The Influence of Molecular Constitution and Temperature on Magnetic Susceptibility

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III. *The Influence of Molecular Constitution and Temperature on Magnetic Susceptibility.*

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CONTENTS.

INTRODUCTION.

THE present communication is a continuation, and in some respects a completion, of several preliminary researches which have been published from time to time during the past three years.

On the hypothesis that a molecule may be distorted by the near approach of its neighbours, it has been shown* how the presence of molecular groups, which vary in

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* 'Proc. Camb. Phil. Soc.,' vol. XVI., p. 486, 1912.

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complexity with change of temperature, may modify the temperature coefficient of the magnetic property of a substance. The large change of molecular constitution during the transition from the liquid to the crystalline state should therefore be accompanied by a sudden change of the magnetic property.

The relation between molecular complexity and specific diamagnetic susceptibility χ_D may be written,* on the above hypothesis, in the form

$$\chi_D = \frac{1}{H} \Sigma n_p \,.\, \Delta M_p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where ΔM_p is the total diamagnetic moment produced in a complex of type p by the application of an external magnetic field H. n_p is the number of complexes of the type p per gramme. During a transition from one degree of complexity to another, several types of complexes may coexist. The summation is extended over all such types.

The corresponding expression for the specific paramagnetic susceptibility χ_P is

$$\chi_P = \Sigma \, \frac{n_p \,.\, c_p}{\vartheta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

where c_p is the Curie constant per particle of type p. Since, in the above equations, n_p is a function of the temperature, characteristic for each substance, it is probable that the irregularities of the temperature susceptibility curves obtained by Prof. HONDA,† Prof. DU BOIS,‡ and Mr. OWEN§ are due to the presence of this variable factor.

The application of (1) and (2) to the case of aqueous solutions of salts of the ferromagnetic elements, for which n_p is approximately a linear function of the temperature, gives indirect evidence of the existence of molecular complexes in solution‖ (see also footnote, p. 134 *infra*).

It is intended in the present research to test more fully the hypothesis stated above, which is involved in (1) and (2), by investigating the magnetic susceptibility of a number of substances over a wide range of temperature. To simplify the problem, the substances chosen are all diamagnetic and consist chiefly of organic compounds. The small electrical conductivity of the latter allows us to neglect any effect which may arise from the presence of moving intermolecular charges.¶ The diamagnetic property will therefore be a concern of the internal structure of the

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* *Loc. cit.*, p. 489.

† 'Ann. der Phys.,' IV., 32, p. 1027, 1910.

‡ 'Versl. Kon. Ak. v. Wetensch.,' Amsterdam, XII., p. 596, 1910.

§ 'Versl. Kon. Ak. v. Wetensch.,' Amsterdam, XIV., p. 637, 1912.

‖ 'Proc. Camb. Phil. Soc.,' vol. XVII., p. 65.

¶ Sir J. J. THOMSON, 'Rapports du Congrès Int. Paris,' 1900, vol. III., p. 148; also SCHRÖDINGER, 'Sitz. d. k. Akad. Wien,' CXXI., p. 1305, 1912. [See, however, the article by H. A. LORENTZ, 'Mathematische Vorlesungen an der Universität Göttingen,' VI., p. 189, 1914.—*Note added March, 1914.*]

molecule and of such modification of that structure as is produced by the mutual actions between the molecules.

Thus stated, the diamagnetic property of a substance depends upon the molecule as a whole. The above hypothesis postulates no definite structure of the atom or molecule beyond that it is capable of assuming a slightly distorted configuration due to the influence of neighbouring atoms or molecules.

The interpretation of the experimental facts (described in Part I. of this communication) by means of the electron theory of magnetism will be withheld until the results have been discussed from the molecular standpoint.

PART I.

(1) THE MEASUREMENT OF MAGNETIC SUSCEPTIBILITY AT AIR TEMPERATURE.

The magnetic potential energy of a body placed in a magnetic field may be written

$$W = -\tfrac{1}{2}\chi M H^2$$

where χ is the specific susceptibility of the substance, M the mass of the body, and H the intensity of the magnetic field. For a small displacement of the body,

$$\delta W = -\chi M H \delta H.$$

If the body be so suspended that its displacement causes work to be done on the suspended system against a mechanical force, F, acting through a distance, δr, we have

$$\delta W + F \,.\, \delta r = 0.$$

Therefore

$$F = \chi M H \frac{\delta H}{\delta r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In the present experiments the body, which was spherical, was placed with its centre at P (fig. 1) with regard to the pole pieces A and B. The mechanical forces acting on the body are therefore by (3)

$$X = \chi M \left(H_x \frac{\partial H_x}{\partial x} + H_y \frac{\partial H_y}{\partial x} + H_z \,.\, \frac{\partial H_z}{\partial x} \right)^* \quad . \quad (4)$$

along Ox, with similar expressions for the forces Y and Z, acting along Oy and Oz. If the body were truly spherical, with its centre at P, the forces Y and Z would be zero. In practice this is never the case, and Y and Z, although small, are not zero. Since, however, in these experiments

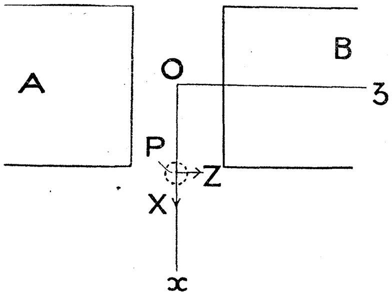

FIG. I

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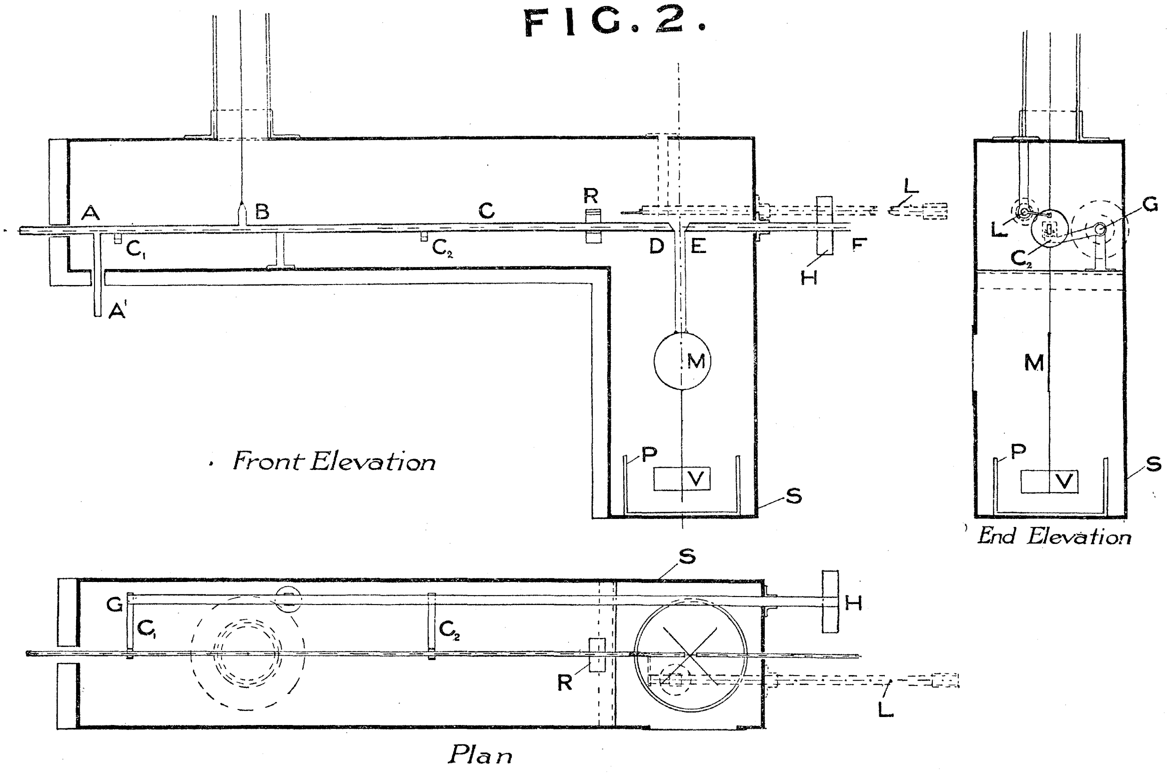
* It should be noted that the term involving H_x is large in comparison with the terms involving H_y and H_z.

the resistance to motion in the directions Oy and Oz is great, the disturbance of the equilibrium of the suspended system, due to these forces, may be neglected.

The method of measuring the force X, or rather the method of comparing X for different substances, is shown in fig. 2. The torsion arm, ABCD, is made of aluminium. The angle through which the torsion arm was twisted when the magnetic field was excited was measured by the double suspension mirror DME. The dash-pot P contained a mixture of paraffin-oil and heavy mineral oil in which four vanes, V, hung. The arm EF is the extremity of a three-dimensional adjustment stage. The brass case S, which surrounded the torsion arm and suspension mirror, was rigidly attached to a brass carrier which was provided with a screw motion and slid upon rails. These rails were screwed to a heavy slate bed which was supported by two large blocks of stone. To prevent the transmission of vibrations to the suspended system from outside, two layers of indiarubber were inserted between the stone blocks and the slate bed. The rod GH provided with the cranks, C_1 and C_2, was used to rest the torsion arm while the substance under investigation was being attached to the end A (see plan and end elevation). To preserve balance of the torsion arm when different masses of substance were used, a rider R was provided which could be moved by the rod L into different positions along the torsion arm. A very fine phosphor-bronze wire, attached to the projection B, suspended the movable parts of the system.

FIG. 2.



The displacement of the substance, due to the action of the force X, was usually about $\frac{1}{200}$ mm. This will not appreciably alter the sensitiveness of the bifilar suspension, and, therefore, the use of torsion to bring the body back to its initial position is not necessary.

The substance was placed in a small glass phial (fig. 3). Form (a) was used for liquids, form (b) for both solids and liquids; (a) was provided with inlet and outlet tubes of fine bore, which admitted only a minimum contact of the substance under investigation with the air, and thereby reduced as much as possible any effect due to evaporation. The stopper consisted of a short piece of indiarubber tubing closed at one end by a glass plug. By this device the bulb could be thoroughly cleaned and easily filled. To fill the phial, the stopper was removed and the liquid drawn into the bulb. By tilting the bulb slightly, the liquid ran out of the shorter limb and the stopper was placed in position. The liquid in the longer limb was removed by means of a fine capillary tube. In this way it was possible to obtain a sphere of the liquid under investigation. This type of phial has been used with some substances which are crystalline at ordinary temperatures by filling the phial in a high temperature enclosure. The type (b) was devised primarily for use with crystals which could not be introduced into (a). It has been used for liquids as a check against any effect which might arise from the motion of the liquid in the lower limb of type (a).

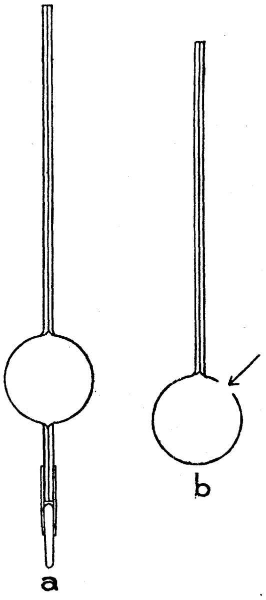


FIG. 3
Crystals introduced at arrow

Let d_1 be the deflection due to phial and contained air.
,, d_2 ,, ,, ,, ,, water.
,, d ,, ,, ,, ,, substance.
,, χ_a ,, specific susceptibility of air.
,, χ_w ,, ,, ,, ,, water.
,, χ ,, ,, ,, ,, substance.

Now $X = pD$, where D is the deflection on the scale, and p is some constant, provided the deflection of the torsion arm is small. Hence from (4)

$$p(d_2-d_1) = (\chi_w m_w - \chi_a m_a)\left(H_x \frac{\partial H_x}{\partial x} + H_y \frac{\partial H_y}{\partial x} + H_z \frac{\partial H_z}{\partial x}\right), \quad . \quad . \quad . \quad (\alpha)$$

$$p(d-d_1) = (\chi M - \chi_a M_a)\left(H_x \frac{\partial H_x}{\partial x} + H_y \frac{\partial H_y}{\partial x} + H_z \frac{\partial H_z}{\partial x}\right) \quad . \quad . \quad . \quad . \quad (\beta)$$

if the phial be placed in the same position relative to the pole pieces. Here M is the mass of the substance taken, M_a that of the air which fills the same volume, m_a is the mass of air which fills the volume m_w occupied by the water. In all the experiments described below the current was kept constant at 8·6* amperes, to within 1 part in 500. Hence the factor involving the magnetic field on the R.H.S. of (α) and (β) is constant, and we get by division

$$\chi M = \chi_a M_a + (\chi_w m_w - \chi_a m_a) \frac{d-d_1}{d_2-d_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\gamma)$$

The specific susceptibilities of water χ_w and air χ_a were taken as $7 \cdot 25 \times 10^{-7}$ and 210×10^{-7} (at 20° C.) respectively.

(2) Experiments Down to the Temperature of Liquid Air.

The apparatus designed for the measurement of susceptibility at low temperatures is shown in fig. 4.

