

# The Influence of Molecular Constitution and Temperature on Magnetic Susceptibility. Part IV: Further Applications of the Molecular Field

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

*Part IV.—Further Applications of the Molecular Field.*

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(1) INTRODUCTION.

THE present work is a continuation of that published in 'Phil. Trans., Royal Society,' vol. 214, pp. 109–146, 1914 (Parts I. and II.) and vol. 215, pp. 79–103, 1915 (Part III).<sup>\*</sup> It will lead to clearness in the following development of the subject if a brief résumé of these papers is given. At the same time, I wish to discuss one or two points in connexion with the views which have been previously advanced and the relation between mechanical and molecular theory.

In Part I. the experimental evidence brought forward has justified the hypothesis of molecular distortion enunciated at the outset. We have thereby been led to regard the molecular configuration of a material medium as a distorted one, and this applies particularly to a substance which is crystalline. The extent of this distortion is small, but is sufficient to account for the observed change of specific susceptibility which occurs on crystallization. Such change will naturally depend upon the particular crystalline symmetry assumed by the substance.

The theoretical treatment given in Part II. is an attempt to account for the phenomena observed by extending the electron theory developed by LANGEVIN so

<sup>\*</sup> For brevity, reference to these researches is given under Parts I., II., and III.

as to include the effects of mutual molecular influences. Such a representation of the facts has led to the recognition of a large molecular force, in all crystalline media, depending upon the nature and proximity of the molecules in any particular crystalline grouping. The existence of this intrinsic molecular field can only be inferred indirectly. Although the actual properties of the crystalline state depend upon the operation of this field, yet, except in the case of substances of a ferro-magnetic nature, there is no direct experimental evidence which discloses its very great magnitude.

From a theoretical point of view, there seems to be no doubt that the mutual actions of the molecules are represented by enormous internal forces in all crystalline media. The usual method of determining the force at an internal point of the material medium is to take a cavity whose dimensions are small in comparison with ordinary lengths (*e.g.*, 1 cm.) and yet large compared with molecular dimensions. A convenient designation of the dimensions of the cavity is contained in the phrase "physically small."\* In molecular theory, the subdivision of the medium into elements is not valid beyond the limits of physical smallness and only in media which are absolutely continuous may the elements be pushed to limits of "mathematical smallness." In a continuous medium our mathematical functions give us an accurate estimate of the forces and potentials operating at internal points; in a medium composed of discrete particles these same functions give us only an approximate estimate. A discussion of the nearness of the approximation which can be obtained for material media is of great importance from the point of view of our subject. For the liquid state the question has been considered by Sir JOSEPH LARMOR† who found that the part contributed to the force at any internal point by the molecules immediately surrounding that point was, on account of rapid motions and irregular distributions of the axes of the molecules, negligibly small. To quote from LARMOR‡: "The general conclusion may be expressed, in an adaptation of CAUCHY'S terminology, by the principle that whenever the integrals in the formulæ for mechanical forces on a material medium cease to be convergent, their principal values must be substituted," and again in the footnote to p. 265,

"This statement (*i.e.*, the above quotation) may be considered to be the mathematical expression of the principle of the mutual compensation of molecular forces, for which, *cf.*, 'Phil. Trans.', A, 1897, p. 260. The principal value of CAUCHY, as regards the completely defined analytical integrals of Pure Mathematics, would be the value at the centre of a minute spherical cavity. But the quantities which, to avoid periphrasis, have been here called integrals, are really summations of contributions from finite though very small, and complexly constituted, polarised molecules; the distribution of these molecules that occupy our minute cavity is entirely

\* LEATHAM, "Volume and Surface Integrals used in Physics," 'Cambridge Monographs,' No. 1, p. 5.

† 'Æther and Matter,' p. 261.

‡ *Loc. cit.*, p. 265.

unknown and may be continually changing, so that the only possible principal value is the one that omits the contribution of neighbouring molecules altogether."

When now we come to the case of crystalline media, the molecules which were removed from our small spherical cavity would affect considerably the value of the forcive at the centre, for there is in this case no averaging out on account of random motions and orientations of the molecules originally occupying the cavity. As we do not know the relative dispositions of the molecules composing the space lattice, or the law of force which is operative between the molecules, it is quite impossible to calculate the value of the intrinsic forcive for a point inside a crystalline medium, and as the method of averages, the application of which is quite satisfactory when the medium is in a fluid state, breaks down in the case of a crystalline medium, it is clear that our only way of progress lies in indirect deduction from experimental facts which record the change of physical properties accompanying the transition from the liquid to the crystalline state. This is the method which has been adopted in the previous portions of this work and it has been shown that the internal forcive at a point of a crystalline medium is extremely large and comparable, if interpreted magnetically, with the molecular field in ferro-magnetic substances ( $10^7$  gauss).

In Part III. it was shown that the potential energy of the molecules forming a crystalline structure was sufficiently large to account for the magnitude of the thermal energy required for fusion. On p. 201 of his "Æther and Matter," LARMOR states: "These various actions (referring to the disturbance of configuration of steady orbits in molecules by action of an applied magnetic field) involve energy terms for each individual molecule, and the sum for all the molecules, if it could be formed, would represent the total energy of the disturbance of the medium. But such a mere aggregate of terms would be of no use for applications to matter in bulk; what we are concerned with there is the mechanical part of the energy, which must be an analytical function of the specification of matter by volume, determined as to mathematical form by the character of the molecular actions, but with coefficients whose values are to be obtained only by direct experiment."

Although for a fluid medium the total energy of the disturbance of the medium, due to the application of a magnetic field, has little significance, yet, in the transition from the liquid to the crystalline state, during which the molecular field becomes operative, the sum total of the energy disturbance of the medium due to the action of this molecular field is representative of the latent thermal energy which is absorbed when the crystalline medium is fused, and has a definite value for each particular substance.

From the point of view of fluids, the intrinsic forcives mutually compensate and the mathematical functions may be treated as analytic, their principal values being taken. In a crystalline structure, however, the functions cannot be treated as analytic. Indirectly we have obtained a measure of the intrinsic forcive in this case with the aid of experimental data. The most we can obtain by direct experiment, however, is a measure of the mean molecular field, which expresses mathematically how the

susceptibility of matter *in bulk* depends upon a transition from the liquid to the crystalline state. When thus considering diamagnetic matter in bulk, the large local forcive which has been shown to bind the molecules of the crystalline structure together need not be considered, since for matter *in bulk* its effects are cut out by the mutual compensation of molecular forcives. It is only when we enquire into the *molecular* structure of the crystalline medium, or to changes in this structure, that we pass to the inner limit where the principles of LARMOR and CAUCHY for the fluid state no longer apply. LARMOR remarks: "The result of the integration still however gave us a valid estimate of the effect of the material system *as a whole*, when we bore in mind that the infinite or rather undetermined term entering at the inner limit really represents the part of the result which depends *solely* upon the local molecular configuration; a part whose actual magnitude could be determined only when that configuration is exactly assigned or known" (*loc. cit.*, p. 125).

It is with this "infinite or rather undetermined term . . . . . which depends *solely* upon the local molecular configuration" that these researches are mainly concerned. It has been called the local molecular field of the crystalline medium (Part III., p. 83).

(2) ON THE ENERGY AND ULTIMATE TENSILE STRENGTH ASSOCIATED WITH CRYSTALLINE MEDIA OR GELS.

The large intrinsic potential energy associated with a crystalline medium has been discussed in para. 5, Part III., pp. 90–95. It now remains for us to examine the accompanying stresses to see how far the elastic properties of material media may be interpreted in terms of these intrinsic forcives. Consider first the case of a liquid which is gradually cooled in liquid air so that it passes into a glass-hard transparent gel when it arrives at the temperature of the liquid air.

It has been suggested (Part III., p. 81) that the appearance of rigidity in the gel is due to an interlocking of the irregularly shaped molecules (arranged at random) whose thermal agitation is sufficiently reduced. On account of this random orientation of the interlocked molecules the gel will be isotropic. At such a low temperature, also, the molecular motions will be highly constrained so that a particular molecule will present practically the same aspect to the surrounding molecules over a long period. If this is the case, then the local molecular forcive between this and a neighbouring molecule will act in a definite direction and will not be rapidly changing its direction as would be the case with the same molecules at a considerably higher temperature (in the ordinary liquid state). It is clear therefore that between the molecules of the gel at low temperature we shall have a large local forcive in operation, due to the interaction of the magnetic systems or revolving electrons within each molecule, but the direction of the action of this forcive between any pair of molecules will be one of random distribution, as we pass from pair to pair of molecules, although at any given point it is fixed in direction.

On further cooling, the molecules continue to readjust themselves and the rigidity increases until a glass is formed. Still lower temperatures, accompanied by further molecular readjustment due to reduction of amplitude, may result in such a distortion of the lines of force binding the pairs of molecules together, that a completely new pairing of molecules takes place, resulting in spontaneous crystallization accompanied by thermal evolution as the more stable crystalline state is formed.

Whatever may be the nature of the forces which hold the molecules of a liquid together, we have, in addition to these forces, the intrinsic field referred to above, when the substance passes into a rigid gel or crystallizes, and it is due to this intrinsic field that the two latter media show rigidity.

If  $H_c$  be this intrinsic field,\*  $I$  the local intensity of magnetization,† the potential energy per unit volume associated with the gel or crystalline medium will be

$$\frac{1}{2} \cdot H_c \cdot I \dots \dots \dots (1)$$

and this will be over and above any potential energy which the molecules of the liquid possess. This is also a measure of the mechanical stress which binds the molecules of the gel or crystalline medium together and determines their rigidity.

In Part III. we have given reasons for locating the source of the local molecular field within the molecule and we found that in the immediate neighbourhood of a

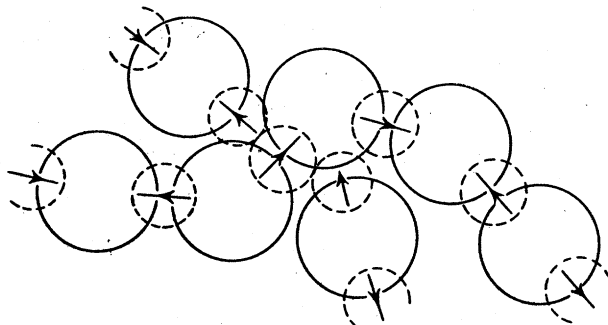


Fig. 1.

molecule the value of this field, as determined from the properties of crystalline media, is of the order  $10^7$  gauss. However the molecule is orientated, provided that orientation is not variable with time, the local force will be of this order of intensity and in some direction determined by the orientations of the two molecules between which it acts. In a gel, as we pass from molecule to molecule, the direction of this stress will be continually changing (fig. 1). Throughout a crystal, on the other hand, its direction will be constant and will in fact be one of the determining factors of a particular form of crystalline symmetry (fig. 1A).

In a gel, the whole collection of molecules is bound together into one homogeneous

\* See Part III., p. 86.

† *Loc. cit.*, p. 90.

isotropic mass (*i.e.*, as viewed in bulk) whereas in a crystalline medium the mass will be æolotropic.

In Part III. evidence was brought forward showing that in the case of diamagnetic media the local intensity of magnetization  $I$  is of the order 100, while the local molecular field  $H_c$  between the molecules is of the order  $10^7$  gauss. The energy of the molecular configuration of the crystalline medium (over and above that due to

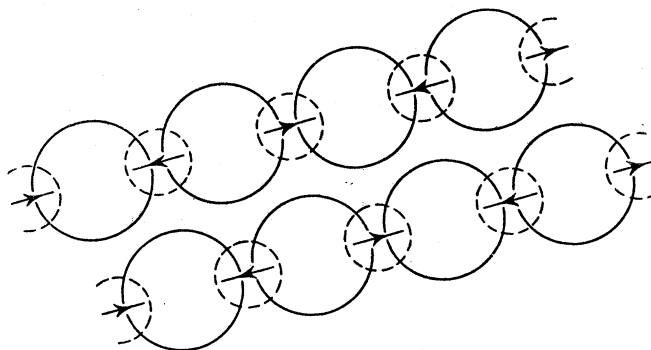


Fig. 1A.

the molecular configuration in the liquid state) or of the gel at low temperatures, will therefore be of the order  $\frac{1}{2} \cdot H_c \cdot I = 10^9$  ergs per unit volume\* and the internal stress  $10^9$  dynes per square centimetre, or 1000 atmospheres approximately. For wrought iron the energy per unit volume will be

$$\frac{1}{2} \cdot H_c \cdot I = \frac{1}{2} \times 6.5 \times 10^6 \times 1700 = 5.5 \times 10^9 \text{ ergs}$$

and the internal stress about 5500 atmospheres.

In nickel the intrinsic pressure is  $1.4 \times 10^9$  dynes per square centimetre or 1400 atmospheres; in cobalt  $4.4 \times 10^9$  dynes per square centimetre or 4400 atmospheres, in cast iron  $4 \times 10^9$  dynes per square centimetre or 4000 atmospheres. These internal stresses are a measure of the forces binding the molecules together and should give an estimate of the ultimate tensile strength or tenacity of the medium. Moreover the tenacities of ferro-magnetic, paramagnetic and diamagnetic media should be roughly of the same order. That this is so is seen from the following values†:—

	Material.	Tenacity (dynes per square centimetre).
Ferro-magnetic	Iron, (wire) . . . . .	$5.0-6.0 \times 10^9$
	Iron, wrought . . . . .	$2.9-4.5 \times 10^9$
	Iron, cast . . . . .	$1.2-1.9 \times 10^9$
	Nickel (wire) . . . . .	$5.3 \times 10^9$
	Mild steel (0.2 per cent. carbon) .	$4.3-4.9 \times 10^9$
	High carbon steel . . . . .	$7.0-7.7 \times 10^9$
	Nickel steel (5 per cent.) . . . . .	$6.2 \times 10^9$

\* This, as we have seen in Part III., p. 93, is compatible with the values of the latent heat of fusion of diamagnetic crystalline media. See also *infra*, pp. 253-4, p. 256.

† KAYE and LABY, 'Physical and Chemical Constants,' 1918, p. 28.

