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J. H. Van Vleck

as I have maintained, they would be expected to perturb the calculated levels. While these extra electronic levels in Dy would not be so close, they would still be present and would be expected to perturb the other levels to a greater or less extent, thereby destroying the validity of the simple calculations.

The agreement of experiment with Penney and Schlapp's theory for Er and Nd is very much better than one has any right to expect when one considers the very simple assumptions which were made when they set up the ex-

pression for the potential function. The agreement with Dy is not good but the disagreement is easily accounted for.

I am extending the experimental work in this field to a large number of salts of as many rare earths as I can obtain and hope to find out shortly whether or not this remarkable agreement continues to persist. I wish to express my indebtedness to Professor Kirkwood who has taken a keen interest in this problem and who spent considerable time discussing with me the theoretical side of the subject.

The Influence of Dipole-Dipole Coupling on the Specific Heat and Susceptibility of a Paramagnetic Salt

J. H. VAN VLECK,
Harvard University, Cambridge, Massachusetts
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The mutual magnetic potential energy of atomic magnetic dipoles is unimportant in salts of high dilution at ordinary temperatures, but becomes important in determining the temperature scale in the new very low region obtained by magnetic cooling. This "dipole-dipole" energy is not to be confused with exchange interaction which is important in concentrated magnetic materials and which is there responsible for ferromagnetism at ordinary temperatures. The partition function, and hence the entropy, specific heat, and susceptibility are calculated for a paramagnetic solid inclusive of dipole and simultaneously also feeble exchange coupling. In Sections 3–4 the computation is made for atoms otherwise free, but in Section 6 they are subjected in addition to a crystalline Stark field. Comparison with experiment is made in the following paper by Hebb and Purcell. Our method of partition functions is to be contrasted with the usual,

essentially static Lorentz method of representing dipole-dipole coupling by a local field, e.g., $H+4\pi M/3$ for a long test body. The Lorentz procedure is shown to be only a first approximation, which is really warranted if the density is so low or the temperature so high that one may neglect all terms but the first in the development of the partition function in $1/T$. Otherwise the usual results of the local field method are obtained only by an extrapolation which is comparable with the assumption in Heisenberg's theory of ferromagnetism of identical energy for all states with the same crystalline spin. Two other types of extrapolation, based on a second approximation, are obtained which correspond respectively to assuming a Gaussian distribution of energies for these states and to use of the local field proposed by Onsager. The latter seems to be much the more satisfactory of the two.

1. INTRODUCTION

THE purpose of the present paper is to calculate the partition function for an ensemble of atoms, each of which carries a magnetic moment, and is subject to both (a) an applied magnetic field and (b) coupling with the moments of other atoms. In Section 6 we shall include simultaneously (c) a crystalline potential of the type used by Bethe, Kramers, Penney and Schlapp, etc.[1] We shall be concerned pri-

marily with media of high magnetic dilution, where the interaction (b) is due mainly to the usual magnetic potential energy of two dipoles, which varies as the inverse third power of their distance of separation. Exchange effects have usually been considered unimportant in media of high magnetic dilution because they fall off exponentially with distance. However, Kramers[2]

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[1] For a general discussion of the influence of crystalline fields on magnetic susceptibilities, exclusive of dipole-dipole interaction, see J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, Chap. XI; also especially the subsequent work of Penney and Schlapp, Phys. Rev. **41**, 194; **42**, 666 (1932), summarized in Chap. X of Stoner's *Magnetism and Matter*.

[2] H. A. Kramers, Physica **1**, 182 (1933).

has shown that because of a complicated coupling via the excited states of intermediate, normally nonmagnetic atoms, the diminution may be sometimes less drastic than exponential. Hence we shall make our computations general enough so that (b) can include some exchange as well as true magnetic coupling.

After the partition function Z per unit volume has been calculated, there are a variety of applications, especially in connection with the production of very low temperatures by the magnetic method, which will be discussed in the following paper by Hebb and Purcell.[3] The specific heat is given by the relation

$$c_v = \frac{\partial}{\partial T}\left(kT^2 \frac{\partial \log Z}{\partial T}\right), \qquad (1)$$

while the free energy F and entropy S are supplied by[4]

$$F = -kT \log Z, \quad S = -\partial F/\partial T. \qquad (2)$$

The formula for the magnetic moment per unit volume is

$$M = kT \partial \log Z/\partial H_0, \qquad (3)$$

where H_0 is the applied magnetic field *before insertion of the test body*. The quotient of M to H_0 we shall call the experimental susceptibility. It is to be distinguished from the susceptibility as usually defined in electrodynamics which is the ratio of M to the field H inside the test body *after* its insertion. The passage from one kind of susceptibility to the other requires the use of "demagnetizing corrections" giving the relation between H_0 and H. Unfortunately H cannot be measured directly, whereas H_0 is usually known from the dimensions of the solenoids, etc.

2. The Hamiltonian Function, and Expansion of the Partition Function

Let μ_i be the magnetic moment of atom i, and let V_i be its crystalline potential, which is a function of the coordinates of all the electrons of the atom. However, those with vanishing

angular momentum enter only in a trivial fashion, merely introducing an additive constant in V_i. The Hamiltonian function is

$$\mathcal{K} = \sum_i V_i + \sum_{i>i} w_{ij} - H_0 \sum_i \mu_{zi}, \qquad (4)$$

with

$$w_{ij} = r_{ij}^{-3}[\mathbf{\mu}_i \cdot \mathbf{\mu}_j - 3(\mathbf{\mu}_i \cdot \mathbf{r}_{ij})(\mathbf{\mu}_j \cdot \mathbf{r}_{ij})/r_{ij}^2] + V_{ij}^{ex}. \qquad (5)$$

Here $\mathbf{r}_{ij}$ is the radius vector connecting atoms i and j, and r_{ij} is the modulus of $\mathbf{r}_{ij}$. We suppose throughout that H_0 is directed along the z axis. The first part of (5) represents the dipole-dipole coupling between atoms i and j, while the last term is the exchange energy. Usually one is interested in an atom for which only one multiplet component is effective, so that one can take

$$\mathbf{\mu}_i = g\beta \mathbf{J}_i, \qquad (6)$$

where $\mathbf{J}_i$ is the angular momentum vector of the atom, measured in multiples of $h/2\pi$, while β is the Bohr magneton $he/4\pi mc$, and g is the Landé factor. If we forget orbital valence, assuming that the exchange integral connecting an electron of atom i and one of j has a value K independent of how the orbital angular momentum of either electron is oriented, and if all electrons not in closed shells are equivalent, then it can be shown[5] that apart from an additive constant

$$V_{ij}^{ex} = v_{ij}\mathbf{\mu}_i \cdot \mathbf{\mu}_j/r_{ij}^3, \qquad (7)$$

where

$$v_{ij} = -\frac{2r_{ij}^3}{g^2\beta^2}\left[\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}\right]^2 K. \qquad (8)$$

Here S, L, and J are, respectively, the spin, azimuthal, and inner quantum numbers of an atom. The atoms of the crystal are to be considered all alike when free, so that it is not necessary to attach subscripts to S, L, and J. The factor $r_{ij}^3/g^2\beta^2$ is included in (8) in order to make v_{ij} dimensionless and facilitate the formal

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[3] M. H. Hebb and E. M. Purcell, J. Chem. Phys. **5**, 338 (1937).

[4] Our free energy F is in a certain sense analogous to the Gibbs rather than Helmholtz definition, as we have $dF = -SdT - MdH$ rather than $-SdT + HdM$.

[5] Eqs. (7-8) are well-known consequences of the Dirac vector model when $J = S$, $L = 0$. See, for instance, Dirac, Proc. Roy. Soc. **123A**, 714 (1929) or Chap. XII of the writer's *Electric and Magnetic Susceptibilities*. The bracketed factor in (8) owes its existence to the fact that only the component of S along J is effective when $L \neq 0$ provided nondiagonal elements in J are neglected. It is squared because one must make the projection along J for both atoms involved in any given coupling term.

simultaneous handling of dipole-dipole and exchange interaction. It is seen that the two types of interaction, though physically quite different are mathematically rather similar, since both couple together the angular momentum vectors of different atoms. The exchange effect, however, is isotropic, as it depends only on the relative orientation of $\mathbf{u}_i$ and $\mathbf{u}_j$, and not on the inclination of either relative to $\mathbf{r}_{ij}$. If the exchange coupling is not direct, but via the excited states of intermediate atoms, an apparent rather than true value is to be used for the exchange integral K.