The phial P, supported from the torsion arm at A′, was surrounded by a thin-walled glass tube G, the latter being sealed at the lower end and supported by the cork flange CC. Conduction of heat from or to the torsion arm was prevented by inserting a strip of wood W between the phial and the projection of the torsion arm. A copper cylinder N, which just fitted into the glass tube, served to keep uniformity

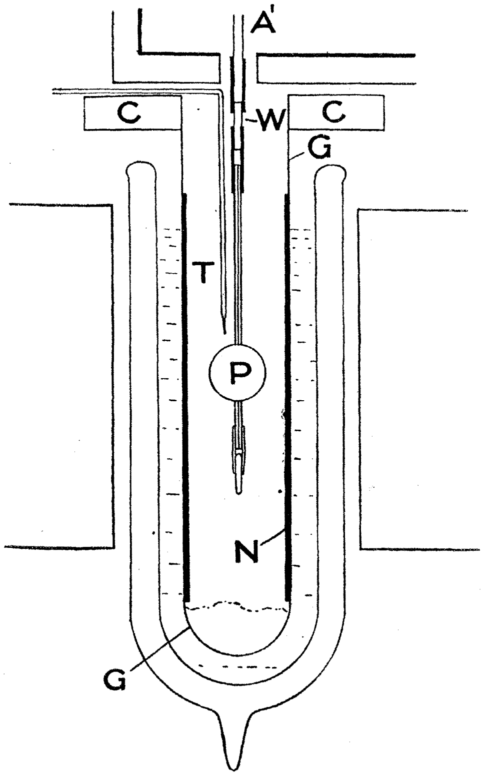


FIG. 4

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* In the last two experiments the current was increased to 9·0 amperes.

of temperature throughout the volume occupied by the phial. A layer of phosphorus pentoxide was placed at the bottom of the glass tube to absorb any moisture and thereby prevent the deposition of water on the phial during cooling. The liquid air tube was brought up from below into the position shown. The flange of cork CC was very broad and prevented any convection currents from disturbing the equilibrium of the suspended system. A copper German-silver thermocouple T was used to measure the temperature, one junction being situated just above the phial. The thermocouple circuit included a delicate D'Arsonval galvanometer. A slight kick, due to induction effects, was observed when the magnetic field was excited. This quickly died away and readings of the deflection of the phial and temperature were taken simultaneously..

(3) EXPERIMENTS UP TO 250° C.

The method of suspension used is essentially that devised by CURIE,[*] and fig. 5 is a diagram of the apparatus, looking along the direction of the axis of the electro-magnet. The phial which was used in these experiments was open above and closed below, as shown at Q. The suspension rod, ASSS, was made of brass and was

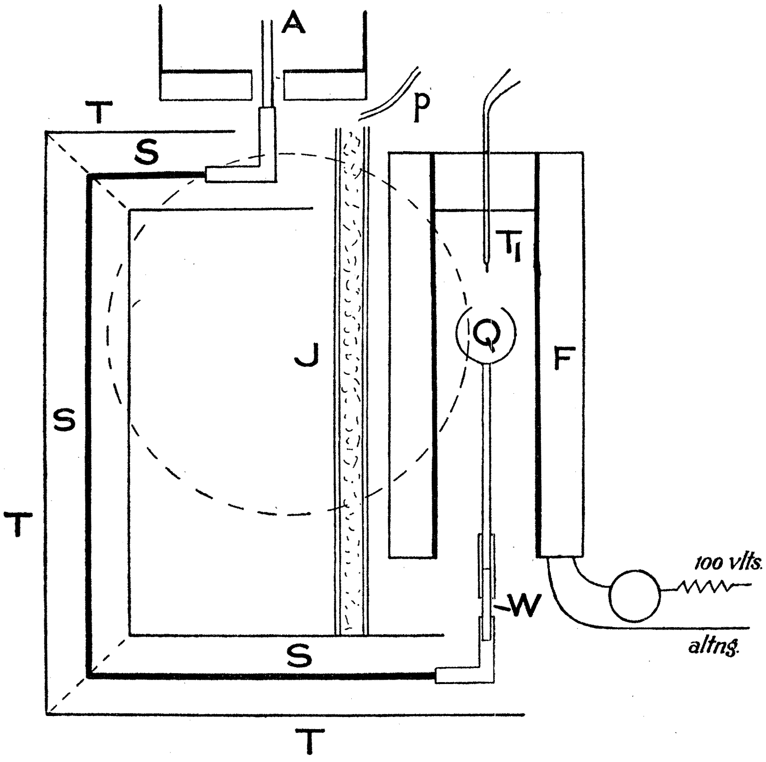

FIG. 5

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[*] 'Ann. de Chim. et de Phys.,' VII., vol. 5, p. 298, 1895.

surrounded by glass tubes, TTT, to prevent disturbances due to air currents. A screen J, formed of two pads of asbestos board, with an intervening layer of cotton-wool kept wet by water from the pipe p, served to prevent disturbances due to air currents from the walls of the electric furnace F. The temperature attained was measured by the copper German-silver couple, T_1 fitted into the top of the furnace, as shown. A support of wood W was inserted between the phial and the main brass suspension to prevent conduction of heat and the accompanying thermal disturbances. In both series of experiments the whole apparatus had to be surrounded with pads of cotton-wool to keep a steady zero.

(4) Discussion of Possible Errors.

In the measurement of magnetic properties over wide intervals of temperature it is necessary to consider the effect of a number of possible sources of error and these will now be considered.

(a) *The Effect of Alteration of Volume during Fusion or Crystallization on the Volume of Air Displaced by the Substance.*

We shall denote the specific susceptibility of the liquid by χ_l, that of the crystals by χ_c. From equation (γ), by division,

$$\frac{d_c - d_1}{d_l - d_1} = \frac{\chi_c M - \chi_a (M_a + \partial M_a)}{\chi_l M - \chi_a M_a} = 1 + \frac{M\partial\chi - \chi_a . \partial M_a}{\chi_l M - \chi_a M_a}$$

$$= 1 + \frac{M . \partial\chi}{\chi_l M - \chi_a M_a} + \frac{\chi'_a . \partial V_a}{7{\cdot}0 \times 10^{-7*}} \text{ where } \partial\chi = \chi_c - \chi_l.$$

∂M_a is the additional mass of air displaced owing to the change of volume of the substance in passing from one state to another, ∂V_a the corresponding change of volume, and χ'_a is the susceptibility of air per unit volume. ($0{\cdot}25 \times 10^{-7}$).

For most substances, $\partial V_a \doteqdot 0{\cdot}1$,[†] if $V_a = 1$, *i.e.*, for the volume of substance experimented on in this research. Hence the variation of deflection due to this cause is $0{\cdot}25 \times 10^{-7} \times 0{\cdot}1/7{\cdot}0 \times 10^{-7}$, or 4 parts in 1000, and is beyond the limit of experimental accuracy. In the above it is assumed that there is no appreciable change of temperature of the system while fusion takes place, so that no effect due to variation of χ_a with temperature enters.

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[*] $-7{\cdot}0 \times 10^{-7}$ is taken as a mean value of $\chi_l . M - \chi_a M_a$.

[†] *Vide* G. Tammann, 'Kristallisieren u. Schmelzen,' Leipzig, 1903, pp. 204 *et seq.* The values of ∂V in cubic centimetres per cubic centimetre for some of the substances investigated in this research are:—

Benzene, 0·10;
Benzophenone, 0·09;
Nitrobenzene, 0·08.
Naphthalene, 0·14;
Mercury, 0·036.

(*b*) *The Effect of Variation of Temperature on χ_a and the Influence of Thermal Expansion over the Wide Range of Temperature used in these Experiments.*

Since

$$\frac{\partial}{\partial\vartheta}(\chi_a\mathrm{M}_a) = \frac{\partial}{\partial\vartheta}(\chi'_a\mathrm{V}_a),$$

and

$$\frac{\partial}{\partial\vartheta}(\chi_{c,l}\,.\,\mathrm{M}) = \frac{\partial}{\partial\vartheta}(\chi'_{c,l}\,.\,\mathrm{V}_{c,l}),$$

where the subscript c, l refers to the crystalline or liquid state, we have, dashing the deflections $d_{c,l}$ and d_1 for the higher or lower temperature,

$$\frac{d'_{c,l}-d'_1}{d_{c,l}-d_1} = \frac{\chi_{c,l}\,.\,\mathrm{M}-\chi_a\mathrm{M}_a+(\vartheta-\vartheta_0)\left[\frac{\partial}{\partial\vartheta}(\chi'_{c,l}\,.\,\mathrm{V}_{c,l})-\chi'_a\frac{\partial\mathrm{V}_a}{\partial\vartheta}-\mathrm{V}_a\frac{\partial\chi'_a}{\partial\vartheta}\right]}{\chi_{c,l}\,.\,\mathrm{M}-\chi_a\mathrm{M}_a},$$

which is the ratio of the deflections due to thermal expansions of the substance and air, and the variation of the susceptibility of the substance and air with temperature over an interval $\vartheta-\vartheta_0$. The necessary data for calculating the magnitude of this correction are not known for most of the substances which have been used in these experiments, but the largest factor involved is that due to the variation of density and susceptibility of the contained air. (The variation of the susceptibility of the air external to the phial is eliminated since the difference between $d'_{c,l}$ and d'_1 is taken.) For a temperature interval of 150° C., this factor amounts to 2 per cent.* (approximately) of the deflection, $d_{c,l}-d_1$, due to the substance. This error is, however, distributed over a range of 150° C. When the data of thermal expansion of the liquid and crystalline states are known, there will be two corrections, one for each state, which will be distributed throughout the range of temperature for which that state exists. It is to be observed that in this and the foregoing correction the thermal expansion of the glass and the variation of its susceptibility with temperature disappear, since they are equally involved in $d'_{c,l}$ and d'_1, the difference of which is taken.

(*c*) *The effect of displacement of the substance* (*liquid*), *as a whole, during cooling* was tested in two ways:—

(i) By actually displacing the liquid and repeating the observations;

(ii) By using, in some of the later experiments, a phial in which the displacement was prevented.

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* This factor is $\dfrac{-0\cdot25\times10^{-7}\times0\cdot00365\times150+1\cdot0\times0\cdot25\times10^{-7}/150}{7\cdot25\times10^{-7}}$.

(*d*) *Correction due to Dissymmetry of the Phial.*

The phials were nearly spherical and were placed with their centres as nearly as possible at the point P (fig. 1) where the force on them is a maximum and error due to displacement a minimum. The present measurements are differential ones, and provided the phial is replaced in the same position, no appreciable error can creep in from this source.

(*e*) *Latent Heat and Thermal Conductivity.*

The possible errors due to latent heat of change of state and thermal conductivity will be considered in more detail when the preliminary experimental curves are discussed.

(*f*) *Effect of Air Dissolved in the Substance.*

The error due to the presence of dissolved air in the substance is reduced to a minimum by heating the substance strongly. In those experiments performed at air temperature, an inappreciable amount of air was evolved on fusion. The error arising from this cause is negligibly small; for if a quantity of air equal in volume to that of the phial were expelled on fusion, it would account for only one-third of the actual effect found. But a small trace of air dissolved in the substance will, in all probability, remain in the substance if a considerably higher temperature is not sufficient to remove it; and although such a trace of air would have a small influence on an absolute measurement of the susceptibility, it will not appreciably affect the difference of susceptibility between the liquid and crystalline states.

(5) METHOD OF EXPERIMENT.

Fig. 6 shows how the value of the force acting on the suspended system varies with x, (a) when the phial is filled with air, (b) when it is filled with water. In each figure the dotted circle shows the size of the phial, and OM is a distance equal to the radius of the pole piece on the same scale. It will be seen that if the phial moves a small fraction of 1 mm. either towards or away from O, the resultant deflecting force remains very nearly constant, because one-half of the substance and phial has a slightly larger force acting on it, while the other half has a slightly smaller force.

The pole pieces were cylindrical, 8 cm. diameter and 4·65 cm. apart, so that the liquid air tube could be inserted for low temperature work and a small electric furnace for high temperature work. The advantage of large pole pieces is that the size of the phial is of less consequence. The hysteresis effect was not appreciable and the deflections were very consistent; a small increase of the current was readily followed by a small increase of the deflection. A Grassot fluxmeter showed that the field intensity was 3000 gauss for a current of 8·6 amperes.

Measurements were first made with the phial filled with air, water, and the substance, at room temperature. If the substance were a liquid it was cooled by liquid air, and after about 1 hour observations were begun and taken at a large number of temperatures as the substance gradually warmed to room temperature. A series of such observations occupied a period of 10 hours. Frequently the heating was too slow to allow the complete interval to be bridged during the day, and in such cases the curve was completed the following day. It will be observed that the lag in temperature of the substance behind the thermocouple, with such a small rate of cooling, will be small, and this lag will be uniform so long as there is no sudden change of the state of the substance. At temperatures considerably higher or lower than the temperature of fusion, the lag will generally be greater than it is at the fusion-point itself. It can easily be seen from the curves given below that the effect of this will be to lessen the difference of susceptibility between the liquid and the crystalline states. The actual difference of susceptibility cannot, therefore, be attributed to this source even if the lag were considerable. A similar series of readings was taken for the phial alone, which, corrected for the variation of the susceptibility of the contained air with change of temperature and subtracted from the readings obtained above, will give the variation of the specific susceptibility of the substance with temperature.