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	Material.	Tenacity (dynes per square centimetre).
Diamagnetic . . .	Lead . . . . .	$0.16 \times 10^9$
	Zinc . . . . .	$1.1 - 1.5 \times 10^9$
	Glass (sometimes paramagnetic) . . . . .	$0.3 - 0.9 \times 10^9$
	Quartz . . . . .	$10 \times 10^9$
	Copper . . . . .	$1.2 - 2.5 \times 10^9$
	Silver (wire) . . . . .	$2.9 \times 10^9$
	Gold (wire) . . . . .	$2.6 \times 10^9$
Paramagnetic . . .	Aluminium . . . . .	$0.6 - 1.5 \times 10^9$
	Tin . . . . .	$0.16 - 0.38 \times 10^9$
	Glass (sometimes diamagnetic) . . . . .	$0.3 - 0.9 \times 10^9$
	Platinum (wire) . . . . .	$3.3 \times 10^9$

We may conclude that the intrinsic stress due to the local molecular field, calculated as above, gives a satisfactory interpretation of the ultimate tensile strength of crystalline media, as observed experimentally, irrespective of the nature of their magnetic property.

The energy associated with the medium, in virtue of this intrinsic pressure of crystallization, is consistent to the right order with the value of the latent heat of fusion of the material.\*

The energies per cubic centimetre of various diamagnetic and paramagnetic media, calculated from the latent heats of fusion, are given below :—

## 1. ORGANIC Compounds Investigated in Parts I. and III.

Substance.	Magnetic nature.	Latent heat.	Density.	Energy (ergs per cubic centimetre).
Benzene . . . . .	diamagnetic	30 (calories per gramme)	0.88	$1.1 \times 10^9$
Xylene . . . . .	"	39	—	—
Chlorobenzene . . . . .	"	30	1.12	$1.4 \times 10^9$
Bromobenzene . . . . .	"	20	1.49	$1.3 \times 10^9$
Aniline . . . . .	"	21	1.02	$0.9 \times 10^9$
Acetophenone . . . . .	"	33	—	—
Benzophenone . . . . .	"	23	1.10	$1.0 \times 10^9$
Phenylhydrazine . . . . .	"	36	1.10	$1.6 \times 10^9$
Pyridine . . . . .	"	22	0.985	$0.9 \times 10^9$
Nitrobenzene . . . . .	"	22	1.19	$1.1 \times 10^9$
Naphthalene . . . . .	"	35	1.15	$1.7 \times 10^9$
Naphthylamine . . . . .	"	22	—	—
Acetic acid . . . . .	"	44	1.05	$1.9 \times 10^9$
Glycerine . . . . .	"	42	1.26	$2.2 \times 10^9$
Carbon tetra-chloride . . . . .	"	4	1.58	$0.26 \times 10^9$

\* See also Part III., p. 93.



## 2. ELEMENTS and Inorganic Compounds.

Substance.	Magnetic nature.	Latent heat.	Density.	Energy (ergs per cubic centimetre).
Bismuth . . . . .	diamagnetic	13 (calories per gramme)	9.8	$5.3 \times 10^9$
Cadmium . . . . .	"	14	8.6	$5.0 \times 10^9$
Lead . . . . .	"	5	11.4	$2.4 \times 10^9$
Silver . . . . .	"	22	10.5	$9.7 \times 10^9$
Zinc . . . . .	"	28	7.1	$8.3 \times 10^9$
Phosphorus . . . . .	"	5	1.8	$0.38 \times 10^9$
Mercury . . . . .	"	3	13.6	$1.7 \times 10^9$
Copper . . . . .	"	43	8.9	$16.0 \times 10^9$
Sulphur . . . . .	"	9	2.0	$0.8 \times 10^9$
Ice . . . . .	"	80	0.9	$3.0 \times 10^9$
Aluminium . . . . .	paramagnetic	77	2.7	$8.7 \times 10^9$
Tin . . . . .	"	14	7.3	$4.3 \times 10^9$
Palladium . . . . .	"	36	11.4	$17.0 \times 10^9$
Platinum . . . . .	"	27	21.5	$24.0 \times 10^9$
Potassium . . . . .	"	16	0.86	$0.56 \times 10^9$
Iron* (transformation $\beta - \gamma$ at $A_3$ point) .	—	1.4 (calories per gramme)	7.9	$0.46 \times 10^9$

In the case of iron at the  $A_3$  point, the transformation is from one cubic crystalline form to another, and we should expect the change of internal energy to be smaller than in the general case of actual crystallization from the liquid state.

We can obtain a measure of intrinsic pressures in crystalline media in another way, which depends on extrapolation of the relation connecting the temperature of the freezing point with applied pressure.

If

- $v_l$  = volume of 1 gramme of liquid,
- $v_c$  = volume of 1 gramme of crystal,
- $\mathcal{S}$  = temperature of fusion,
- $p$  = pressure, in atmospheres,
- $L$  = latent heat,

we know that

$$\frac{\partial \mathcal{S}}{\partial p} = \frac{(v_l - v_c) \cdot \mathcal{S}}{L} = \frac{\delta V \cdot \mathcal{S}}{L}.$$

If the applied pressure be such that  $v_l = v_c$  then  $\delta V = 0$ , and if we can determine the pressure  $\pi$  for which this condition exists, we have determined the intrinsic pressure due to the crystalline grouping, for if the latter were greater than, or less than,  $\pi$  there would be a change of volume on crystallization. If  $v_l = v_c$  since, as the curve of fusion shows, both  $\mathcal{S}$  and  $L$  are finite,  $\frac{\partial \mathcal{S}}{\partial p}$  must be zero, *i.e.*, we have to

\* A. E. OXLEY, 'Trans. Faraday Society,' vol. XI., Part 2, February, 1916.

determine the value of the applied pressure corresponding to the maximum of the closed area on the  $\mathfrak{S}$ ,  $p$  diagram. We cannot expect this method to give us anything but an approximate value of  $\pi$  because the extrapolation beyond laboratory pressures is considerable, but the results of the calculation are suggestive.

The relations between the temperature of fusion ( $\mathfrak{S}$ ) and applied pressure ( $p$ ) in atmospheres, for the substances\* here referred to are taken from 'Kristallisieren und Schmelzen' by G. TAMMANN, Leipzig, 1903, p. 204, *et seq.*

For *water* TAMMANN found

$$\mathfrak{S} - 22 = 0.00438 \cdot (p - 2200) - 77 \times 10^{-8} \cdot (p - 2200)^2.$$

Differentiating and equating  $\frac{\partial \mathfrak{S}}{\partial p}$  to zero,

$$\frac{\partial \mathfrak{S}}{\partial p} = 0.00438 - 154 \times 10^{-8} \cdot (p - 2200) = 0,$$

or

$$\begin{aligned} \pi &= \frac{0.00438 + 154 \times 2200 \times 10^{-8}}{154 \times 10^{-8}} \\ &\doteq 5000 \text{ atmospheres} \doteq 5 \times 10^9 \text{ dynes/square centimetre.} \end{aligned}$$

*Benzophenone*—

$$\mathfrak{S} = 48.11 + 0.02757p - 0.00000136 \cdot p^2.$$

Differentiating and equating  $\frac{\partial \mathfrak{S}}{\partial p}$  to zero we find the intrinsic pressure

$$\pi \doteq 10,000 \text{ atmospheres.}$$

*Acetophenone*—

$$\mathfrak{S} = 19.2 + 0.0235p - 0.00000152 \cdot p^2$$

$$\pi \doteq 7700 \text{ atmospheres.}$$

*Aniline*—

$$\mathfrak{S} = -6.1 + 0.0203p - 0.00000112 \cdot p^2$$

$$\pi \doteq 9000 \text{ atmospheres.}$$

*Nitrobenzene*—

$$\mathfrak{S} = 5.67 + 0.02344p - 0.00000116 \cdot p^2$$

$$\pi \doteq 10,000 \text{ atmospheres.}$$

*Xylene*—

$$\mathfrak{S} = 13.2 + 0.03438p - 0.00000171 \cdot p^2$$

$$\pi \doteq 10,000 \text{ atmospheres.}$$

*Benzene*—

$$\mathfrak{S} = 5.43 + 0.0283p - 0.00000198p^2$$

$$\pi \doteq 7100 \text{ atmospheres.}$$

\* Most of these substances show a change of diamagnetic susceptibility on crystallization. See Part I., pp. 120-131; Part III., pp. 96-97.

*Naphthalene*—

$$\mathfrak{S} = 79.95 + 0.03657p - 0.00000180p^2$$

$$\pi \doteq 10,100 \text{ atmospheres.}$$

*Carbon tetra-chloride*—

$$\mathfrak{S} = -23.0 + 0.0350p - 0.00000147p^2$$

$$\pi \doteq 11,900 \text{ atmospheres.}$$

*Ethylene di-bromide*—

$$\mathfrak{S} = 9.85 + 0.0252p - 0.00000125p^2$$

$$\pi \doteq 10,000 \text{ atmospheres.}$$

*Formic acid*—

$$\mathfrak{S} = 7.75 + 0.01276p - 0.00000080p^2$$

$$\pi \doteq 7980 \text{ atmospheres.}$$

*Potassium*—

$$\mathfrak{S} = 59.5 + 0.0146p - 0.0000007p^2$$

$$\pi \doteq 10,000 \text{ atmospheres.}$$

*Phosphorus*—

$$\mathfrak{S} = 43.93 + 0.0275p - 0.00000050p^2$$

$$\pi \doteq 27,500 \text{ atmospheres.}$$

*Sulphur, rhombic-monoclinic\**

$$\mathfrak{S} = 95.4 + 0.03725p + 0.00000213p^2$$

$$\pi \doteq -8700 \text{ atmospheres.}$$

*Solid CO<sub>2</sub>*—

$$\mathfrak{S} = -56.8 + 0.01999p - 0.00000075p^2$$

$$\pi \doteq 13,300 \text{ atmospheres.}$$

These values, it is true, appear rather high when compared with those found from other considerations, but due importance must be attached to the difficulties of experimental work of this nature and to the fact that the experimental data have been extrapolated over a considerable pressure interval (several thousands of atmospheres).

Comparing these results with those given on pp. 252 to 254 it is considered that a mean value of the intrinsic stress in diamagnetic crystalline media, viz.,  $2 \times 10^9$  dynes per square centimetre is representative of the true order of magnitude of the force which binds the molecules in the space lattice of a crystalline medium. This implies that the energy per unit volume of the diamagnetic crystalline medium, in virtue of the crystalline grouping, is comparable with  $2 \times 10^9$  ergs.

\* This transition of sulphur from the rhombic to the monoclinic form is accompanied by thermal absorption. Since  $\frac{\partial^2 \mathfrak{S}}{\partial p^2}$  is positive the transition line for different pressures will be convex to the  $p$ -axis.

As the corresponding stresses and energies are of the same order in the ferro-magnetic metals, and, further, since it has been shown (see Part II., pp. 143, 145 and Part III., pp. 84–87) that the local molecular force in diamagnetic media is of the same order as that in the ferro-magnetic metals, we may conclude that the local intensities of magnetization in the two types of media are comparable.

Since

$$\frac{1}{2} \cdot H_c \cdot I \doteq 2 \times 10^9 \text{ ergs,}$$

and

$$H_c \doteq 10^7 \text{ gauss (see Part III., p. 86),}$$

we find

$$I \doteq 400,$$

and

$$\alpha'_c = \frac{H_c}{I} \doteq 2.5 \times 10^4.$$

In a diamagnetic crystalline medium the local forces are comparable with those in iron, and, since the latter medium shows hysteresis in a magnetic field, we may enquire whether a similar phenomenon will be shown by diamagnetic media. If the diamagnetic molecules are magnetically unsymmetrical, the application of an external magnetic field will tend to orientate them.\* But this will be a differential effect on our conception of a diamagnetic molecule, and thus the tendency of the applied field to produce new molecular groupings will be small. We should therefore expect that hysteresis due to magnetization will be inappreciable in diamagnetic media. In iron, on account of the unbalanced magnetic nature of the molecules or atoms, new groupings are actually produced under fields of moderate intensity and the formation of these implies a loss of energy which is measured by the area of the hysteresis loop.

If, however, we take a diamagnetic copper wire and subject it to mechanical strain, the medium shows mechanical hysteresis. If sufficiently large stresses are employed, a permanent set is produced within the individual crystalline grains, new groupings of the molecules are formed, and a certain amount of energy is dissipated. All media, whether they are ferro-, para-, or diamagnetic, will show mechanical hysteresis. The difference from a magnetic point of view lies merely in the compensated nature of the diamagnetic molecule as compared with the uncompensated nature of the ferro-magnetic molecule, but the local forces are comparable, so that under mechanical stress the mechanical hysteresis effects will be comparable.

### (3) A COMPARISON OF THE ELASTICITIES OF SOME DIAMAGNETIC CRYSTALS WITH THOSE OF CRYSTALLINE PARAMAGNETIC AND FERRO-MAGNETIC MEDIA.

It is well known that the application of an external magnetic field alters the distribution of stress in a mass of iron crystals. On our theory we see how the

\* This orientation in a diamagnetic liquid gives rise to the induced magnetic double refraction. See Part III., p. 87.

molecules orientate themselves during crystallization under the influence of the local forcives which are characteristic of the molecular configuration. The influence of these local forcives will produce in the crystalline medium a distribution of internal stress which will in general be different across different planes, and in this way the planes of cleavage can be defined. In the direction where the stress is greatest, we should expect the elastic properties of the crystal to be abnormally high, comparable in fact with the elastic properties of steel.

In other directions we should expect the elastic properties to be less pronounced, and indeed the shearing of crystals, merely by the insertion of a knife blade and the application of small pressure parallel to a plane of cleavage, is evidence of this.

The following values of YOUNG'S Modulus of Rigidity for various ferro-magnetic, paramagnetic, and diamagnetic media show that the power to resist distortion is of the same order whatever the magnetic nature of the crystalline medium.

