

The Influence of Molecular Constitution and Temperature on Magnetic Susceptibility. Part III: On the Molecular Field in Diamagnetic Substances

A. E. Oxley

Phil. Trans. R. Soc. Lond. A 1915 **215**, 79-103

doi: 10.1098/rsta.1915.0003

Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

To subscribe to *Phil. Trans. R. Soc. Lond. A* go to: <http://rsta.royalsocietypublishing.org/subscriptions>

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

Part III. On the Molecular Field in Diamagnetic Substances.

By A. E. OXLEY, M.A., M.Sc., *Coutts Trotter Student, Trinity College, Cambridge,*
Mackinnon Student of the Royal Society.

Communicated by Prof. Sir J. J. THOMSON, O.M., F.R.S.

Received June 24,—Read June 25,—Revised December 2, 1914.

CONTENTS.

	Page
(1) Introduction	79
(2) On the local molecular polarization and the local molecular forces within diamagnetic fluid and crystalline media	80
(3) The mean and local molecular fields of a diamagnetic crystalline substance	81
(4) On the magnitude of the local molecular field	84
(5) On the stresses and energy associated with the molecular field	90
(6) Additional experiments	96
(7) A relation between the magnetic double refraction of organic liquids and the change of magnetic susceptibility due to crystallization	97
(8) On the nature of the molecular field	100

(1) INTRODUCTION.

IN the present communication an attempt is made to examine to what extent the crystalline state of diamagnetic substances (which form a very large proportion of the whole number of substances known to us) involves mutual actions between the constituent molecules and to obtain a measure of the forces which hold the molecules together in a definite space lattice characteristic of the substance. The work is thus a continuation of that published in 'Roy. Soc. Phil. Trans.,' vol. 214, pp. 109–146, 1914, wherein it was shown how from determinations dealing with the change of diamagnetic property on crystallization information could be derived concerning the inner structure of crystalline media and the intensity of the interacting molecular forces.

In the paper cited (p. 143) it was suggested that the local molecular field within diamagnetic crystalline media may be comparable with the ferro-magnetic molecular (525.)

[Published February 16, 1915.]

field. In the light of the experimental results on aromatic substances there described and of those given by DU BOIS, HONDA and OWEN, which are concerned with elementary substances, this suggestion has been found to lead to interesting results. It is clear that we can easily test whether such an intense local molecular field exists; for if so it must be of import in connection with the transition from the liquid to the crystalline state in general, and the changes of other physical properties which accompany this change of state must also depend directly or indirectly upon the molecular field. The object of the present communication is to test the experimental and theoretical work which has already been completed by applying the results obtained to a wider range of physical phenomena. Evidence of a change of specific diamagnetic susceptibility owing to crystallization has been obtained with about forty substances, but with some substances the change, if it exists, is exceedingly small. Ten additional substances have been investigated, and the results, in conjunction with the other physical properties, are used to extend the ideas concerning the molecular field to diamagnetic crystalline media in general.

PART III.

(2) ON THE LOCAL MOLECULAR POLARIZATION AND THE LOCAL MOLECULAR FORCES WITHIN DIAMAGNETIC FLUID AND CRYSTALLINE MEDIA.

The passage from a purely mechanical theory of the properties of material media to the actual discrete molecular theory, as interpreted electro-dynamically, involves an examination of the local polarizations which act in the immediate neighbourhood of the point considered within the medium. It has been shown by Sir JOSEPH LARMOR* that the forces exerted at such a point by the surrounding polarized medium can be separated into two parts, a purely local part and a part due to the rest of the medium. If we neglect the forces due to the former then those due to the latter are derivable from a potential due to the combined volume and surface density distributions of POISSON. With fluid media we can go further and determine, at least approximately, the forces due to the purely local part. This is attained by imagining a cavity scooped out round the point and determining the force due to the surface distribution of polarization over its walls. The removed molecules are now put back in the cavity and the additional force which they contribute is found by applying the method of averages. The molecules of a fluid are in rapid motion and the force at a point in the interior of the cavity due to these replaced molecules averages out to a small corrective polarization. It can be shown that the force due to the immediately neighbouring molecules is represented by $(\frac{1}{3}+s)P$ where P is the

* 'Roy. Soc. Phil. Trans.,' A, vol. 190, p. 233, 1897; and LORENTZ, 'Theory of Electrons,' pp. 137 and 303.

polarization due to the applied field and s is the coefficient of the corrective polarization—the effect of the replaced molecules.

Within a crystalline structure, however, this method of averages applied to the molecules within the cavity is not valid, for each molecule is orientated so as to occupy some definite position with respect to its neighbours. In such a case the local force, due to a molecule which is close to the point under consideration, is uncompensated, and we have to resort to indirect deduction from experimental facts to obtain a measure of the polarization effect due to the molecules immediately surrounding the point. It is to this uncompensated effect that we have attributed the rigidity of the crystalline medium.* In order to avoid the complexity introduced by the elasticity of crystalline media LARMOR confined his investigations to fluids; but, as we are attempting to ascribe to these very elastic forces a nature which permits of their interpretation in terms of a local molecular field binding the molecules together, the treatment for crystalline substances is the same in kind as that for fluid substances.

The rigidity of gels at low temperatures is of a different nature and is probably due to an interlocking of the molecules (arranged at random) whose thermal agitation is sufficiently reduced. This is in accordance with the work of TAMMANN† who found that at very low temperatures the power and velocity of crystallization were very small.

(3) THE MEAN AND LOCAL MOLECULAR FIELDS OF A DIAMAGNETIC CRYSTALLINE SUBSTANCE.

In a former paper‡ the author has shown that the change of specific susceptibility, which accompanies the transition from the liquid to the crystalline state for many substances, can be satisfactorily interpreted in terms of a *mean* molecular field which operates to an appreciable extent only in the crystalline state. The nature of this molecular field need not be definitely specified, and it will suffice for our purpose to regard it as a magnetic field limited to such a magnitude as to produce in the molecules of the substance a distortion, or polarization, such as is equivalent to that actually produced by the mutual forces of the molecules of the crystalline structure.§

In Part II. of the work referred to, the mean molecular field was represented magnetically by the term $\alpha_c \cdot \Delta H$, where α_c is a coefficient (the constant of the

* 'Roy. Soc. Phil. Trans.,' A, vol. 214, p. 143, 1914.

† WHETHAM, 'Theory of Solution,' p. 44, and references to TAMMANN'S work there given.

‡ 'Roy. Soc. Phil. Trans.,' A, vol. 214, p. 109, 1914. This paper contains Parts I. and II. of the present work, and, for brevity, reference is made to these in what follows.