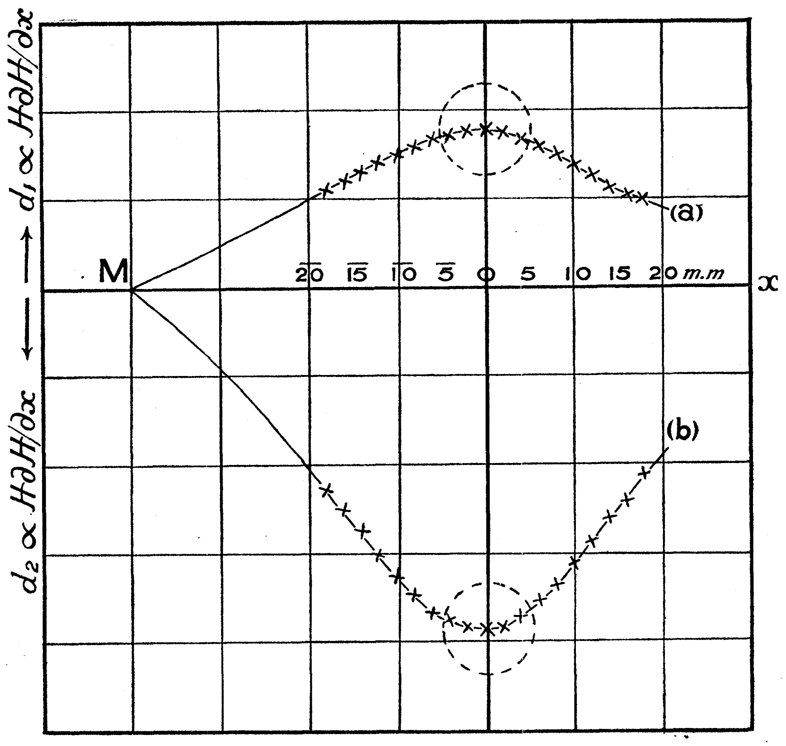

FIG. 6.

Similar experiments have been made, using hot water and other liquids in the Dewar tube, but it was difficult to take readings at temperatures higher than 100° C.

without the aid of the electric furnace and the inverted system of suspension, due to Curie, described above. With the latter, experiments have been made up to 250° C., and observations could be taken both with rising and falling temperatures.

(6) The Experiments.

A sufficiently large number of compounds has been investigated to establish a general theory of the dependence of magnetic property on the transition from the liquid to the crystalline state. Preliminary experiments were made on the phial filled (1) with air, (2) with nitrobenzene. The glass from which the phials were

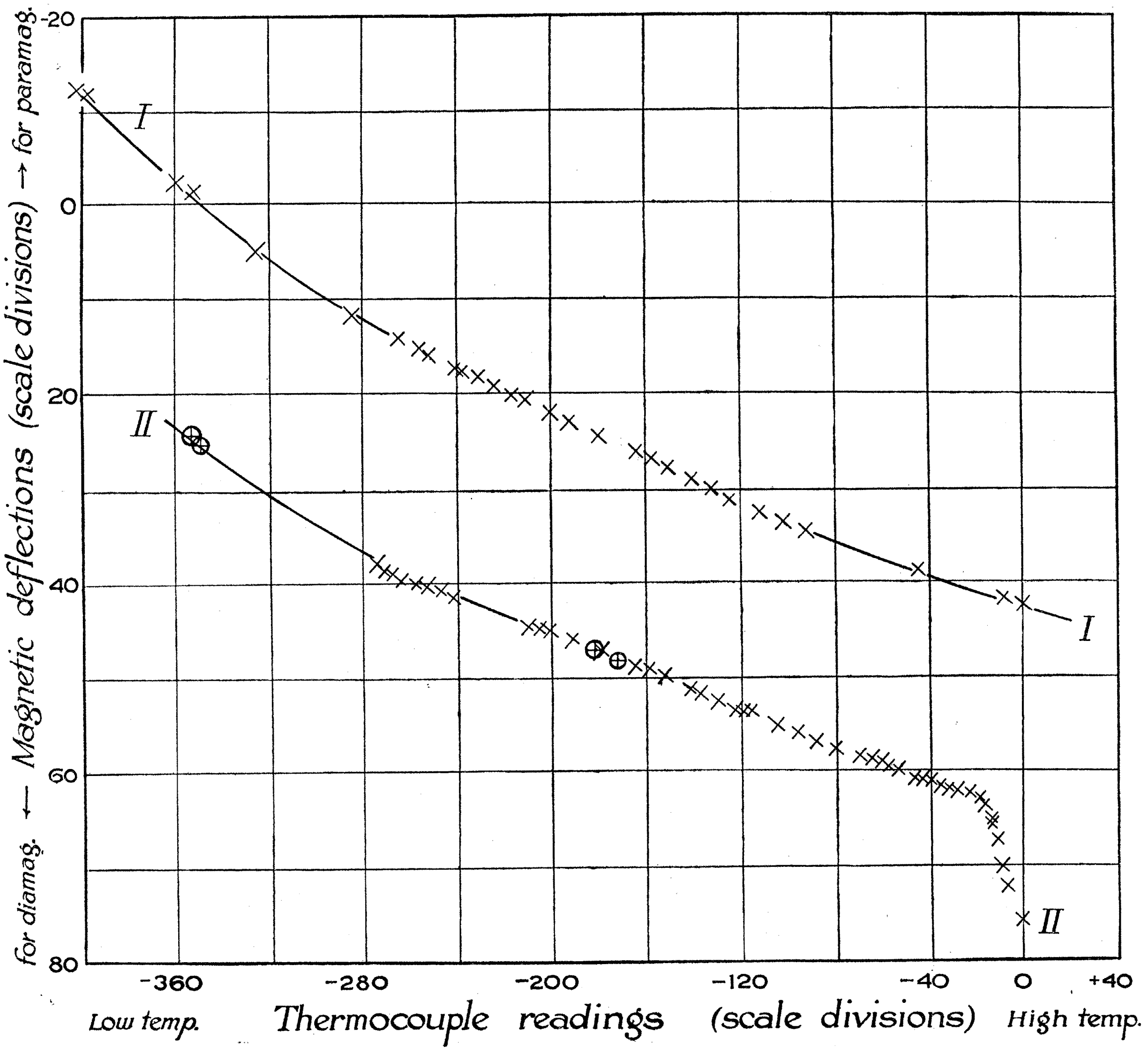

FIG 7

The ordinates of curve I have been reduced 70 scale divisions, so that the two curves may be more readily compared.

The four points marked ⊕ on curve II were obtained by recooling after the crystals had been melted.

constructed was slightly paramagnetic, and the variation of its susceptibility with temperature is represented in fig. 7, Curve I. In this figure the ordinates are deflections in millimetres, and are proportional to the forces acting on the phial at any temperature. The abscissæ are temperatures in divisions of the thermocouple scale (T). Some of the observations are given in Table I.

TABLE I.

− T.	Deflection (d_1).	− T.	Deflection (d_1).	− T.	Deflection (d_1).
483	− 103·0	246	− 53·5	159	− 43·0
469	− 102·5	239	− 52·5	152	− 42·5
447	− 95·0	231	− 52·0	142	− 40·9
404	− 82·0	225	− 51·0	133	− 39·7
355	− 71·5	212	− 48·8	125	− 38·5
322	− 65·5	201	− 48·0	113	− 36·2
288	− 58·5	193	− 47·0	93	− 35·5
264	− 56·0	180	− 45·5	8	− 28·0
254	− 54·3	165	− 43·6	0	− 27·5

The current was adjusted to 8·6 amperes for each observation. Weight of phial = 1·223 gr.

The corresponding observations when the phial was filled with nitrobenzene are plotted in fig. 7, Curve II. Some of the observations are given in Table II.

TABLE II.

− T.	Deflection (d).	− T.	Deflection (d).	− T.	Deflection (d).
275	38·0	115	54·0	19	63·0
257	39·7	97	56·0	17	64·0
248	40·7	89	57·0	13	65·5
205	44·7	80	57·8	11	67·5
192	46·0	70	58·7	9	70·5
180	46·7	65	59·0	7·5	72·5
171	48·0	59	59·7	1	76·0
160	49·0	51	60·0	− 2	76·0
153	49·8	40	60·9	182	47·0
142	51·5	35	61·8	173	48·0
130	52·7	30	62·0	353	25·2
122	53·4	23·5	62·5	349	24·5

The current was adjusted to 8·6 amperes for each observation. Weight of phial and nitrobenzene = 2·273 gr.

T = 0 corresponded to atmospheric temperature, 16° C.

It will be seen that the curves are approximately parallel until a point corresponding to the temperature 5° C. is reached, which is the melting-point of the crystals. It appears, therefore, that the liquid is more diamagnetic than the crystals. By subtracting the ordinates, we get the values of $d-d_1$ at different temperatures. These, in conjunction with the value of d_2-d_1 for water at air temperature, give the specific susceptibility* of nitrobenzene at different temperatures. The two curves in fig. 8 show how the specific susceptibility of nitrobenzene varies with temperature; curve (a) for phial of type (a), curve (b) for phial of type (b).

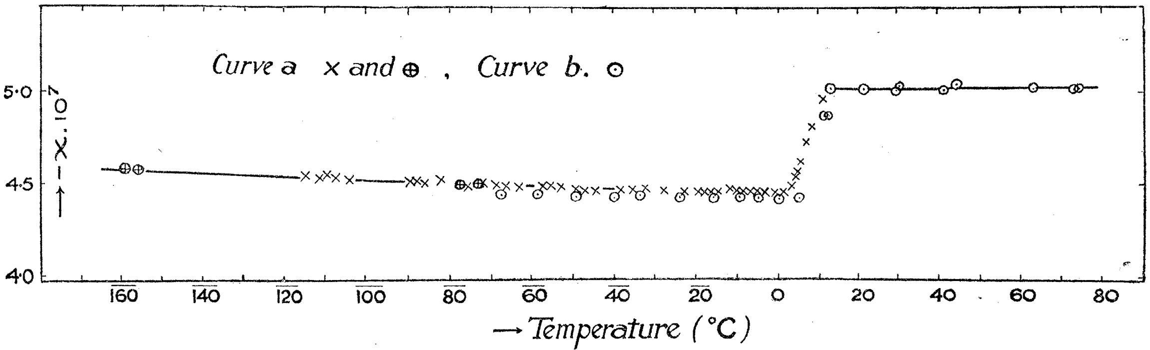

FIG. 8

As the crystals were very gradually melted by heat conducted through the walls of the phial, no effect due to latent heat would be expected to enter. Moreover, if the crystals were taking heat from the phial faster than it was supplied by the surrounding enclosure, the temperature of the phial would be colder than that indicated by the thermometer. The phial could not get hotter than the enclosure unless the latent heat were negative. The only way in which latent heat might affect the observations, therefore, is by cooling the phial below the temperature indicated by the thermometer. But this effect would increase the deflection due to the glass and accordingly reduce that due to the diamagnetic substance contained in it. This result would make any correction due to latent heat of opposite sign to the difference actually found. A good test of the absence of any error due to this cause is obtained by showing that the change of susceptibility is permanent. If the effect were due to absorption or emission

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* The calculation is as follows:—

d_2 for 0·75 gr. water = 80 scale divisions.

$d_2-d_1 = 80+28 = 108$ scale divisions; $d-d_1 = 76+28 = 104$ scale divisions.

$M = 2{\cdot}273-1{\cdot}223 = 1{\cdot}050$ gr.; $m_w = 0{\cdot}75$ gr.; density of nitrobenzene = 1·22.

Using equation (γ), we find

$$\chi = \frac{1}{1{\cdot}050}\left[\frac{0{\cdot}25\times1{\cdot}050}{1{\cdot}22} - \{7{\cdot}25\times0{\cdot}75+0{\cdot}25\times0{\cdot}75\}\frac{104}{108}\right]10^{-7} = -4{\cdot}98\times10^{-7}.$$

Also

$$\partial\chi = \frac{1}{1{\cdot}050}\left\{0{\cdot}25\,\partial V_a - \frac{7{\cdot}5\times0{\cdot}75}{108}\,.\,\delta(d-d_1)\right\}.\,10^{-7}.$$

At the fusion-point

$$\partial V_a \doteqdot 0{\cdot}08;\ \delta(d-d_1) = 13 \text{ scale divisions.}$$

Hence

$$\partial\chi/\chi \doteqdot 12 \text{ per cent.}$$

of heat on change of state, this could not be the case. The change of susceptibility cannot be ascribed to an alteration of thermal conductivity for, as will be seen later, the same difference has been obtained at air temperature between crystals and supercooled liquid, each having stood long enough to take up the temperature of the room.

The experiments on about twenty substances* will now be briefly summarised, for the most part in the order in which they have been investigated. In one or two cases, substances, which are chemically closely related, have been classed together.

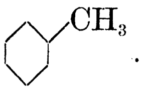
The results are shown graphically in figs. 8–14. A short account of any peculiarity will be given and the curves will be more fully discussed later. For brevity, in what follows, the specific diamagnetic susceptibility will be referred to generally by χ, the absolute temperature by ϑ, and a curve showing the relation between χ and ϑ will be called a $\chi-\vartheta$ curve.

About seventy experiments have been made and some of the substances have been investigated several times, using both types of phial described above (fig. 3).