Substance.	Magnetic nature.	YOUNG'S modulus (dynes per square centimetre).	Rigidity (dynes per square centimetre).
* { Iron (0·1 per cent. carbon) Steel (1 per cent. carbon) . Nickel . . . . . Aluminium . . . . . Tin . . . . . Glass . . . . . Platinum . . . . . Lead . . . . . Zinc . . . . . Copper . . . . . Silver . . . . . Gold . . . . . Bismuth . . . . . Quartz (fibre) . . . . .	ferro-magnetic	$2 \cdot 13 \times 10^{12}$	$8 \cdot 3 \times 10^{11}$ (calc.)
	"	$2 \cdot 09 \times 10^{12}$	$8 \cdot 1 \times 10^{11}$
	"	$2 \cdot 02 \times 10^{12}$	$7 \cdot 7 \times 10^{11}$ (calc.)
	paramagnetic	$7 \cdot 05 \times 10^{11}$	$2 \cdot 67 \times 10^{11}$
	"	$5 \cdot 43 \times 10^{11}$	$2 \cdot 0 \times 10^{11}$ (calc.)
	(sometimes diamagnetic)	$6 \cdot 5 - 7 \cdot 8 \times 10^{11}$	$2 \cdot 6 \times 10^{11}$
	paramagnetic	$1 \cdot 68 \times 10^{12}$	$6 \cdot 1 \times 10^{11}$
	diamagnetic	$1 \cdot 62 \times 10^{11}$	$0 \cdot 56 \times 10^{11}$ (calc.)
	"	$1 \cdot 25 \times 10^{12}$	$5 \times 10^{11}$
	"	$1 \cdot 23 \times 10^{12}$	$4 \cdot 55 \times 10^{11}$
	"	$7 \cdot 9 \times 10^{11}$	$2 \cdot 87 \times 10^{11}$
	"	$8 \cdot 0 \times 10^{11}$	$2 \cdot 77 \times 10^{11}$
	"	$3 \cdot 19 \times 10^{11}$	$1 \cdot 2 \times 10^{11}$ (calc.)
	"	$5 \cdot 18 \times 10^{11}$	$3 \cdot 0 \times 10^{11}$
		Principal YOUNG'S moduli (dynes per square centimetre).	Principal rigidity (dynes per square centimetre).
† { Quartz (crystalline) . . . Beryl . . . . . Topaz . . . . . Rock salt . . . . . Potassium chloride . . . Fluor spar . . . . . Pyrites . . . . .	diamagnetic	$1 \cdot 00 \times 10^{12}$	$5 \cdot 7 \times 10^{11}$
	paramagnetic	$2 \cdot 06 \times 10^{12}$	$6 \cdot 54 \times 10^{11}$ }
		$2 \cdot 25 \times 10^{12}$ }	$9 \cdot 6 \times 10^{11}$ }
	diamagnetic	$2 \cdot 25 \times 10^{12}$ }	—
		$2 \cdot 83 \times 10^{12}$ }	—
		$2 \cdot 60 \times 10^{12}$ }	—
	"	$0 \cdot 41 \times 10^{12}$	$1 \cdot 27 \times 10^{11}$
"	$0 \cdot 36 \times 10^{12}$	$0 \cdot 64 \times 10^{11}$	
"	$1 \cdot 44 \times 10^{12}$	$3 \cdot 4 \times 10^{11}$	
—	$3 \cdot 46 \times 10^{12}$	$10 \cdot 5 \times 10^{11}$	

\* KAYE and LABY, 'Physical and Chemical Constants,' p. 27, 1918.

† A. E. H. LOVE, "The Mathematical Theory of Elasticity," 'Camb. Univ. Press,' p. 160. In the cases of beryl and topaz the different values correspond to bars whose lengths are in the directions of the different axes of symmetry.

As LOVE points out, the values of these elastic constants for beryl and topaz are remarkable in that they are greater than the corresponding constants in ordinary steel. The values of the elastic coefficients for most of the other substances in the above table are comparable with the constants for steel, and it is considered that these results give very strong evidence in favour of the large intermolecular forcive operative in diamagnetic crystalline media and confirm the suggestion made in Part II., p. 143, that this local forcive is comparable with that in ferro-magnetic media.

If a crystalline medium be heated, then as long as the crystalline state prevails, rotational vibrations of large amplitude are prevented, so that the specific heat of the crystalline medium is lower than that of the supercooled liquid.\* In the latter case, the liquid at low temperatures passes into a rigid gel, and when this is heated, the molecules acquire rotational vibrations gradually until finally the ordinary liquid state is reached, possessing no appreciable rigidity. It is important to note that the molecules are vibrating under a local forcive to which we are ascribing the elastic properties of the medium, and therefore the theory is consistent with the theory of specific heat developed by DEBYE, in which the forces which control the thermal vibrations of the molecules are identical with those which determine the elastic constants of the medium. MADELUNG and SUTHERLAND have similarly suggested that the elastic forces resisting mechanical strain are just those forces which determine the infra-red optical vibrations of the atoms in the solid substance. It has been found possible to calculate the infra-red frequencies from a knowledge of the mechanical properties. In the present researches it has been shown that we can calculate both the optical frequencies† and the mechanical stresses from the local molecular forcive. *Within* the core of the atom the local controlling force may be more intense, and although such an intense forcive would not be directly operative in determining the state of crystallization, yet it might be responsible for determining frequencies on the ultra-violet side comparable with X-ray frequencies. (See *infra*, pp. 273 and 278.)

#### (4) THE CHANGE OF DENSITY ON CRYSTALLIZATION INTERPRETED AS A MAGNETO-RESTRICTION EFFECT OF THE MOLECULAR FIELD.

If we subject a liquid to a magnetic field, a change of volume occurs to such an extent that the internal pressure is reduced by an amount equal to the potential energy per unit volume of the magnetic field. This change of internal pressure (see Part III., p. 91) is

$$\frac{1}{2} \cdot k_l \cdot H^2 + \frac{1}{2} \cdot \lambda \cdot k_l^2 \cdot H^2 \dots \dots \dots (2)$$

where

$k_l$  is the susceptibility of the liquid per unit volume,

$\lambda$ , a constant equal to 1/3,

and

H, the applied field intensity.

\* Part III., p. 94.

† A. E. OXLEY, 'Roy. Soc. Proc.,' A, vol. 95, p. 58, 1918, and Part III., p. 84.

As  $k_l$  for diamagnetic media is of the order  $-7 \times 10^{-7}$ , the second term in (2) is insignificant in comparison with  $\frac{1}{2} \cdot k_l \cdot H^2$ .

If  $c$  be the compressibility of the liquid, the change of volume in cubic centimetres per cubic centimetre will be given by

$$\delta v = \frac{1}{2} \cdot c \cdot k_l \cdot H^2. \quad (3)$$

This relation has been experimentally verified by QUINCKE.\* The compressibility  $c$  is of the order  $10^{-10}$ , particular values for different substances being:—

Substance.	$c \times 10^{10}$ .
Benzene . . . . .	0·8
Chlorobenzene . . . . .	0·7
Toluene . . . . .	0·8
Xylene . . . . .	0·7
Water . . . . .	0·5
Carbon tetrachloride . . . . .	0·9
Acetic acid . . . . .	0·4
Carbon bisulphide . . . . .	0·9

Substance.	$c \times 10^{12}$ .
Mercury . . . . .	3·7
Potassium . . . . .	31·5
Sodium . . . . .	15·4
Lead . . . . .	2·2
Tin . . . . .	1·7
Bismuth . . . . .	2·8
Iron . . . . .	0·4

Since the largest magnetic field at our disposal is 50,000 gauss, the largest value of  $\delta v$  is

$$-\frac{1}{2} \times 10^{-10} \times 7 \times 10^{-7} \times 2 \cdot 5 \times 10^9 = -8 \times 10^{-8} \doteq -10^{-7} \text{ c.c./c.c.}$$

Now we have shown (Part III., p. 90) that the potential energy term corresponding to (2) for a crystalline medium is

$$\frac{1}{2} \cdot k_l \cdot H^2 + \frac{1}{2} \cdot \alpha'_c \cdot I^2$$

per unit volume, where  $\alpha'_c$  is the constant of the local molecular field and  $I$  is the aggregate of the local intensity of magnetization per unit volume. The term  $\frac{1}{2} \cdot \alpha'_c \cdot I^2$  is associated with each cubic centimetre of the crystalline structure whether

\* See G. T. WALKER, "Aberration and the Electromagnetic Field," 'Camb. Univ. Press,' pp. 72-83.

H be zero or not. It is really due to the spontaneous *local* intensity of magnetization per unit volume and corresponds to the similar energy term,  $\frac{1}{2}NI^2$  (WEISS), due to the spontaneous magnetization in iron. Using the values which have already been assigned to  $\alpha'_c$  and I,\* viz.,

$$\left. \begin{aligned} \alpha'_c &\doteq 2.5 \times 10^4 \dagger \\ I &\doteq 400 \end{aligned} \right\}, \dots \dots \dots (4)$$

we see at once that this term is large in comparison with  $\frac{1}{2} \cdot k_i \cdot H^2$  and therefore the change of volume to which the potential energy term  $\frac{1}{2} \cdot \alpha'_c \cdot I^2$  gives rise will be large in comparison with that which we can produce artificially in a liquid by applying the largest field available in the laboratory.

When a diamagnetic substance crystallizes, the alteration of internal pressure will be  $\frac{1}{2}\alpha'_c \cdot I^2$  and therefore the accompanying change of volume in cubic centimetres per cubic centimetre will be

$$\delta V = \frac{1}{2} \cdot c \cdot \alpha'_c \cdot I^2,$$

and substituting from (4) we find

$$\delta V = \frac{1}{2} \cdot 0.8 \times 10^{-10} \times 16 \times 10^4 \times 2.5 \times 10^4 = 0.16 \text{ c.c./c.c.}$$

to the appropriate order.

Some values of  $\delta V$  in cubic centimetres per cubic centimetre are:—

Substance.	$\delta V$ .	
Benzene . . . . .	0.10	}
Naphthalene . . . . .	0.14	
Benzophenone . . . . .	0.19	
Di-phenylamine . . . . .	0.10	
Formic acid . . . . .	0.10	
Sodium . . . . .	0.03	
Potassium . . . . .	0.03	}
Mercury . . . . .	0.036	
Lead . . . . .	0.03	
Tin . . . . .	0.03	
Bismuth . . . . .	0.03	
Iron (at $A_3$ point) . . . . .	0.003	

The values calculated agree as well as could be expected with the experimental determinations, since we know the orders of magnitude only of  $\alpha'_c$  and I, for these are

\* See p. 257 *supra*.

† A physical explanation of this large value of  $\alpha'_c$  and of the corresponding constant N in ferromagnetism is given on p. 267 *infra*.

‡ G. TAMMANN, 'Kristallisieren u. Schmelzen,' Leipzig, 1903, pp. 204 *et seq.*

§ DESCH, 'Metallography,' p. 242.



unknown functions of the molecular structure and space lattice of each substance. It will be noticed that those substances showing a small value of  $\delta V$  have low compressibilities.

The case of iron at the  $A_3$  transformation is particularly interesting. From the curves given by CHARPY and GRENET,\* dealing with the expansion of iron and iron-carbon alloys between  $200^\circ \text{C.}$  and  $1000^\circ \text{C.}$ , we can show that the extent of linear contraction which occurs suddenly at the  $A_3$  point ( $900^\circ \text{C.}$ ) is of the order 0.003 centimetre per centimetre. The change of volume will be of this order of magnitude, which is small in comparison with the change of volume accompanying the crystallization of many organic compounds, but is very large compared with the magnetostriction effect which can be induced in either a ferro-magnetic or diamagnetic substance with a field of 50,000 gauss.

Taking into account the small compressibility of iron,† which is only  $0.4 \times 10^{-12}$ , or about 1/200 that of the liquids above referred to, this change of volume may be interpreted as due to a change of internal energy represented by  $\frac{1}{2} \cdot N \cdot I^2$  where  $N$  is the constant of the ferro-magnetic field, of the order  $0.38 \times 10^4$ ,‡  $I$  the saturation intensity of magnetization, of the order 1760. For we have

$$\begin{aligned} \delta V &= \frac{1}{2} \cdot c \cdot N \cdot I^2 \\ &= \frac{1}{2} \times 0.4 \times 10^{-12} \times 0.38 \times 10^4 \times 1.76^2 \times 10^6 \\ &= 0.002 (4) \text{ c.c./c.c.} \end{aligned}$$

which is of the order of magnitude found experimentally. The molecular field exists in an unmagnetized piece of iron and is accompanied by the large spontaneous magnetization of that element throughout an individual grain, but as these grains have all types of orientation, the large molecular field and the accompanying spontaneous magnetization are hidden in a piece of iron large enough to contain many grains. The molecular field will nevertheless produce the magnetostriction effect referred to above.§ Let us suppose that such a piece of iron is subjected to an external magnetic field. The molecules of all the grains will tend to come into alignment with the applied field and there will be a new distribution of stress. In an unmagnetized piece of iron, taken as a whole, the stress may be regarded as equal in all directions, but when an external field is applied, this is no longer the case and the iron shows a new magnetostriction effect consisting of an expansion in one direction and a contraction in the other. The extent of the redistribution of stress should be determined by a term of the form  $\frac{1}{2} \cdot \alpha'_c \cdot I^2$  where  $\alpha'_c$  is the constant of the molecular field

\* *Loc. cit.*

† RICHARDS, 'Journ. Chem. Soc.,' vol. 99, p. 1201, 1911.

‡ WEISS and BECK, 'Journ. de Phys.,' sér. iv., vol. 7, p. 249, 1908.

§ See *infra*, p. 265. It is assumed here that the molecular field disappears just above the  $A_3$  point, at least in so far as it is effective in causing spontaneous magnetization. This is in accordance with the small paramagnetic susceptibility of iron above  $A_3$ .

and  $\iota$  is the resultant intensity of magnetization induced in the direction of the external field. The compressibilities will now be different along and perpendicular to this direction, and the change of volume should be proportional to  $\iota^2$  for the particular value of the applied field. This result agrees with experiment.\*

We can see in a general way how the sign of  $\delta V$  on crystallization may sometimes be positive and sometimes negative. Usually the molecular packing in the crystalline state will be closer than that in the liquid state, but it may happen that the configuration of the molecule is such that, when the parts which have the strongest magnetic attraction for each other are in the position of minimum potential energy, the packing is more open than in the liquid state. The appearance of the internal force on crystallization will in this case be accompanied by expansion. In the former case the appearance of the internal force will be accompanied by contraction.

The region of stability of the crystalline state is represented on the pressure temperature diagram by a closed area (fig. 2).

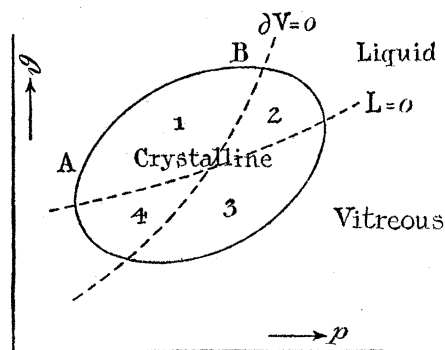


Fig. 2.