In most cases important in the production of very low temperatures, the atom is effectively in an S state, so that in (6–7–8) etc. one can take $J=S$, $L=0$. One then often speaks of the dipole-dipole coupling as spin-spin interaction; as in the following paper by Hebb and Purcell. In many instances, notably in gadolinium compounds or in those containing manganous or ferric ions, the paramagnetic ingredient is actually in an S state, while in other examples furnished by salts of the iron group, the orbital angular momentum is quenched by the crystalline field, leaving us only the spin to consider.

The partition function is

$$Z = \sum_\lambda \exp\left(-W_\lambda/kT\right)$$

$$= \sum_\lambda \left\{ 1 - \frac{W_\lambda}{kT} + \frac{W_\lambda^2}{2k^2T^2} - \cdots \right\}, \quad (9)$$

where the sum is over all the states of the crystal, regarded as a single unit. Eq. (9) may also be written

$$Z = \eta \left[1 - \frac{\mathcal{3C}_{Av}}{kT} + \frac{(\mathcal{3C}^2)_{Av}}{2k^2T^2} \right.$$

$$\left. - \frac{(\mathcal{3C}^3)_{Av}}{6k^3T^3} + \frac{(\mathcal{3C}^4)_{Av}}{24k^4T^4} + \cdots \right], \quad (10)$$

where η is the total number of states. The precise value of η is of no interest in connection with specific heat or susceptibility, as (1) and (3) do not depend upon η since η is independent of H_0 or T. The subscript Av denotes a quantum-mechanical mean value, in other words the diagonal sum or spur divided by the total number of rows or columns in the matrix representing $\mathcal{3C}$.

Now in virtue of the invariance of the spur, this average can be calculated in any system of representation. This fact is a tremendous aid in problems of the present sort, as Waller has already shown.[6] It obviates the necessity of determining the characteristic values W_λ of $\mathcal{3C}$, a practically hopeless task, and enables us to use systems of representation appropriate to one individual atom. Consequently we can use the familiar system which diagonalizes the component m_{zi} of angular momentum of each atom i in the direction of the applied field, even though m_{zi} is not really a constant of the motion because of perturbations due to dipole-dipole and exchange coupling between atoms.

Our development (9) or (10) of the partition function as a series in $1/T$ is obviously applicable only if the temperature is not too low. An alternative method of approximation valid in the vicinity of $T=0$ is being investigated by Professor H. A. Kramers.

Each member of (10) can be developed as an ascending series in the field H_0. From considerations of symmetry there will be no odd powers of H_0 so that

$$Z = Z^0(1 + Z^{(2)}H_0^2 + \cdots). \quad (11)$$

Throughout the paper, zero superscripts imply absence of the applied magnetic field, whereas zero subscripts imply absence of the material or of its dipole-dipole interaction.

3. CALCULATION OF Z^0 AND THE SPECIFIC HEAT FOR ATOMS NOT EXPOSED TO CRYSTALLINE FIELDS

Usually one is interested in the specific heat and entropy in the absence of applied field, so that in connection with (1) and (2) it suffices to determine the portion Z^0 of the partition function which persists when $H_0=0$. In the present section we shall hence compute Z^0, deferring until Section 4 the determination of $Z^{(2)}$ which is needed for the susceptibility. For simplicity, the crystalline potential terms V_i will be omitted until Section 6.

With $H_0 = V_i = 0$, one has

$$\mathcal{3C} = \sum_{i>i} w_{ij}, \quad (12)$$

[6] I. Waller, Zeits. f. Physik **79**, 370 (1932).

where by (5), (6) and (7)

$$w_{ij} = g^2\beta^2 r_{ij}^{-3}[(1+v_{ij})(\mathbf{J}_i \cdot \mathbf{J}_j)$$
$$- 3(\mathbf{J}_i \cdot \mathbf{r}_{ij})(\mathbf{J}_j \cdot \mathbf{r}_{ij})/r_{ij}^2]. \quad (13)$$

The average of the expression (13) can be taken over atoms i and j independently since the complete diagonal sum factors into the diagonal sum for individual atoms. Furthermore

$$(J_{xi})_{\mathrm{Av}} = (J_{vi})_{\mathrm{Av}} = (J_{zi})_{\mathrm{Av}} = 0, \quad (14)$$

as is obvious from symmetry considerations or from the fact that positive and negative values of the magnetic quantum number can be matched in pairs. Hence

$$\mathcal{K}_{\mathrm{Av}} = 0. \quad (15)$$

Terms in $\mathcal{K}^2$. To compute the quadratic term in (10), one uses, besides (14), the relations

$$0 = (J_{zi}J_{vi})_{\mathrm{Av}} = (J_{vi}J_{xi})_{\mathrm{Av}} = \cdots = (J_{zi}J_{xi})_{\mathrm{Av}};$$

$$(J_{xi}^2)_{\mathrm{Av}} = (J_{vi}^2)_{\mathrm{Av}} = (J_{zi}^2)_{\mathrm{Av}} = \tfrac{1}{3}J(J+1). \quad (16)$$

The reader should be careful to distinguish between $\mathbf{J}_i$ and J. The former is a vector matrix, whereas the latter is the usual inner quantum number, which is by hypothesis the same for all atoms. On the other hand the spatial components J_{xi}, J_{vi}, J_{zi} vary from atom to atom.

On performing the spatial averaging of the direction cosines and using (13), (14), (16), one finds that

$$(\mathcal{K}^2)_{\mathrm{Av}} = (\sum_{j>i} w_{ij})^2_{\mathrm{Av}} = \sum_{j>i} (w_{ij}^2)_{\mathrm{Av}}$$
$$= \tfrac{1}{2}N\sum_j (w_{ij}^2)_{\mathrm{Av}} = \tfrac{1}{6}g^4\beta^4 J^2(J+1)^2 N^3 Q, \quad (17)$$

where N is the number of atoms/cc and

$$Q = N^{-2}\sum_j r_{ij}^{-6}(2+v_{ij}^2). \quad (18)$$

The most important contribution to the sum (18) comes from the coupling between adjacent atoms. If all other interactions are disregarded and each atom is surrounded by z neighbors at equal distances r, (18) becomes

$$Q = zr^{-6}N^{-2}(2+v^2), \quad (19)$$

where v is the value of v_{ij} connecting adjacent atoms. For cubic arrangements, the dipole-dipole part of (18) may readily be summed accurately. If one neglects exchange except between neighbors, then one finds

$$Q_{sc} = 12(1.40 + \tfrac{1}{2}v^2), \quad Q_{fc} = 12(1.20 + \tfrac{1}{2}v^2),$$
$$Q_{bc} = (256/27)(1.53 + \tfrac{1}{2}v^2). \quad (20)$$

If dipole-dipole forces are included only between neighbors, the factors 1.40, 1.20, 1.53, are replaced by unity. The subscripts sc, bc, fc refer, respectively, to the simple, body, and face centered cube structures.

Terms in $\mathcal{K}^3$. We now proceed to the terms in $\mathcal{K}^3$. Here there are two types of terms. One kind arises because $(w_{ij}^3)_{\mathrm{Av}} \neq 0$ inasmuch as

$$(J_{xi}J_{vi}J_{zi})_{\mathrm{Av}} = -(J_{vi}J_{xi}J_{zi})_{\mathrm{Av}} = \tfrac{1}{2}i(J_{zi}^2)_{\mathrm{Av}} = \tfrac{1}{6}iJ(J+1). \quad (21)$$

Formulas (21) are consequences of the relations

$$J_{xi}J_{vi} - J_{vi}J_{xi} = iJ_{zi}, \quad \text{etc.} \quad [(J_{xi}J_{vi})_{\mathrm{Av}} + (J_{vi}J_{xi})_{\mathrm{Av}}] = 0, \quad (22)$$

which are well-known commutation rules or else are readily established by partial integration of the angular momentum operator integrals. Eqs. (21) give the only type of nonvanishing third-order term in w_{ij}^3, since

$$(J_{xi}^3)_{\mathrm{Av}} = (J_{xi}^2 J_{vi})_{\mathrm{Av}} = (J_{xi}J_{vi}J_{zi})_{\mathrm{Av}} = 0, \quad \text{etc.} \quad (23)$$

Thus one finds that

$$(w_{ij}^3)_{\mathrm{Av}} = \tfrac{1}{2}g^6\beta^6 J^2(J+1)^2 r_{ij}^{-9}(1 + \tfrac{3}{2}v - \tfrac{1}{2}v^3). \quad (24)$$