(*a*) *A Study of Benzene Derivatives.*

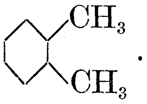
For the most part, the simpler benzene derivatives have been selected, because in many cases their crystalline forms have been investigated and it was hoped that an interpretation of the results would thereby be rendered more feasible.

Toluene.



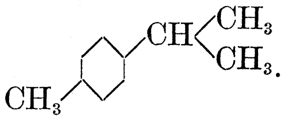
Liquid toluene is more diamagnetic than crystalline toluene, $\partial\chi/\chi$ amounting to 5 per cent. Two curves for this substance have been obtained and the break in the curve occurred in each case at −96° C. The melting point is at −92° C. (fig. 9*a*).

Ortho-xylene.



The liquid is more diamagnetic than the crystals, the change of χ taking place at −26° C. and $\partial\chi/\chi = 4{\cdot}8$ per cent. The melting point of the crystals is at −28° C. (fig. 9*b*).

Cymene.



The curve for the phial filled with cymene was parallel to that for the empty phial over the interval 20° C. to −150° C. (see note under *pyridine* below).

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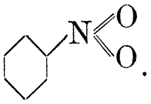
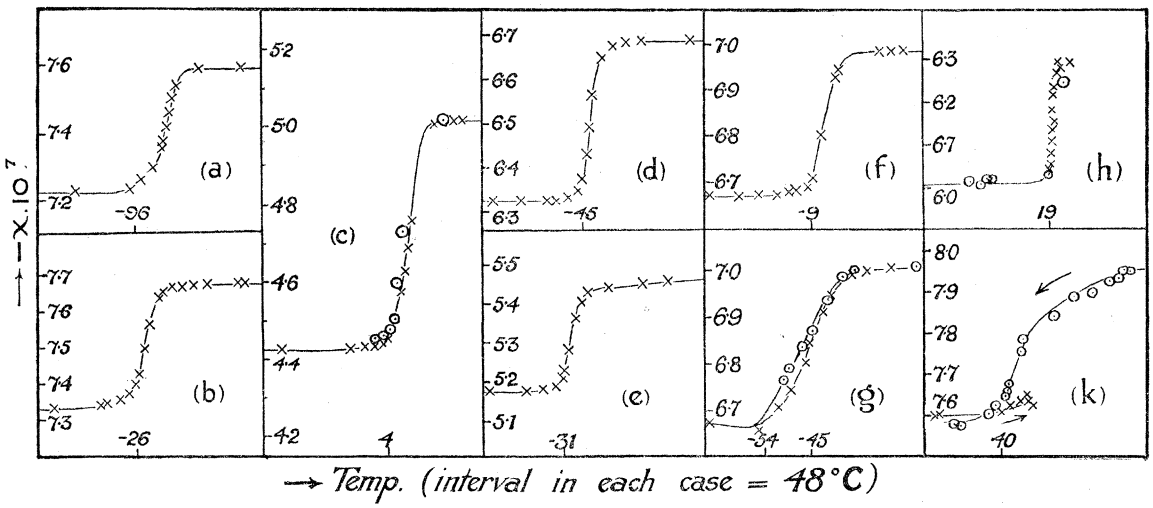
* Over thirty substances have been investigated. An account of these additional experiments will be given in a future paper.

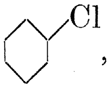
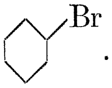
Nitrobenzene. 

Two additional experiments have been made on this substance (1) using phial of type (a); (2) using phial of type (b). In each case the liquid was found to be more diamagnetic than the crystals, the value of $\partial\chi/\chi$ being 13 per cent. The results obtained in the preliminary experiments with this substance are therefore confirmed. The melting point deduced from the magnetic property is 4° C. (fig. 9*c*).

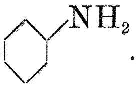


(*a*) Toluene (*b*) o-Xylene (*c*) Nitrobenzene (*d*) Monochlorobenzene (*e*) Monobromobenzene
(*f*) Aniline (*g*) Benzylchloride (*h*) Acetophenone (*k*) α-Naphthylamine

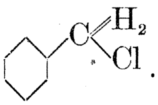
FIG 9

Monochlorobenzene and Monobromobenzene.  ,  .

Each liquid is more diamagnetic than the corresponding crystals. $\partial\chi/\chi$ in each case is 5 per cent. Type (a) of phial was used with the chlorine derivative, type (b) with the bromine derivative. The melting point of the chlorine compound, as deduced from the dip of the $\chi-\vartheta$ curve, is −45° C.; that of the bromine compound is −31° C. (figs. 9*d* and 9*e*).

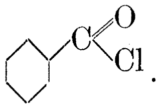
Aniline. 

Liquid aniline is 5 per cent. more diamagnetic than crystalline aniline; the melting point derived from the $\chi-\vartheta$ curve is at −9° C. (fig. 9*f*).

Benzyl Chloride. 

Liquid benzyl chloride is more diamagnetic than the crystalline form. The transition, as fig. 9*g* shows, appeared to be less abrupt than usual.* The melting point, if it corresponds to the beginning of the dip, is at −54° C. The middle of the dip is at a temperature −45° C., which is very nearly equal to the value of the melting point (−43° C.) obtained by other methods. The value of $\partial\chi/\chi$ is 5 per cent.

Benzoyl Chloride.



This substance showed a departure from the general rule that for benzene compounds the liquid state is more diamagnetic than the crystalline state. Five experiments have been made with this substance and two of the curves are shown in fig. 10, Curve I. The liquid, which is oily, is seen to be less diamagnetic than the crystals

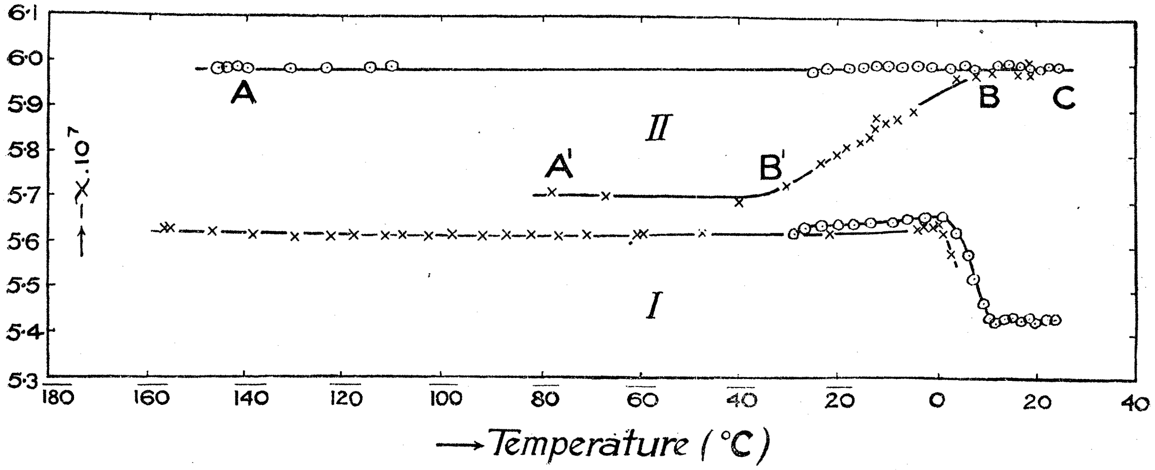
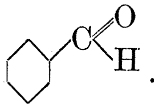


FIG. 10

by an amount 5 per cent. of the value of χ. Taking the point where the decrease of χ begins, as the temperature of fusion, we deduce −3° C. for the melting point. Other methods give −1°·0 C.

This substance will be considered later in conjunction with several other compounds showing similar properties.

Benzaldehyde.



The first experiment made on this substance showed that it possessed the hitherto unique property of constancy of the magnetic susceptibility through the normal fusion point down to the temperature −150° C., as shown by the curve ABC (fig. 10, Curve II). But on taking away the metal cylinder (used to preserve a uniform temperature over

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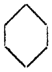
* This may be an effect of too rapid heating of the enclosure combined with low conductivity of the substance.

the space occupied by the substance) during a repetition of this experiment, it was discovered that the benzaldehyde had not crystallized but had passed into a transparent jelly-like mass. By plunging the phial containing the benzaldehyde into liquid air, the benzaldehyde again assumed this jelly form, but on warming, followed by a further slight cooling, a white crystalline mass was obtained. This was now cooled to the temperature of liquid air, withdrawn, suspended from the torsion balance and quickly surrounded by liquid air. An experiment carried out on the benzaldehyde after this treatment is shown in fig. 10, Curve A′B′BC. It will be seen that approximately the normal dip, 5 per cent., was obtained, the liquid being more diamagnetic than the crystals, but the transition stage was considerably drawn out and appeared to have an intermediate step or stable state.

Shortly after this difference in magnetic property between the gelatinous and the crystalline states of benzaldehyde had been established, a research appeared by M. CHAUDIER,* who had discovered that the specific magnetic rotation of organic substances behaves in a similar way. He found that if the substance passed into a gelatinous state, on being cooled below the normal fusion point, there was no discontinuity of the magnetic rotation in passing from the liquid to the gelatinous state. The rotation, on the other hand, disappeared totally if the substance passed into a crystalline form on being cooled. The two phenomena—magnetic rotation and magnetic susceptibility—are doubtless closely allied and each is affected by a transition from the liquid to the crystalline state. An attempt is made in Part II. to connect theoretically these effects. It does not appear that CHAUDIER obtained the same substance in both gelatinous and crystalline forms, and it would be interesting to carry out an experiment on the magnetic rotation of a substance capable of existing in either form at a given temperature. CHAUDIER shows that the discontinuity exists for benzene, aniline, and nitrobenzene on crystallization, and that the rotation remains constant in the cases of amyl-alcohol, glycerine, and essence of terebene, which pass into the gelatinous form on cooling below the normal freezing point. The phenomenon with the last substance is made complex on account of optical activity.

Benzene.  .

This substance shows an anomaly different from that of any other benzene compound investigated. Five experiments have been made and one of the curves is drawn in fig. 11. The pit in the $\chi - \vartheta$ curve occurs in every case at the normal fusion point, 5° C. On either side of this point, the curve rises, the distant parts of the curve corresponding to the liquid and crystalline states being continuous, as shown by the dotted line. This dotted line appears to correspond to no real physical state as it was found impossible to make the substance pass along this path. The depth of the pit

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* 'Comptes Rendus,' vol. 156, p. 1529, May, 1913.

was not always the same—this may be explained by the slightly different rates of cooling in the different experiments—for the outer layers of the sphere of benzene crystals will melt first, and these may have reached the stage where an increase of temperature causes a rise of χ, while the inner layers of the sphere are still falling to pass through the pit.

This fall and rise of χ may be connected with the perfect symmetry of the benzene molecule.

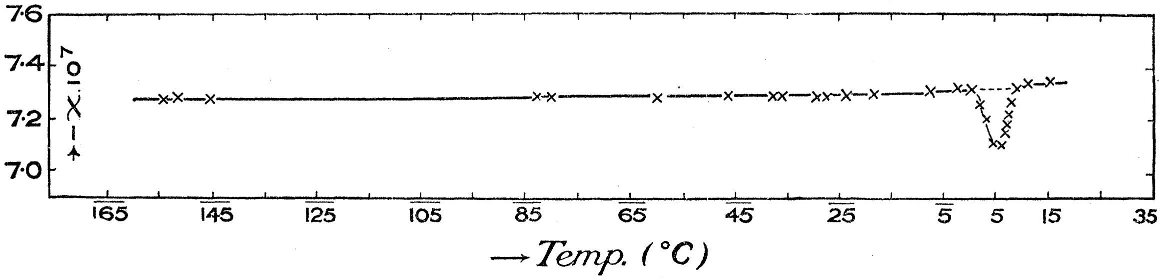


FIG. 11

Pyridine.

The curve for the phial filled with pyridine was parallel to the curve for the empty phial throughout a range of temperature, 20° C. to $-150°$ C. In liquid air, the pyridine passed into a stiff jelly state, as in the case of benzaldehyde. On slightly warming and again cooling, a white crystalline mass appeared.

Similar freezing experiments were made on cymene. The gelatinous state appeared turbid and on recooling, crystallization took place; the substance being transformed into a white mass which quickly melted on withdrawal from the liquid air.

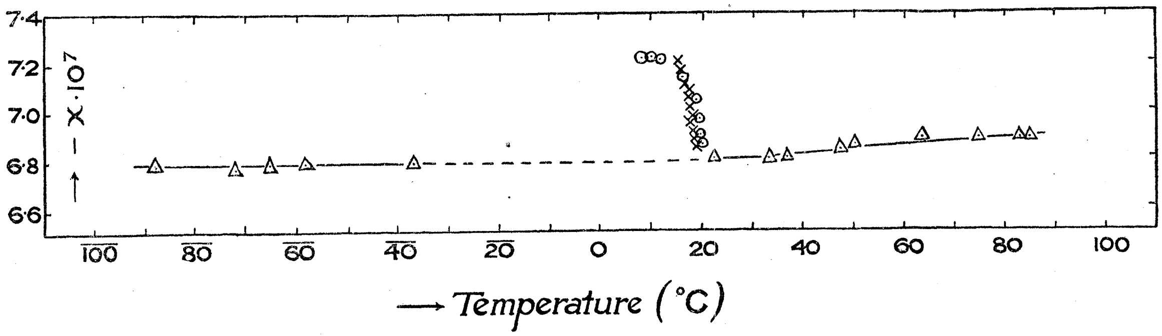
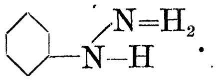
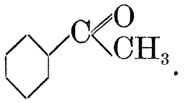


FIG. 12

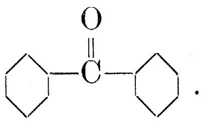
Phenylhydrazine.