This area will in general be divided into four quadrants by the loci of the lines  $\delta V = 0$  and  $L = 0$ , where  $\delta V$  is the change of volume on crystallization and  $L$  is the latent heat.

In the four quadrants the following conditions hold :—

Quadrant.	$L$ .	$\delta V$ .	$\frac{\partial \delta}{\partial p}$ .	$\frac{\partial^2 \delta}{\partial p^2}$ .
1	+	+	+	-
2	+	-	-	-
3	-	-	+	+
4	-	+	-	+

If the melting-point is at some point along the arc  $AB$  of the first quadrant, increase of pressure raises the m.p. and  $\delta V$  and  $L$  are positive. This corresponds

\* NAGAOKA and HONDA, 'Phil. Mag.,' vol. 46, p. 268, 1898.

with the case for benzophenone. In the case of water the diagram is as in fig. 3 and for  $p = 1$  atmosphere,  $\delta V$  is negative and  $L$  is positive. The m.p. is in this case located on the arc  $A'B'$  in the second quadrant. A similar case is that of pure iron as the temperature is raised through the critical point  $A_3$  (see fig. 4). At  $A_3$ ,  $\delta V$  is negative and  $L$  is positive, while  $\frac{\partial \mathcal{S}}{\partial p}$  is negative.

Now

$$\frac{\partial \mathcal{S}}{\partial p} = \frac{(v_\gamma - v_\beta) \cdot \mathcal{S}}{L} = \frac{\delta V \cdot \mathcal{S}}{L}.$$

Therefore  $v_\beta > v_\gamma$  which gives a shrinkage in iron on heating through the  $A_3$  point at about  $900^\circ \text{C}$ .

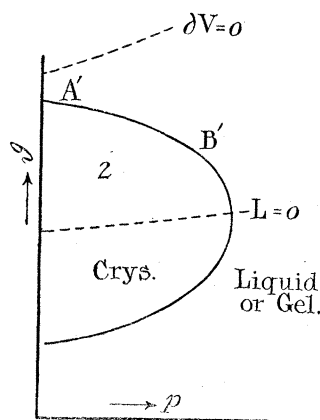


Fig. 3.

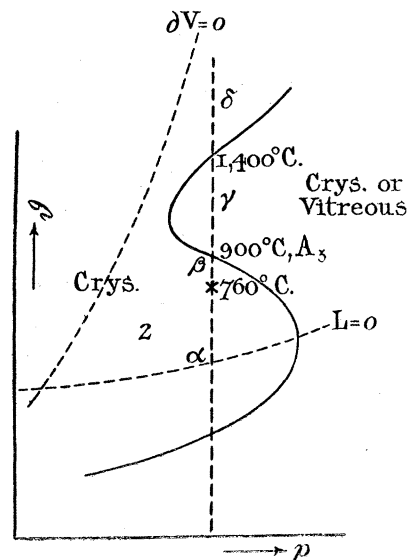


Fig. 4.

The application of the relation

$$\frac{\partial \mathcal{S}}{\partial p} = \frac{(v' - v'') \cdot \mathcal{S}}{L} = \frac{\delta V \cdot \mathcal{S}}{L}$$

is interesting in connexion with some abnormalities of heats of recalescence in ferromagnetic media. The change of volume  $\delta V$ , both expansion and contraction; the absorption or evolution of heat of the amount  $L$ , depend solely upon the shape of the region of crystalline stability and its position relatively to the  $\mathcal{S}$ ,  $p$  axes.

Thus nickel steel with no carbon and pure cobalt show no recalescence at the magnetic change points. In these cases  $L$  is very small and since  $\delta V$  and  $\mathcal{S}$  are finite,  $\frac{\partial \mathcal{S}}{\partial p}$  will be large (fig. 5). In other words, under the pressure of one atmosphere, the path of the crystallization curve cuts the line  $AB$  at a steep angle in the neighbourhood of the intersection of the fusion curve with the neutral line  $L = 0$ ,

The apparent discontinuities of the susceptibility temperature curve are suggestive in this connexion (fig. 6). The upper branch of the curve AB for the so-called  $\beta$ -iron is practically continuous with the branch CD for the  $\delta$ -range above  $1400^{\circ}\text{C}$ . Between B and C there is a break, the branch BE representing  $\beta$ -iron over a somewhat narrow range just below the critical temperature  $\mathcal{D}_c$  and the branch EF representing paramagnetic  $\gamma$ -iron. The locus BEFC corresponds to a crystalline modification of iron which is more stable over this temperature interval than the crystalline grouping or groupings over the ranges AB and CD.

If this view is correct, the molecular field is operative in iron over a temperature interval from  $1400^{\circ}\text{C}$ . upwards as well as below the critical temperature. The existence of this force above  $1400^{\circ}\text{C}$ . implies a crystalline symmetry involving an appreciable mutual action between the molecules consistent with the enhanced susceptibility found by CURIE\* and by WEISS and FOEX† over this range. In the

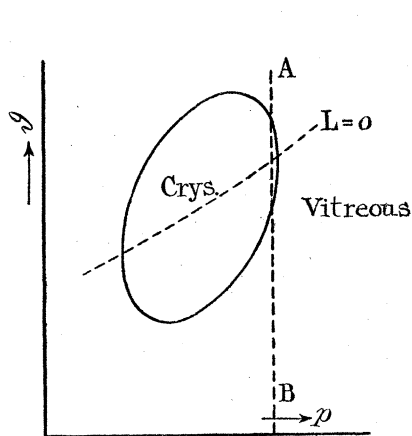


Fig. 5.

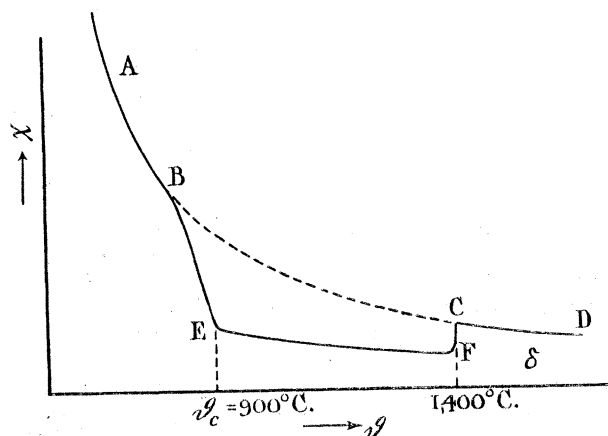


Fig. 6.

intermediate range, between  $900^{\circ}\text{C}$ . and  $1400^{\circ}\text{C}$ ., iron shows a paramagnetic quality only. Perhaps we may regard the molecular state in this range as more allied to a gel, consisting of very small interlocked grains, each with relatively few molecules,‡ rather than to a coarse grain crystalline arrangement of the molecules. The orientations of the molecular axes as we pass from one small grain to another will be different, so that each grain is, as it were, surrounded by a surface of vitreous material. As stated on p. 251 the molecular field would then be non-effective in so far as the production of

\* 'Annales de Chimie et de Physique,' sér. iv., vol. v., p. 289, 1895.

† 'Archives des Sciences, Genève,' sér. 4, vol. xxxi., p. 88, 1911.

‡ This smallness of grain structure above  $A_3$  in wrought iron or mild steel is consistent with the experiments of J. E. STEAD, 'Iron and Steel Institute,' 1898, No. 1, p. 145. The reverse effect, that of a coarse structure on cooling from above  $A_3$ , observed by STEAD and CARPENTER ('Iron and Steel Institute,' No. 11, p. 119, 1913) in the case of thin strips of electrolytic iron, may possibly be attributed to surface forces. See also a paper "On the Part Played by the Amorphous Phase in the Hardening of Steels," by J. C. W. HUMFREY, 'Trans. Faraday Soc.,' May, 1915.

spontaneous magnetization is concerned, but the tenacity might even surpass that of the chaotic  $\beta$ -state since the transition  $\beta$ - $\gamma$  is accompanied by shrinkage. Such an increase of tenacity was actually found by ROSENHAIN and HUMFREY.\*

The effects of prolonged heating on the plasticity of mild steel are interesting in this connexion. EWING and ROSENHAIN† have shown that the plasticity of a material is caused by slips occurring on cleavage or "gliding" surfaces *within each* of the crystalline grains, although the elementary portions of the crystals retain their primitive form and the crystalline structure of the metal as a whole is preserved. In the case of mild steel, exposure to a temperature of 1200° C. or higher temperatures for several hours may cause the material to lose much of its plasticity, while some specimens of soft iron after prolonged exposure at 700° C. to 800° C. (less than the critical temperature) have been made brittle. These results are consistent with a similarity of molecular configuration for temperatures above 1200° C. and below the critical temperature (about 850° C.). On the other hand an exposure at 900° C. or 1000° C. (*i.e.*, in the region of the paramagnetic state), followed by a slow or fairly rapid cooling, induces considerable plasticity in the material, and this treatment may even be used to remove brittleness originating from heating to the higher or lower ranges of temperature mentioned above. As the plasticity is produced by slipping on cleavage surfaces *within* the crystalline grains, this smallness of the grain structure may, under stress, determine a molecular rotation. EWING and ROSENHAIN‡ have shown that in some metals, in addition to slips or motions of pure translation, there results a molecular rotation from strain which gives rise to twin-crystals. It is interesting to note that the formation of twin-crystals is common in iron through the  $\gamma$ -range, but has not been observed in the  $\beta$  and  $\alpha$  ranges.

As the temperature falls below 1400° C. there is some modification of the crystalline cubic arrangement, resulting in a closer packing of the molecules, and accompanied by an interlocking of the fine grains. Thus iron in the  $\gamma$ -range (1400° C. to 900° C.) will be paramagnetic. At a lower temperature than 900° C., this state is unstable and another modification of the crystalline grouping occurs, accompanied by expansion, thermal evolution, and the appearance of spontaneous magnetization. This latter effect seems inconsistent with a more open packing of the molecules, but an analogy is found in the case of water, where the molecular influence in the liquid just above 0° C. is small compared with that in ice just below freezing point, although the packing of the molecules in the liquid state is closer than that in the crystalline state (see *supra* p. 264). As the temperature is lowered the transformation progresses rapidly until a point B is reached, after which the increase of magnetic quality is somewhat less rapid. On continued cooling, the iron passes into the  $\alpha$ -range where the magnetic property is capable of attaining a saturation value.

\* 'Roy. Soc. Proc.,' A, vol. 83, 1909; 'Iron and Steel Institute,' No. 1, 1913.

† 'Phil. Trans. Roy. Soc.,' A, vol. 193, p. 279.

‡ See EWING, 'The Strength of Materials,' p. 47, 1906.

(5) FURTHER DISCUSSION OF THE NATURE OF THE LOCAL MOLECULAR FIELD  
IN FERRO-MAGNETIC AND DIAMAGNETIC MEDIA.

This subject has already been discussed in Part III, pp. 89 and 100, but no interpretation was then given to the magnitudes of the constants  $N$  and  $\alpha'_c$  of the local ferro-magnetic and diamagnetic fields. The values of  $N$  given by WEISS and BECK\* are  $0.38 \times 10^4$  for iron, and  $1.27 \times 10^4$  for nickel. For diamagnetic crystalline media  $\alpha'_c$  is of the order  $2 \times 10^4$ .

EWING and LOW† have shown that in very strong magnetic fields the relation between induction ( $B$ ) and applied field ( $H$ ) may be represented by the equation

$$B = H + a \text{ constant.} \dots \dots \dots (1)$$

This constant has the value  $4\pi I$  (where  $I$  is the saturation intensity) and is equal to 21,360 in wrought iron, 6470 in nickel and 16,300 in cobalt.

In the case of wrought iron

$$B = H + 21360. \dots \dots \dots (2)$$

Suppose we could apply a field equal to the molecular field,  $6.53 \times 10^6$  gauss for iron. The limiting value of the permeability  $\mu_L$  for this field will be from (2)

$$\mu_L = 1 + \frac{21360}{6.53 \times 10^6},$$

and the limiting susceptibility per unit volume

$$\chi_L = \frac{\mu_L - 1}{4\pi} = \frac{21360}{4\pi \times 6.53 \times 10^6} = 2.60 \times 10^{-4},$$

and

$$\frac{1}{\chi_L} = 0.38 \times 10^4.$$

This is equal to the value of  $N$ , the coefficient of the molecular field, as we should expect.

Similar calculations may be made for nickel and cobalt, the limiting susceptibilities being respectively

$$\chi_L = 0.81 \times 10^{-4} \text{ for nickel,}$$

$$\chi_L = 2.0 \times 10^{-4} \text{ for cobalt.}$$

Now we may ask the question, why is it that, in spite of the fact that all the molecules are ordered into a definite space lattice under the influence of the respective molecular fields, the materials still show a finite susceptibility to magnetization? The

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

† 'Phil. Trans. Roy. Soc.,' A, p. 242, 1889.

explanation, I think, is to be found in the finite though small angular oscillations which constitute a portion of the thermal energy of the molecules. The molecules are fixed relative to one another and form a definite space lattice but they are oscillating with small amplitude under the molecular field. This allows them to retain a finite susceptibility. Suppose we could double the molecular field, the limiting susceptibility would become one-half its former value and the saturation intensity of magnetization would be slightly increased. If we could increase the molecular field indefinitely, the susceptibility would get indefinitely small, the product of the two however tending to a finite limit equal to the *true* saturation intensity of magnetization. The amplitude of the molecular oscillations would, under the influence of this indefinitely large force, be indefinitely small. This state might be attained in a practical manner by cooling the substance, say in liquid hydrogen, when the limiting susceptibility would become vanishingly small.

