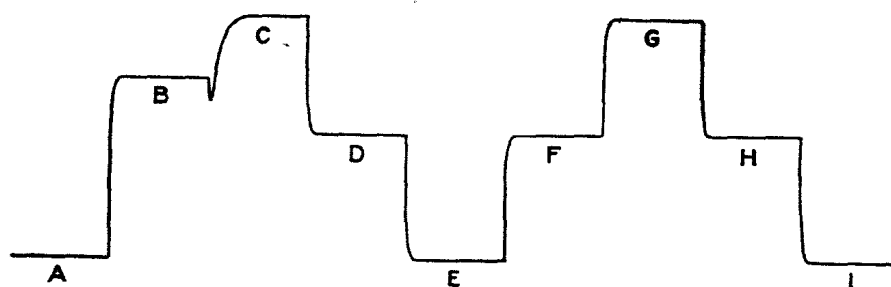


Fig. 2. Perpendicular magnetic field of 1100 Gauss.

The figures 2 and 3 show the phenomenon for a field of 1100 Gauss.

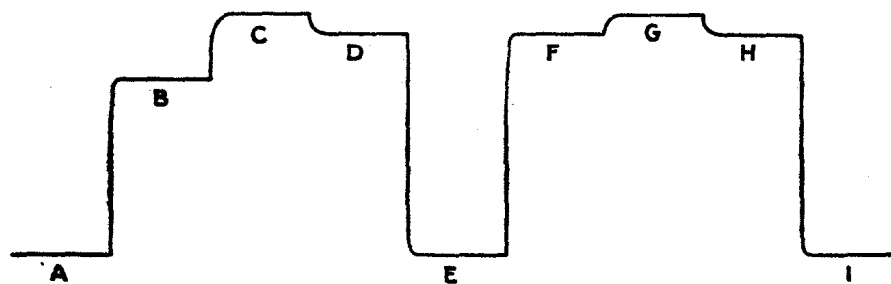


Fig. 3. Horizontal magnetic field of 1100 Gauss.

In order to understand their meaning it may be stated that to magnify the ordinates implies the diminishing of the extinction.

The difference between the two phenomena is very characteristic. Whereas the perpendicular field excited for the first time a temporary increase of the extinction, nothing of the sort is observed

when the horizontal field is excited. Whereas after the breaking up of the perpendicular field the extinction is much larger than in the virginal state, the extinction is much smaller than before after the removal of the horizontal field. This condition of diminished extinction seems to be stable, it holds during some hours; the condition of increased extinction, as is left after removal of the perpendicular field, is of a transitory nature, gradually the virginal state being restored.

We expected from theoretical considerations which will be treated more fully hereafter that the effect of the temporary increase of the extinction when a vertical field is excited would appear more clearly in the case of weaker fields (compare the temporary drop of the curve between B and C in fig. 2). At the same time we expected that in the case of a sufficiently weak perpendicular field it might occur that the extinction of the field is on, would remain larger than before.

The experiments confirmed our expectation completely as is shown by the following figures

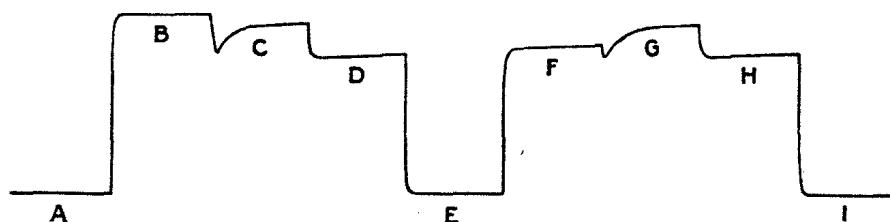


Fig. 4. Perpendicular field of 300 Gauss.

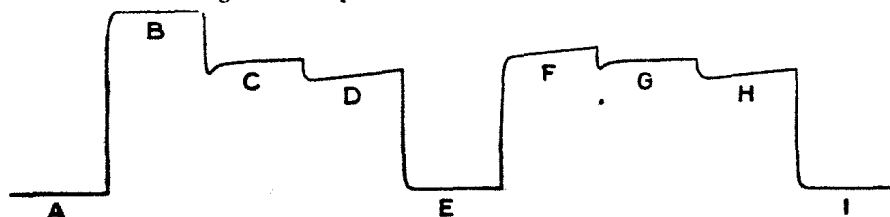


Fig. 5. Perpendicular field of 100 Gauss.

We have also examined whether commutation of the magnetic field has any influence on the extinction, but we could not state such an influence.<sup>1)</sup>

<sup>1)</sup> Considering the very different character which the influence of a magnetic field on the same preparation may have, it is easily understood that various observers, by visual examination of the extinction have come to quite contradictory results. Moreover, small impurities of the preparation and especially the state of the surface of the glass are of decisive influence. A further research on the influence of the surrounding surfaces is being prepared; we only want to remark that we performed these measurements with plates of glass which were not chemically cleared.

§ 3. *Attempt at a theory of the phenomena.*

Finely we want to make a few remarks containing a provisional elementary explanation of the observed phenomena, reserving to give afterwards a more mathematical theory.

We suppose that the molecules of para-azoxyanisol, as may be expected from the chemical constitution are of an oblong form, and that therefore a magnetic field will try to place their longitudinal axes parallel to the field.