Another contribution to the mean of $\mathcal{K}^3$ comes from products of the form $w_{ij}w_{jk}w_{ki}$. The mean of such products is sensitive to the type of geometrical arrangement or symmetry in the crystal. We now make the restriction that the crystal be a simple cube as far as the spacing of paramagnetic ions is concerned. The most important terms of the present sort are then those in which two of the w's in the triple product relate to coupling between adjacent atoms, while the third involves atoms separated by an amount $\sqrt{2}r$. In other words, the three atoms i, j, k form the three corners of an isosceles right-angle triangle. In calculating the mean value of any individual product, one must allow for the fact that r_{ij} has different directions for the various sides of the triangle. Hence

$$w_{ij}w_{jl}w_{li} = [\beta^6 g^6/r^9(\sqrt{2})^3][(1+v)J_{xi}J_{xj} + (1+v)J_{vi}J_{vj} + (v-2)J_{zi}J_{zj}][(1+v)J_{xj}J_{xk} + (v-2)J_{vj}J_{vk} + (1+v)J_{zj}J_{zk}]$$
$$\times [J_{xk}J_{xi} - (J_{vk} + J_{zk})(J_{vi} + J_{zi}) + \tfrac{1}{2}(J_{vk} - J_{zk})(J_{vi} - J_{zi})]. \quad (25)$$

Here, we have supposed, for simplicity, but without loss of generality, that the y and z axes are directed along the two

legs of the triangle. Also we have included exchange coupling only between neighbors, i.e. along the two short sides of the triangle. This approximation is warranted if the exchange interaction diminishes much more rapidly with distance than does the dipole-dipole. Using (16), one finds that

$$(w_{ij}w_{jk}w_{ki})_{Av} = [3\beta^6 g^6/r^9\sqrt{2}^3][\tfrac{1}{3}J(J+1)]^3(1+v). \tag{26}$$

In connection with (24), it will suffice to consider only the coupling between neighbors, as (24) involves $J(J+1)$ to a lower power than does (26), and so need not be evaluated especially accurately. With this approximation, there are $3N$ terms of the type (24). There are $72N$ terms of the triangular form assumed in (26). There are also many other triangular ones in which one or both of the two shorter sides of the triangle do not connect adjacent atoms. Their effect is calculated in a fashion analogous to (25-6) and it is found that with the simple cubic arrangement the effect of including all the larger triangles is the same as though they were neglected, and the $72N$ terms of type (26) each increased by a factor approximately $(1.3+1.3v)/(1+v)$. Thus one finds

$$(\mathcal{3C}^3)_{Av} = Ng^6\beta^6 J^2(J+1)^2 r^{-9}(1+\tfrac{3}{2}v-\tfrac{1}{2}v^3) + 2N\sqrt{2}g^6\beta^6 r^{-9}J^3(J+1)^3(1.3+1.3v). \tag{27}$$

Terms in $\mathcal{3C}^4$. The fourth-order term $\mathcal{3C}^4$ in (13) involves nonvanishing terms of three types, *viz.* $w_{ij}^2 w_{kl}^2$, w_{ij}^4, and $w_{ij}^2 w_{jl}^2$, where it is to be supposed that all atoms denoted by different letters are distinct, i.e. $i \neq l$, etc. Clearly

$$(w_{ij}^2 w_{kl}^2)_{Av} = (w_{ij}^2)_{Av}(w_{kl}^2)_{Av} = [\tfrac{2}{3}g^4\beta^4 J^2(J+1)^2]^2 r_{ij}^{-6} r_{kl}^{-6}(1+\tfrac{1}{2}v^2)^2 \tag{28}$$

since the mean of w_{ij}^2 has already been computed in connection with (17).

A rather long calculation shows that

$$(w_{ij}^4)_{Av} = \frac{g^8\beta^8 J^4(J+1)^4}{r^{12}}\left[\frac{24}{25}(1+v_1) - \frac{16}{25}\frac{(1+v_1)}{J(J+1)} + \frac{11}{25}\frac{(1+v_2)}{J^2(J+1)^2}\right], \tag{29}$$

where v_1, v_2 are terms due to exchange, whose explicit values are

$$24v_1 = -16v + 36v^2 + 5v^4, \qquad 33v_2 = 28v + 12v^2 + 10v^4. \tag{30}$$

The mean values needed in obtaining the result (30) are supplied by

$$(J_{z_i}^4)_{Av} = \left[\frac{J^2(J+1)^2}{5}\right]\left[1 - \frac{1}{3J(J+1)}\right], \qquad (J_{x_i}^2 J_{z_i}^2)_{Av} = \frac{1}{15}J^2(J+1)^2 + \frac{1}{30}J(J+1), \tag{31}$$

The terms in (30) with $J(J+1)$ in the denominator arise from the noncommuting property of angular momentum, which requires us to observe carefully the ordering of products in the factors, as by (21) and (22) the corrections for noncommutation give contributions which do not average to zero.

If we include only coupling between neighbors, the terms in $w_{ij}^2 w_{jl}^2$ are of two types, *viz.*, those in which atoms ijk are on the same straight line, and those in which r_{ij} forms an angle of 90° with r_{jl}. One-fifth of the terms are of the former and four-fifths of the latter type. When the two types are weighted in this fashion, one finds

$$(w_{ij}^2 w_{jk}^2)_{Av} = (32/75)Ng^8\beta^8 J^4(J+1)^4 r^{-12}[1 - \tfrac{1}{3}(J^2+J)^{-1}](1+v_3), \tag{32}$$

where $v_3 = (75v^4 + 252v^2 + 48v)/288$.

Now $\mathcal{3C}^4$ is composed of $9N(3N-11)$ terms of structure (28), $3N$ of the type (29) and $90N$ of the class (32). This is all on the assumption that we consider only coupling between neighbors. A rough allowance for the interaction between non-neighbors can be made by multiplying the dipole-dipole parts (i.e., parts independent of v) of (28) and (32) by 1.4^2. The reason for this statement is that the multiple sums encountered can almost be factored into two sums of the form (18), for which the cubic non-neighbor correction factor is 1.4.

When one utilizes (15), (18), (27), (28), (29), (32), together with the remarks in the preceding paragraph on the structure of $\mathcal{3C}^4$, one finds that if one stops with fourth-order terms, the partition function (10) becomes[7]

$$Z^0 = \eta\left\{1 + N\frac{\tau^2}{T^2}(1.4+\tfrac{1}{2}v^2) - \frac{N\tau^3}{T^3}\left[\frac{(2+3v-v^3)}{12J(J+1)} + \frac{\sqrt{2}(1.3+1.3v)}{3}\right] + \frac{N^2\tau^4}{2T^4}(1.4+\tfrac{1}{2}v^2)^2\right.$$

$$+ \frac{N\tau^4}{T^4}\left[-\frac{11}{6}(1.4+\tfrac{1}{2}v^2)^2 + \frac{3}{25}(1+v_1) - \frac{2}{25}\frac{(1+v_1)}{J(J+1)} + \frac{11}{200}\frac{(1+v_2)}{J^2(J+1)^2}\right.$$

$$\left.\left. + \frac{8}{5}\left(1-\frac{1}{3J(J+1)}\right)(1.4+v_3)^2\right] + \cdots\right\}. \tag{33}$$

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[7] Although (33) involves the square of N explicitly, only the first power appears in F or c_v (cf. Eq. (35)), except implicitly through τ, as F is of the form $(aN+bN^2+\cdots)/(1+cN+\cdots)$ with $c = +b/a$.

Here it has been convenient to introduce a characteristic temperature τ defined by

$$\tau = g^2\beta^2 NJ(J+1)/k. \qquad (34)$$

The specific heat corresponding to (33) can immediately be obtained from (1). If, to make the formulas short, we neglect exchange and hence set $v=0$, and if we assume that J is a large number, then (1) becomes

$$c_v = Nk[2.8(\tau/T)^2 - 3.7(\tau/T)^3 \\ - 4.0(\tau/T)^4 + \cdots]. \qquad (35)$$

It is to be cautioned that this formula is only valid for a simple cubic arrangement. However, the coefficient of the first term is adapted to any arrangement by replacing 2.8 by $\frac{1}{6}Q$, where Q is given in (18). This first term in c_v has also been computed independently by I. Waller,[8] and to this approximation our results and methods are identical with his. With the face and body centered cubic arrangements, it can be shown that the coefficient of τ^3/T^3 becomes, respectively, 3.4 and 3.5 instead of 3.7. The remaining term, in τ^4/T^4, is subordinate if the temperature is high enough that the convergence is good, and then not much harm will be done in using the simple cubic arrangement for this term even if the actual crystalline arrangement is different. Unfortunately, one is often interested in temperatures comparable with the characteristic temperature τ. Under such circumstances, (35) cannot be used, as the higher order terms in τ^5/T^5 etc., omitted in (35) would surely come into play. If we were to use (35) as it stands without additional terms, one could obtain something so fantastic as a negative total specific heat by taking τ/T sufficiently large! Under such circumstances, it is probably better to stop with the first term of (35). This procedure is equivalent to replacing $(\mathcal{H}^{2n})_{\text{Av}}$ by $[(2n!)/n!2^n] [(\mathcal{H}^2)_{\text{Av}}]^n$, $(\mathcal{H}^{2n+1})_{\text{Av}}$ by zero, and has a certain resemblance to the approximations in Heisenberg's theory of ferromagnetism[9] in its simplest form, which on the whole nevertheless work surprisingly well. In fact, in the following paper by Hebb and Purcell, where comparison is made with experiment, it is found that the agreement is usually better if one uses only the first term rather than the complete expression (35). A possible extrapolation of (35) by means of the Onsager model is discussed at the very end of the present article.