As  $N$  is the reciprocal of the limiting susceptibility the constant of the molecular field will become indefinitely large. WEISS, however, supposes  $N$  to be constant.\* The tendency of  $\chi_L$  to approach a small limiting value as the temperature is lowered is confirmed experimentally for ferro-magnetic substances† and is particularly noticeable in the case of weak magnetic fields. The reduction of the amplitude of vibration of the molecules as the absolute zero is approached merely implies a higher frequency of angular oscillation under the increasing molecular field and does not necessarily imply that the rotational energy becomes vanishingly small. In this case it should be noted that the saturation intensity of magnetization we are considering is smaller than that which would be given by the simple summation of all the magnetic moments of the molecules in unit volume. In other words, the difficulty of producing this latter saturation by an external field becomes increasingly difficult on account of the larger molecular force at low temperatures, in agreement with the vanishingly small susceptibility referred to above. At higher temperatures the susceptibility to an external field is far greater; the molecules are, as it were, helped over their difficulties with respect to the molecular field, when the external field is applied, by the increased energy of the rotational oscillations, and having passed this critical point they are held in new combinations. Beyond the critical point the molecular state is chaotic, the molecules being interlocked (*cf.* p. 265), and the external field has sufficient control to produce a paramagnetic effect only.

\* Following WEISS, we have taken the molecular field proportional to  $I$ . WEISS writes the molecular field  $NI$  and assumes  $N$  to be constant. This applies with sufficient accuracy in a temperature region just below the critical temperature, but cannot be true over the whole region down to absolute zero, because, as the molecular translational vibrations die down, the molecules approach one another more closely and the molecular field must necessarily increase considerably although  $I$  remains practically constant. This increase is accounted for by the increase of the coefficient  $N$ , which is the reciprocal of the limiting susceptibility.

† EWING, 'Magnetic Induction in Iron and other Metals,' p. 172 *et seq.*, where curves are given for iron, hard steel, nickel and various nickel steels. See also p. 269 *infra* and EWING, *loc. cit.*, p. 354.

The fall off in the value of  $\chi$  as the temperature is reduced, may, in part, be explained by the increased value of the molecular field, due to the nearer approach of the molecules. As the local molecular field becomes very big, the induced diamagnetic effect in each molecule will become big, in the same proportion, and this will tend to reduce the value of  $\chi$  and make this quantity tend to a limiting value. If the molecular field is of the order  $10^7$  gauss at ordinary temperatures, we have seen that the ratio of the induced diamagnetic moment  $\Delta M$  to the magnetic moment of the electron orbit  $M$ , is of the order  $1/100$ . If the molecular field at low temperatures approaches  $10^9$  gauss, owing to closer proximity of the magnetic elements in neighbouring molecules, the diamagnetic effect would be comparable with the ferro-magnetic effect.\* On our view this does not imply that diamagnetic substances should acquire a large diamagnetic susceptibility at very low temperatures. For taking the molecules in pairs, locally they are paramagnetic and the action of the local molecular field is to reduce this paramagnetic effect so that the local magnetic moment becomes smaller and the susceptibility to an external field tends to zero as in iron.

According to EWING† experiments carried out to test this effect have neither proved nor disproved this theory, probably because the external fields were not sufficiently strong. But during crystallization we are applying unconsciously to each molecular current a magnetic field 500 or 1000 times stronger than the largest field we can apply externally, and probably even greater local intensities are attained at low temperatures, since the interacting magnetic elements in adjacent molecules may be almost touching one another. The mutual induction and temperature effects combine to cause  $\chi$  to approach the limit zero at the absolute zero or in very powerful external fields.

In diamagnetic media we have seen that the constant of the local molecular field  $\alpha'$ , (which corresponds to  $N$  in WEISS's ferro-magnetic field) is of the order  $2.5 \times 10^4$  and the reciprocal of this, viz.,  $+4 \times 10^{-5}$ , is the order of magnitude of the *local positive limiting susceptibility* of a diamagnetic crystalline medium. (At ordinary temperatures the diamagnetic susceptibility per unit volume is of the order  $-10^{-6}$ ). The parts of molecules adjacent to one another in a diamagnetic crystalline medium attract in a similar manner to the adjacent parts of molecules of a ferro-magnetic or paramagnetic medium.

In a ferro-magnetic medium, as the temperature is raised, the susceptibility increases up to a certain point just below the critical temperature and then falls off rapidly. The temperature controls the susceptibility in two ways; first, by helping the molecules to overcome the difficulties of orientation, produced by the neighbouring molecules, to a point just below the critical temperature; second, by overdoing this effect and by giving the molecules too much rotational energy, at the critical temperature and above, so that the susceptibility to magnetization falls very rapidly.

\* In nickel the molecular field is  $6.3 \times 10^6$  gauss. An applied field of  $10^6$  gauss would make a substance as diamagnetic as bismuth have a saturation value equal to that of nickel.

† 'Magnetic Induction in Iron and other Metals,' p. 353.



In a diamagnetic crystalline medium, as the temperature is raised, the local positive susceptibility will obey a similar law, the temperature of fusion now corresponding to the critical temperature in the ferro-magnetic case. Although locally the relation between susceptibility and temperature is the same in the two cases, the effect passes unnoticed in the diamagnetic case because the molecule has a total zero magnetic moment. Nevertheless, the effect of temperature acts in its two antagonistic ways in diamagnetic as well as in ferro-magnetic media. When the temperature is above the melting point, the rotational energy of the molecules annuls the local force (liquid state), when it is very low the molecules become interlocked and cannot readjust themselves in a space lattice (gel state). There is an intermediate region of temperature where opportunity is offered for the tendency of self-orientation under the mutual local forces to display itself, and over this range crystallization may take place. This intermediate temperature range defines the closed region of stability of the crystalline form on the pressure temperature diagram of equilibrium of the crystalline and amorphous states (see p. 263).

A discussion as to how far we may regard it as proved that the local molecular field in crystalline media is of magnetic nature was given in para. 8, of Part III. The conclusion reached was that the molecular field is certainly in part magnetic. It is possible to bring forward further evidence of the truth of this deduction. In some noteworthy researches\* published by TYNDALL, as long ago as 1870, it was shown that magnetic properties of crystalline media bear a close relation to molecular aggregation. About 100 different crystals were examined and from the deportment of these, when subjected to a magnetic field, TYNDALL found that "if the arrangement of the component particles of any body be such as to present different degrees of proximity in different directions, then the line of closest proximity, other circumstances being equal, will be that chosen by the respective forces for the exhibition of their greatest energy. If the mass be magnetic this line will stand axial, if diamagnetic, equatorial."†

The exactness of the dependence of magnetic deportment on the position of cleavage planes is remarkably shown in these experiments. Whatever the crystal examined, it was found that the magnetic deportment disclosed accurate information of the planes of cleavage. TYNDALL describes the results of his important experiments in such elegant language that it may be permissible to quote some of them at length. Thus he continues:—"From this point of view, the deportment of the two classes of crystals represented by Iceland spar and carbonate of iron, presents no difficulty. This crystalline form is the same, and as to the arrangement of the particles, what is true of one will be true of the other. Supposing then, the line of closest proximity to coincide with the optic axis; this line, according to the principle expressed, will stand axial or equatorial, according as the mass is magnetic or diamagnetic, which is

\* 'On Diamagnetism and Magne-crystalline Action,' 1870.

† *Loc. cit.*, p. 23.

precisely what the experiments with these crystals exhibit. Analogy as we have seen justifies the assumption here made. It will, however, be of interest to enquire, whether any discoverable circumstance connected with crystalline structure exists upon which the difference of proximity depends and knowing which, we can pronounce with tolerable certainty, as to the position which the crystal will take up in the magnetic field.

“The following experiments will perhaps suggest a reply.

“If a prism of sulphate of magnesia be suspended between the poles with its axis horizontal, on exciting the magnet the axis will take up the equatorial position. This is not entirely due to the form of the crystal; for even when its axial dimension is shortest, the axis will assert the equatorial position, thus behaving like a magnetic body, setting its longest dimension from pole to pole.

“Suspended from its end with its axis vertical, the prism will take up a determinate oblique position. When the crystal has come to rest, let that line through the mass which stands exactly equatorial be carefully marked. Lay a knife-edge along this line, and press it in the direction of the axis. The crystal will split before the pressure, disclosing shining surfaces of cleavage. This is the only cleavage the crystal possesses and it stands equatorial. Sulphate of zinc is of the same form as sulphate of magnesia, and its cleavage is discoverable by a process exactly similar to that just described. Both crystals set their planes of cleavage equatorial. Both are diamagnetic.

“Let us now examine a magnetic crystal of similar form. Sulphate of nickel is, perhaps, as good an example as we can choose. Suspended in the magnetic field with its axis horizontal, on exciting the magnet the axis will set itself from pole to pole, and this position will be persisted in, even when the axial dimension is shortest. Suspended from its end, the crystalline prism will take up an oblique position with considerable energy. When the crystal thus suspended has come to rest, mark the line along its end which stands *axial*. Let a knife edge be laid along this line and pressed in a direction parallel to the axis of the prism. The crystal will yield before the edge and discover a perfectly clean plane of cleavage.

“These facts are suggestive. The crystals here experimented with are of the same outward form; each has but one cleavage, and the position of this cleavage with regard to the form of the crystal, is the same in all. The magnetic force, however, at once discovers a difference of action. *The cleavages of the diamagnetic specimens stand equatorial; of the magnetic, axial.*

“A cube cut from a prism of scapolite, the axis of the prism being perpendicular to two of the parallel faces of the cube, suspended in the magnetic field, sets itself with the axis of the prism from pole to pole.

“A cube of beryl of the same dimensions with the axis of the prism from which it is taken also perpendicular to two of the faces, suspended as in the former case, sets itself with the axis equatorial. Both these crystals are magnetic.

“The former experiments showed a dissimilarity of action between magnetic and diamagnetic crystals. In the present instances, both are magnetic, but still there is a difference; the axis of the one prism stands axial, the axis of the other equatorial. With regard to the explanation of this, the following fact is significant. Scapolite cleaves *parallel* to its axis, while beryl cleaves *perpendicular* to its axis; the cleavages in both cases, therefore, stand axial, thus agreeing with sulphate of nickel. The cleavages hence appear to take up a determinate position regardless of outward form, and they seem to exercise a ruling power over the deportment of the crystal.

“A cube of saltpetre, suspended with the crystallographic axis horizontal, sets itself between the poles with this axis equatorial.

“A cube of topaz, suspended with the crystallographic axis horizontal, sets itself with this axis from pole to pole.

“We have here a kind of complementary case to the former. Both these crystals are diamagnetic. Saltpetre cleaves parallel to its axis; topaz perpendicular to its axis. The planes of cleavage, therefore, stand in both cases equatorial, thus agreeing with sulphate of zinc and sulphate of magnesia.

“Where do these facts point? A moment's speculation will perhaps be allowed us here. May we not suppose these crystals to be composed of layers indefinitely thin, laid side by side, within the range of cohesion, which holds them together, but yet not in absolute contact? This seems to be no strained idea; for expansion and contraction by heat and cold compel us to assume that the particles of matter in general do not touch each other; that there are unfilled spaces between them. In such crystals as we have described these spaces may be considered as alternating with the plates which compose the crystal. From this point of view it seems very natural that the magnetic laminæ should set themselves axial, and the diamagnetic equatorial.

“Our fundamental idea is, that crystals of one cleavage are made up of plates indefinitely thin, separated by spaces indefinitely narrow. If, however, we suppose two cleavages existing at right angles to each other, then we must relinquish the notion of plates and substitute that of little parallel bars; for the plates are divided into such by the second cleavage. If we further suppose these bars to be intersected by a cleavage at right angles to their length, then the component crystals will be little cubes, as in the case of rock-salt and others. By thus increasing the cleavages, the original plates may be subdivided indefinitely, the shape of the little component crystal bearing special relation to the position of the planes. It is an inference which follows immediately from our way of viewing the subject, that if the crystal have several planes of cleavage, but all parallel to the same straight line, this line, in the case of magnetic crystals, will stand axial; in the case of diamagnetic, equatorial. It also follows that in the so-called regular crystals, in rock-salt, for instance, the cleavages annul each other, and consequently, no directive power will be exhibited, which is actually the case.”

The above quotation from TYNDALL's work clearly shows how closely allied are the

different forces of crystallization in different directions (which forces determine the planes of cleavage) with the magnetic behaviour of the crystallized medium and lead us to suspect that the forces of cohesion are probably of magnetic nature. The fine points are so completely explained by the magnetic deorientation that it is difficult to dissociate the crystalline forces from a magnetic origin. If we assume that these forces are of an electrostatic nature, then it must be admitted that the electrostatic axis of the molecule must coincide with the magnetic axis if the action of a magnetic field is to be decisive, as TYNDALL proved it to be, in isolating the planes of cleavage. But if the electrostatic and magnetic symmetries of the molecules are coincident the application of a field of either nature should induce a double refraction of the same kind in a given liquid. This, however, is not true experimentally, the electric induced double refraction in liquid carbon bisulphide being opposite in sign to the magnetic induced double refraction.\* Moreover, in crystalline media, the greatest axes of the ellipsoids representing the magnetic and electric properties of the molecule do not in general coincide. We may therefore say that the evidence points to the conclusion that the force which holds the molecules together in a crystalline space lattice is magnetic in nature and not electrostatic.†

DRUDE,‡ in his experiments on the relation between valency and dispersion,

\* COTTON and MOUTON, 'Comptes Rendus,' vol. 155, p. 1232, December, 1912.

† [Note added April 26, 1919.—After the present communication had passed out of my hands, an important paper "On the Origin of Spectral Series" was published by Sir J. J. THOMSON ('Phil. Mag.,' April, 1919). In this a new theory of atomic structure is suggested in which the atomic nucleus and the revolving electrons play similar rôles to those described on p. 274. Within the contour of the atom, according to Prof. THOMSON, the electrostatic force due to the nucleus is of a periodic character and determines a series of spherical or approximately spherical surfaces where the electric force vanishes and over which the periodic motion of the boundary electrons is determined solely by the magnetic field of the atom. This magnetic field is supposed to be radial. If this is the case, these intra-atomic fields must be of the order of magnitude  $10^8$  gauss (as a simple calculation shows, since  $\nu = \frac{H\epsilon}{2\pi m}$ ) to account for the frequencies of the visible spectrum. Still larger intra-atomic fields will exist nearer to the nucleus, of the order  $10^9$  gauss. These will be sufficient to account for the frequencies of the K series. The infra-red series will be accounted for by fields of the order  $10^7$  gauss. But this latter value is of the order of the intermolecular magnetic field which has been deduced independently in various ways in the present researches. Moreover, it is to this local field that we have ascribed the rigidity and other properties of crystalline media in general. The frequencies of the infra-red series will, on this view, correspond with the elastic vibrations of the rigid medium in conformity with the quantum theory of specific heats of EINSTEIN and DEBYE as already stated (see Part III., p. 94, and *supra*, p. 259). Reasons have already been given for assigning a magnetic nature to the intermolecular field in crystalline media (see Part III., pp. 101–3, and *supra*, pp. 270–276). This intermolecular magnetic field, which is of the order  $10^7$  gauss, is suggestive in connexion with Prof. THOMSON'S theory, referred to above. On p. 274 (footnote) it was suggested that the forces determining crystalline cohesion are magnetic in nature, the symmetry of the magnetic forces being determined, however, by the electrostatic action of the nucleus. Therefore, in this fundamental sense, the present theory and that of Sir J. J. THOMSON are identical.]