§ A force of electrostatic nature will modify the electron orbits, and therefore the susceptibility, an effect which we may represent magnetically. If the revolving electrons are controlled by molecular magnets (as on RITZ'S theory), a magnetic field would be the true interpretation of the molecular field. Probably both types of molecular field co-exist (*vide infra*, p. 22, for a discussion of the nature of the molecular field).

molecular field) defining the extent of the polarization of the molecules in the crystalline state and depending upon the definite space lattice which the molecules assume. $\frac{\Delta H}{H}$, where H is the applied field, defines the distortion produced in an electron orbit by the forces exerted by surrounding molecules when the substance is in the liquid state. ΔH is the polarization (proportional to the applied field H) due to this distortion. As we do not know the actual disposition or the proximity of the molecules in the structure, the difficulty in attempting to calculate α_c is insuperable and we are compelled to try the more indirect method afforded by experiment. A rough estimate of the value of α_c has been obtained from CHAUDIER'S observations on the change of magnetic rotatory power when aniline, benzene and nitrobenzene crystallize, the order of magnitude deduced being at least 10^2 .* The corresponding value of α_l for the liquid state, deduced from theoretical considerations, is of the order $\frac{1}{3}$.† Thus in the liquid state the mean molecular field is represented by $\frac{1}{3} \cdot \Delta H$. The distortion of the molecules in the liquid state of the substance is therefore insignificant compared with that for the crystalline state and, neglecting α_l in comparison with α_c , it was shown that

$$\chi_c \cdot H = \chi_l \cdot [H + \alpha_c \cdot \Delta H], \quad (1)$$

where H is the intensity of the applied magnetic field, χ_c and χ_l are the specific susceptibilities of the crystalline and liquid states respectively. Thus we may ignore the mutual influences of the molecules of the crystalline state providing we supply a mean molecular field whose magnetic equivalent is $\alpha_c \cdot \Delta H$. Equation (1) shows that the actual change of χ on crystallization (a few per cent. with aromatic compounds) demands that $\Delta H/H$ shall be of the order $5 \cdot 10^{-4}$; which implies a small and reasonable distortion of the molecules of a liquid due to the surrounding molecules. It should be noted that this is a maximum value of the distortion for the liquid state. The value will be smaller if, as is probable, α_c is of a higher order than 10^2 . At present no physical interpretation has been put upon the large value of α_c , but we see that it is representative of the local part of the force in the crystalline state just as the smaller constant α_l is representative of the local part of the force in the liquid state.

On the theory of magnetism developed by LANGEVIN, a diamagnetic molecule contains oppositely spinning systems of electrons which counterbalance one another externally so that the molecule possesses no initial magnetic moment.‡ When an external magnetic field is applied the period of one system of electrons is lengthened, that of the other system is shortened, and the molecule becomes slightly polarized or distorted. This small differential effect, which is compatible with the Lorentz

* Part II., p. 141.

† LARMOR, 'Roy. Soc. Phil. Trans.,' A, vol. 190, p. 233, 1897.

‡ This null initial magnetic moment corresponds to the null electric moment possessed by a molecule of a dielectric which is not subjected to an external electrostatic field.

explanation of the Zeeman effect, is the origin of the small negative moment possessed by diamagnetic substances when subjected to a magnetic field. The smallness of the diamagnetic susceptibility in general is due to the self-compensation of the forces (produced by the oppositely rotating systems of electrons or any other magnetic system in the molecule) which takes place at points whose distances from the molecules are large in comparison with molecular dimensions. But quite close up to the molecule these forces will not compensate and the local force will be comparable with that due to an unbalanced revolving electron or other magnetic element of the molecule. It is with this *local* field that the present communication is mainly concerned. I shall call it the local molecular field of the diamagnetic substance. In the crystalline state we may regard the space lattice as defined by the local forces exerted between a system of electrons in one molecule upon another system in an adjacent molecule and so on throughout the crystalline structure.

As was shown in Part II., p. 142, the mean molecular field is proportional to the intensity of magnetization of the substance, and we may write

$$\alpha_c \cdot \Delta H = \alpha'_c \cdot N \cdot \Delta M \cdot \rho \dots \dots \dots (2)$$

where α'_c is the new constant of the molecular field, of the order 10^5 , N the number of molecules per gram., ΔM the diamagnetic moment induced in a molecule by applying an external magnetic field H , and ρ is the density of the substance. The local molecular field will have the same constant of proportionality but we must replace the

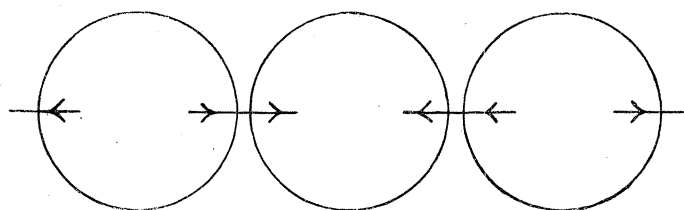


Fig. 1.

diamagnetic moment ΔM of the molecule as a whole by the local moment associated with a pair of molecules. We have no means of measuring directly the value of this latter quantity, but it is probably very large in comparison with ΔM , and it was suggested at the end of Part II. that it may be so large that the local molecular field is comparable with the molecular field in ferro-magnetic substances.* On account of the null initial moment which has been prescribed for the diamagnetic molecule the local molecular field will be of an alternating character, the distance over which it is unidirectional being comparable with the distance between the molecules, as the diagram above shows.

* It should be noted that this *local* molecular field will exist in all crystalline substances, whether they are subjected to an external magnetic field or not. On the other hand, the *mean* molecular field is a differential effect and depends on ΔM , the diamagnetic moment which is induced by the external field.

The small value of α_l possessed by fluid substances implies a mean molecular field much smaller than that associated with a crystalline structure. But how much larger the mean and local molecular fields of the crystalline state are compared with those of the liquid state has not been ascertained at present. All that has been shown in Parts I. and II. is that the minimum value of the mean molecular field in some diamagnetic crystalline media is large compared with that in liquids. We shall now proceed to obtain an estimate of the intensity of the local molecular field in crystalline media from the small variation of χ which occurs on crystallization.

(4) ON THE MAGNITUDE OF THE LOCAL MOLECULAR FIELD.

If we apply a strong magnetic field to a diamagnetic liquid whose molecules possess dissymmetry, LANGEVIN* has shown that the liquid becomes doubly refracting and that a very small proportion of the unsymmetrical molecules suffer an orientation under the action of the field. The amount of orientation which can be produced by the largest magnetic field obtainable is not sufficient to affect the value of the susceptibility appreciably.† When, however, the liquid crystallizes and all the molecules are similarly orientated, we should expect that the susceptibility will be different in different directions if the molecules are not symmetrical. But this cannot be the explanation of the change of χ observed in the experiments of Part I. (and in those carried out by HONDA and OWEN). For in these experiments the crystals were small and their axes would be distributed at random. In some cases the crystals were observed to grow in such a way. The explanation here put forward, and which has already been advanced in Parts I. and II., is that each molecule of the substance is distorted when it forms part of a crystalline structure by the local forces due to the neighbouring molecules. This mutual action between the molecules is necessary to account for the rigidity of the crystalline structure and for the existence of planes of cleavage (see p. 92, *infra*). We can therefore find the intensity of the local molecular field by making it of such magnitude as to produce a change of susceptibility of the same order of magnitude as that actually observed in the crystallization experiments.

We may write‡

$$\frac{\Delta M}{M} = -\frac{H\tau\epsilon}{4\pi m} = -10^{-9} H \dots \dots \dots (3)$$

where ΔM is the change of moment produced in an electron orbit of moment M by applying a field H , τ is the period of the electron, approximately 10^{-15} sec., and ϵ/m the ratio of the charge to the mass of an electron, 1.7×10^7 . The largest field which

* 'Le Radium,' vol. 7, p. 249, 1910.

† *Loc. cit.*, p. 252.

‡ LANGEVIN, 'Ann. de Chim. et de Phys.,' sér. VIII., vol. 5, p. 96, 1905.

can be produced in the laboratory is of the order 10^5 gauss, and therefore the largest moment which we can induce is given by

$$|\Delta M| < 10^{-4} \cdot M.$$

This induced moment is sufficiently large to account for the diamagnetic susceptibility of the substance.

From equation (3) we have

$$\frac{\Delta M_l}{M_l} = -\frac{\epsilon \tau_l H}{4\pi m}, \quad \dots \dots \dots (4)$$

$$\frac{\Delta M_c}{M_c} = -\frac{\epsilon \tau_c H}{4\pi m}, \quad \dots \dots \dots (5)$$

where the subscripts l and c refer to the liquid and crystalline states respectively.