Two curves for the transition from the crystalline to the liquid state and one curve for the gelatinous state down to the temperature $-90°$ C., are shown in fig. 12. As phenylhydrazine melts at 20° C., there was no need to use the copper cylinder, which ordinarily surrounded the phial, and so it was possible to watch the substance throughout the transition. The crystals were found to be more diamagnetic than the liquid and the mean value of $\partial\chi/\chi$ was 4·7 per cent. The gelatinous form was stable at low temperatures and had a susceptibility equal to that of the liquid above the normal fusion point. The crystals obtained at low temperatures gave rise, on warming, to a large number of small bubbles, which prevented observations being made on the crystals at temperatures much below the freezing point.

Acetophenone. 

The liquid was frozen to a white crystalline mass which melted at 19° C., accompanied by an increase of diamagnetism amounting to 4·5 per cent. On allowing the liquid to stand for two days crystals again appeared, but these were transparent and very much larger. The susceptibility of these crystals was smaller than that of the liquid by 4 per cent. The crystals were again tested after three days but no further decrease of diamagnetism was observed (fig. 9*h*).

Benzophenone. 

Two curves for this substance are shown in fig. 13. It will be seen that in each case the benzophenone passed into the gelatinous state on cooling. This state appears to be unstable and, on cooling sufficiently, crystallization sets in, which is accompanied by a decrease of χ amounting to 6 per cent. (approximately). In the first experiment the transition took place when the liquid had been super-cooled about 30° C.; in the

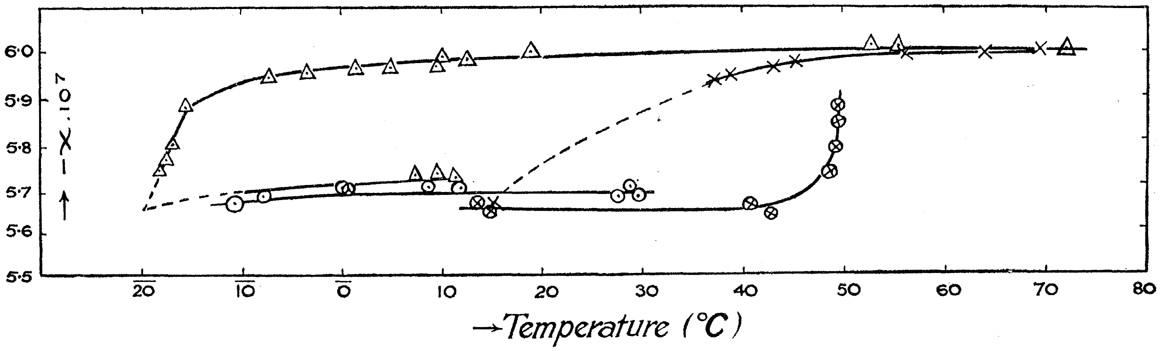


FIG. 13

second experiment, crystallization took place at a temperature 70° C. below the normal melting point. In each case, when the crystals were heated, fusion took place at the normal temperature, 48° C. The substance was melted by hot water contained in a Dewar tube, and the temperatures below that of the room were obtained with a tube which had been cooled by liquid air.

It is apparent that with this substance a definite hysteresis effect, due to temperature, is obtained, similar to that which was discovered by the late Prof. HOPKINSON*, in the case of nickel-steels. If we regard the paramagnetic state of the nickel-steel as isotropic†, the temperature hysteresis effects in the two cases are completely analogous. The paramagnetic solid corresponds to the diamagnetic liquid. On cooling, the nickel-steel passes the critical temperature‡ without crystallizing just as the benzophenone passes the normal fusion point and assumes a gelatinous form. Continued cooling in each case causes the more stable crystalline form to appear. This is accompanied by a large rise of the paramagnetism of the nickel-steel (ferro-magnetism) and by a fall of the diamagnetism of the benzophenone. If now the nickel-steel be heated, it loses its ferro-magnetism at the critical temperature—a temperature which is characteristic for a given alloy and is lower the greater the proportion of nickel in the steel—while the benzophenone regains its larger diamagnetic property at the normal fusion point—a temperature which is lower the greater the impurity present. Further, the heat produced (recalescence) when the ferro-magnetic state appears on crystallization of the nickel-steel is analogous to the heat produced (heat of formation of the crystals) when the benzophenone crystallizes. The molecular changes are of the same nature in the two cases; the only difference is in the character of the magnetic property possessed by the molecules and by which such molecular changes are indicated.§

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* 'Roy. Soc. Proc.,' vol. XLVIII., p. 1, 1890; or EWING'S 'Magnetic Induction in Iron and other Metals,' p. 184, *et seq.* HOPKINSON referred to the paramagnetic state above the critical temperature as the non-magnetizable state.

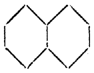
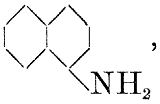
[† At least we may regard it as an allotropic modification of the alloy. See the article by GUILLAUME, 'Rapports du Congrès Int. Paris,' 1900, vol. 1; also DUMAS, 'Journ. of the Iron and Steel Institute,' 68, p. 255, 1905. It should be mentioned that the results described in this communication concerning change of state are in accordance with the work of TAMMANN, 'WIED. Ann.,' LXII., p. 285, 1897. See also the article by SPRING, 'Paris Reports,' 1900, and WHETHAM'S 'Theory of Solution,' Chap. II., where additional references to TAMMANN'S work are given.—*Note added March, 1914.*]

‡ It would be more correct to speak of the "range of temperature of transformation" instead of "critical temperature."

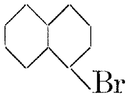
[§ Mr. M. OWEN has observed that the specific susceptibility of super-cooled *gallium*, between 30° C. and 16° C., is constant and equal to that of the liquid above the normal fusion point. The crystalline state is much more diamagnetic and χ_c remains nearly constant until the fusion point, 30° C., is reached.

My attention was drawn to this point of priority, after my work had been completed, by the curve given in OWEN'S paper, 'Ann. der Phys.,' IV., 37, p. 693 (fig. 4F), 1912. The English translation of this paper, 'Versl. Kon. Ak. v. Wetensch.,' Amsterdam, XIV., p. 637, 1912, which first came to my notice, contains no diagrams and I had overlooked the brief reference there made, at the foot of p. 642, to the behaviour of *gallium.*—*Note added March, 1914.*]

(*b*) *A Study of Naphthalene Compounds.*

Naphthalene, , *α-Naphthylamine,* 

, *and*

α-Bromonaphthalene, 

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In each case the liquid state is more diamagnetic than the crystalline state. The change of susceptibility on crystallization was 4·5 per cent. for each substance, and took place at 80° C. with naphthalene, at 40° C. with α-naphthylamine (fig. 9*k*), and at 4° C. with α-bromonaphthalene.

The rather low value of $\partial\chi$ for naphthalene and its derivatives may be due to the two carbon atoms "condensed" in the naphthalene nucleus, which differ considerably in their chemical nature from the remaining carbon atoms of the naphthalene system.

(*c*) *Mercury.*

The liquid state was found to be more diamagnetic than the crystalline state, the value of $\partial\chi/\chi$ amounting to 14 per cent. The curves are shown in fig. 14. These were obtained by first cooling the mercury with liquid air and observing the susceptibility as the temperature gradually rose. In the curve ABCD, when the point C had been reached, the mercury was re-cooled to a temperature just below that of the freezing-point (−37° C., as determined from the position of the dip) and afterwards to −85° C., and the points marked ⊗ were obtained. Between −37° C. and 70° C. the diamagnetic property remained constant.

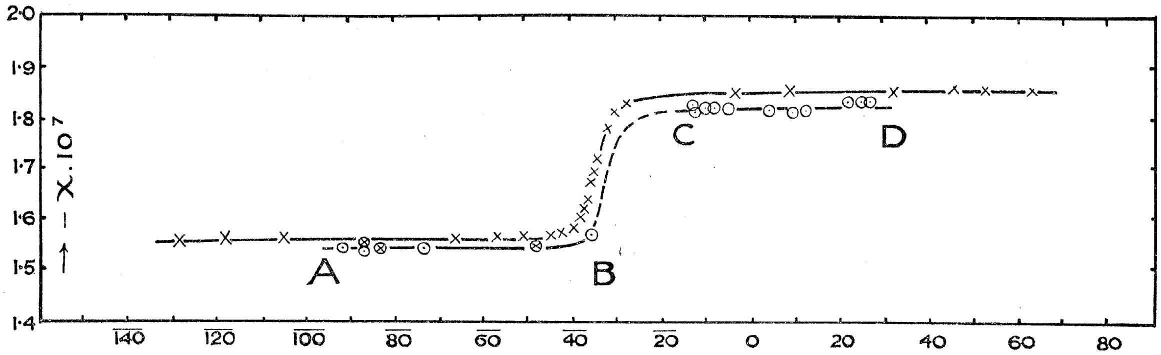

FIG. 14

Experiments on Substances which show a Liquid Crystal State.

Cholesteryl Chloride, $C_{27}H_{45}Cl$, *and Para-azoxyanisol,* 

$$CH_3.O.C_6H_4.N\underset{\diagdown O \diagup}{-}N.C_6H_4.O.CH_3.$$

In each case the diamagnetic property decreased during the transition from the true crystalline to the true liquid state. The value of $\partial\chi/\chi$ for para-azoxyanisol was 6 per cent. A smaller and less definite value was obtained with cholesteryl chloride, and after the liquid state had appeared the susceptibility continued to decrease, probably owing to further dissociation of molecular complexes. M. PASCAL* has recently investigated para-azoxyphenetol,  $C_2H_5.O.C_6H_4.\underset{\diagdown O \diagup}{N-N}.C_6H_4.O.C_2H_5$, and has discovered that the red liquid form is less diamagnetic than the yellow crystalline form, the value of $\partial\chi/\chi$ being 18 per cent. This substance appears to behave like para-azoxyanisol, but gives a larger value of $\partial\chi$.

In the case of para-azoxyanisol, the $\chi-\vartheta$ curve for ascending temperature was similar to that for descending temperature, but the two curves were slightly displaced owing to thermal lag. Fusion took place at 120° C.

The sign of $\partial\chi$ for each of these liquid crystal compounds is the same as that for benzoyl chloride and phenylhydrazine. Through the kindness of Prof. POPE, I have been able to examine some crystals of the last substance under the crystallization microscope, but no trace whatever of a doubly refracting layer at the boundaries of the crystals could be discerned.

It may perhaps be supposed that the transition of all substances, from the true liquid to the true crystalline state, takes place over a finite though small interval of temperature. This does not imply that all substances should show the liquid crystal state, but merely that a labile state exists, which may or may not be doubly refracting, in which the molecular grouping is determining how the substance will crystallize on further cooling.

(7) GENERAL DISCUSSION OF THE EXPERIMENTAL RESULTS.

The dependence of diamagnetic property on crystallization readily follows as a result of the production of homogeneously close-packed assemblages of atomic spheres of influence.† The difference of structure of the crystalline and amorphous states of a substance is due to the distribution of the restraining forces acting on the molecules of the crystalline structure, which will necessarily produce a small distortion of each molecule; while in the amorphous or gelatinous structure, the molecules will possess a more symmetrical shape on account of the withdrawal of the restraining forces. This deformation effect in every molecule of the crystalline structure is in accordance with the hypothesis stated at the beginning of this communication—a deformation of the atom presumably producing a modification of the internal structure which will in turn modify the diamagnetic property. In Part II., an attempt will be made to interpret this change of diamagnetism in terms of the change of self induction of the electron orbits contained in the atom. The inappreciable deformation of the molecules when

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* 'Ann. de Chim. et de Phys.,' VIII., vol. 25, p. 375, 1912.

† BARLOW and POPE, 'Trans. Chem. Soc.,' vol. LXXXIX., p. 1675, 1906.

the substance assumes a gelatinous or liquid form is in accordance with the constancy of the magnetic property which is observed when the substance super-cools or passes into a jelly. Until we postulate some definite internal structure of the atom or molecule, it is impossible to say what the precise effect of the adjustment, from the symmetrical shape of the molecule of the gelatinous state to the non-symmetrical shape of the crystalline state, will be, either as regards magnitude or sign.

Providing the molecular complexity does not change, the diamagnetic property does not depend upon the temperature, and it can therefore be represented by a series of straight lines parallel to the temperature axis. Continuity between these straight lines is represented by the equation

$$\chi_D = \frac{1}{H}\Sigma n_p \,.\, \Delta M_p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

During the transition from one state to another, different types of particles co-exist, n_p characterizing the growth of the number of particles of type p. ΔM_p, the diamagnetic moment produced by the applied field H, in a complex of type p, is dependent upon the molecular distortion of the complex.