‡ 'Ann. der Phys.,' vol. 14, p. 677 and p. 936, 1904.

suggested that the electron couples constituting the molecule were of two kinds: (1) those of the atoms themselves, the sum of which presumably determine the atomic weight; (2) those of valency which alone are sufficiently free to vibrate synchronously with light waves and hence are particularly concerned in the refraction and dispersion of light.

The valency or boundary electrons are vibrating under the control of the nucleus, but are less firmly held in the system than those near the nucleus. These valency electrons which have periods corresponding with luminous vibrations are affected by an external magnetic field in accordance with the well-known Zeeman and diamagnetic effects. The highly constitutive nature of the magnetic susceptibility is consistent with this view that the origin of the magnetic property is partly located near the molecular boundary. The nuclear electrons in the free atom will determine symmetry of the molecule, and are directly responsible, by their magnetic effect, for the symmetry of the crystalline grouping. This latter will therefore be determined by the nucleus, which controls the nuclear and boundary electrons, in an indirect manner and the distribution of atomic nuclei in accordance with crystalline symmetry as disclosed by X-ray methods is apparent.

W. H. and W. L. BRAGG have shown the difficulty, even in simple cases, of defining the molecular boundaries in a crystalline space lattice, although in some cases this is possible. But to determine by the X-ray method whether in any given crystal any atom has a special relation to a neighbouring atom would be practically impossible. The X-ray effects which they investigate are determined only by the nucleus or core of the atom and the outer electrons of the atom which contribute to its magnetic property, though they are controlled by the nucleus, are probably distorted by the influences of neighbouring magnetic elements. This distortion, which explains a large number of observed phenomena, defines the molecular boundary within the space lattice and determines a definite chemical molecule. These outer regions of the atom or molecule remain undetected by the X-ray experiments.\*

\* A. E. OXLEY, 'Nature,' No. 4, 1915. The core or electrostatic part of the atom is at a much greater distance from the atomic boundary than are the circular currents which give rise to the magnetic properties. As the intensity of the magnetic field due to a circular current varies inversely as the cube of the distance, and as in a crystalline structure two such circuits may approach so as almost to touch, each electron describing a *small* circle, the local magnetic force may be sufficiently large to account for the facts.

The view that the cohesive force in crystalline media is of a magnetic nature was expressed in Part II. of this research, pp. 83-86. It was there stated that in a diamagnetic crystalline medium the molecules are held together by the local magnetic forces due to the revolving electrons. It is possible that each electron is completely bound to its own nucleus by a narrow tube of force, when the molecules would be capable of attracting or repelling one another electromagnetically according to their directions of rotation. The advantage of an electromagnetic cohesive force lies in the fact that by it we can readily see how similar molecules will cling together. Electrostatically such attraction implies an electron transfer which, we know, does not always take place. Reasons are given on p. 277 that the atomic forces which determine the structure of the molecule are in part at least of a magnetic nature. The advantage of

The theory propounded by TYNDALL was called by him the "theory of reciprocal induction," and the direction within the crystalline medium where the molecules had the closest proximity and along which the greatest energy was displayed, he called the "line of elective polarity." This theory is identical with our hypothesis of mutual molecular distortion enunciated at the beginning of Part I. and subsequently confirmed in a variety of ways by other physical phenomena. The direction of closest approach of the molecules, *i.e.*, the line of elective polarity is the line along which the crystal shows the maximum elastic properties. TYNDALL'S explanations of the phenomena he had discovered were prophetic. The diamagnetic forces were known to be so minute that the theory of reciprocal induction appeared incredible, and, as a correspondence between Lord KELVIN and TYNDALL shows,\* the former expressed emphatically his view that this theory was quite incapable of accounting for the effects observed. On our modern conception of the magnetic structure of matter, this doubt is dispelled and the smallness of the diamagnetic property is no barrier to the theory of reciprocal induction. The effect of applying pressure to a diamagnetic medium, produced, in the direction of the pressure, an increase in the diamagnetic property. This was attributed by TYNDALL to the mutual actions of the diamagnetic polarities which are so minute that their effects, as then understood, would be of such a small order of magnitude that they could not be detected by experiment. On our view of a diamagnetic molecule, which maintains that such a molecule is paramagnetic locally, the effects observed by TYNDALL can be accounted for quantitatively for the local molecular forcives are comparable with those in para- and ferro-magnetic media.

But even in the case of ferro-magnetic media it is not obvious that the magnetic forces are sufficient to explain the mechanical phenomena unless we realise the localised nature of the forcive. If we take, for example, a crevasse of the usual assigning a magnetic nature to the forces of valency is clear, for in this way, without admitting an electron transfer between the various atoms forming the molecule, we can secure the necessary attraction, and this by a fixed or directed force which at the same time is compatible with a characteristic orbital frequency such as appears to be necessary to account for ordinary absorption, magnetic rotation, and diamagnetic phenomena. The possibility of a satisfactory interpretation of many problems suggested by stereochemistry, in terms of the magnetic force due to revolving electrons, has been ably expounded by A. L. PARSON ('Smithsonian Miscellaneous Collections,' vol. 65, No. 11, a paper to which, on account of war service, I have only recently had access). Though PARSON'S theory involves new difficulties in connexion with the distribution of positive electricity in the atom, the advantages from a chemical standpoint which he secures by the introduction of magnetic forces of chemical combination cannot be denied. Granting this, it is natural to suppose that the cohesive forces, which hold the molecules in position in a space lattice, will be residual magnetic forces, and that they will closely resemble, in distribution at least, the atomic forces determining the configuration of the molecule. It will be of great interest to see how far such magnetic cohesive forces are capable of interpreting the spacing of molecules in a crystalline lattice in accordance with the distribution disclosed by X-ray analysis. Magneocrystalline action, as we have seen, is explicable in this way.

\* Various letters, 'On Diamagnetism and Magneocrystalline Action,' 1870.

conventional dimensions, within an iron crystal where the saturation intensity is  $I$ , the mechanical stress is  $2\pi I^2$ , which is far smaller than the ultimate tensile strength of the iron. Indeed, EWING\* remarks "we may, if we please, regard the magnetic molecules as pulling at one another across any imaginary interface, while the stress with which they pull is balanced by thrust in the framework of the iron, but neither the pull nor the thrust is competent to explain the mechanical strains." The above value of the stress, viz.,  $2\pi I^2$  is obtained by taking a crevasse whose gap, although "physically small," is sufficiently wide to accommodate several molecules in line. If we take a narrower crevasse, approaching "mathematical smallness" in width of gap, we obtain a measure of the force acting between the molecules, and this includes the localised force  $NI$  or  $\alpha'_c I$  which is of the order  $10^7$  gauss. The localised stress across this interface is  $\frac{1}{2}NI^2$  or  $\frac{1}{2}\alpha'_c I^2$ , which we have seen to be of the order  $2 \times 10^9$  dynes per square centimetre. This is of the same order as the ultimate tensile strength of crystalline media both ferro-magnetic and diamagnetic.

The magnetic resistance of joints is interesting in connexion with the localised nature of the molecular field in iron. It has been shown by Sir J. J. THOMSON and H. F. NEWALL† that the susceptibility of an iron bar is much reduced if it is severed and the two parts put in contact. Later, Sir JAMES EWING and W. Low‡ investigated this effect in a more exhaustive manner when the joints were carefully trued up and also for rough joints, under varying pressures. They found that for a carefully planed joint a compressive stress of 226 kilogrammes per square centimetre restored almost completely the loss of magnetic property produced by cutting, but that this stress had only a small restorative effect in the case of a rough joint. In the latter case, we may suppose that the number of points of contact between the two parts of the bar is small, in the former that the two portions are in contact over a large percentage of the available area of contact. Under a compressive stress of 226 kilogrammes per square centimetre, it appears that in the trued-up specimens the order of contact of the molecules is the same as in the uncut metal and therefore this stress is a measure of the internal stress within the material. As 226 kilogrammes per square centimetre is equal to  $0.5 \times 10^9$  dynes per square centimetre, this stress, although lower, is comparable with that calculated on p. 252, and we may regard the width of the resulting crevasse as approaching mathematical smallness, the spheres of influence of the molecules on either side of it overlapping to an extent comparable with the overlap in the interior of the uncut bar (see also Part III., p. 89). But even with the most carefully faced junction there will be irregularities, coarse compared with molecular dimensions, and in such regions the localised nature of the molecular field will determine a finite air gap which would account for the difference of stress mentioned above. Perfectly faced surfaces of soft iron or mild steel (annealed) might be

\* 'Magnetic Induction in Iron and other Metals,' p. 254.

† 'Proc. Camb. Phil. Soc.,' 1887.

‡ 'Phil. Mag.,' September, 1888.

expected, under the influence of an external magnetic field, to form a perfect junction, in other words to become welded together.

TAYLOR JONES\* has obtained an induction as high as 74,200 Maxwells in soft iron under strong fields. The tension necessary to pull the surfaces apart in this case will be  $\frac{B^2}{8\pi} = \frac{7.4^2 \times 10^8}{8\pi}$ , or  $2 \times 10^8$  dynes/square centimetre, which is about a twenty-fifth of the tensile strength of the material.

#### (6) ON A MAGNETIC THEORY OF CHEMICAL COMBINATION.

On the theory of chemical action developed by Sir J. J. THOMSON,† the determining feature of an atom from the point of view of chemical combination is the number of positive valency electrons it possesses. These electrons are dragged from their loose attachment to the nucleus, during chemical combination, and pass from one atom to another. The two originally neutral atoms thus become oppositely charged and so attract one another and form, as it were, an electric doublet. Let us look at this problem from the magnetic standpoint. Each electron orbit is equivalent to a small magnetic doublet and it is interesting to enquire how far the magnetic forces of such doublets may represent the force of chemical affinity. Recent work on radio-activity, the wide deflections of  $\beta$ -rays, and the diffraction of X-rays, all point to a localisation of the electrostatic charges in a minute core or nucleus. Round this nucleus, and under its control, the valency electrons (in part responsible for the magnetic properties) rotate. It is conceivable, therefore, that the magnetic forces, in addition to the important role they play in crystallization, may also in part be responsible for the forces of chemical affinity.‡

If, during chemical combination, there is a definite transfer of valency electrons from one atom to another, we should expect to find an abrupt change in the magnetic behaviour of an atom before and after chemical combination. If, on the other hand, there is no such electron transference, we might expect that the atoms would preserve their magnetic properties, which would be more or less of an additive nature. In a remarkable series of investigations, PASCAL§ has shown that in a very large number of organic compounds, the molecular susceptibility is the sum of the atomic susceptibilities of the component atoms, provided the molecule contains no peculiarity of molecular configuration—such, for instance, as the ethylene linkage, unsaturated atom, or complex nucleus. Thus if  $\chi_M$  is the molecular susceptibility, and  $\chi_A$  the atomic susceptibility of a component atom, we have

$$\chi_M = \sum \chi_A + \lambda$$

where the summation extends to all the atoms in the molecule and  $\lambda$  is a positive or

\* 'Phil. Mag.,' vol. xli., p. 165, 1896.

† 'The Corpuscular Theory of Matter,' 1907, Chap. VI.

‡ See footnote p. 274. Also W. M. HICKS, 'Roy. Soc. Proc.,' A, vol. 90, p. 356.

§ 'Ann. de Chim. et de Physique,' sér. 8, vol. 19, p. 5, 1910.



negative constant for a certain type of peculiarity of molecular configuration. In normally saturated compounds  $\lambda = 0$ . The elements carbon, hydrogen, chlorine, bromine and iodine have constant atomic susceptibilities in a large variety of simple and complex organic compounds. This suggests that the origin of the valencies of these elements is also the origin of a definite amount of diamagnetism, under the influence of a definite magnetic field. In other words, a hydrogen atom, in whatever organic compound it is found, has a constant atomic susceptibility equal to  $-30.5 \times 10^{-7}$ , while the carbon atom has a constant atomic susceptibility equal to  $-62.5 \times 10^{-7}$ , and so on.

This result of PASCAL'S, in conjunction with—

- (1) The enormous magnitude of the local molecular field in diamagnetic media, and
- (2) The conception of diamagnetism as due to an induction effect in oppositely spinning electrons (as developed in Parts I., II. and III.), led me to suspect that the magneton may be a constituent of the diamagnetic hydrogen molecule. The calculation showed\* that if there is one electron in each hydrogen atom whose period is equal to

\* 'Roy. Soc. Proc.,' A, vol. 95, p. 58, 1918.

At the time this paper was written, I was out of touch with the latest available data concerning the values of AVAGADRO'S constant ( $N$ ) and the ratio  $\epsilon/m$ . The calculation was to determine  $M$  from the relation

$$M = - \frac{\chi \cdot 4\pi m}{N \cdot n \cdot \epsilon \cdot \tau}.$$

Taking

- $\chi$  = molecular susceptibility of hydrogen,
- =  $-61.0 \times 10^{-7}$  (PASCAL),
- $N$  =  $6.06 \times 10^{23}$  (MILLIKAN),
- $\epsilon/m$  =  $1.77 \times 10^7$  e.m.u. (BUCHERER),
- $n$  = 2, the number of electrons per molecule,
- $\tau$  =  $2.19 \times 10^{-15}$  sec., the period of revolution for the line  $H\alpha$ ,

we find on calculation

$$M = 16.3 \times 10^{-22} \text{ for the moment of the magneton.}$$

This gives for  $r$ , as calculated from  $M = \frac{\pi e r^2}{\tau}$ , the value  $0.85 \times 10^{-8}$  cm.