The characteristic temperature τ defined in (34) has a simple physical interpretation, as follows. In classical theory, the dipole-dipole interaction is represented by the artifice of taking the local field acting upon the molecule to be $H_0 + \Phi M$ rather than H_0. The extra part ΦM arises from two causes: (I) The macroscopic field H in the test body is not the same as the field H_0 before its insertion. The portion of Φ arising from this source is negative, and its absolute value is often called the demagnetizing coefficient.[10] (II) There is the correction because of the fact that in a solid any given atom is in a privileged position, so that the field at the atom is not the same as the mean field. Instead in a body with cubic symmetry the atom may be regarded as at the center of a spherical cavity, and by a well-known argument, Lorentz[11] showed that the resulting contribution to Φ is $4\pi/3$. The value of Φ resulting from the two combined causes is shape dependent; with a spherically molded body Φ vanishes, a very long slab placed parallel to the field yields $\Phi = 4\pi/3$, while for a very wide body $\Phi = -8\pi/3$, provided in each case the atoms are on the average cubically spaced. If the effective field acting upon the moment is $H_0 + \Phi M$, and if saturation is neglected, the familiar quantum-mechanical version of the Langevin formula[12] for the moment is

$$M = [g^2\beta^2 NJ(J+1)/3kT][H_0 + \Phi M]; \qquad (36)$$

whence by (34)

$$M = \tfrac{1}{3}\tau H_0/(T - \tfrac{1}{3}\Phi\tau). \qquad (37)$$

Clearly, except for a factor $\frac{1}{3}\Phi \leq 4\pi/9$, our characteristic temperature τ is the same as the "Curie" temperature at which formula (37) fails due to zero denominator and at which it is necessary to consider saturation, so that ferromagnetism sets in. Numerically τ is very small ($\sim 0.05°$K), as is obvious from the fact that

[8] I. Waller, Zeits. f. Physik **104**, 132 (1936).
[9] For a description of Heisenberg's theory of ferromagnetism see, for instance, his original paper, Zeits. f. Physik **49**, 619 (1928) or reference 17.

[10] An excellent discussion of demagnetization corrections is given in Stoner, *Magnetism and Matter*, pp. 38–40.
[11] Cf. H. A. Lorentz, *The Theory of Electrons*, note 54.
[12] See, for example, p. 285 of reference 10.

Curie temperatures of ordinary size are obtained in the Weiss theory[13] only by artificially giving Φ enormous values ($\sim 10^5$) rather than taking $\Phi \leqq 4\pi/3$.

It is to be noted that our formula (35) for specific heat is independent of shape, unlike that (36) for moment. The reason is that the expression Q defined in (18) and any other grating sums encountered in the derivation of (35) involve only inverse sixth or other high negative powers of the interatomic distance and so are practically independent of boundary conditions, whereas this is not true of Φ, which involves a sum of inverse third powers (cf. later Eq. (43)).

4. CALCULATION OF $Z^{(2)}$ AND THE SUSCEPTIBILITY FOR ATOMS NOT EXPOSED TO EXTERNAL FIELDS

In the present section we shall consider only the ordinary susceptibility for fields not powerful enough to cause saturation, and so it will suffice to compute the coefficient $Z^{(2)}$ in the development (11). If in (10) we neglect terms beyond the fourth order in $\mathfrak{K}$, this coefficient has the value

$$Z_2^{(2)} = \eta Z_0^{-1} \left[\frac{(a^2)_{\mathrm{Av}}}{2k^2T^2} - \frac{p(aab)_{\mathrm{Av}}}{6k^3T^3} + \frac{p(aabb)_{\mathrm{Av}}}{24k^4T^4} \right] \quad (38)$$

with the abbreviations

$$a = -\sum_i J_{zi} g\beta H_0, \quad b = \sum_{j>i} w_{ij}, \quad (39)$$

and with w_{ij} as in (5). The symbol p means that in averaging, all possible orders of the factors in the following product are to be used; e.g.

$$paab = \tfrac{1}{3}(a^2b + aba + ba^2). \quad (40)$$

It is necessary to distinguish between the various orders because a and b do not commute in multiplication.

The first term of (38) is simply the usual magnetic part of the partition function obtained by disregarding the interaction between elementary magnets. Use of (16) gives immediately

$$(a^2)_{\mathrm{Av}}/2k^2T^2 = NH_0^2g^2\beta^2J(J+1)/6k^2T^2. \quad (41)$$

To evaluate the next term in (38), we note that $J_{zi}J_{zj}J_{qk}J_{ql}$ vanishes on the average unless the subscripts coincide in pairs, and unless in

13 A convenient summary of the Weiss theory is given on p. 352ff. of reference 10.

addition $q=z$ rather than $q=x, y$. The nonvanishing form is $J_{zi}J_{zj}J_{zi}J_{zj} = J^2(J+1)^2/9$. These statements are also valid even if the order of the factors is permuted. Thus one finds[14]

$$p(aab)_{\mathrm{Av}} = \tfrac{2}{3}H_0^2g^4\beta^4J^2(J+1)^2$$
$$\times \sum_{j>i}[1 + v_{ij} - 3\cos^2(z, r_{ij})]/r_{ij}^3. \quad (42)$$

Let us set

$$\Phi = -N^{-1}\sum_j[1 - 3\cos^2(z, r_{ij})]/r_{ij}^3. \quad (43)$$

Then $M\Phi$ is the z component of the field at atom i due to a grating constructed by placing a dipole of strength M/N at each atom j of the crystal (except $j=i$) with axis always parallel to the field H, i.e., to the z axis. Hence Φ as defined by (43) is the same as the factor Φ in the customary local field $H+\Phi M$ discussed preceding Eq. (36).[15] In particular, in a spherically molded cubic crystal Φ vanishes, since the mean value of $\cos^2(H, r_{ij})$ in (43) is $1/3$. This agrees with the fact in such a body the demagnetizing and Lorentz corrections cancel. In a nonspherical specimen, one cannot take this mean value equal to $1/3$, as atoms near the boundary make an important contribution to the sum (43), and spoil the symmetry.

The exchange terms presumably vary much more strongly with distance than in the inverse third fashion. Hence, to a sufficient approximation, we can regard v_{ij} as having a nonvanishing value v only when it connects adjacent atoms, so that $\sum_j v_{ij}/r_{ij}^3 = vz'N$ where $z' = z/Nr^3$ and where z is the number of neighbors possessed by any atom. For a simple cubic arrangement z and z' are identical.

When we use (43) and the above simplification of the exchange terms, (42) becomes

$$p(aab)_{\mathrm{Av}} = -\tfrac{1}{3}NH_0^2g^4\beta^4J^2$$
$$\times (J+1)^2[N\Phi - Nvz']. \quad (44)$$

If we retain only the part of (38) through aab, i.e., through $\mathfrak{K}^3$ in (10), Eqs. (38), (41), (44) and

14 A factor 2 appears on the right side of (42) because of the two possibilities $i=k$, $j=l$, or $i=l$, $k=j$. This factor disappears in (44) because ij and ji count as one term in a double sum such as (42), so that there are $N/2$ single sums of the form (43).

15 That essentially the same results will be obtained with discrete grating sums such as (43) as with the classical Lorentz continuum, as long as there is isotropy, has been demonstrated by Ewald, Ann. d. Physik 49, 1 (1916).