In the crystalline and liquid states,

$$\chi_{D_c} = \frac{N}{H} \,.\, \Delta M_c, \qquad \chi_{D_l} = \frac{N}{H} \,.\, \Delta M_l,$$

where ΔM_c and ΔM_l are the diamagnetic moments produced in a distorted molecule of the crystalline and liquid states respectively, and N is the number of molecules per gramme of the substance. The magnitude and sign of the change of susceptibility will be determined by the nature of the crystalline structure, while the shape of the curve of transition* depends on the variation of n_p with temperature.

Below the melting points of benzaldehyde, benzophenone, and phenylhydrazine, two distinct $\chi-\vartheta$ curves have been obtained. In each case the velocity of crystallization of the super-cooled liquid was small, for observations showed that, several hours after cooling, the susceptibility of the gelatinous state was indistinguishable from that of the true liquid.

For benzene derivatives, the diamagnetic property of the crystalline state is in general less than that of the liquid state; but in addition to those compounds which show a liquid crystal state, there are two important exceptions, viz., benzoyl chloride and phenylhydrazine, in which the crystals are more diamagnetic than the liquid. It is interesting to notice that there exists for benzene and its derivatives an alternative kind of packing which is found in the crystalline structure of some of the halogen derivatives. This alternative or cubic system is highly symmetrical for

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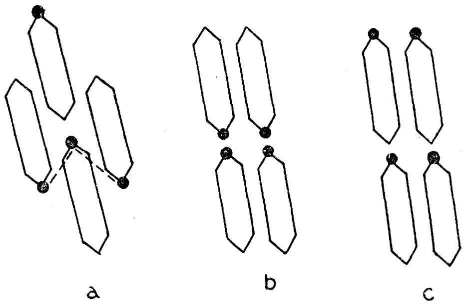
* In the experiments which have been described the shape of this curve is masked by the effect of low thermal conductivity of the substance.

benzene itself, but the presence of a halogen atom destroys the symmetry of the complex, the latter being sheared in various directions. It is by a process of shearing, similar to that which corresponds to the change from the cubically to the hexagonally derived complex, that we may account for the different diamagnetic properties accompanying polymorphism and by which we may, at any rate provisionally, explain the abnormal results obtained with benzoyl chloride and phenylhydrazine. Diagrammatically, we may represent such a shear by the accompanying figures (a) and (b), where the black dot represents the substituent of the benzene complex. During crystallization it frequently happens that pairs of molecules assume mirror-image positions—(a) and (b) are types of this arrangement. In the case shown at (c), the mirror-image formation is absent. The forces of crystallization will be different in the three cases. On the whole, the resultant of the forces between the molecules will act inwards on each ring system in case (a), and outwards in case (b). Each of these types differs from (c) where the forces on the whole may act neither inwards nor outwards on any given ring system.



Hence we may regard the substituent as a directive agent, and in so far as it influences its own complex and the neighbouring complexes, there is a reversal of the effects produced by the forces of crystallization in case (b) as compared with case (a). This reversal of the interaction of substituent and nucleus with respect to any particular molecule will produce a distortion of the internal structure of an opposite kind.

For convenience and clearness the disposition of the six carbon atoms of the benzene ring is represented as uniplanar. This need not be the case. It is possible now to explain the two abnormal cases of benzoyl chloride and phenylhydrazine without having to assume that the liquid state possesses a greater molecular complexity or a closer packing of molecules than the corresponding crystalline state. I have had the opportunity of discussing, with Prof. Pope, this question of a reversal of the change in magnetic property due to crystallization, and he informed me that the demands of this explanation are in accordance with the modern views of chemists and crystallographers.

The nature of the irregularity of the $\chi-\vartheta$ curves does not appear to be directly connected with the change of volume on crystallization; for in the case of water* the effect is small, and is normal as far as sign is concerned, while a large expansion takes place on crystallization. In the case of benzene there is a fall and a rise of χ on crystallization, while the change of state involves a contraction simply.

With regard to the crystalline forms of the elements, BARLOW and POPE† point out that those elements which show allotropic modifications crystallize in forms of low symmetry, while other elements not so easily obtainable in allotropic forms crystallize in forms of high symmetry. It seems necessary, therefore, to distinguish between the forces holding the atoms in position in the molecule and the forces holding the molecules together in the crystal structure. The atoms of an element are assumed to be identical, and the molecular aggregate to which they give rise and the accompanying distortion depend upon the kind of packing which these equal atomic spheres of influence assume. The only element which has been investigated in this research is mercury. The large change of χ on freezing indicates a large change of molecular configuration.

The allotropic forms of an element, which possess characteristic crystalline structures, will have different molecular distortions and consequently different magnetic properties. Moreover, as these forms are of different degrees of stability, the disintegration of the structure with change of temperature will in general be different for each form. The $\chi - \vartheta$ curves may therefore be expected to show irregularities. Reference has already been made to the work of DU BOIS and HONDA‡ on the magnetic properties of the allotropic modifications of phosphorus, antimony, carbon, and tin. But these authors used the irregularities which their observations disclosed as an argument against the truth of the foundations of LANGEVIN'S electron theory of diamagnetism instead of interpreting them as due to the variation of molecular complexity. The experiments described above show that the peculiarities of the $\chi - \vartheta$ curves can in all cases examined be traced to the variation of molecular complexity. In the liquid state most of the compounds that have been investigated are unassociated, and the absence of any variation of χ with ϑ is conclusive proof of the truth of the Curie law of diamagnetism when the molecules are not appreciably distorted. This law is true for distorted molecules, if the distortion is not a function of the temperature, as the parallelism of the curves for the various crystals and for the empty phial shows.

It is clear from the experimental results that diamagnetism is not wholly an atomic property, for the near approach of the molecules, which takes place on crystallization,

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* PICCARD, 'Comptes Rendus,' vol. 155, p. 1497, December 23, 1912, and WEISS and PICCARD, 'Comptes Rendus,' vol. 155, p. 1234, December 9, 1912. These authors find that the variation of the diamagnetic property of water with temperature can be interpreted as due to the co-existence of two types of complexes, one type growing at the expense of the other as the temperature is varied. This explanation is in accordance with equation (1) which I had published earlier.

† 'Trans. Chem. Soc.,' vol. LXXXIX., p. 1741, 1906.

‡ 'Versl. Kon. Ak. v. Wetensch.,' Amsterdam, XII., p. 601, 1910.

is able to modify the susceptibility appreciably. From the decrease of diamagnetism accompanying the crystallization of benzene derivatives, it appears that the process of crystallization implies the utilization of the residual forces between the molecules which tends to make them more normally saturated. The value of $\partial\chi$ is not constant for the different members of the same class of compounds, and in benzene derivatives it is a function not only of the ring system but also of the substituent.

Before the extent of this adjustment of the diamagnetic property—due to the juxtaposition of unsaturated groups—can be of value, it is necessary to examine different classes of compounds each containing a large number of members.

It will have been seen that a satisfactory interpretation of the variations of the diamagnetic property found in this research can be given in terms of molecular theory. All that has been assumed concerning the structure of the molecule is that it is a unit which can be distorted by the near approach of other units. In order that we may inquire more fully into the nature of the distortion and the forces which cause it, we must postulate some definite structure of the molecule. We shall assume, in the investigation which follows (Part II.), that the molecule consists of a congeries of electrons; and that the positive charges, which keep the electrons whirling in their orbits, are fixed in the molecule.

For the present, looking at the problem from a purely molecular point of view, the hypothesis stated at the beginning concerning the molecular distortion which accompanies crystallization, has been found justifiable, and has led to results in harmony with the views of chemists and crystallographers.

Little has been said in this communication concerning the Curie law of paramagnetism, which may be written in the form

$$\chi_{\mathrm{P}} = \Sigma \frac{n_p \,.\, c_p}{\vartheta}.$$

The recent work of Prof. KAMERLINGH ONNES,* on the variation of paramagnetism at low temperatures, shows how we may interpret departures from the simple Curie law, $\chi_{\mathrm{P}} = c/\vartheta$, by a modification of the Curie constant. The above expression for χ_{P} shows that if the change of aggregation or the process of crystallization modifies the structure of the molecule, then for every type of complex p, we shall have a new Curie constant c_p per particle of this type. In addition to this, the above expression provides a continuity of the magnetic property during the transition stage where there will be a co-existence of various types of particles. The passage from the liquid to the crystalline state modifies the paramagnetic as well as the diamagnetic property. ONNES† has shown that there is a sudden change of the value of χ_{P} during the crystallization of liquid oxygen.

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* 'Versl. Kon. Ak. v. Wetensch.,' Amsterdam, XV., p. 322, 1912.

† 'Versl. Kon. Ak. v. Wetensch.,' Amsterdam, XIV., p. 674, 1912.

It appears therefore that these two expressions for the diamagnetic and paramagnetic properties are generally applicable and explain the variation of susceptibility with temperature in terms of two Curie laws. These laws are exact to within the limits of experimental accuracy, and any variation of the magnetic property which is apparently not in accordance with them can be attributed to variation of the molecular complexity.

PART II.

(1) A THEORY OF THE PHENOMENA FOUND IN THE ABOVE EXPERIMENTAL RESEARCHES IN TERMS OF THE ELECTRON THEORY OF MAGNETISM.

The theory of LORENTZ, which postulates no free magnetism, but attributes magnetic phenomena to the motion of electric charges, accounts admirably and in a simple way for the main characteristics of the Zeeman effect and for the rotation of the plane of polarisation in a magnetic field. Each of the latter phenomena appears to be closely related to the diamagnetic property of a substance; for LANGEVIN has shown that the magnetic moment produced in a molecule by the application of an external magnetic field is such as would lead to diamagnetism by a process which is compatible with the simple explanation of the Zeeman effect given by LORENTZ. Further, the fact that the magnetic rotation produced by the ferromagnetic elements is proportional to the intensity of magnetization, and not simply to the intensity of the applied magnetic field, shows that we must take into consideration the magnetic property in this case also.

No theory has yet been devised, however, which is completely consistent with the principles of mechanics and the phenomena—optical and electric—of the luminiferous medium, and in adopting the theory of LORENTZ, we are merely seeking to obtain a fuller interpretation, on certain hypotheses, of the experimental facts obtained in Part I. But it is evident that whatever theory be adopted with regard to the origin of the diamagnetic property, any distortion of the molecular system, such as is produced by crystallization, must be accompanied by an adjustment of the magnitude of that property.

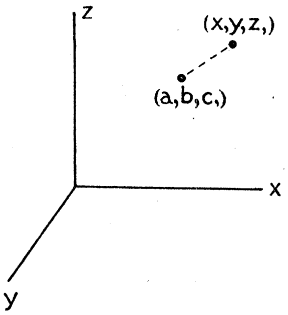
To obtain a satisfactory interpretation of the phenomena which have been observed in the experiments of Part I., we must take into consideration the forces which the systems of rotating electrons in different molecules exert on each other. LORENTZ has shown that the force exerted on an electron (surrounded by neighbouring systems) by an electric force E is not simply ϵE, where ϵ is the charge on the electron. A term $\epsilon . f(P)$ must be added, where P is the electric polarisation of the medium, and the function f characterizes the grouping of the molecules for any particular state of the substance. The total mechanical force acting on an electron is therefore

$$\epsilon [E + f(P)].$$

We may regard the crystalline state as isotropic to a first approximation, since the crystals formed in the experiments have all kinds of orientations. The introduction of the term $f(\mathrm{P})$ will then represent the effect due to the modification of the internal motions of an atom or molecule, by the process of crystallization, and will no longer characterize the different properties which the substance really possesses along its crystalline axes.

We shall follow the electron theory of M. LANGEVIN* and refer the electron system of any molecule to axes fixed in direction relative to the æther, but whose origin always coincides with the centre of gravity of the whole system of electrons. Let x, y, z be the co-ordinates of a particular electron. Then $\Sigma x = \Sigma y = \Sigma z = 0$, and since the medium is assumed to be isotropic,

$$\Sigma xy = \Sigma yz = \Sigma zx = 0.$$



Let a, b, c be the co-ordinates of the centre of gravity of a molecule. Then, since the medium is isotropic,

$$\Sigma a = \Sigma b = \Sigma c = 0$$

and

$$\Sigma ab = \Sigma bc = \Sigma ca = 0.$$

The co-ordinates of an electron, with respect to the centre of the molecule in which it is situated, will be denoted by

$$(\xi,\ \eta,\ \zeta) = (x-a,\ y-b,\ z-c).$$

The above equations give

$$\Sigma\xi = \Sigma\eta = \Sigma\zeta = \Sigma\xi\eta = \Sigma\eta\zeta = \Sigma\zeta\xi = 0.$$

The areal velocity of an electron, with reference to the centre of gravity of the molecule, will have a component along Oz given by

$$\Omega_z = \tfrac{1}{2}(\xi\dot{\eta}-\eta\dot{\xi}), \quad \ldots \ldots \ldots \quad (1)$$

and, assuming that we can interpret the magnetic effect of the electrons spinning in their orbits by the magnetic moment M_z where

$$\mathrm{M}_z = \Sigma\epsilon\,.\,\Omega_z, \dagger \quad \ldots \ldots \ldots \quad (2)$$

we may write from (1) and (2)

$$\dot{\mathrm{M}}_z = \frac{\epsilon}{2}\Sigma(\xi\ddot{\eta}-\eta\ddot{\xi}). \quad \ldots \ldots \ldots \quad (3)$$

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* 'Ann. de Chim. et de Phys.,' VIII., vol. 5, p. 70, 1905. For clearness I have borrowed the treatment up to equations (4) directly from M. LANGEVIN'S paper.