In this connexion it should be pointed out that, on PLANCK'S theory of quanta of energy, the constant  $h$  is consistent with the existence of a unit of magnetism. Assuming, as NICHOLSON and BOHR have done, that the angular momentum of the electron is an integral multiple of  $\frac{h}{2\pi}$ , CHALMERS showed that the magnetic moment of the electron orbit is

$$M = \frac{\epsilon}{m} \cdot \frac{h}{4\pi}.$$

This gives  $M = 92.4 \times 10^{-22}$  e.m.u., which is 5 times the experimental value of the moment of the magneton. If we leave aside PLANCK'S theory of energy quanta and adopt instead SOMMERFELD'S theory of quanta of action, LANGEVIN showed that a remarkable relation between  $h$  and  $M$  exists. He found

$$M = \frac{\epsilon}{m} \cdot \frac{h}{24\pi},$$

when the law of attraction between the nucleus and the electron is the inverse square. This gives for the magnetic moment of the electron orbit  $M = 15.4 \times 10^{-22}$  e.m.u., a value nearly equal to the most recent experimental value of the moment of the magneton, viz.,  $18.5 \times 10^{-22}$  e.m.u.

that of the line  $H_a$ , then the molecular diamagnetic susceptibility of hydrogen ( $-61.0 \times 10^{-7}$ ) can be accounted for, and each electron orbit of radius  $10^{-8}$  cm. has a magnetic moment  $+16.3 \times 10^{-22}$ , nearly equal to that of the magneton,  $+18.5 \times 10^{-22}$ .

The atomic susceptibility of carbon in combination is shown by PASCAL to be  $-62.5 \times 10^{-7}$ , and in connexion with the additive law this value is consistent with the experimental values of the molecular susceptibilities. The mean experimental value of the atomic susceptibility of diamond is  $-59.0 \times 10^{-7}$ .\* The mean of these values is  $-60.7 \times 10^{-7}$ , which is probably as accurate a value as is available at present. But this value is almost exactly twice that of the atomic susceptibility of hydrogen  $-30.5 \times 10^{-7}$ . Probably therefore the atom of carbon contains two magnetons. As to the period of revolution we have

$$M = \frac{1}{2} \cdot e \cdot \omega r^2 = \frac{\pi e r^2}{\tau}$$

where

- M = moment of orbit,  
 $e$  = electron charge in e.m.u.,  
 $r$  = radius of orbit,  
 $\tau$  = period,

and this implies that the period  $\tau$  for the carbon atom is not equal to that of the line  $H_a$  unless  $r = 10^{-8}$  for the carbon atom.

The sum of the atomic susceptibilities of the atoms in the group  $CH_2$  is

$$-123.5 \times 10^{-7}.$$

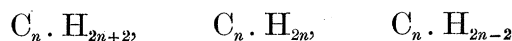
Experimentally, PASCAL showed that the difference of molecular susceptibility in a number of compounds whose constitution differed by this group was

$$-118.7 \times 10^{-7}.$$

The mean of these two values is  $-121.1 \times 10^{-7}$  which is probably very near the true value. But this is almost exactly four times the value of the atomic susceptibility of hydrogen, viz.,  $-30.5 \times 10^{-7}$ , and in this combination,  $CH_2$ , we may say that each hydrogen atom has one magneton and the carbon atom has two magnetons.

An ethylene linkage, according to PASCAL, lowers the diamagnetic molecular susceptibility of the compound by  $+57 \times 10^{-7}$ , while two or more such linkages lower it by  $+110 \times 10^{-7}$ . These values are respectively nearly equal to twice and four times the atomic susceptibility of hydrogen.

As the additive law holds in the case of the simpler liquid hydrocarbons, it will hold for all the others which differ only by  $CH_2$  groups, and therefore, taking the values of  $\lambda$  into account, any member of the three homologous series



\* HONDA, 'Ann. der Phys.,' vol. 32, p. 1044, 1910, gives  $-59.5 \times 10^{-7}$ ; OWEN, 'Ann. der Phys.,' vol. 37, p. 693, 1912, gives  $-58.5 \times 10^{-7}$ .

may be considered as containing respectively

$$4n + 2, \quad 4n - 2, \quad 4n - 6 \text{ magnetons.}$$

Moreover, PASCAL has shown that the magnitude of  $\chi_{\text{CH}_2}$  is quite independent of the presence of nitrogen, oxygen, or sulphur in the compound, so that, where the additive law holds for such complex molecules, it will hold for the whole series of *additive* compounds formed with the group.

PASCAL also investigated the halogens, fluorine, chlorine, bromine and iodine. The atomic susceptibilities of these elements, as deduced from the molecular susceptibilities of organic compounds in which they are contained, are given in column 2, the approximate number of magnetons per atom is given in column 3.

Substance.	$\chi_A \cdot 10^7$ .	$n$ .
Fluorine . . . . .	- 65.5	2
Chlorine . . . . .	- 209.5	7
Bromine . . . . .	- 319.2	10
Iodine . . . . .	- 465.0	15

It must be admitted, however, that these last four results do not warrant an extension of the magneton theory to these elements. Moreover, although the results for the hydrocarbons mentioned above are very suggestive, yet there remain difficulties, such for example as the values of  $\lambda$ , which for the benzene ring is equal to  $-15 \times 10^{-7}$ , the interpretation of which does not fall into line with the magneton view. Further difficulties are met with in the cases of nitrogen and oxygen.

Perhaps these difficulties should be expected, since it has been proved that the additive law breaks down for many atoms, especially as regards the metallic elements. When, in addition, we take into consideration that the mutual disturbances of the electron orbits, in atoms containing a relatively large number of electrons, have been neglected, the agreement is probably as good as could be expected. Thus in the case of the hydrocarbons considered above, compounds which show no electrolytic dissociation and in the formation of which no transfer of electrons takes place from one atom to another on combination, we might expect that the addition of a hydrogen atom or a  $\text{CH}_2$  group would add a definite amount of diamagnetism to the compound. But in the case of the metals and some other elements, chemical combination may be accompanied by the transference of electrons, *i.e.*, by a breakdown of the magnetic elements of the atoms. In such cases the additive law could not hold.

Thus iron-carbonyl ( $\text{Fe}(\text{CO})_5$ ) and nickel-carbonyl ( $\text{Ni}(\text{CO})_4$ ) are diamagnetic\*; potassium ferri-cyanide is paramagnetic, while potassium ferro-cyanide is diamagnetic.† It would appear that in these cases the loss of magnetic property of the iron and nickel atoms is due to a transfer of valency electrons, *i.e.*, it involves an electric charging up of the atoms. The behaviour of the oxygen atom in organic compounds, in compounds with chlorine and in metallic oxides, where it acts always as an electronegative element, may possibly be accounted for in the same way. Free oxygen and ozone are strongly paramagnetic, but no semblance of an additive nature of the magnetic property is found in any of the oxygen compounds.

The appearance of strong magnetism in the Heusler alloys and its disappearance in manganese steels, are similar effects, dependent on the formation of intermetallic chemical compounds accompanied by an electron transfer.

There are many paramagnetic substances which possess molecular magnetic moments comparable with, and in some cases much superior to, those shown by ferromagnetic substances. The apparent feeble susceptibility they possess is due to the fact that, with the largest magnetic field which can be applied, we can never produce anything like a saturation effect. In fact, according to WEISS, the molecule of cobalt chloride,  $\text{Co.Cl}_2$ , contains 25 magnetons, while an atom of cobalt below the critical temperature contains 9 magnetons. We may well ask ourselves—what is the nature of the process by which the addition of a diamagnetic substance,  $\text{H.Cl}$  to cobalt, produces such a large increase in the number of magnetons per molecule.‡ Assuming the work of WEISS holds good, and there is certainly a very considerable amount of evidence in favour of his theory, we can interpret this result either by supposing that the atom of cobalt really contains more than 9 magnetons,§ or else that the *diamagnetic* acid supplies the additional magnetons when it acts on the cobalt to form the chloride. In either case, it seems that we must admit that a molecule may possess systems of magnetons which, in certain circumstances, are so arranged to counterbalance one another, producing no additional moment of the molecule.|| These magnetons would contribute nothing to the paramagnetic or ferro-magnetic property of a substance and could not be included in WEISS's theory. The grouping of these "latent" magnetons, according to our extended view, would be perturbed by the union of the cobalt atom with the  $\text{Cl}$  ion, in a manner similar to that by which an external field reveals the spontaneous magnetization in iron (as interpreted on EWING's theory) by orientating groups which were formerly so constituted as to show no magnetic effect externally. If this is so, then we are only justified in assuming that purely diamagnetic molecules contain groups of magnetons so arranged that the

\* A. E. OXLEY, 'Proc. Camb. Phil. Soc.,' vol. 16, p. 102, 1911.

† J. S. TOWNSEND, 'Phil. Trans. Roy. Soc.,' A, vol. 187, p. 547, 1896.

‡ The specific susceptibility of cobalt chloride is  $90 \times 10^{-6}$ , that of hydrochloric acid  $-0.80 \times 10^{-6}$ .

§ Some of which are self-compensated.

|| *I.e.*, of the molecule as a whole.

molecule possesses no resultant magnetic moment. For example, while iron below the critical temperature possesses, according to WEISS, 11 magnetons to the atom, the molecule of ferric sulphate possesses 30, ferric chloride 28, sodium ferro-pyrophosphate 26, sodium ferrous oxalate 27.\* Again, nickel below the critical temperature possesses 3 magnetons to the atom, above the critical temperature either 8 or 9 magnetons to the atom, while a molecule of nickel sulphate contains 16 magnetons. In general the number of magnetons, per molecule of a salt of a ferro-magnetic element, is large compared with the number of magnetons associated with an atom of the pure ferro-magnetic. The fact that cupric salts are paramagnetic while cuprous ones are diamagnetic is interesting from our point of view. Although copper is diamagnetic, yet a molecule of cupric sulphate contains 10 magnetons. It seems as if the large local atomic fields, which have been recognised in diamagnetic and ferro-magnetic molecules, have the power, when the molecules approach so that their fields overlap, to upset the equilibrium of the atoms in combination and redistribute their magnetic elements. This is easily possible when the great intensity of the local molecular field is borne in mind. In most cases a diamagnetic molecule, on account of its symmetry, would, under the influence of such a field, remain diamagnetic, but each orbit would be distorted by the field and the susceptibility of the substance would be slightly modified.

#### (7) ON SOME ANOMALIES IN THE MAGNETIC ROTATION EFFECT.

Diamagnetic media are in general dextro-gyric. The only exception is titanium chloride which is lævo-gyric.† Paramagnetic media are sometimes dextro-gyric and sometimes lævo-gyric, while the ferro-magnetic elements, iron, nickel and cobalt are all dextro-gyric. At present no theory seems capable of accounting for these anomalies and it is therefore interesting to examine to what extent the local molecular field may cause the effects observed. At one time it was thought that the direction of rotation probably depended merely on the diamagnetic or paramagnetic property of the molecule, but experiment soon disproved this generalisation. VOIGT‡ suggested that the production of an intense reverse field, when the external field was applied, would account for the effects, but no physical explanation of a possible origin for this intense reverse field was given.

On the views of diamagnetic and paramagnetic polarity developed in these researches, the necessary fields demanded by VOIGT are found in the immediate neighbourhood of the molecular boundary. In diamagnetic liquids the molecules have zero magnetic moments and their axes are distributed at random. The application of

\* 'Journal de Phys.,' vol. 1, sér. v., p. 974, 1911.

† For solutions of salts in water it should be noted that VERDET'S constant for the solute is to be regarded as negative if VERDET'S constant for the solvent is less than 0·0130, which is the value of the constant for pure water at 20° C.

‡ See P. ZEEMAN, 'Researches in Magneto Optics,' p. 185.

an external field produces a minute diamagnetic polarity, which differential effect determines the magnitude and sign of the rotation. When a polarised ray passes over such molecules, it will be rotated considerably locally, but only to be rotated in the opposite direction to an almost equal extent in a neighbouring molecule or in another part of the same molecule.

This will also be true if the diamagnetic medium is crystalline. Hence the final rotation will be a relatively small differential effect compatible with the diamagnetic effect of the medium in bulk. We shall omit the exceptional case of titanium chloride for the present and pass on to consider the ferro-magnetic media iron, nickel and cobalt.

In ferro-magnetic media, on account of the continuity of magnetic induction, there is an enormous reverse local field, and if this acts over regions of the molecule containing magnetically active electrons, a large rotation will be produced, which will not be compensated in neighbouring molecules, when the ferro-magnetic material is saturated. Hence we should expect a very large rotation to be produced by such media. This has been confirmed experimentally, in the cases of iron, nickel and cobalt, by KUNDT.

Paramagnetic solutions lie in an intermediate category. The application of an external magnetic field causes a certain amount of molecular orientation depending on the temperature. Such orientation causes a reverse field over a part of the system, but over the neighbouring molecules in combination with the one considered, the field depends upon the difference between the reverse local field and the applied field, which difference may be positive or negative. If, in such regions, there are electrons capable of orientating the polarised beam, the rotation may be dextro- or lævo-gyric, according as the resultant field is opposite to, or in the same direction as, the applied field. This will not explain the exceptional case of titanium chloride unless this molecule possesses some peculiar dissymmetry, whereby, in spite of its diamagnetic nature, it becomes orientated under the applied field. Such orientation is the basis of the magnetic double refraction theory developed by LANGEVIN\* and confirmed experimentally in some respects by COTTON and MOUTON† (see Part III., p. 87). An alternative explanation of the behaviour of the titanium chloride molecule may be found in a rotation of the paramagnetic titanium atom relative to the compound molecule.

BECQUEREL has deduced an interesting relation‡ connecting the magnetic rotation ( $r$ ) with the Zeeman coefficient ( $Z = \frac{\epsilon}{4\pi m}$ ), the applied field  $H$ , wave-length  $\lambda$  and refractive index  $\mu$ , viz.,

$$r = -2\pi \cdot \frac{ZH\lambda}{c} \cdot \frac{\partial\mu}{\partial\lambda}, \dots \dots \dots (1)$$

where  $c$  is the velocity of light.

\* LANGEVIN, 'Le Radium,' vol. 7, p. 251, 1910.

† 'Ann. de Chim. et de Phys.,' sér. viii., vol. 19, p. 155, 1910.

‡ SCHUSTER, 'Theory of Optics,' p. 307.