(34) show that the formula (3) for the moment gives

$$M = (\tau H/3T)[1 + \tfrac{1}{3}(\Phi - z'v)_\tau T^{-1}]. \quad (45)$$

To first powers of Φ this formula is, apart from exchange corrections equivalent to (37), as one sees by expanding (37) as an ascending series in Φ. Thus to linear terms in Φ, the treatment by means of the partition function agrees with the method of the local field. To see whether this similarity also holds to Φ^2, we must now proceed to examine the fourth order (i.e., $\mathfrak{IC}^4$) part of the partition function. Before so doing we must caution that even the expressions of the first degree in Φ are rigorous only for ellipsoidal test bodies, as only bodies of such shape have a uniform polarization and so admit a constant demagnetizing factor or in other words a value of the sum (43) independent of the position of

atom i. Actually, cylinders are often used experimentally, and the best that one can do is to approximate them by ellipsoids. Because of other difficulties (e.g., insufficiency of Eq. (37) when we come to higher powers of Φ) the resulting error is probably not usually of paramount concern. The exchange corrections are seen to have the effect of replacing Φ by $\Phi - z'v$. Eq. (8) shows that v has the opposite sign from the exchange integral K. Hence if the latter is negative, as in most nonferromagnetic materials, the exchange terms have the effect of decreasing the apparent value of Φ, or in other words a demagnetizing tendency. In ferromagnetic media, on the other hand, K is positive and large because of high magnetic density. Under these conditions exchange is in the present first approximation equivalent to an enormous positive value of Φ, as in the Weiss theory of the molecular field.

Terms in $\mathfrak{IC}^4$. By (38–39), the fourth degree position of the partition involves

$$\eta p(aabb)_{\mathrm{Av}}/24Z^0k^4T^4 = (\eta g^2\beta^2/Z^0k^4T^4)p[\tfrac{1}{2}\sum_{i>i}(J_{zi}J_{zj}w_{ij}w_{ij})_{\mathrm{Av}} + \tfrac{1}{2}\sum_{j>i}(J_{zi}J_{zi}w_{ij}w_{ij})_{\mathrm{Av}}$$
$$+ \tfrac{1}{4}(N-2)(J_{zk}^2)_{\mathrm{Av}}\sum_{i>i}(w_{ij}^2)_{\mathrm{Av}} + \sum_{i>i}\sum_{k(\neq i)}(J_{zi}J_{zk}w_{ij}w_{jk})_{\mathrm{Av}}], \quad (46)$$

where k is not to equal i or j, and p has the same meaning as in (40). On using (16), (21), (31) and taking care to include all possible orderings of the noncommutative factors, one finds after some calculation that

$$p\sum_{i>i}(J_{zi}J_{zj}w_{ij}w_{ij})_{\mathrm{Av}} = -Ng^4\beta^4[J(J+1)/6]^2 \cdot \tfrac{1}{3}\sum_j r_{ij}^{-6}(v_{ij}^2 - 1), \quad (47)$$

$$p\sum_{i>i}(J_{zi}J_{zi}w_{ij}w_{ij})_{\mathrm{Av}} = (N/18)g^4\beta^4[J^3(J+1)^3 - \tfrac{1}{3}J^2(J+1)^2]\sum_j(v_{ij}^2 + 2)/r_{ij}^6, \quad (48)$$

$$(J_{zk}^2)_{\mathrm{Av}}\sum_{i>i}(w_{ij}^2)_{\mathrm{Av}} = \tfrac{1}{2}g^4\beta^4N[\tfrac{1}{3}J(J+1)]^3\sum_j(3v_{ij}^2 + 6)/r_{ij}^6, \quad (49)$$

$$p\sum_{i>i}\sum_{k(\neq i)}(J_{zi}J_{zk}w_{ij}w_{jk})_{\mathrm{Av}} = \tfrac{1}{2}[\tfrac{1}{3}J(J+1)]^3Ng^4\beta^4[(-N\Phi + Nvz')^2 - \sum_j r_{ij}^{-6}(2 + v_{ij}^2)]. \quad (50)$$

The derivation of (50) requires some comment, as here the spatial averaging is complicated by exclusion of $k=i$, which prevents easy factorization. However, one can add and subtract the term $k=i$. Thus one can write, with the aid of (16)

$$\sum_{i>i}\sum_{k(k\neq i)}(J_{zi}J_{zk}w_{ij}w_{jk})_{\mathrm{Av}} = \tfrac{1}{2}[\tfrac{1}{3}J(J+1)]^3Ng^4\beta^4[\{(\sum_j r_{ij}^{-3}f_{ij})_{\mathrm{Av}}\}\{\sum_k(r_{jk}^{-3}f_{jk})_{\mathrm{Av}}\}$$
$$- \sum_j(r_{ij}^{-6}f_{ij}^2)_{\mathrm{Av}}], \quad (51)$$

where $f_{ij} = [1 + v_{ij}] - 3\cos(z, r_{ij})[\cos(x, r_{ij}) + \cos(y, r_{ij}) + \cos(z, r_{ij})]$ and where on the right side the sum includes $k=i$. In (51) it is possible to average separately, i.e., replace the average product by the product of averages, because after the inclusion of $k=i$ there is no statistical correlation between the directions of r_{ij} and r_{jk}. In the first part of the right side of (51), convenient use may be made of the definition (43) of Φ and the relations $0 = \sum_j r_{ij}^{-3}\cos(x, r_{ij})\cos(y, r_{ij})$, etc. which are consequences of the fact that the Lorentz local field is parallel to the direction z of the applied field, at least in an isotropic body. The exchange contributions are simplified as after Eq. (43). In the last part of (51) one may take

$$[\cos^2(x, r_{ij})]_{\mathrm{Av}} = \tfrac{1}{3}, \quad [\cos(x, r_{ij})\cos(z, r_{ij})]_{\mathrm{Av}} = 0, \quad [\cos(x, r_{ij})\cos^3(z, r_{ij})]_{\mathrm{Av}} = 0, \quad \text{etc.} \quad (52)$$

provided the crystal has cubical symmetry, or provided we desire only the powder susceptibility if the arrangement is not cubic. This condition we suppose to be met. Use of (52) is then allowed regardless of the shape of the body, since the last part of (51) involves inverse sixth powers of the distance and so boundary conditions do not enter. For similar reasons, relations such as (52) can be used in obtaining (47–48–49). In view of all the above, (51) finally can be thrown into the form (50).

Substituting (47–50) in (46) and using (41–42), one finds that the partition function (38) becomes

$$Z^{(2)} = (\tau/6kT^2)[1 + \gamma T^{-1} + \gamma^2 T^{-2} - \delta T^{-2}], \quad (53)$$

where τ, Q are defined as in (34), (18) and

$$\gamma = \tfrac{1}{3}\tau(\Phi - vz'), \quad \delta = xQ\tau^2/9. \quad (54)$$

with

$$x = 1 + [(3 + 3v^2zr^{-6}N^{-2}Q^{-1})/(8J^2 + 8J)]. \quad (55)$$

In obtaining (53) we have used the explicit value of $1/Z^0$, which by (33) or (10–15–17) to the present degree of approximation is

$$1/Z^0 = \eta^{-1}[1 + \tfrac{1}{3}Q(\tau/2T)^2]^{-1} = \eta^{-1}[1 - \tfrac{1}{3}Q(\tau/2T)^2].$$

By (3) and (11), the moment is $M = 2kTZ_2H$. Hence we can write

$$M = \tfrac{1}{3}H\tau/(T - \gamma + \delta T^{-1}), \quad (56)$$

since to the present stage of approximation there is no distinction between $1 + \gamma T^{-1} + \gamma^2 T^{-2}$ and $1/(1 - \gamma T)$ or between $1 - \delta T^{-2}$ and $1/(1 + \delta T^{-2})$.

Reference to (37) shows that if we omit δT^{-1}, Eq. (56) is exactly what one gets by taking the local field to be $H + (\Phi - vz')M$. The presence of the last term δT^{-1}, however, shows that it is not accurate to represent the dipole-dipole interaction by means of the customary local field. We must, of course, examine whether the modifications due to this extra term are appreciable. Clearly it is unimportant if the actual temperature T is large compared with the characteristic temperature τ. This condition is met in paramagnetic salts except at very low temperatures. In the electric case, the analogous correction term can be important even at room temperatures, as we will discuss in another paper. Even with paramagnetic substances of fairly high magnetic dilution, the influence of the last term is by no means negligible in the celebrated experiments at Leiden and elsewhere on the production of very low temperatures. In the case of $Gd_2(SO^4)8H_2O$, for instance, τ equals 0.19°K. If we neglect exchange, doubtless warranted at this magnetic dilution, and assume a spherically molded body, so that $\Phi = 0$, the effect of the extra term is to make the moment at $T = \tau$ less than half as large as it would be otherwise.