In passing from the liquid to the crystalline state the alteration of M_l produced by the local molecular field H_c is $\Delta M'_l$ where

$$\frac{\Delta M'_l}{M_l} = -\frac{\epsilon \tau_l H_c^*}{4\pi m}, \quad \dots \dots \dots (6)$$

$$M_c = M_l \pm \Delta M'_l. \quad \dots \dots \dots (7)$$

It should be noted that although H_c alternates as we pass from molecule to molecule of the crystalline structure, still the sign of $\Delta M'_l$ will everywhere remain the same, for when H_c changes sign M_l also changes sign, so that every molecule of the crystalline structure suffers a definite distortion due to the action of the local molecular field. The ambiguity of sign in the above formulæ simply implies that the arrangement of molecules may be such that M_l is increased or decreased by the particular kind of packing which the molecules assume and corresponds to a reversal of the sign of $\partial \chi$. (See Part I., p. 133, and Part II., p. 143.)

From equations (6) and (7), we find

$$M_c = M_l \left(1 \mp \frac{\epsilon \tau_l H_c}{4\pi m} \right), \quad \dots \dots \dots (8)$$

and therefore from (5)

$$\frac{\Delta M_c}{M_l} = -\frac{\epsilon \tau_c H}{4\pi m} \left(1 \mp \frac{\epsilon \tau_l H_c}{4\pi m} \right). \quad \dots \dots \dots (9)$$

Hence

$$\frac{\Delta M_c - \Delta M_l}{M_l} = -\frac{\epsilon \tau_c H}{4\pi m} \left(1 \mp \frac{\epsilon \tau_l H_c}{4\pi m} \right) + \frac{\epsilon \tau_l H}{4\pi m}, \quad \dots \dots \dots (10)$$

which gives by (4)

$$\frac{\Delta M_c - \Delta M_l}{\Delta M_l} = \frac{\tau_c}{\tau_l} \left(1 \mp \frac{\epsilon \tau_l H_c}{4\pi m} \right) - 1. \quad \dots \dots \dots (11)$$

* H_l , the molecular field within the liquid, is insignificant compared with H_c and is therefore neglected in equations (6) and (7).

The electrons which give rise to diamagnetism also give rise to the Zeeman effect, a slight alteration of their periods accounting for both phenomena.* The order of magnitude of the local molecular field H_c will not be effected by assuming that the electrons in a molecule have a mean natural period τ_l , when the substance is in the liquid state, which becomes modified to $\tau_c = \tau_l \pm \delta\tau$, when crystallization sets in. The change of period $\delta\tau$ indicates the order of magnitude of the displacement of an absorption band owing to the transition from the liquid to the crystalline state.

Now

$$\chi_c = \frac{Nn}{H} \cdot \Delta M_c, \quad \chi_l = \frac{Nn}{H} \cdot \Delta M_l, \quad \partial\chi = \chi_c - \chi_l = \frac{Nn}{H} (\Delta M_c - \Delta M_l),$$

where n is the number of electrons per molecule and N the number of molecules per gram. Therefore

$$\begin{aligned} \frac{\partial\chi}{\chi} &= \frac{\Delta M_c - \Delta M_l}{\Delta M_l} = \frac{\tau_c}{\tau_l} \left(1 \mp \frac{\epsilon\tau_l H_c}{4\pi m} \right) - 1 \\ &= \left(1 \pm \frac{\delta\tau}{\tau_l} \right) \left(1 \mp \frac{\epsilon\tau_l H_c}{4\pi m} \right) - 1. \end{aligned}$$

The change of period $\delta\tau$ is produced by the local molecular field H_c , and therefore

$$\frac{\delta\tau}{\tau_l} = \frac{\epsilon\tau_l H_c}{4\pi m}.$$

Hence

$$\frac{\partial\chi}{\chi} = \left(1 \pm \frac{\epsilon\tau_l H_c}{4\pi m} \right) \left(1 \mp \frac{\epsilon\tau_l H_c}{4\pi m} \right) - 1. \quad \dots \dots \dots (12)$$

This equation gives us a value of the local molecular field H_c when we know the extent to which χ is modified on crystallization. With all the substances investigated in Part I. and with many of the elements examined by HONDA and OWEN, $\partial\chi/\chi$ amounts to a few per cent. Hence either

$$\frac{1}{100} \doteq \frac{\epsilon^2 \cdot \tau_l^2 \cdot H_c^2}{16\pi^2 m^2} \quad \text{or} \quad \frac{1}{100} \doteq \frac{\epsilon \cdot \tau_l \cdot H_c}{2\pi m}.$$

Taking $\tau_l \doteq 10^{-15}$ sec., $\epsilon/m = 2 \times 10^7$, we get either

$$H_c \doteq 6 \times 10^7 \text{ gauss} \quad \text{or} \quad H_c \doteq 3 \times 10^6 \text{ gauss},$$

and in either case H_c is of the order 10^7 gauss.

We have no experimental evidence at present as to how far an absorption line is displaced when a substance passes from the liquid to the crystalline state, but such

* LANGEVIN, 'Ann. de Chim. et de Phys.,' vol. 5, p. 97, 1905.

evidence would be a direct test of the value of H_c .* The above deduction is an interesting confirmation of the suggestion made at the end of Part II., p. 143, with regard to the intensity of the local molecular field in diamagnetic crystalline substances.

In a crystalline substance which shows natural double refraction we may regard the molecules as held in position in the crystalline structure by this intense local field, and in that case the double refraction of the medium would be a consequence of the orientation of the molecules due to the operation of this field when the substance crystallizes. Now the magnetic double refraction induced in a liquid is proportional to the square of the field intensity.† Let us assume that this law holds good for much larger fields than the largest we can apply in the laboratory.‡ If we take 5×10^4 gauss as the maximum value of this external field then the magnetic double refraction of the liquid will be represented by $C \times 2.5 \times 10^9$, where C is a constant independent of the applied field. If we could apply a field of 10^7 gauss the magnetic double refraction would be $C \times 10^{14}$, *i.e.*, 40,000 times as great. This is of the order of magnitude of the ratio of the double refraction of quartz to liquid nitrobenzene, the latter being subjected to a field of 3×10^4 gauss.

Conversely, if we assume that on crystallization there is an internal local molecular field, which if interpreted as a magnetic field is of the order 10^7 gauss, we can see how under its influence the molecules would become orientated to such an extent as to give rise to a crystal possessing the high natural double refraction of quartz.

All elements and compounds which show on fusion a small percentage change of χ must possess a molecular field whose local value, if interpreted magnetically, is of the order 10^7 gauss. This value is also supported by observations on the artificially induced and natural double refractions of other liquid and crystalline media.

It is known that most uniaxal crystals have a double refraction comparable with that of quartz, and of a much higher order of magnitude than that which has been induced in a liquid by the largest magnetic field at our disposal.§ Thus the abnormally high double refraction of Iceland spar is about 100 times that of quartz. On the other hand, the double refraction of ice is only about $\frac{1}{100}$ of that of quartz.

* It will be shown later that the mechanical interpretation of the large local molecular field is the internal stress which accounts for the rigidity of a crystalline medium. Now it has been shown by HUMPHREYS ('Astrophys. Journal,' vol. 35, p. 268) that there is a direct relation between the pressure shift of spectral lines and the Zeeman effect. Hence it is very probable that the shift of an absorption band on crystallization would be determined by the Zeeman effect of H_c .

† This results from both the theory of HAVELOCK, 'Roy. Soc. Proc.,' A, vol. 77, p. 170, 1906, and that of LANGEVIN, 'Le Radium,' vol. 7, p. 251, 1910. The law is found to hold experimentally, CORRON and MOUTON, 'Ann. de Chim. et de Phys.,' sér. VIII., vol. 19, p. 155, 1910.