We shall assume that this relation applies to all media. On our theory  $H$  will be the sum of the applied and local fields and will be considered positive if it is in the direction of the external field.  $Z$  we shall take to be negative, *i.e.*, the negative electron is always responsible for the Zeeman effect.

*In diamagnetic media*, in general,  $H$  is positive,  $\frac{\partial\mu}{\partial\lambda}$  is negative, and therefore  $r$  is negative, or clockwise looked at along the direction of  $H$ . The rotation is dextro-gyric.

*In ferro-magnetic media*,  $H$  is the resultant of the applied field and a very large reverse molecular field, so that  $H$  is very large and negative;  $\frac{\partial\mu}{\partial\lambda}$  is positive. Hence again  $r$  is negative and the rotation is dextro-gyric as in diamagnetic media.

*In paramagnetic solutions*,  $H$  may be positive or negative over magnetically active atoms, and therefore the sign of  $r$  may be positive or negative. Hence some paramagnetic solutions will be dextro- and some lævo-gyric.

In the ferro-magnetic elements the magnitude of the rotation is remarkably high. Thin films of saturated iron show a rotation of the order 260 million times that of carbon bi-sulphide subjected to an external field of one gauss. To test this we may write

$$r_{\text{Fe (saturated)}} = -2\pi \cdot \frac{Z_{\text{Fe}} \cdot H_c}{c} \cdot \lambda \cdot \frac{\partial\mu_{\text{Fe}}}{\partial\lambda} \text{ for iron,}$$

$$r_{\text{CS}_2 (H = 1 \text{ gauss})} = -2\pi \cdot \frac{Z_{\text{CS}_2} \cdot H}{c} \cdot \lambda \cdot \frac{\partial\mu_{\text{CS}_2}}{\partial\lambda} \text{ for carbon bisulphide.}$$

where  $H_c$  is the reversed molecular field, of the order  $-6.5 \times 10^6$  gauss,  $H = 1$  gauss. The Zeeman coefficients  $Z_{\text{Fe}}$  and  $Z_{\text{CS}_2}$  we shall take to be of the same order, hence:—

$$\frac{r_{\text{Fe (saturated)}}}{r_{\text{CS}_2 (H = 1 \text{ gauss})}} = + \frac{H_c \cdot \frac{\partial\mu_{\text{Fe}}}{\partial\lambda}}{H \cdot \frac{\partial\mu_{\text{CS}_2}}{\partial\lambda}} \dots \dots \dots (2)$$

For iron\*

$\lambda \times 10^8$ .	$\mu$ .
2570	1.01
4410	1.28
5890 (D)	1.51

Near

$$\lambda = 5890 \times 10^{-8}, \quad \frac{\partial\mu_{\text{Fe}}}{\partial\lambda} = + \frac{0.23}{1480 \times 10^{-8}}.$$

\* 'Smithsonian Physical Tables,' p. 196.

For carbon bisulphide\*

$\lambda \times 10^8$ .	$\mu$ .
4340 ( $H_\gamma$ )	1'6920
4860 ( $H_\beta$ )	1'6688
5890 (D)	1'6443

Near

$$\lambda = 5890 \times 10^{-8}, \quad \frac{\partial \mu_{\text{CS}_2}}{\partial \lambda} = -\frac{0\cdot0255}{1030 \times 10^{-8}}.$$

From (2)

$$\frac{r_{\text{Fe (saturated)}}}{r_{\text{CS}_2 (H = 1 \text{ gauss})}} = + \frac{6\cdot53 \times 10^6 \times 0\cdot23 \times 1030 \times 10^{-8}}{0\cdot0255 \times 1480 \times 10^{-8}} \doteq 40 \times 10^6.$$

For nickel†

$\lambda \times 10^8$ .	$\mu$ .
2750	1'09
4410	1'16
5890 (D)	1'30

Near

$$\lambda = 5890 \times 10^{-8}, \quad \frac{\partial \mu_{\text{Ni}}}{\partial \lambda} = +\frac{0\cdot14}{1480 \times 10^{-8}},$$

and

$$\frac{r_{\text{Ni (saturated)}}}{r_{\text{CS}_2 (H = 1 \text{ gauss})}} = + \frac{6\cdot35 \times 10^6 \times 0\cdot14 \times 1030 \times 10^{-8}}{0\cdot0255 \times 1480 \times 10^{-8}} \doteq 25 \times 10^6.$$

For cobalt‡

$\lambda \times 10^8$ .	$\mu$ .
2750	1'41
5000	1'93
6500	2'35

Near

$$\lambda = 5890 \times 10^{-8}, \quad \frac{\partial \mu_{\text{Co}}}{\partial \lambda} = +\frac{0\cdot42}{1500 \times 10^{-8}}.$$

Taking the reverse molecular field equal to that in iron

$$\frac{r_{\text{Co (saturated)}}}{r_{\text{CS}_2 (H = 1 \text{ gauss})}} = + \frac{6\cdot53 \times 10^6 \times 0\cdot42 \times 1030 \times 10^{-8}}{0\cdot0255 \times 1500 \times 10^{-8}} \doteq 87 \times 10^6.$$

These values, although rather small, are comparable with the enormous ratios of the rotations of saturated ferro-magnetics to diamagnetics, as actually observed

\* *Loc. cit.*, p. 192.† *Loc. cit.*, p. 196.‡ *Loc. cit.*, p. 195.



experimentally, and point to the importance of the local molecular force in magneto-optic phenomena. It should be noted that the value of the reverse field we have taken is that of the *intermolecular* field. Within the atom the reverse field will probably be greater than  $-6.5 \times 10^6$  gauss. If it is of the order  $-5 \times 10^7$  gauss, the above ratios become  $320 \times 10^6$  for iron,  $200 \times 10^6$  for nickel and  $700 \times 10^6$  for cobalt. Intra-atomic fields of the order  $10^8$  gauss are required by HUMPHRIES\* to explain the pressure shift of spectral lines and by RITZ† in his theory of spectral series (see also Part III, p. 100, and *supra*, p. 273, footnote).

#### (8) SUMMARY OF CONCLUSIONS.

(I.) The applications of the local molecular force, in diamagnetic, paramagnetic and ferro-magnetic media, have in the present research been extended to interpret the ultimate tensile strength of crystalline and vitreous media. It has been shown by EWING and ROSENHAIN that the permanent set which occurs prior to breaking is due to slipping along the cleavage planes *within* the individual crystalline grains. We should therefore expect that the material would be fractured when the applied mechanical stress is equal to that produced internally by the local molecular force. The internal stress within the material is shown to be of the order  $2 \times 10^9$  dynes per square centimetre which is approximately the mean value of the ultimate tensile strengths of crystalline and vitreous media (pp. 250–259).

(II.) As a consequence of this internal stress, the energy per unit volume will be  $2 \times 10^9$  ergs, and this energy, which is over and above that which exists in the fluid state, should be a measure of the latent heat of fusion per cubic centimetre. This test which was applied in Part III. to test the order of the local force, has been extended to a variety of organic and inorganic media, including the metals and is found to accord with the experimental values to the right order (pp. 253–4).

(III.) Since the forces under which the molecules vibrate are those to which we ascribe the elastic properties of crystalline media, the results obtained are consistent with the theory of specific heats developed by DEBYE, in which the specific heat is attributed to purely translational vibration, and it has been shown (Part III.) that, near the fusion point, the rotational energy acquired by the molecules will give a measurable departure from this theory which is actually observed experimentally. As we should expect, it is found that the elastic constants of a variety of ferro-magnetic, diamagnetic and paramagnetic media are of the same order, several diamagnetic and paramagnetic media even surpassing steel in their power to resist distortion (pp. 257–259).

(IV.) Any change of internal pressure will be accompanied by a change of volume defined by the compressibility of the medium and dependent as to sign upon

\* ‘Astrophysical Journal,’ vol. 23, p. 232, 1906; vol. 35, p. 268, 1912.

† ‘Ann. der Phys.,’ vol. 25, p. 660, 1908.

peculiarities of the molecular configuration. It has been shown that the energy change which occurs on crystallization is compatible with a volume change of the same order of magnitude as that accompanying crystallization, and we may therefore interpret the change of volume on crystallization as a magneto-striction effect of the local molecular force. The magneto-striction effect depends on molecular orientation which is proportional to the square of the magnetic force (pp. 259–263). In Part III. it was shown that the double refraction of crystalline media can be interpreted as due to the magnetic double refraction effect of the local molecular force which orientates the molecules into a crystalline space lattice. This effect is also proportional to the square of the magnetic force and the two effects mutually support one another.

(V.) The above results are interesting in connexion with TAMMANN'S theory of the closed region of stability of the crystalline state, as represented on the pressure temperature diagram. TAMMANN'S experimental work gives an alternative method of determining intrinsic pressures, but the results are notably higher than those found in other ways. Possibly this is due to extrapolation over a wide pressure range. The pressure temperature diagrams showing the fusion curve are instructive in dealing with problems relating to thermal evolution (or absorption), and volume changes and possible interpretations of these peculiarities in the ferro-magnetic elements, iron, nickel and cobalt, have been given (pp. 263–266).

(VI.) A physical interpretation has been given of the large values of the coefficients,  $N$  and  $\alpha'_e$ , of the molecular fields in ferro-magnetic and diamagnetic crystalline media respectively. These coefficients are the reciprocals of the limiting local susceptibilities of the media under field strengths equal to the respective molecular fields. The local susceptibility of a diamagnetic molecule is comparable with that of a ferro-magnetic molecule and the two vary in the same way with field strength and temperature. In diamagnetic media, however, magnetic hysteresis will be inappreciable, since the molecule as a whole possesses a zero magnetic moment. Nevertheless, mechanical hysteresis in diamagnetic media will be of the same order as in ferro-magnetic media (pp. 267–270 and p. 257).

(VII.) From TYNDALL'S experiments on the deportment of paramagnetic and diamagnetic crystals in a magnetic field, the positions of the planes of cleavage can be traced. These results show that the forces responsible for crystalline symmetry are very probably of a magnetic nature. If the forces are of an electrostatic nature, then, since an electric field must disclose the same planes of cleavage, the electric and magnetic symmetries must coincide. This is not the case however. The magnetic forces are partly due to the valency or boundary electrons whose orbits are controlled by the atomic nuclei. The nuclei determine the crystalline symmetry, indirectly, through the medium of the magnetic forces of the electrons. This conclusion is not at variance with the results of X-ray diffraction experiments; the latter determine only the positions of the diffuse diffracting cores and give no

indication as to the outer regions of the atom which determine the valency forcives. Hence, in spite of the disclosure of the X-ray methods, it is maintained that within a crystalline medium the molecules, though distorted, are still essentially integral units and that it is possible to imagine a surface enclosing each (pp. 270–277).

(VIII.) The smallness of the nucleus disclosed by recent work on radio-activity suggests that in addition to the part played by the magnetic forces in crystallization, these forces are in part responsible for chemical combination (footnote, p. 274). The theory of chemical combination developed by Sir J. J. THOMSON implies the transference of electrons from one atom to another whereby the atoms become oppositely charged. Such a transference of the valency electrons implies a complete readjustment of the magnetic property and therefore this property could not be of an additive nature. This is borne out by a large amount of experimental evidence.

If the chemical combination takes place without a transference of the valency electrons from one atom to another, which probably happens in many organic compounds in which electrolytic dissociation does not take place, we might expect the magnetic properties to be more or less of an additive nature. PASCAL'S work confirms this view (pp. 277–281).

(IX.) The author has previously shown that the magneton may be a constituent of the diamagnetic hydrogen molecule. It appears that this idea may be extended to carbon and the hydrocarbons in general, where the molecular susceptibility can be directly calculated from the atomic susceptibilities of the component atoms. The results, however, are not so convincing when extended to other elements, but the fact that departures from the additive law occur in such cases leads us to suppose that some disturbing influence has been neglected. WEISS'S work on salts of the ferro-magnetic elements, taken in conjunction with our present conception of diamagnetism, suggests that diamagnetic substances contain magnetons, compensated so as to produce a diamagnetic effect of the medium in bulk. The forces of chemical combination may, however, perturb this state, and by rearranging the magnetic elements give rise to a compound possessing more magnetons than are contained in an unbalanced state in a ferro-magnetic element. Examples of this are given and also of the reverse effect which may equally well arise (pp. 281–282).

(X.) The principle of the continuity of magnetic induction, as applied to the local molecular forcive, suggests a possible interpretation of known anomalies of the magnetic rotational effect. In paramagnetic solutions, the dextro-gyric or lævo-gyric property is attributed to a differential effect of the reversed local field and the applied field over rotationally active electrons, the sign of the effect depending on the direction of the resultant field acting over these electrons.

The very powerful rotational effect of thin films of iron, nickel and cobalt, in comparison with that shown by carbon bisulphide, has also received an interpretation in terms of the local molecular forcive (pp. 282–286).

(XI.) It is considered that the above conclusions when conjoined with those obtained in Parts I., II., III., which bring the theory into line with the magnetic atom fields of RITZ and probably suggest an origin of spectral series, amply justify the importance of the magnetic force in crystalline and vitreous media. The magnitude of this local magnetic force, first calculated to interpret the change of diamagnetic susceptibility observed on crystallization of a large number of organic compounds experimented upon in Parts I. and III., has been found capable of correlating a number of additional physical phenomena of wide difference of origin. It is hoped to continue these applications to other branches of optics including spectral series and optical activity.

(XII.) [*Added February 28, 1920.*—It has been established that the intermolecular field, in all crystalline media, is of the order  $10^7$  gauss. The electrons, within the free atom, are controlled by electrostatic, and possibly also by magnetic, forces, whose origin lies in the core. When the atoms are grouped into a definite space lattice, the cohesive force between them is of a magnetic nature, and the rigidity of such media is due to the localised mechanical stress, exerted at definite points across the atomic "surface"; the electrons revolving in small circles in adjacent atoms (p. 274). This mechanical stress, due to the local magnetic forces, is responsible for the change of specific susceptibility, and other properties, on crystallization; and is balanced by the stress due to the distortion of the internal electrostatic configuration of the atoms. In this way, a balance is secured between the electrostatic and magnetic stresses; these stresses predominating alternately, as we pass through the crystalline structure, thus giving rise to a system in equilibrium.

The rotation of electrons in *small* circles, at definite points near the atomic "surface," is suggestive in connexion with the theory of directed valencies required to explain stereo-chemical phenomena (p. 274, footnote).]

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