5. Comparison with Heisenberg's Gaussian Calculation and Onsager's Method. Can Dipole-Dipole Coupling Ever Produce Ferromagnetism?

Of course, as soon as the temperature is so low that our new term in (56) is important, there is immediately the difficulty that the whole series development is not convergent. There are many different formulas which agree with ours to the degree of accuracy of the the calculation, but which would yield completely different results when T is comparable with τ. For instance, we might omit the last term from the denominator of (56) and add $-\tfrac{1}{3}H\tau\delta/T^3$ to its right side. Our reason for writing our result in the form (56) is that (56) has a form analogous to that obtained in Heisenberg's theory of ferromagnetism when a Gaussian distribution of energy values is assumed. In fact, (56) agrees exactly with Heisenberg's Gaussian formula (except for his saturation terms) when one neglects everything but exchange,[16] and takes $J = \tfrac{1}{2}$, the case considered by him.

The derivation of a formula substantially equivalent to (56) may also be made in a completely different way. Instead of our computation by series development of the partition function, one may attempt a calculation by Heisenberg's method in which in the first approximation all states belonging to the same magnetic quantum number M' for the entire crystal are regarded as having the same energy, and in which in the second approximation a Gaussian distribution is assumed for these states. (It is usually stated that identity or else Gaussian distribution of energies is assumed for all states with the same total angular momentum J' for the whole crystal. However, corresponding assumptions can equally well be made for

[16] When only exchange is included, Φ vanishes. Also then the factor x defined in (55) reduces to $1 + \tfrac{3}{4}(J^2 + J)^{-1}$, as Q becomes $N^{-2}zr_0^{-6}v^2$.

all states with the same M', since owing to the enormity of J' the overwhelming fraction of states with a given J' have M' nearly equal to J' when $H \neq 0$.) The difference as compared with Heisenberg's original calculations is, of course, that we must include dipole-dipole rather than just exchange coupling. There is immediately one difficulty, as in our problem the total dipole-dipole interaction energy $\sum_{j>i} w_{ij}$ does not commute either with $M' = \sum J_{zi}$ or with $\mathbf{J}'^2 = (\sum J_{xi})^2 + (\sum J_{yi})^2 + (\sum J_{zi})^2$. Hence one cannot really talk about the states belonging to a given value of M' or J'. This is one reason why we presented the calculation in the way we have, rather than by a method analogous to Heisenberg's, since the latter thus cannot be applied at all rigorously to our problem. Our other reasons are that our scheme of series development of the partition function presents an interesting alternative to the Heisenberg procedure, and especially that, unlike the latter, it need not be specialized to $J = \frac{1}{2}$ as soon as the calculation is extended beyond the first or nonspreading approximation. If, nevertheless, as close a parallel as possible with Heisenberg is desired, the mean energy, mean square energy, etc. may formally be evaluated for a given M' and J', in the sense that these means are taken proportional to the appropriate matrix spur or diagonal sum. We shall not give the details of the calculation. They are made by means of the vector model, after a manner explained elsewhere.[17] If identity of energy for all states of a given M' is assumed, and if saturation effects are disregarded inasmuch as we are considering only weak fields, a formula is found which is exactly the same as (56) except that the last term δT^{-1} in the denominator is missing. This is just what one would expect to be true. To obtain this term, it is necessary to go to the second approximation, in which a Gaussian spread of energies for a given M' is assumed. Here there is the usual difficulty that with present mathematical machinery[18] it is possible to make the calculation only with $J = \frac{1}{2}$. With such a specialization the computation can be carried through, and one obtains a formula not quite identical with (56). The difference is only that the definition (55) of x becomes $x = 1 + [(-3 + 9zv^2 r^{-6} N^{-2} Q^{-1})/8(J^2 + J)]$. The cause of this slight discrepancy is, however, not hard to find. The Heisenberg method is really applicable only when $\sum J_{zi} g \beta H$ commutes with the rest of the Hamiltonian function. Therefore to obtain an expression comparable with that furnished by his procedure, one ought erroneously to write all the b terms in front of the a (or vice versa) in (38), or in other words omit the operator p. When this change is made, the results by the two methods are similar.

In order to have ferromagnetism, it is necessary for the denominator of (56) to vanish for a real value of T. The resulting value of T, which may be called the Curie temperature, is

$$T_c = \tfrac{1}{6}\tau(\Phi - vz) \pm \tfrac{1}{6}\tau[(\Phi - zv)^2 - 4Qx]^{\frac{1}{2}}. \quad (57)$$

[17] See Chap. XII of the writer's *Electric and Magnetic Susceptibilities*.
[18] Cf. footnote, p. 329 of reference 17.

Let us consider the case of no exchange, i.e., $v = 0$, since the possibility of ferromagnetism resulting from exchange has already been dealt with by Heisenberg. If $J = \infty$, i.e., $x = 1$, Eq. (20) shows that for a simple cubic arrangement (57) is real if and only if $\Phi \geqq 8.2$. For the face-centered and body-centered cube, the corresponding inequalities are both $\Phi \geqq 7.6$. Even larger values of Φ are required if J is finite. Now from the mode of definition, the maximum value of Φ that can occur physically in an isotropic material is that $4\pi/3 = 4.2$ appropriate to a very long test body. Hence if formula (56) is granted, dipole-dipole interaction is never adequate to produce ferromagnetism. This is a quite different result than if one represents this interaction by means of a local field $H_0 + \Phi M$, as then ferromagnetism sets in at the temperature $\tfrac{1}{3}\Phi\tau$ (cf. Eq. (37)).

We thus conclude that according to (56) no plausible arrangement of atoms is sufficient to give ferromagnetism from dipole-dipole effects alone. The situation is consequently different from that in the usual ferromagnetism due to exchange. Here Heisenberg found that if $J = \frac{1}{2}$ there could be ferromagnetism even with a Gaussian distribution provided $z > 8$ and the exchange integral has the proper sign. This result can also be seen[16] by omitting all of (57) except the terms involving v. Of course one can question whether the Gaussian approximation is a good one. In the case of ordinary, i.e., exchange ferromagnetism, it is known that a formula where all the states of the same spin are regarded as having the same energy works better empirically than the more elaborate expression based on the Gaussian approximation. A partial theoretical explanation has been given by Fay,[19] who was able to take into account half the spin-spin interactions rigorously, and thus found formulas agreeing well with those obtained by the nonspreading approximation. Extension of this method to the dipole-dipole coupling is, however, not feasible.

The second order or fluctuation effects are entirely ignored by using the usual Lorentz or Weiss local field, and are undoubtedly over-recognized in formulas like (56) based on a Gaussian distribution. However, these effects

[19] C. H. Fay, Proc. Nat. Acad. Sci. **21**, 537 (1935).
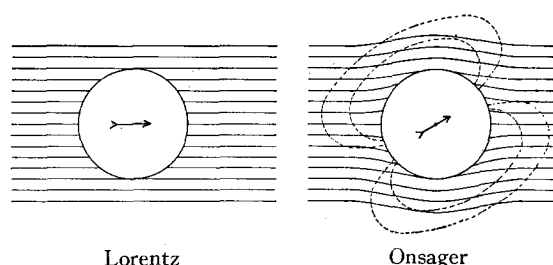
Lorentz   Onsager

Fig. 1. In the Lorentz method, the field inside the cavity is computed on the assumption that the lines of induction outside the cavity are unmodified by the existence of the latter. With the Onsager model, the distribution of these lines is revised by elementary electrostatics to take cognizance of the cavity. The resulting portion of the local field may be called the direct part. In addition, Onsager has a "reaction field" which is shown by dashed lines in the figure and which arises because the dipole itself will polarize the surrounding medium. The direct and reaction contributions to the local field are given by the first and second terms of our later Eq. (85). The reaction field on the dipole is clearly always parallel to it and has no influence on the latter's orientation. So in dealing with permanent rather than induced polarization, only the direct portion need be considered. Eq. (58) is thus obtained by taking the moment M equal to the product of the polarizability $\psi/4\pi$ and the first member of (85), and then solving for M. In the case of induced polarization, the elementary dipoles are all parallel to the field, and the sum of Onsager's direct and reaction fields is identical with the Lorentz expression.

are considerably more important in the dipole-dipole than in the exchange case. In the latter, raising z from 6 to 8 was sufficient to give ferromagnetism even in a Gaussian calculation,[20] but with dipole-dipole forces, the values of Φ which would be necessary are far too large to be permissible even if $z=12$. The physical basis for this situation is not hard to see. In the dipole-dipole case, the mean energy is relatively small. In fact, for a spherically molded specimen it is exactly zero. Hence, the mean square of the dipole-dipole energy can be radically different from the square of the mean, and the fluctuation corrections correspondingly important.