‡ There are good reasons for supposing that this law is not accurate for such large fields, for a saturation effect must come in. But the result of assuming that it holds is suggestive, and probably indicates the true order of the effects.

§ *Vide* note, p. 99.

But COTTON and MOUTON have shown that the magnetic double refraction induced in water by the largest magnetic field they were able to apply ($3 \cdot 10^4$ gauss) is insignificant compared with that of liquid nitrobenzene subjected to the same field. In general the natural double refraction of a crystalline medium is of a high order compared with the artificial double refraction which we can produce in a liquid using a field of $3 \cdot 10^4$ gauss. The intrinsic molecular field, if interpreted magnetically, must therefore be large compared with $3 \cdot 10^4$ gauss in all crystalline diamagnetic media. This result will be used later in the extension of our ideas concerning the molecular field to diamagnetic crystalline media in general.

In Part II. the change of specific susceptibility due to the crystallization was represented by the difference, $(\alpha_c - \alpha_l) \Delta H$, of the mean molecular fields of the crystalline and liquid states. $\frac{\Delta H}{H}$, where H is the applied field, defines the distortion

produced in an electron orbit by the forces exerted by surrounding molecules when the substance is in the liquid state and subjected to a field H . ΔH is the polarization (proportional to the applied field H) due to this distortion. α_l is the constant of the molecular field for the liquid state and is approximately equal to $\frac{1}{3}$. Now the molecules of a liquid are moving about rapidly in all directions, and therefore the polarization defined by ΔH is an average effect. In the crystalline state, on the other hand, the molecules are orientated into definite positions with respect to one another, and therefore the polarization due to the mutual influences of the molecules in this case (as disclosed by applying an external field H) is large compared with ΔH . Let $\alpha_c \cdot \Delta H$ be this new polarization. Then α_c , which is large compared with α_l , is a factor defining the polarization which results from the complete orientation of the molecules in the crystalline medium. α_c will also depend upon the proximity of the molecules.

Now reverting to equation (8) of Part II., the variation of χ on crystallization may be written

$$\frac{\partial \chi}{\chi} = (\alpha_c - \alpha_l) \cdot \frac{\Delta H}{H} = \alpha_c \cdot \frac{\Delta H}{H},$$

if α_c is large compared with α_l . The large value of α_c implies a correspondingly small value of $\Delta H/H$, *i.e.*, a small value for the molecular distortion in the liquid state in order to account for a given change of χ on crystallization.

As in § 3 we may write the mean molecular field $\alpha_c \cdot \Delta H$, which accounts for the change $\partial \chi$ on crystallization, in the form $\alpha'_c \times$ (diamagnetic moment per unit volume) $= \alpha'_c \cdot N \cdot \Delta M \cdot \rho$, and the value of α'_c , the new constant of the molecular field, is of the order 10^5 for those substances which show a small percentage change of χ on crystallization.

Now the local molecular field H_c is of the order 10^7 gauss. We may write $H_c = \alpha'_c \cdot I$ where I is the aggregate of the local intensity of magnetization per unit volume. α'_c , the constant of the local molecular field, will be equal to the constant of

the mean molecular field, for the relationship of the molecules to one another in the crystalline structure determines their common magnitude. Hence $H_c \doteq 10^7 \doteq 10^5 \cdot I$ and $I \doteq 100$.

We can now use these values to form an estimate of the potential energy associated with a diamagnetic crystalline medium in virtue of the local molecular field and the local molecular polarization.

But before passing on to this, it will be interesting to compare the above deductions with regard to the local molecular force in diamagnetic crystalline media with those of WEISS which are concerned with the force in ferro-magnetic media.

Imagine a spherical cavity, large compared with molecular dimensions but lying wholly within the same crystal of (1) a diamagnetic; (2) a ferro-magnetic medium. On account of the structure which has been assigned to the diamagnetic molecule, the force at the centre of the cavity (when there is no external field) will be zero in case (1). In (2) the force will be $\frac{1}{3} \cdot I$ where I is the spontaneous intensity of magnetization. Now let us move our point of observation from the centre of the cavity out towards the surface. When the point approaches within a range comparable with molecular dimensions, in case (2), the force increases, and when the point is at a distance from the wall equal to that which separates two molecules of the crystalline structure the force is represented by NI where N is the constant of WEISS's molecular field, of the order 10^4 . If we move our point of observation in case (1) (the diamagnetic medium) from the centre of the cavity to the surface, then as the point approaches to within a distance comparable with molecular dimensions the local force is due almost entirely to the molecule which is nearest to the point. This molecule maintains a definite orientation with respect to the point, and when the latter is so close to the molecule as to be almost on its surface the polarization is comparable with the saturation intensity in iron. This is the interpretation of the large values of H_c and NI which are each of the order 10^7 gauss. As $H = \alpha_c' \cdot I$, we may suppose that the large coefficients N and α_c' determine the enormous magnitude of the forces quite close to a molecule in the respective crystalline structures. These local forces we could hardly hope to calculate directly for we do not know the proximity of the molecules in the structure or the law of force which holds at such a close range. The local molecular field of a diamagnetic crystalline substance alternates as we pass from molecule to molecule of the structure and is therefore localized. If we could take a crevasse between two molecules of the structure then the induction across it would give us a measure of H_c . Similarly in the ferro-magnetic case a crevasse of such small dimensions would give us a measure of WEISS's field NI . If we take a crevasse in the ferro-magnetic medium, which is large compared with molecular dimensions, the force in the gap is $H + 4\pi I$ and this is small compared with NI . The difference between these forces must be attributed to the localization of the intense fields associated with the iron atom. We then get continuity of magnetic induction while the intense field is still capable of modifying the structure of a neighbouring molecule.

The crystallization of a diamagnetic substance may be regarded as accompanied by the production of a spontaneous *local* intensity of magnetization. We have up to the present regarded the molecular field as a magnetic field, and a close analogy has been found between the phenomena shown by ferro-magnetic and diamagnetic substances. The question as to how far we are justified in regarding the molecular fields as magnetic fields will be discussed in § 8.

(5) ON THE STRESSES AND ENERGY ASSOCIATED WITH THE MOLECULAR FIELD.

In the previous work evidence has been given which shows that the forces associated with a diamagnetic crystalline structure are exceedingly large, and therefore the potential energy of the crystalline state will be considerable. If $|\iota|$ be the local magnetic moment which in conjunction with the local molecular field $|H_c|$ binds one molecule to another in the crystalline structure, and if all such elementary systems (each system consisting of the adjacent parts of a pair of molecules which are bound together by the local forces) are independent, then the energy possessed by 1 c.c. of the substance in virtue of a particular crystalline grouping may be written

$$\frac{1}{2} \sum |\iota| \cdot |H_c|.$$

Let n be the number of molecules per cubic centimetre. Then

$$\frac{1}{2} \sum |\iota| \cdot |H_c| = \frac{1}{2} n |\iota| \cdot H_c,$$

where H_c corresponds to the molecular field in ferro-magnetism. If we put $n \cdot |\iota| = I$ and $H_c = \alpha'_c I$, we find for the energy associated with 1 gr. of the substance

$$\frac{1}{2\rho_c} \cdot \alpha'_c \cdot I^2 \dots \dots \dots (13)$$

Here α'_c is the constant of the molecular field, I the aggregate of the local intensity of magnetization per unit volume, and ρ_c the density of the substance. This is the amount of potential energy which the molecules contained in 1 gr. possess in virtue of their grouping, and is additional to the energy possessed by 1 gr. of the liquid. We may treat the crystalline substance as a fluid whose molecules do not influence one another, providing the energy term represented by (13) is superposed upon any energy which 1 gr. of the fluid may possess. Therefore if the crystalline structure be submitted to a magnetic field H , the potential energy associated with 1 gr. may be written

$$\frac{1}{2\rho_l} \cdot [k_l \cdot H^2 + \alpha'_c \cdot I^2], \dots \dots \dots (14)$$

where k_l and ρ_l are the susceptibility and mass per unit volume of the liquid. Let us now compare this with the expression given by LARMOR* for the potential energy per