Further we suppose the particles to undergo a directing couple from the glass-wall, so that the wall tries to direct them parallel to itself. The forces proceeding from the wall extend like all molecular influences only to a very small distance from the wall.

Let us admit further, that the particles influence each other,<sup>1)</sup> in such a way that particles try to turn their axes reciprocally parallel.

The result of the influences is that with given temperature and pressure two phases in equilibrium are possible, one of them being very sensible to a cause of outward direction, and the other not being so.

In the first (the liquid crystalline) phase, there will appear in consequence of the orientating influence of the molecules on each other regions, wherein the axes of the molecules are grouped around a direction of preference. In several parts of this phase the directions of preference will be divided accidentally, and as a consequence of irregular refraction such an unarranged condition will be opalescent.

In the other phase the effects of the molecules cannot cause suchlike directed regions and therefore there is no extinction. We hope to come back to the thermodynamics of these phases as well theoretically as experimentally.

Besides the forces mentioned above the influence of the molecular motion, which is always opposed to the directing effect has to be taken into consideration. In the following we will not go into the details of the optical problem of extinction, but we will use in our consideration the plausible supposition that the extinction will be the smaller according as the arrangement is more regular.

Let us begin our explication at the virginal state. By the influ-

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<sup>1)</sup> These latter influences cause a clustering tendency. For, if a molecule is at a certain point with a given direction of axis, this fact will influence the probability of the direction of the axis of a neighbouring molecule. Consequently the problem with which we are occupied at present shows an analogy with the problem of the clustering tendency in the neighbourhood of the critical point, treated by ZERNIKE and one of us,

ence of the wall, added to the reciprocal effect of the molecules (correlation) the axes will show a preference for lying in horizontal planes. In the horizontal plane itself, however, each direction is equivalent.

Now, when we excite a perpendicular magnetic field, it tries to turn the molecules in a direction perpendicular to the plane of preference in virginal state; and the first result will be a disturbance of the order existing in the virginal state and therefore an increase of the extinction. Soon however a magnetic field of sufficient intensity will bring about a higher order i. e. a smaller extinction as is shown at C in fig. 2. A weak magnetic field however will only diminish the originally existing order i. e. increase of the extinction (see fig. 5). But a strong magnetic field has also to overcome the resistance of the reciprocal influence between the originally horizontally directed particles; therefore the slow rising towards C (fig. 2) is quite intelligible; whereas after F (fig. 2) a quicker rising can be explained, as the state of the matter there is such that no preference for directions parallel to the wall of glass is shown even at a very small distance from it.

Let us now proceed to consider the case represented in fig. 3. In the virginal state (B) the molecules were lying by preference in the horizontal planes, the exciting of the horizontal magnetic field (C) not only increases this preference, but moreover calls into existence in that horizontal plane a direction of preference. From this it follows that there can be no question of a temporary rising of the extinction at the exciting of a horizontal field.

The different conduct at the removal of the field can be explained too.

After the removal of the vertical field (*D* and *H* in fig. 2) the heat motion has free play as no direction of preference exists at some distance of the walls. The directing influence of the wall restores but slowly the original order by means of the mutual influences of the molecules. In the mean time (compare *FG* in fig. 4) if the field which has disturbed the order, is weak, the wall will sooner be able to recover the original state. Totally different is the case after the removal of the horizontal field (*D* and *H* in fig. 3). Here the influences proceeding from the wall, united with the mutual action of the molecules, practically maintain the higher order originated by the field.

The fact that the commutation of the magnetic field has no influence on the extinction shows that the particles themselves possess no polar peculiarities. A research which Mr. ROCHELL is working out

in the Physical Laboratory, had proved already that the substance we had under consideration is paramagnetic.

For the moment these principal points may suffice. Perhaps we will discuss these questions when publishing further experimental results.

We gladly use the occasion to thank Prof. VAN ROMBURGH for his kindness in putting his preparation at our disposal.

*Summary.*

1. A new method is described to measure with the aid of thermopile and galvanometer the extinction of liquid-crystalline substances.

2. The very different influence on the extinction of a vertical (longitudinal) and a horizontal (transversal) magnetic field is traced.

3. An explanation of the observed phenomena is drawn in outline whereby the principal supposition is that the wall of glass directs the particles in planes parallel, directs then according the lines of force.

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*Utrecht, October 1916.*

**Physics.** — "*The clustering tendency of the molecules at the critical point*". By Prof. L. S. ORNSTEIN. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of May 27, 1916).

In a former communication by Dr. F. ZERNIKE and the author<sup>1)</sup> the arrangement of the molecules in space using a new method of probability is described, more accurately than this was possible in the considerations of VON SMOLUCHOWSKI and EINSTEIN; by this method it was also possible to calculate the opalescence at the critical point itself, which was impossible with the formulas of KEESOM-EINSTEIN.

We introduced a function  $f$ , defined in the following way. Suppose that space is divided into a great number of elements of volume  $dV_0, dV_1, \dots, dV_s$ , etc. The numbers  $r_0, r_1, r_s$ , etc. may represent the deviations of the average number of molecules in these elements. Then, if the *deviations* in all the surrounding elements of the working sphere are *given* ( $r_1, r_s$ , etc.), the average deviation in the element  $dV_0$  may be represented by:

<sup>1)</sup> Accidental deviations of density and the opalescence at the critical point of a single substance. These Proc. XVII, p. 793, 1914.