Onsager's method.—Another, entirely different approach to the problem has been given recently by Onsager.[21] The gist of his observations is that the usual Lorentz field is not the best possible

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[20] Incidentally, the present calculation shows as a corollary that in the ferromagnetic case of exchange rather than dipole-dipole coupling, Heisenberg's conclusion that use of a Gaussian spread prevents ferromagnetism is only true when $J=\frac{1}{2}$. Namely, as soon as one uses $J=1$ in (57) and omits all but exchange terms, one can still have a real positive Curie temperature even when $z=6$. Heisenberg obtained the same result, but his calculations were voided (reference 18) by an error which makes use of his group methods impossible when $J>\frac{1}{2}$.

[21] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

choice of a local field in an essentially static method. The reason is that the ordinary procedure assumes that the lines of force are the same outside the classical spherical cavity as though this cavity did not exist. Actually there will be a "back-action" of the dipole at the center of the cavity on the surrounding medium, and this effect will depend on how the given dipole is aligned. The distinction between the Lorentz and Onsager models is illustrated in Fig. 1. Onsager thus derives a new local field which is claimed to be a better approximation than the usual one. For further details, the reader is referred to his interesting paper.[21] It leads to the formula

$$M=(3/16\pi)H[-1+\psi+(1+\tfrac{2}{3}\psi+\psi^2)^{\frac{1}{2}}]$$
$$=(H/4\pi)[\psi+\tfrac{1}{3}\psi^2-(1/9)\psi^3$$
$$-(1/27)\psi^4+\cdots], \quad (58)$$

with

$$H=H_0+\tfrac{1}{3}(3\Phi-4\pi)M, \quad \psi=4\pi N\mu^2/3kT. \quad (59)$$

The difference between H_0 and H simply represents the "demagnetizing correction," H_0 and H being respectively fields before and after insertion of the sample. This distinction is not discussed in Onsager's paper, as he considered dielectric media, but the adaptation to magnetic rather than electric dipoles is immediate. To make a fair comparison with (56), we must assume that the dipoles are distributed continuously rather than discretely. Then, apart from exchange corrections, (18) becomes

$$Q=8\pi N^{-1}\int_a^\infty r^{-4}dr=2(4\pi/3)^2 \quad (60)$$

as the volume of the classical cavity is to be chosen equal to the mean volume associated with an atom (or molecule), giving $1/N=4\pi a^3/3$. If we use (60), development of (56) gives the same series as (58) to terms in ψ^3 inclusive, provided we neglect exchange terms and provided we replace the noncommutation correction factor x by unity. It is not clear how either of the two latter effects could be introduced into Onsager's formula, since his *modus operandi* is entirely classical. The usual Lorentz procedure would give $\psi+\tfrac{1}{3}\psi^2+(1/9)\psi^3+\cdots$. The Onsager field is thus seen to be a better approximation than the Lorentz one at least if ψ is not too large.

The physical arguments in Onsager's paper gave one good reason to expect this, but at the same time it is reassuring to have examined the situation analytically by use of the partition function. In this connection it is to be emphasized that (56) is only rigorous to ψ^3 and so the comparison cannot be made to a higher approximation. Onsager, of course, did not claim complete accuracy for his result.

The Onsager formula (58) agrees with the Gaussian one (56) in predicting that dipole-dipole interaction can never give ferromagnetism. Furthermore, (58) demands that the moment always increases as the temperature is lowered. With (56) this is unfortunately not true, since (56) has a maximum at $T = \sqrt{\delta}$. We thus believe that Onsager's formula is better than one based on a Gaussian distribution. Distinct experimental evidence that (58) or even (37) works better than (56) is given in the following paper of Hebb and Purcell.

To summarize, it must at present be regarded as uncertain theoretically whether or not ferromagnetism can result from dipole-dipole coupling. Alternative methods of calculation better suited to the vicinity of $T = 0$ are greatly to be desired, which would decide whether or not the state of lowest energy is magnetic. The Bloch-Slater method applies unfortunately only for the exchange case. In dielectrics the analog of ferromagnetism does not occur nearly so often as (37) would demand, as we will discuss in a paper in a later issue of this journal. There are some magnetic experiments on long test bodies, notably $FeNH_4(SO_4)_2 12H_2O$ at which no ferromagnetism is found at temperatures considerably below the critical temperature at which (37) fails. However, Hebb and Purcell find that this difficulty practically disappears when one includes the effect of the crystalline field (i.e. uses our later Eq. (83) rather than (37)) which greatly lowers the susceptibility and hence the Curie temperature in the local field model. There are certain salts at which residual magnetization is found at very low temperatures, though rather curiously often no saturation curvature in weak fields.[22] Eq. (37) would predict both effects and (56) or (58) neither! All told, the actual behavior is probably intermediate between (37) and (58). This situation seems comprehensible, since the continuum model basic to (58) involves an excessively high value of Q. Namely (60) is over twice as large as any of the estimates (20) appropriate to discrete arrangements, and so (58) may over-accentuate the corrections to the Lorentz expression.

6. Calculation for Atoms Subject to Crystalline Fields

We shall now compute the specific heat and magnetic susceptibility for an ensemble of atoms subject to a crystalline field in addition to the applied external field and the dipole-dipole interaction.

Let us choose a system of representation which diagonalizes the energy of an individual atom subject to the crystalline and the applied fields. The matrix elements of the magnetic moment of atom i in this scheme, which are Hermitean, will be denoted by

$$\mu_{x_i}(m_i; m_i'), \quad \mu_{y_i}(m_i; m_i'), \quad \mu_{z_i}(m_i; m_i'). \tag{61}$$

We suppose the applied field along the z axis. The letter m_i symbolizes the totality of quantum numbers which come into play for atom i. Therefore m_i includes a "crystalline quantum number" which determines the spatial orientation of the atom, but which is not the same as the ordinary magnetic quantum number unless the field has axial symmetry. In addition m_i contains the inner quantum number if several multiplet components are excited. The determination of the matrix elements (61) has been discussed in detail by Penney and Schlapp,[1] and need not be considered explicitly here. The point which we would like to stress here is that the calculation of these elements involves the solution of a "one-atom problem," and so is tractable by direct methods involving solution of algebraic equations of low degree. On the other hand we must use perturbation theory to

[22] N. Kürti, P. Lainé, Bernard-Vincent Rollin and F. Simon, Comptes rendus **202**, 1576 (1936); **204**, 675, 754 (1937). By the absence of saturation curvature we mean the failure of additional remanence to appear in feeble fields as long as they exceed 7 gauss.

handle the dipole-dipole interactions. Their influence has not been included in (61), and can only be treated by successive approximations, inasmuch as the dipole-dipole forces couple together the enormous number of atoms in the crystal, thereby spoiling the factorization into one-atom problems.

The characteristic values of the energy of atom i for the unperturbed problem will be denoted by $W_i(m_i)$. The total unperturbed energy of the crystal is then

$$W_M = \sum_i W_i(m_i).$$ (62)

To simplify printing, we omit attaching zero subscripts to the amplitudes μ_i and energies W_i, but it is nevertheless to be understood that they are throughout to be calculated in the unperturbed system of representation, i.e., exclusive of dipole-dipole coupling. Note that our unperturbed system is inclusive of portions, *viz.* crystalline and applied fields, which are usually regarded as belonging to the perturbing potential. Instead, the latter consists solely of the dipole-dipole and exchange energy, and therefore takes the form $\sum_{j>i} w_{ij}$ where (cf. Eq. (5) or (13))

$$w_{ij}(M; M') = w_{ij}(m_i m_j; m_i' m_j') = r_{ij}^{-3} \sum_{q, \ q'=x, \ y, \ z} [(1 + v_{ij})\delta(q; q')$$

$$- 3 \cos (q, r_{ij}) \cos (q', r_{ij})] \mu_{qi}(m_i; m_i') \mu_{q'j}(m_j; m_j').$$ (63)

To the second approximation in the dipole-dipole coupling, i.e., to the second order in $(1/r_{ij}^3)$, the partition function is

$$Z = Z_0 [1 + A + B + \cdots],$$ (64)

where

$$Z_0 = \sum_M \exp (- W_M/kT) = [\sum_{m_i} \exp (- W_i(m_i)/kT)]^N,$$ (65)

$$A = A^0 + A^{(2)}H_0^2 + \cdots = - (1/kTZ_0)\sum_M \sum_{j>i} w_{ij}(M; M) \exp (- W_M/kT),$$ (66)

$$B = B^0 + B^{(2)}H_0^2 + \cdots = (1/2k^2T^2 Z_0)\sum_{=M, \ M'} \sum_{j>i} w_{ij}(M; M') \sum_{l>k} w_{kl}(M'; M) \exp (- W_M/kT)$$

$$+ (1/kTZ_0)\sum'_{M, \ M'} \{ \sum_{j>i} w_{ij}(M; M') \sum_{l>k} w_{kl}(M'; M)/(W_{M'} - W_M)\} \exp (- W_M/kT).$$ (67)

Here Z_0 denotes the partition function in the absence of dipole-dipole coupling. It is not to be confused with Z^0, as Z^0 includes this coupling, but not the applied field, while the reverse is true of Z_0. In writing (66–7) we have utilized the fact that the amplitudes, energies, etc. and hence A, B can be developed as power series in H_0. The letter M denotes the totality of quantum numbers for some state of the entire crystal, and so comprises N times as many quantum numbers as m_i.