* 'Roy. Soc. Proc.,' A, vol. 52, p. 63, 1892.

gramme of a diamagnetic liquid the molecules of which have a small mutual influence. If k_i be the susceptibility per unit volume, this energy is shown to be

$$\frac{1}{2\rho_i} \cdot [k_i \cdot H^2 + \lambda \cdot k_i^2 \cdot H^2], \quad \dots \quad (15)$$

where λ is a constant approximately equal to $\frac{1}{3}$ (our α_i). In accordance with our notation we have $k_i \cdot H = n \cdot \Delta M_i$, where n is the number of molecules per cubic centimetre, and ΔM the diamagnetic moment induced in each by H . Therefore, instead of (15), we may write

$$\frac{1}{2\rho_i} \cdot [k_i \cdot H^2 + \lambda (n \cdot \Delta M_i)^2]. \quad \dots \quad (16)$$

Comparing (14) with (16) we may identify α'_c with λ and I with $n \cdot \Delta M_i$. Further, the applied field H is associated with the moment $n \cdot \Delta M$, which it produces, in the same manner as the molecular field H_c is associated with the aggregate of the local intensity of magnetization per unit volume, I , which it produces. The analogy is complete. In (14) we are concerned with the local forces of the crystalline structure which, on account of the relative fixity of the molecules, do not average out; whereas in (16) we are concerned with the average forces within the fluid, the large local forces having become averaged out on account of the motions of the molecules round any point.

Prof. LARMOR has pointed out an interesting case in which the term in λ predominates.* If we suspend a bunch of iron nails from the pole of a magnet, we find that they adhere to each other endwise and repel one another sideways, while non-adjacent nails have no action on one another. This is analogous to the result disclosed by (14) for a diamagnetic crystalline substance. Each molecule may be considered as possessing two little magnets opposing one another, and these molecules fit together in such a way that the magnets nearest to one another in adjacent molecules help one another.

In the case of a fluid λ and k_i^2 are small, so that the predominant term in the expression for the energy is $\frac{1}{2\rho_i} \cdot k_i \cdot H^2$, as is ordinarily assumed. For a crystalline medium taken as a whole the corresponding energy term is $\frac{1}{2\rho_c} \cdot k_c \cdot H^2$, the expression usually taken in measuring k_c .† It is only when we are inquiring into the local forces binding the molecules together into a crystalline lattice, the energy term of which is $\frac{1}{2\rho_c} \cdot \alpha'_c \cdot I^2$, that we get the true diamagnetic analogy with the bunch of iron nails. The molecules of the diamagnetic structure are held together endwise, so to speak, but we may have attractive forces in a perpendicular direction depending

* *Loc. cit.*, p. 64.

† Strictly speaking, to each of these expressions for the energy should be added a term proportional to k^2 , which is very small.

upon the configuration of the molecule. These latter forces will, in general, be different from the former, and will give rise to a difference of cohesion which accounts for the greater ease of cleavage of crystals in certain directions. [*Here, again, we have further proof of the truth of the hypothesis of molecular distortion in crystalline media. It is true that if to a liquid we could apply such an intense field that all its molecules are orientated, that liquid would possess a double refraction equal to that of a crystal, but as long as there is no mutual action between the molecules this doubly refracting medium could show no signs of rigidity and no preference for cleavage along certain planes.† Clearly the process at work in the formation of a crystalline structure is that of a binding force (mutual induction in our case) between two unbalanced parts of two adjacent molecules. All magne-crystallic properties can readily be interpreted in terms of such a mutual effect. It is important to note, however, that unless we recognize the enormous intensity of the local molecular field, which, together with the large local intensity of magnetization in diamagnetic crystals, binds the molecules together and by a mutual induction effect distorts them, we could not account for the rigidity of the crystalline medium, or the extent of its double refraction. It appears that TYNDALL'S explanation‡ of the deportment of diamagnetic crystals when placed in a magnetic field as due to a mutual action between the diamagnetic molecules is sufficient to account qualitatively for the behaviour observed, but it is difficult to see, on TYNDALL'S view of a simple and very minute diamagnetic polarity, where such large forces as those demanded for crystalline media could have their origin. On our view a diamagnetic molecule as a whole possesses a small diamagnetic polarity, an induction effect of the applied field, and the force due to it at a point considerably removed from the molecule is small. But in between a pair of molecules the internal forces are unbalanced, and the intensity of the local field is comparable with that in ferro-magnetic substances. On the other hand, quite close up to the diamagnetic molecule conceived by TYNDALL, the force binding it to a neighbouring molecule is not intense enough to account for the difference of magnetic property in different directions, as Lord KELVIN pointed out. The explanation of magne-crystallic action formulated by TYNDALL (this is the theory of reciprocal molecular induction) accounts qualitatively for the phenomena but certainly fails from a quantitative point of view. The present conception of a diamagnetic molecule surmounts the latter difficulty.]

As this question of determining the order of intensity of the local forces and local polarizations within diamagnetic crystalline media is of the greatest importance, any additional proof of the correctness of the values assigned to them is valuable. Let us therefore try to form some estimate of the magnitude of the term $\frac{1}{2\rho_c} \cdot \alpha'_c \cdot I^2$, which

* [Added November 12, 1914.]

† Cf. the liquid crystalline state.

‡ TYNDALL, 'On Diamagnetism and Magne-crystallic Action,' 1870, p. 69.

is large compared with the other term of equation (14). Taking the value of the local molecular field, $H_c = \alpha'_c I = 10^7$, we find since $\alpha'_c \doteq 10^5$, that I , the aggregate of the local intensity of magnetization per unit volume, is of the order 100. This is comparable with the saturation intensity of ferro-magnetic substances. If $\rho_c = 1$,

$$\frac{1}{2\rho_c} \cdot \alpha'_c \cdot I^2 \doteq 10^9 \text{ ergs.},$$

which is the amount of potential energy associated with 1 gr. of the crystalline medium in virtue of its molecular grouping. The thermal equivalent of this will be of the order $10^9/4 \cdot 10^7 = 25$ gr. calories, which represents the heat energy required to destroy the crystalline structure, *i.e.*, the latent heat of fusion. This is of the right order of magnitude for many diamagnetic substances—organic compounds and elements.* The above reasoning applies only to the order of magnitude of the latent heat. It is obvious that until we know the disposition of the molecules within the crystalline structure the value of α'_c is somewhat vague. But the experimental fact that the latent heat of transformation of iron from the ferro-magnetic to the para-magnetic state is of the same order of magnitude as the latent heat of fusion of many diamagnetic crystalline substances is powerful evidence that the local forces and local polarization which we have assigned to diamagnetic crystalline structures are enormous, comparable, in fact, as the above and preceding calculations have shown, with the intense forces and polarization of ferro-magnetic substances.