† Sir JOSEPH LARMOR ('Phil. Trans.,' 1897, A, p. 230), has shown that this relation implies the existence of a constraint to prevent the accumulation of displacement during the action of a steady magnetic field on a system of spinning electrons. See also LEATHEM, 'Roy. Soc. Proc.,' vol. 89A p. 31, 1913.

In addition to the forces due to external sources acting on the electrons contained in a given molecule, there will be internal forces having components X, Y, Z, which are determined by the configuration of the molecule. If the origin move with velocity (u, v, w) the velocity of any electron will be $(u+\dot{x}, v+\dot{y}, w+\dot{z})$, and LANGEVIN writes the equations of motion in the form

$$\left.\begin{aligned} m\ddot{\xi} &= \mathrm{X}+\epsilon\mathrm{E}_x+\epsilon\mathrm{H}_z(v+\dot{y})-\epsilon\mathrm{H}_y(w+\dot{z})-m\ddot{a}-m\dot{u} \\ m\eta &= \mathrm{Y}+\epsilon\mathrm{E}_y+\epsilon\mathrm{H}_x(w+\dot{z})-\epsilon\mathrm{H}_z(u+\dot{x})-m\ddot{b}-m\dot{v} \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad (4)$$

where E and H are the electric force and magnetic force and m is the mass of an electron.

If we wish to take into account the forces due to neighbouring molecules, when crystallization takes place, we must add the term $\epsilon f(\mathrm{P})$ to these equations. Now, in a crystalline structure, the motion of a molecule will consist of oscillations about a centre, and, therefore, if we take a mean value of this polarisation term and add it to the equations (4) we shall include the effect of the presence of neighbouring molecules. Assuming that the medium is isotropic (which is permissible since the crystals will have all kinds of orientations, and we are seeking the effect of close approach of the molecules only and not any particular property in a specified direction) the new equations are

$$\left.\begin{aligned} m\ddot{\xi} &= \mathrm{X}+\epsilon\left[\mathrm{E}_x+f(\mathrm{P}_x)\right]+\epsilon\mathrm{H}_z(v+\dot{y})-\epsilon\mathrm{H}_y(w+\dot{z})-m\ddot{a}-m\dot{u} \\ m\ddot{\eta} &= \mathrm{Y}+\epsilon\left[\mathrm{E}_y+f(\mathrm{P}_y)\right]+\epsilon\mathrm{H}_x(w+\dot{z})-\epsilon\mathrm{H}_z(u+\dot{x})-m\ddot{b}-m\dot{v} \end{aligned}\right\}. \quad . \quad . \quad . \quad (4)'$$

On account of the small dimensions of the elementary system considered, the electric force E and the electric polarisation term $f(\mathrm{P})$ will be nearly constant throughout its extent, so that denoting the value of E and $f(\mathrm{P})$ at the centre of the elementary system by E_0 and $f(\mathrm{P}_0)$, we have, expanding and neglecting higher powers than the first,

$$\mathrm{E}_x = \mathrm{E}_{0x}+x\left(\frac{\partial \mathrm{E}_x}{\partial x}\right)_0+y\left(\frac{\partial \mathrm{E}_x}{\partial y}\right)_0+z\left(\frac{\partial \mathrm{E}_x}{\partial z}\right)_0$$

and $\quad . \quad . \quad . \quad . \quad . \quad (5)$

$$f(\mathrm{P}_x) = f(\mathrm{P}_{0x})+x\left[\frac{\partial f(\mathrm{P}_x)}{\partial x}\right]_0+y\left[\frac{\partial f(\mathrm{P}_x)}{\partial y}\right]_0+z\left[\frac{\partial f(\mathrm{P}_x)}{\partial z}\right]_0$$

Calculating $\dot{\mathrm{M}}_z$ from (3), (4)′, and (5), and using the relations given on p. 137 for an isotropic medium, we find (writing $\Sigma\xi^2 = \Sigma\eta^2 = \Sigma\zeta^2 = \mathrm{A}/2$)

$$\begin{aligned} \dot{\mathrm{M}}_z = \frac{\epsilon^2}{4m}\Bigg[&\mathrm{A}\left\{\left(\frac{\partial \mathrm{E}_y}{\partial x}\right)_0-\left(\frac{\partial \mathrm{E}_x}{\partial y}\right)_0\right\}+w\mathrm{A}\left\{\left(\frac{\partial \mathrm{H}_x}{\partial x}\right)_0+\left(\frac{\partial \mathrm{H}_y}{\partial y}\right)_0\right\} \\ &-\mathrm{A}\left\{u\left(\frac{\partial \mathrm{H}_z}{\partial x}\right)_0+v\left(\frac{\partial \mathrm{H}_z}{\partial y}\right)_0\right\}-\mathrm{H}_{0z}\frac{d\mathrm{A}}{dt}\Bigg] \\ &+\frac{\epsilon^2}{4m}\left[\mathrm{A}\left\{\left(\frac{\partial f(\mathrm{P}_y)}{\partial x}\right)_0-\left(\frac{\partial f(\mathrm{P}_x)}{\partial y}\right)_0\right\}\right]+\frac{\epsilon^2}{2m}\Sigma(\xi\mathrm{Y}-\eta\mathrm{X}) \end{aligned}$$

The last term is zero if each molecule has no initial moment, as LANGEVIN'S theory of diamagnetism requires. Leaving aside the subscript 0 and using the equations of the electromagnetic field

$$\frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} = -\frac{\partial H_z}{\partial t}, \qquad \frac{\partial H_x}{\partial x} + \frac{\partial H_y}{\partial y} + \frac{\partial H_z}{\partial z} = 0,$$

and

$$\frac{\partial H_z}{\partial t} + u \, . \, \frac{\partial H_z}{\partial x} + v \, . \, \frac{\partial H_z}{\partial y} + w \, . \, \frac{\partial H_z}{\partial z} = \frac{dH_z}{dt},$$

we get, following LANGEVIN,

$$\dot{M}_z = -\frac{\epsilon^2}{4m} \cdot \frac{d}{dt}(H_z A) + \frac{\epsilon^2}{4m}\left\{A\left[\frac{\partial f(P_y)}{\partial x} - \frac{\partial f(P_x)}{\partial y}\right]\right\}.$$

Integrating this equation from time O $(H = 0)$ to time τ $(H = H_z)$ we find

$$\Delta M_z = -\frac{\epsilon^2}{4m} \, . \, H_z A + \frac{\epsilon^2 A}{4m}\int_0^\tau \left[\frac{\partial}{\partial x} f(P_y) - \frac{\partial}{\partial y} f(P_x)\right] dt,$$

where ΔM_z is the magnetic moment produced in the molecule during this interval. The second term on the R.H.S. of (6) will depend upon the molecular configuration of the substance and implies a modification of the electron circuits which will change their self-induction. Now any change of the self-induction may be represented by a small change of the intensity of the applied magnetic field.

We may write

$$f(P) = \alpha \, . \, P,^*$$

where "α" characterizes the grouping of the molecules and therefore

$$\left[\frac{\partial}{\partial x} f(P_y) - \frac{\partial}{\partial y} f(P_x)\right] = \alpha\left(\frac{\partial P_y}{\partial x} - \frac{\partial P_x}{\partial y}\right) = -\alpha \frac{\partial}{\partial t}(\delta H_z),$$

where $\alpha \, . \, \delta H_z$ is the elementary change in the external field during a small interval of time δt.

Therefore

$$\Delta M_z = -\frac{\epsilon^2}{4m} H_z A - \frac{\epsilon^2 A \alpha}{4m} \, . \int_0^\tau \frac{\partial}{\partial t}(\delta H_z) \, . \, \partial t$$

$$= -\frac{\epsilon^2 H_z A}{4m} \, . \left[1 + \frac{\alpha \, . \, \Delta H_z}{H_z}\right], \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

where $\alpha \, . \, \Delta H_z$ is the total variation of H_z due to establishing this magnetic field when the electron orbits are modified by the presence of neighbouring molecules.

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* LORENTZ, 'Theory of Electrons,' p. 137.

If N be the number of molecules in one gramme of the substance we may write the specific susceptibility

$$\chi = \frac{\mathrm{N}\Delta\mathrm{M}_z}{\mathrm{H}_z} = -\frac{\mathrm{N}\epsilon^2\mathrm{A}}{4m}\cdot\left[1+\frac{\alpha\,.\,\Delta\mathrm{H}_z}{\mathrm{H}_z}\right]. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

and it is clear that the value of χ is modified by crystallization, for the polarisation term $\alpha\mathrm{P}$ varies with the state of the substance. If $\alpha = 0$, (7) reduces to the Langevin expression for diamagnetic susceptibility in which the mutual influences of the molecules are neglected.

The variation of χ on crystallization may be written

$$\frac{\partial\chi}{\chi} = (\alpha_c - \alpha_l)\,.\,\frac{\Delta\mathrm{H}_z}{\mathrm{H}_z}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

where α_c and α_l are the electric polarisation constants for the crystals and liquid respectively; α_l is of the order 1/3 for most liquids.* It now remains for us to examine the amount of this change and to do this we must determine α_c. The value of the polarisation constant for any substance is positive and may be very large compared with the value 1/3 which it usually possesses for the liquid state; but its exact determination in any particular case is difficult since it depends upon the actual distribution of the molecules, about which we know very little.

It appears, however, that we can deduce an approximate value of the magnitude of α_c from CHAUDIER's researches on the change of magnetic rotatory power with change of state. This deduction leads to a reasonable value.

It has been shown by BECQUEREL, BICHAT, and later by CHAUDIER,† that the magnetic rotatory power of the liquid and vapour states is not generally the same, and it is reasonable to suppose that a similar but more pronounced effect will be found in the passage from the liquid to the crystalline state, but the phenomenon will usually be complicated in the latter case owing to the appearance of double refraction. The researches of GOUY‡ and CHAUVIN§ show that in the case of Iceland spar the effects of double refraction and magnetic rotation are simply superposed. Now CHAUDIER‖ has established that the magnetic rotatory power disappears completely during the crystallization of aniline, benzene, and nitrobenzene (all of which have been investigated in Part I.). If this is a true discontinuity of the magnetic rotatory power, apart from any effect due to double refraction, then we can use this fact to obtain an estimate of

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* *Loc. cit.*, p. 138, or LARMOR, 'Phil. Trans. Roy. Soc.,' 1897, A, p. 233.

† 'Comptes Rendus,' vol. 156, p. 1008, 1913.

‡ 'Journ. de Phys.,' sér. II., vol. 4, p. 149, 1885.

§ 'Journ. de Phys.,' sér. II., vol. 9, p. 5, 1890.

‖ 'Comptes Rendus,' vol. 156, p. 1529, 1913.

the value of α_c for the crystalline forms of these substances. The value deduced* (see footnote) on these assumptions must be at least of the order 10^2 and may be larger. Now reverting to equation (8), we see that the experimental value of $\partial\chi/\chi$, approximately 5 per cent., will be in accordance with the above theory of the effect of crystallization if the change of self-induction of an electron orbit of a substance in the liquid state, due to the presence of neighbouring molecules, be such that

$$\Delta H_z/H_z = 5 \times 10^{-4}.\dagger$$

The value of this ratio will be still smaller if α_c possesses a greater value than 10^2. In the crystalline state, the modification of the electron orbit will be determined by $\alpha_c \Delta H_z/H_z$ and since α_c is large, this term accounts for the variation, $\partial\chi$, found in the experimental investigation of Part I. In the case of liquids, where $\alpha_l = 1/3$, this term produces no appreciable effect on the value of χ, as equation (7) shows.

(2) The Mean Molecular Field of a Diamagnetic Crystalline Substance.

The large value of the electric polarisation constant α_c is compatible with the considerable rigidity possessed by crystalline structures. The term $\alpha_c \,.\, \Delta H_z/H_z$ will therefore be important in the crystalline state. For a super-cooled liquid we may write

$$\chi_l = -\frac{N\epsilon^2 A}{4m},\ddagger$$

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* An extension of the theory of magnetic rotation has just been published by G. H. Livens ('Phil. Mag.,' vol. 26, p. 362, 1913), in which the influence of the electric polarisation due to neighbouring molecules is taken into consideration. Livens shows that the rate of rotation of the plane of polarisation by a solution may be written

$$w = \frac{\epsilon H n^2}{\mu c} \,.\, \Sigma \frac{\epsilon^2}{m^2 (n_0^2 - n^2)^2} \bigg/ \left(1 - \Sigma \frac{a\epsilon^2}{m (n_0^2 - n^2)}\right)^2,$$

where n is the frequency of the light wave, n_0 the restoring coefficient due to displacement of an electron, a the constant of electric polarisation, and ϵ, H, μ, and c have their usual interpretation. The Σ extends to all the electrons in unit volume.

If $a = 0$ we get the result of Drude's theory, where the mutual influences of the molecules are neglected; w is of the order 10^{-2} for the liquid state, and if w is reduced to 1 per cent. of this value when crystallization sets in, the value of

$$\Sigma \frac{a_c \epsilon^2}{m (n_0^2 - n^2)}$$

must be at least of the order 10. Now $\epsilon \doteqdot 10^{-10}$ E.S.U., $m \doteqdot 10^{-27}$, and $n^2 \doteqdot n_0^2 \doteqdot 10^{30}$. As there are about 10^{22} electrons per cubic centimetre, a_c must be of the order 10^2 at least.