In the crystalline state we must regard the molecules as orientated into definite positions with respect to their neighbours by these large intermolecular forces. If at the higher temperatures the molecules undergo rotational vibrations about their mean positions, then it would be expected that the value of I^2 will be somewhat lessened by these vibrations, and we should therefore expect that a small fraction of the energy associated with the grouping would be dissipated as the temperature is raised towards the fusion point. The effect this would have on the variation of the specific

* The following values of the latent heat for some diamagnetic substances with which we are directly concerned are taken from 'Recueil des Constantes Physiques,' Paris, 1913, pp. 323-4 :—

Benzene	30	Acetic acid	44
Xylene	39	Carbon tetrachloride	4
Chlorobenzene	30		
Bromobenzene	20		
Aniline	21	Bismuth	13
Acetophenone	33	Cadmium	14
Benzophenone	23	Lead	5
Phenylhydrazine	36	Silver	22
Pyridine	22	Tin	14
Nitrobenzene	22	Zinc	28
Naphthalene	35	Gallium	19
Naphthylamine	22	Iron (ferro-magnetic)	59

heat with temperature would be to add to the normal variation, expressed by DEBYE'S theory, the following positive term

$$\frac{1}{2\rho_c J} \cdot \alpha'_c \cdot I \cdot \frac{\partial I}{\partial \mathfrak{S}}, \dots \dots \dots (17)$$

where \mathfrak{S} is the absolute temperature and J the mechanical equivalent of the calorie. In a former paper the author has shown that a term of this nature is necessary to represent the variation of the specific heat of substances in the neighbourhood of the fusion point.* A corresponding term explains, on WEISS'S theory, the variation of the specific heat of ferro-magnetic substances in the neighbourhood of the transformation temperature, on the supposition of a ferro-magnetic molecular field of the order 10^7 gauss.† [‡The fact that NERNST and LINDEMANN§ have found experimentally an abnormal increase of the specific heat of diamagnetic substances in addition to the normal variation due to purely translational vibrations, as the fusion point is approached, is additional evidence of the importance of the rotational term (17). DEBYE'S quantum theory of specific heats is concerned with translational vibrations of the molecules only, and, away from the fusion point, it agrees well with experiment. Incidentally, in order that (17) may be a measurable fraction of the specific heat, α'_c and I must be large, for, from experimental data showing the departure from DEBYE'S theory near the fusion point, the interval of temperature over which the molecules have effective rotational vibrations amounts to several degrees at least, so that the large value of (17) cannot be attributed solely to a large value of the gradient $\frac{\partial I}{\partial \mathfrak{S}}$. Unless α'_c and I have values of the order we have already found for them, it would be impossible to account for the measurable departure of the specific heat near the fusion point from DEBYE'S values. Only a fraction of the energy term $\frac{1}{2\rho_c} \cdot \alpha'_c \cdot I^2$ will be dissipated below the fusion point, the major portion disappears at the fusion point and corresponds to the latent heat (as described above).

The departure of the specific heat from the value calculated on DEBYE'S theory is important in connection with the quantum theory, for if the latter be valid, the above term, due to the rotation of the molecules, implies that the angular velocities of the molecules go in definite units. We cannot have the quantum theory holding for translational motion and not for rotational. The remarkable fact is that the rotational term (17) is insignificant except near the fusion point. This means that away from the fusion point the translational motion of the molecules is sufficient to

* A. E. OXLEY, 'Proc. Camb. Phil. Soc.,' vol. XVII., p. 450, 1914.

† WEISS and BECK, 'Journ. de Phys.,' sér. IV., vol. 7, p. 249, 1908.

‡ [Added November 12, 1914.]

§ 'La Theorie du Rayonnement et les Quanta,' Paris, 1912; particularly p. 272 and the memoirs of NERNST and EINSTEIN.

account for the observed specific heat. JEANS, in his "Report on Radiation and the Quantum Theory," published by the Physical Society of London, refers on p. 77 to the necessity of the rotational term, which was pointed out by the author in 'Proc. Camb. Phil. Soc.,' vol. XVII., p. 450, 1914. JEANS adds: "The absence of a noticeable contribution to the specific heats is accounted for, on the quantum theory, by supposing that the *forces opposing rotational movements of the atoms inside the solid are so large that the corresponding vibrations are of very high frequency, and so, normally, possess very little energy.* As far as pure theory goes, there is no question that to the terms in the specific heat contemplated by NERNST'S theory there ought to be added an additional term of a form exactly similar to the Einstein term, but having $x = \frac{h\nu_3}{RT}$, where ν_3 is the frequency (or average frequency) of the vibrations which depend on the rotations of the atoms.

"It is worthy of note that sodium and mercury show an increase, beyond that accounted for by the theories we have considered, in the specific heats as the fusion points is approached, when, presumably, the intensity of the forces which prevent the atom from rotating is relaxed, and NERNST and LINDEMANN find that in general the same is true for the substances they have examined."]

Before passing on to further experimental work and the extension of our results to crystalline diamagnetic media in general, it will be convenient to collect the results which have been obtained in the preceding pages. The work contained in Parts I. and II. has received full support and been confirmed with regard to the enormous intensity of the local molecular field in about 40 diamagnetic substances which show a measurable change of χ on crystallization. Evidence that the magnitude of this field is comparable with that of the ferro-magnetic field has been obtained from the following independent sources:—

(1.) The change of susceptibility observed on crystallization demands a local molecular field of this order of intensity.

(2.) The natural double refraction of a crystalline substance as compared with the artificial double refraction which can be induced in a liquid by the strongest magnetic field at our disposal is consistent with the value of the local molecular field implied by (1) for diamagnetic crystalline media.

(3.) (1) and (2) together imply that the aggregate of the local intensity of magnetization per unit volume of a diamagnetic substance is comparable with the saturation intensity of magnetization of a ferro-magnetic substance.

(4.) The above results lead to a correct estimate of the energy (potential) associated with the crystalline structure, in virtue of the molecular grouping, as tested by the magnitude of the latent heat.

(5.) Lastly, unless the forces binding the diamagnetic molecules together were of the order of magnitude stated, we should not be able to detect a departure of the experimental value of the specific heat near the fusion point from the value calculated

on DEBYE'S theory. Every substance investigated by NERNST and LINDEMANN discloses such a departure.

The above evidence is sufficient to establish the existence of an intense local molecular field of the order 10^7 gauss, if interpreted magnetically, in those diamagnetic crystalline substances (about 40 of which have been investigated) which show a measurable change of χ on crystallization. We shall now pass on to some additional experiments with the object of extending the above conclusions to diamagnetic crystalline media in general.

(6) ADDITIONAL EXPERIMENTS.

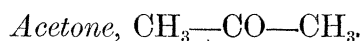
COTTON and MOUTON have found that aromatic liquids show an abnormally large double refraction compared with aliphatic liquids when subjected to the same external magnetic field. According to the theory of molecular orientation, which (in the opinion of these authors) is unique in accounting for all the observed phenomena of induced double refraction, the extent of the double refraction is directly proportional to the degree of dissymmetry of the molecule. Now assuming this to be so, we should expect that an unsymmetrical molecule, whose electrons are more readily displaced in one direction than in another, would have a distortion produced in it, when subjected to the local field of a neighbouring molecule, this distortion being characterized by the molecule's own dissymmetry. Therefore those liquids which show the larger induced double refraction when acted on by a magnetic field should also be the ones which show a large value of $\partial\chi$ on crystallization. All the aromatic liquids examined in Part I. show an appreciable change of χ on crystallization and, according to COTTON and MOUTON, all these show an easily measurable magnetic double refraction. With regard to aliphatic compounds, COTTON and MOUTON found that liquid hexane, chloroform, carbon-tetrachloride, acetone, hexamethylene, ethyl and methyl alcohols, had no appreciable induced magnetic double refraction. I therefore examined some of these for a change in the value of χ on crystallization. The results will now be briefly summarised.

All the experiments were made with the apparatus designed for low temperature work and most of the substances were investigated three times, the method being exactly as described in Part I.

Carbon tetrachloride, C.Cl₄.

At the fusion point (-30° C.) χ passed through a minimum value, as in the case of benzene, and, on further cooling the crystals, the susceptibility appeared to be the same as that of the liquid. An effect of the same nature has been observed by HONDA* with sulphur, χ being a minimum at the fusion point (115° C.).

* 'Ann. der Phys.,' vol. 32, p. 10 8, 1910.

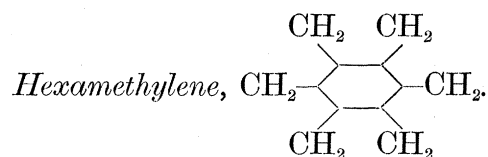


This substance behaved like carbon tetrachloride.



Five experiments made on these fatty acids showed that the change of χ on crystallization was less than 1 per cent. in each case.

Aromatic Substances.



Three experiments showed that no change of χ takes place at the fusion point (6°C.).



The susceptibility of the crystals did not differ appreciably from that of the liquid.

A control experiment on nitrobenzene gave the abnormally large value 12 per cent. (which agrees with the earlier experiments with this substance) for $\partial\chi$.

(7) A RELATION BETWEEN THE MAGNETIC DOUBLE REFRACTION OF ORGANIC LIQUIDS AND THE CHANGE OF MAGNETIC SUSCEPTIBILITY DUE TO CRYSTALLIZATION.

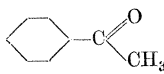

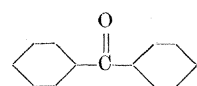
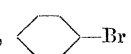
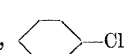
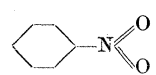


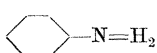
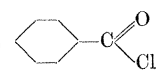

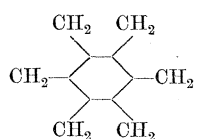
A Comparison of Experimental Results.

The general facts which have been described with regard to the large value of $\partial\chi$ during the crystallization of aromatic compounds and the relatively small value which has been obtained in the later experiments for substances of an aliphatic nature form an interesting parallel with those relating to the magnetic double refraction of aromatic and aliphatic liquids investigated by MM. COTTON and MOUTON.* The parallelism is particularly striking with nitrobenzene and hexamethylene. For the former the induced magnetic double refraction and the value of $\partial\chi$ are abnormally large while with the latter both effects are inappreciable.†

I propose to give a table showing the values of the percentage change of susceptibility on crystallization ($\partial\chi/\chi$) and the magnetic double refraction (M), each referred to nitrobenzene as unit, for a number of substances investigated by COTTON

* 'Ann. de Chim. et de Phys.,' sér. VIII., vol. 19, p. 153, 1910; and sér. VIII., vol. 20, p. 194, 1910.

† 'Journ. de Phys.,' sér. V., vol. 1, p. 23, 1910.

Substance and constitution.	$\partial\chi/\chi$.	M.
Acetophenone, 	0.35	0.49
Benzene, 	0.23	0.23
Benzophenone, 	0.46	0.57
Bromobenzene, 	0.35	0.26
Chlorobenzene, 	0.35	0.29
Nitrobenzene, 	1.0	1.0
Toluene, 	0.38	0.24
Xylene (Ortho), 	0.37	0.28
Aniline, 	0.38	0.2
Benzoylchloride, 	0.38	0.5
Pyridine, 	0.2	0.25
Hexamethylene, 	small	0.0
Carbon tetrachloride, C.Cl ₄	„	0.0
Acetone, CH ₃ .CO.CH ₃	„	0.0
Acetic acid, CH ₃ .COOH	„	0.0
Propionic acid, CH ₃ .CH ₂ .COOH	„	0.0
Chloroform, CH.Cl ₃	„	0.0
Water, H ₂ O	0.15*	0.0

* α -bromonaphthalene is also an exception. The value of $\partial\chi/\chi$ is 4.5 per cent., while COTTON and MOUTON find that it shows a magnetic birefringence equal to that of nitrobenzene.

It is interesting to note in passing that not only does the Kerr electric effect follow the same laws as the magnetic double refraction with regard to variation of field strength and wave-length, but also that it shows a rough parallelism with M for individual substances.

and MOUTON and myself. From the table it is clear that there is some connection between these two effects. In each case the benzene nucleus plays an important rôle. According to COTTON and MOUTON all liquids whose molecules contain such nuclei have a magnetic double refraction which is easy to detect experimentally. These liquids also show a large value of $\partial\chi$ on crystallization. If the nucleus be modified by substitution of a monovalent atom or group for one of the hydrogen atoms the magnetic double refraction may increase or diminish but always retains the same order of magnitude. The parallelism in this respect is well represented by the benzene derivatives investigated in Part I. All these show a value of $\partial\chi/\chi$ of the same order except nitrobenzene. In this substance the substituent $-\text{NO}_2$, which is so active in augmenting the induced double refraction of the liquid, also contributes an abnormally large part to $\partial\chi$ as would be expected.

Both effects appear to depend also upon the degree of unsaturation of the substance, and if by any process we can lessen the number of double linkages associated with the nuclear carbon atoms there is a sudden diminution both of double refraction and $\partial\chi$. Hexamethylene is particularly interesting from this point of view, for here all six double linkages are destroyed by the additional six hydrogen atoms. In their later experiments COTTON and MOUTON have found that most organic liquids and some inorganic ones show a feeble double refraction in the strongest magnetic fields. These would be accounted for if the molecules possess a slight degree of dissymmetry, for then they would become partially orientated by the external field. As regards the change of χ with such substances on crystallization, we should expect that the large molecular field which comes into play would produce a polarization or distortion in any molecule characterized by the molecule's own dissymmetry, while the distorting force would depend upon the degree of unsaturation of the molecule. Although the extent of this distortion is small, yet the forces which produce it must be large, for even with the most unsaturated and unsymmetrical molecules $\partial\chi$ amounts to a few per cent. only when the molecular field is of the order 10^7 gauss.

With more delicate means of detection and a more intense magnetic field, COTTON and MOUTON conclude that a double refraction would be shown by all substances. But this is exceedingly small compared with the natural double refraction of the crystalline medium, as far as experimental data on this question are available up to the present,* and this increase of double refraction in passing from the liquid to the crystalline state demands a value for the local molecular field large in comparison with the strongest magnetic field which we can produce in the laboratory (§ 4).

It is expected too, that if we could use a more delicate means of measuring χ we

* A large number of ordinary and extraordinary refractive indices are given in 'Recueil des Constantes Physiques,' published by the French Physical Society. These, however, refer to minerals which occur in sufficiently large crystals for optical experiments to be readily carried out. Among the few organic crystals which have been investigated are cane sugar, $n_e = 1.570$, $n_o = 1.537$; benzile, $n_e = 1.563$, $n_o = 1.659$.

should be able to detect a change of magnetic property when every substance crystallizes. This again implies an enormous value for the local molecular field, even if the change of χ produced is so small as to be only on the verge of detection by our present methods, as the first part of § 4 shows.

Among organic compounds aromatic substances show both these effects to an exalted degree and it is from a study of these that the large molecular forcives in diamagnetic crystalline media were first recognized. By the argument of the present section it appears only justifiable to extend these results to diamagnetic crystalline media in general. Such an extension is warranted also by the values of the latent heat.

(8) ON THE NATURE OF THE MOLECULAR FIELD.