We have assumed that the medium is isotropic, but as the crystals are differently orientated this assumption will not change the order of a_c.

† This ratio corresponds to a small alteration of the area of an electron orbit to the maximum extent of 1 in 2,000, a magnitude which is quite permissible.

‡ This equation is in accordance with the observations of M. Chaudier, who has shown that, if a substance super-cools or assumes a gelatinous form, the magnetic rotation is the same as for the normal liquid state (*i.e.*, $a \doteqdot \frac{1}{3}$ for the gelatinous state).

neglecting the term $\alpha_l \,.\, \Delta H_z/H_z$ since $\alpha_l \doteqdot 1/3$. For the crystals, at the same temperature, we have

$$\chi_c = -\frac{N\epsilon^2 A}{4m} \,.\, \left[1+\alpha_c \,.\, \frac{\Delta H_z}{H_z}\right].$$

Hence

$$\chi_c = \chi_l \,.\, \left[1+\alpha_c \,.\, \frac{\Delta H_z}{H_z}\right],$$

or

$$\chi_c \,.\, H_z = \chi_l \,.\, [H_z+\alpha_c \,.\, \Delta H_z].$$

I shall call $\alpha_c \,.\, \Delta H_z$ the mean molecular field of the diamagnetic crystals. Now for a given change of the electron orbits due to crystallization, ΔH_z will be proportional to H_z. Hence we may neglect the mutual forces between the diamagnetic molecules when the substance crystallizes providing we supply a molecular field which is proportional to H_z, and therefore to ΔM_z, or to the intensity of magnetization of the substance (equation (6)). For the liquid and gelatinous states this molecular field is negligibly small, because α_l is small, but for the crystalline state α_c is large, and the molecular field is comparable with the external field H_z.

This is exactly analogous to the theory of ferro-magnetism developed by M. Weiss, in which the molecular field is **NI**, where **I** is the magnetic moment produced by the external field and **N** is a constant determined by the intermolecular forces of the crystalline ferro-magnetic material. **N** corresponds to the polarisation constant α_c of the diamagnetic theory. We ought, however, to compare **N** with α_c', where the molecular field

$$\alpha_c \,.\, \Delta H_z = \alpha_c' \,.\, N \,.\, \Delta M_z \rho,$$

ρ, the density of the substance, is of the order 1.

If $\alpha_c = 10^2$, this gives (since $\Delta H_z = H_z/2\times 10^3 = N \,.\, \Delta M_z/\chi \times 2\times 10^3$)

$$\alpha_c' = \alpha_c/\chi \times 2 \times 10^3.$$

Assuming $\chi = 5\times 10^{-7}$, we find $\alpha_c' = 10^3\alpha_c$. Hence the constant of the diamagnetic field is 10^5. The corresponding values of **N** given by Weiss and Beck* are $0{\cdot}38\times 10^4$ for iron, $1{\cdot}27\times 10^4$ for nickel, and $3{\cdot}32\times 10^4$ for magnetite. The mean molecular fields are enormously greater in the cases of ferro-magnetic substances on account of the large value of the intensity of magnetization as compared with that for diamagnetic substances. The values of **NI** (the saturation molecular field) are 6, 530, 000 gauss for iron, 6, 350, 000 gauss for nickel, and 14, 300, 000 gauss for magnetite, while the corresponding value of $\alpha_c' \,.\, \Delta M_z$ for a diamagnetic substance is of the order 150 gauss for an applied field of 3000 gauss, the field used in the above experiments.

To account for the phenomena of the Zeeman effect, magnetic rotation of the plane of polarisation, and diamagnetism, it is necessary to assume that an atom contains

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* 'Journ. de Phys.,' sér. IV., vol. 7, p. 249, 1908.

oppositely rotating systems of electrons. A diamagnetic molecule, on LANGEVIN'S theory, has no initial magnetic moment but there can be complete compensation of the electro-magnetic forces due to the spinning electrons only at points considerably removed from the molecule. Although these forces are compensated at an external point, and the magnetic property observed corresponds to diamagnetism, yet between the molecules the forces will be large and the local intensity of magnetization may be comparable with that of ferro-magnetic substances.* It is interesting that the value of a_c', which defines the crystal structure of a diamagnetic substance, should be at least of as high an order of magnitude as the constant **N** of the ferro-magnetic field. It is probable that these large values of the coefficients of the molecular fields are the origin of the stability and rigidity of crystal structure in general.

Since we may interpret the effect of the surrounding molecules by means of the term aP, it follows that if from any cause the polarisation P suffers a reversal of sign, then the sign of ΔH_z will change, *i.e.*, the variation of χ on crystallization will correspond to the abnormal cases referred to in Part I. The mechanism by which this reversal of $\partial\chi$ is brought about may be attributed to a directive influence of the substituent (or other dissymmetry of the complex molecule) which will produce an electric polarisation effect of opposite kind in a neighbouring nucleus, according to the direction of the force between the substituent and the nucleus.

The liquid state will be more diamagnetic than the crystalline state if $\Delta H_z/H_z$ is negative, *i.e.*, if the process of crystallization involves a small reduction of the self-induction of the electron orbits. This corresponds to the majority of cases investigated in Part I.

In the above theory no account has been taken of the small reaction forces† which will arise from the production of the diamagnetic moment ΔM_z. Since, however, χ (and therefore ΔM_z) does not vary by more than a few per cent. as the substance passes from the liquid to the crystal state, these small reaction effects will appear in both states approximately to the same extent and therefore the value of $\partial\chi$ will not be affected on their account.

SUMMARY OF CONCLUSIONS.

The experimental results described in Part I. have established an almost complete parallelism between the dependence of diamagnetic and ferro-magnetic susceptibilities upon molecular constitution. The molecular changes are of the same nature and the only difference between the two classes of magnetic phenomena lies in the character of the magnetic property possessed by the molecules and by which the variation of molecular complexity is disclosed.

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[*] See Note added, p. 145.

[†] LANGEVIN, 'Ann. de Chim. et de Phys.,' VIII., vol. 5, p. 88, 1905, concludes that such effects would not produce an appreciable change in the magnitude of χ.

In the liquid and crystalline states, providing there are no molecular complexes whose constitutions vary with the temperature, the diamagnetic property involves no temperature co-ordinate and is represented by a series of straight lines parallel to the temperature axis. The work of MM. WEISS and KAMERLINGH ONNES has shown that ferro-magnetic and paramagnetic properties can be represented by a series of hyperbolæ. In either case, I have shown that if the substance forms aggregates, or assumes a crystalline structure, the transition stage is represented by the equations

$$\chi_D = \frac{1}{H} \Sigma n_p \, . \, \Delta M_p \text{ (diamag.)}, \qquad \chi_P = \Sigma \frac{n_p \, . \, c_p}{\vartheta} \text{ (paramag.)}$$

which take into account the coexistence of molecular complexes of different types.

These two expressions are generally applicable and represent the variation of magnetic property with temperature in terms of the two Curie laws, and the superposed effect of the change of molecular complexity with temperature.

For most of the substances examined, the liquid state is more diamagnetic than the crystals. The cases of benzoyl chloride, phenylhydrazine and the liquid crystal compounds, cholesteryl chloride and para-azoxyanisol, are abnormal. Nearly all benzene derivatives show a change of susceptibility on crystallization, amounting to 5 per cent. (approximate). The sign of this change is attributed to the directive action of the substituent.

The experiments show that diamagnetism is not wholly an atomic property; for the process of crystallization, involving simply a closer approach of the atomic spheres of influence, is able to modify the susceptibility.

The existence of a gelatinous or super-cooled liquid state, possessing in all the cases examined a diamagnetic property equal to that of the liquid above the normal fusion point, corresponds to the existence of a supercooled paramagnetic state of nickel-steels below the critical temperature. Definite hysteresis loops with respect to temperature have been obtained, similar to those discovered by the late Prof. HOPKINSON for nickel-steels. The heat of formation of the diamagnetic crystals corresponds to the heat evolved at the critical temperature of the nickel-steel.

The constancy of the diamagnetic property when the substance supercools or passes into a jelly is in harmony with the constancy of the closely related phenomenon of the magnetic rotation of the plane of polarisation by that substance when a gelatinous form is assumed. The process of crystallization is accompanied by a modification of the susceptibility and of the magnetic rotation.

The hypothesis of molecular distortion stated at the beginning of this communication has been justified, and the interpretation of the effect of crystallization as due to a slight modification of the internal structure of the molecule is in agreement with the conceptions of chemists and crystallographers concerning the nature of crystal structure.

In Part II., the extension of Langevin's theory shows that an exceedingly small and reasonable deformation of the molecules in the liquid state is sufficient, owing to the large value of the constant a_c, to account for the change of susceptibility actually observed when the substance crystallizes.

Moreover, the introduction of the idea of a molecular field of the diamagnetic crystals allows us to neglect the mutual influences of the diamagnetic molecules in exactly the same way as the molecular field of Weiss allows us to express the phenomena of ferro-magnetism, without bringing into consideration the mutual influences of the molecules. Both the molecular field of Weiss and the molecular field of the diamagnetic crystals are proportional to the intensity of magnetization, in the respective cases, and the minimum value of the constant of the latter field, deduced from the variation of magnetic rotatory power when crystallization sets in, is of the same order as that of the ferro-magnetic field.

Although on account of a particular structure of the molecules the magnetic properties of different substances, observed externally, may vary enormously, yet, within the substances, the local intensities of magnetization and the forces between the molecules will be large in all crystalline substances. These forces determine the rigidity of the crystalline structures.

These investigations have been made in the Cavendish Laboratory and I wish to thank Prof. Sir Joseph Thomson for placing the necessary apparatus at my disposal and for the interest he has shown in the work.

I am indebted to Prof. Pope for supplying me with many substances for investigation and also for a valuable discussion on the subject of crystal structure.

[It will have been observed that the theoretical treatment given in Part II. consists of an interpretation of the polarisation term, $\frac{\epsilon^2 A}{4m} \cdot \int_0^\tau \left[\frac{\partial}{\partial x} f(P_y) - \frac{\partial}{\partial y} f(P_x)\right] dt$, (which represents that part of the diamagnetic moment due to the distortion of a molecule by the influences of neighbouring molecules of the crystalline structure) by means of a magnetic field. This field is superposed upon the applied field and it has been shown that we may disregard the mutual influences of the molecules forming the crystalline structure if the resultant of these fields is substituted for the applied field.

This corresponds to the interpretation, given by M. Weiss, of the mutual influences of the molecules of ferro-magnetic substances by a uniform magnetic field, **NI**, superposed upon the applied field.

Since the work described in Parts I. and II. was communicated to the Royal Society, a paper has appeared by Weiss ('Comptes Rendus,' vol. 157, No. 25, p. 1405, December 22, 1913) which deals more fully with the nature of the molecular field in ferro-magnetic substances. It is there shown that the large forces which act between the molecules are not necessarily magnetic but may be of any other nature. A consideration of the continuity of magnetic flux has led WEISS to abandon the idea that the magnetic field is actually a *uniform* magnetic field. The difficulty may be surmounted by assuming the molecular field to be localized. This localized nature is a necessary property of the molecular field in diamagnetic crystalline substances. But, as WEISS points out, it is rather difficult to see how the molecular magnets, or the electron orbits, in adjacent molecules, can approach one another so closely that, in spite of thermal agitation, the local field between the molecules should amount to the enormous value of 10^7 gauss.

In any case, whatever may be the nature of the local forces which hold the molecules of a crystalline structure together, we may interpret the accompanying distortion by means of a magnetic field of such magnitude that it produces in the molecules the same change of moment as the actual forces within the crystalline structure will produce. This statement holds whether the substance be ferro-magnetic or diamagnetic.

The large value of this local magnetic field in diamagnetic substances has been briefly mentioned at the end of Part II. It can be shown that a local field, comparable in intensity with the ferro-magnetic field of WEISS, will produce, according to LANGEVIN'S theory, a modification of the electron orbits in the molecules of a diamagnetic substance such as would account for the change of χ observed on crystallization in the experiments of Part I. In a subsequent paper I hope to describe in detail several extensions of the work contained in Parts I. and II., and I should like to make a brief reference here to one or two points because they furnish additional support to the conclusions which have already been mentioned. Further experiments have been made, similar to those described in Part I., and the change of susceptibility on crystallization has been correlated with the magnetic double refraction of the same substance observed by MM. COTTON and MOUTON. The large double refraction of a crystalline structure, as compared with that of a liquid subjected to the strongest magnetic field which we can produce in the laboratory, is compatible with the relatively large local magnetic field by which we may express the forces which hold the molecules in position in the crystal.

Perhaps these large local fields between the molecules of a crystalline structure may be identified with the intense intra-atomic fields of RITZ ('Ann. der Phys.,' IV., vol. 25, p. 660, 1908) which give us a direct interpretation of BALMER'S and RYDBERG'S expressions for spectral series, or with the magneton of WEISS. This would imply that the molecules in the crystal structure are exceedingly close together and that their oscillations are of extremely small amplitude. It is possible that the magneton will prove to be a constituent of diamagnetic as well as of para-magnetic and ferro-magnetic matter.—*Note added March, 1914.*]