The large *local* molecular field which has been recognized in diamagnetic crystalline substances must have its origin in the individual atoms or molecules. In a liquid the effects of these forces at any point within the medium average out to a small resultant effect only as already indicated. When the substance crystallizes the molecules are fixed in definite positions with regard to one another, and the polarization or distortion produced in a molecule owing to the forces exerted by its neighbours is no longer an average value. The modifications of the physical properties of substances at the fusion point readily fall into line with this view. When the substance is vaporized we must still assume that the force quite close up to the molecules is very large and rapidly falls off on account of the compensating action of the other half of the same molecule. If the pressure of the vapour were sufficiently increased so that the local fields overlap, then we should expect that any physical property possessed by the vapour would become modified. Thus HUMPHREYS* has advanced the view that the pressure shift of spectral lines may be due to the co-operation of intense magnetic fields located in neighbouring atoms. The pressure shift can be accounted for if the intra-atomic field, interpreted magnetically, has an intensity of the order 10^8 gauss. Further, RITZ† has shown how to deduce the expressions of BALMER and RYDBERG for the representation of spectral series, providing we assume that the electrons are vibrating under an electromagnetic field whose order of intensity is 10^8 gauss. For this intensity of the intra-atomic field the frequency of vibration of the electrons corresponds to that of visible light. If in the crystalline structure the surrounding molecules exert a local field of the order 10^7 gauss, the electron in the particular atom we are considering would have its orbit modified by an amount which would account for a few per cent. change in the diamagnetic susceptibility. It is not improbable that the intense intra-atomic fields of RITZ may be identified with the field due to the magneton, the molecular field being the result of their mutual action

* 'Astrophysical Journal,' vol. 23, p. 232, 1906, and vol. 35, p. 268, 1912.

† 'Ann. der Phys.,' vol. 25, p. 660, 1908.

between the molecules of the crystalline structure. In addition it is important from our point of view to notice that these large fields are required by RITZ and HUMPHREYS in order to explain certain spectral phenomena, and therefore they are required apart from the magnetic nature of the atoms or molecules under consideration.

[*Let us now compare the theory which has been developed above and in Parts I. and II. with the theory of ferro-magnetism given by WEISS. The intense magnetic properties of iron below the critical temperature are attributed to the mutual effects exerted by the molecules of iron. WEISS has shown that if we regard these effects as purely magnetic, then the large increase of specific susceptibility due to the transformation from the paramagnetic to the ferro-magnetic state may be represented by a molecular field \mathbf{NI} , where \mathbf{N} is a constant of the order 10^4 and \mathbf{I} is the intensity of magnetization for a field strength H . For saturated iron \mathbf{NI} has the value 10^7 gauss (approximately). This internal field is called into action when an external field H is applied, and its presence determines the abnormally large susceptibility of iron below the critical temperature.

In a similar way it has been shown that the change of specific diamagnetic susceptibility when a diamagnetic substance crystallizes can be represented by a mean magnetic molecular field which is proportional to the intensity of magnetization (diamagnetic moment per unit volume) and whose constant of proportionality is comparable with \mathbf{N} . On account of the zero moment possessed by a diamagnetic molecule initially, this mean molecular field is small relative to \mathbf{NI} , but reasons have been given in previous work which show that the local value of this field is comparable with the ferro-magnetic molecular field. It is this local field which distorts the electron orbits on crystallization and gives rise to a small change of diamagnetic susceptibility. This and other considerations have shown that the intensity of the molecular field in diamagnetic substances is of the order 10^7 gauss locally.

Up to the present the representation of this field as a magnetic field has not been justified except in so far as we have seen that it is in harmony with the important work of RITZ, whose molecular magnets have moments not inconsistent with that associated with the magneton,† and whose magnetic field intensity is comparable with the ferro-magnetic molecular field of WEISS and the molecular field within diamagnetic crystalline substances. It is important for our purpose to observe that the intra-atomic fields of RITZ are required to represent the distribution of lines in spectral series, whether the substance be ferro-, para- or diamagnetic.

Now very good evidence that molecular magnets do exist in ferro-magnetic substances has been obtained. The fields due to these must contribute to the molecular field (\mathbf{NI}). Taking the moment of the magneton as 16.5×10^{-22} , we find for

* [Added November 12, 1914.]

† P. ZEEMAN, 'Researches in Magneto-optics,' p. 178.

the saturation intensity of magnetization of iron $\frac{16.5 \times 10^{-22} \times 6.8 \times 10^{23} \times 11^*}{7} = 1760$,

which is nearly equal to the experimental value. Therefore the increase of χ on passing from the paramagnetic to the ferro-magnetic state can be represented by a purely magnetic molecular field due to the magnetons contained in the iron molecules. This increase of χ is represented on WEISS's theory by the molecular field $\mathbf{NI} \doteq 10^7$ gauss, and therefore 10^7 gauss is the magnetic field due to the magnetons when the iron is saturated. The continuity of magnetic induction demands that this field is to a large extent localized (see p. 89 *supra*).

Now reverting to diamagnetic substances we are led, in the light of RITZ's theory, to identify the local molecular field (10^7 gauss) in their case as due to the existence of molecular magnets, so arranged that for any particular molecule the moment is zero. It seems that we could readily account on such a view for the fact that the chemical combination of two diamagnetic substances can give rise to a paramagnetic substance possessing magnetons. This is the case for instance with the union of copper (diamagnetic) and sulphuric acid (diamagnetic) resulting in the formation of cupric sulphate (which is paramagnetic and contains 10 magnetons to the molecule). The forces which come into play during the chemical combination we may regard as upsetting the magnetic equilibrium of each component.

If these molecular magnets do exist in diamagnetic substances then the local molecular field of the diamagnetic substance will be comparable with the molecular field in ferro-magnetic substances, and will be represented as far as they are concerned by a true magnetic field of intensity 10^7 gauss (approximately). In this case the localized nature of the field is a necessary consequence of zero moment which has been assigned to the diamagnetic molecule.

In both ferro-magnetic and diamagnetic cases we have represented the molecular fields as due to *magnetic* force. Now electrostatic forces, or indeed forces of any other nature, may distort the configuration of a molecule in the crystalline structure, and their effect could be represented by a *magnetic* field for both diamagnetic and ferro-magnetic substances. Hence part of the molecular field for diamagnetic and ferro-magnetic substances may be a true magnetic field and part a magnetic representation of the distortion produced by forces of a different nature. At any rate we cannot deny that the parallelism which has been found between ferro-magnetic and diamagnetic phenomena, taken in conjunction with the work of WEISS on the magneton and that of RITZ on spectral series, points to the conclusion that the molecular field in diamagnetics and ferro-magnetics is represented in part (at least) by a true magnetic field. In this connection the introductory remarks of

* An atom of iron has 11 magnetons, and the gramme-atom of iron (56 gr.) contains 6.8×10^{23} atoms, therefore 1 c.c. of iron (whose density is taken as 8) will contain $\frac{6.8 \times 10^{23}}{7}$ atoms.

Prof. J. W. NICHOLSON during the discussion on "The Structure of the Atom" (issued with 'Roy. Soc. Proc.' for July 20) are interesting :—

"I think that Prof. RUTHERFORD has made it clear that the nuclear atom is, as a matter of fact, the only basis upon which profitable discussion of the constitution of the atom can really be carried on. The main rival theory, as Prof. HICKS has just indicated, is the magneton theory. It seems that just recently in the course of a discussion it has been shown that the magneton theory and the nuclear theory do probably amount to exactly the same thing."

Future work will test this. But in the meantime it is clear that the magnetic forces cannot be neglected.]

Note added February 1, 1915.

While this work has been passing through the press, some further extensions have been made. In particular, there is one which I should like to refer to here because it bears directly upon the foregoing work.

It can be shown that the magnitude of the change of volume observed on crystallization may be interpreted as the magneto-striction effect of the local molecular field. We have seen that the natural double refraction of a crystalline medium may be represented as due to the complete orientation of the molecules by the local molecular field. As the magneto-striction effect produced in a liquid and the induced magnetic double refraction are each proportional to the square of the applied field intensity, these results mutually support one another.

The further extension of the work is concerned with the validity of the quantum theory as applied to magnetic phenomena. A discussion of the nature of the magnetic properties of HEUSLER'S alloys, from the points of view developed in the present work, will also be given. I hope to publish an account of these extensions in a future communication.