The equality signs and primes attached to the summations over M' require some explanation. They denote, respectively, inclusion and exclusion of those values of M' for which $W_M = W_{M'}$ (or in the later Eq. (72), those m_i', m_j' for which $W_i(m_i) + W_j(m_j) = W_i(m_i') + W_j(m_j')$). The situation $W_M = W_{M'}$ can arise primarily because of resonance degeneracy. Clearly the energy will be unaffected if we de-excite one atom and excite another one by the same amount. In other words, a partition $W_i(m_j) + W_j(m_i)$ between atoms i and j carries the same total energy as $W_i(m_i) + W_j(m_j)$.

For proof of (64), the reader is referred to a paper by R. Serber.[23] Eq. (64) can also be established by substituting in (9) the usual formulas for the second order perturbed energy, provided the perturbing potential λH_1 is taken as $\sum_{j>i} w_{ij}$. Eq. (64) is then obtained when one expands the exponentials in the partition function to terms of the order λ^2. There is, however, one simplification when working with the partition function rather than individual energy levels. Namely, it is not necessary to worry about the resonance degeneracy difficulties associated with the possibility of atoms trading quantum numbers. These difficulties enter in connection with the determination of the characteristic values of the energy even in the first approximation. However, because of the invariance of the spur, there is no trouble in constructing the partition function, and it is not necessary for us to solve the secular problem connected with resonance degeneracy.

[23] R. Serber, Phys. Rev. **43**, 1011 (1933), especially first form of his Eq. (13).

In virtue of (62), (65), and the first part of (63), Eqs. (66)–(67) may be written

$$A = -k^{-1}T^{-1}\sum_{j>i}(w_{ij})_{\mathrm{Av}},$$

$$B = \tfrac{1}{2}k^{-2}T^{-2}\{\sum_{ijkl}(w_{ij})_{\mathrm{Av}}(w_{kl})_{\mathrm{Av}} + 2\sum_{ijk}(w_{ij}w_{jk})_{\mathrm{Av}}\}_{j>i,\ l>k(i,\ j\neq k,\ l)} + \alpha, \quad (68)$$

with

$$(w_{ij})_{\mathrm{Av}} = d_i d_j \sum_{m_i m_j} w_{ij}(m_i m_j;\ m_i m_j)\ \exp\left[-(W_i(m_i)+W_j(m_j))/kT\right], \quad (69)$$

$$(w_{ij}w_{jk})_{\mathrm{Av}} = d_i d_j d_k \sum_{m_i m_j m_k}[2kT\sum'_{m'_j} w_{ij}(m_i m_j;\ m_i m_j')w(m_j' m_k;\ m_j m_k)/(W_j(m_j')-W_j(m_j)$$

$$+ w_{ij}(m_i m_j;\ m_i m_j)w_{jk}(m_j m_k;\ m_j m_k)]\ \exp\left[-(W_i(m_i)+W_j(m_j)+W_k(m_k))/kT\right], \quad (70)$$

$$d_i = 1/\sum_{m_i}\exp\left[-W_i(m_i)/kT\right], \quad (71)$$

$$\alpha = \alpha^0 + \alpha^{(2)}H^2 + \cdots = \tfrac{1}{2}k^{-2}T^{-2}\sum_{i>j}d_i d_j \sum^=_{m_i m_j m' i m' j}|w_{ij}(m_i m_j;\ m_i' m_j')|^2\ \exp\left[-(W_i(m_i)\right.$$

$$+ W_{ij}(m_j))/kT] + k^{-1}T^{-1}\sum_{i>j}d_i d_j \sum'_{m_i m_j m' i m' j}\{\,|w_{ij}(m_i m_j;\ m_i' m_j')|^2/(W_i(m_i')+W_j(m_j')$$

$$- W_i(m_i)-W_j(m_j))]\ \exp\left[-(W_i(m_i)+W_j(m_j))/kT\right]. \quad (72)$$

In (68), we are to exclude values of k and l which are equal to either i or j, whereas this exclusion was not made in (67).

Calculation of Z^0 and the specific heat.—First we will consider the form of the partition function in the absence of the applied field H_0, and so deal with the portions Z^0, A^0, B^0 of Z, A, B. In computing (64), (65), (68) we may, of course, then use the moment matrix elements and the energies appropriate to $H_0=0$, which we may denote by $\mu_{qi}{}^0(m_i;\ m_i')$, $W_i{}^0(m_i)$ $(q=x,\ y,\ z)$. Now to every state with a given value of the moment, there exists in general a state of equal and opposite moment with the same energy as long as no external field is applied, and as long as the crystalline field has a center of symmetry at each atom, which we shall suppose to be the case. Thus we have

$$\sum_{m_i}\mu_{qi}{}^0(m_i;\ m_i)\ \exp\left[-W_i{}^0(m_i)/kT\right] = 0. \quad (73)$$

Eq. (72) for α is perfectly general. The various atoms need not be alike, and in particular can differ in the size and orientations of their crystalline fields—a not unusual situation since staggered arrangements are common in crystals. If we assume that all atoms are equivalent, i.e. have similar crystalline fields, then the subscripts i, j can be omitted from W, μ, d, etc. If, for simplicity, we further suppose that directions of r_{ij} are either oriented at random, or else that the paramagnetic ions are spaced in a simple, body or face-centered cubic field, without, however, the crystalline field necessarily having cubic symmetry, then we find

$$\alpha^0 = \tfrac{1}{4}N^3 Q k^{-2}T^{-2}d^2\sum_{q=x,\ y,\ z}\{[\sum_{m_i}\mu_q{}^0(m_i;\ m_i)^2\ \exp(-W^0(m_i)/kT)]^2$$

$$+ \sum_{m_i m_j(m_i\neq m_j)}|\mu_q{}^0(m_i;\ m_j)|^4\ \exp\left[-(W_i{}^0(m_i)+W_j{}^0(m_j))/kT\right]$$

$$+ 2kT\sum'_{m_i m_j m' i m' j}[\,|\mu_q{}^0(m_i;\ m_i')|^2|\mu_q{}^0(m_j;\ m_j')|^2/(W_i{}^0(m_i')-W_j{}^0(m_j')$$

$$- W_i{}^0(m_i)-W_j{}^0(m_j)]\ \exp\left[-(W_i{}^0(m_i)+W_j{}^0(m_j)/kT)]\}. \quad (74)$$

Here Q is defined as in (18–19–20). The second term in (74) arises because of the interchange degeneracy previously mentioned. If the crystalline field is not cubic, the mean square magnitudes of $\mu_x,\ \mu_y,\ \mu_z$ appearing in (74) need not be equal, unlike the case of free atoms considered in Section 4 where there was isotropy except for dipole-dipole forces.

Eq. (73) shows that $A^0=0$, $B^0=\alpha^0$. Consequently the specific heat is by (1), (64–5),

$$c_v = N\frac{d}{dT}\left[d\sum_{m_i}W^0(m_i)\ \exp(-W^0(m_i)/kT)\right] + \frac{d}{dT}\left[kT^2\frac{d\alpha^0}{dT}\right]. \quad (75)$$

Here the first term is simply the specific heat of an atom in the crystalline field alone, and arises

from the redistribution of atoms among the various Stark levels as the temperature is varied.[24] The second term is the specific heat due to dipole-dipole interaction between the atoms bound in the crystalline field.

Explicit formulas for α^0 for Fe^{+++} and Gd^{+++} are given in the following paper by Hebb and Purcell, along with graphs of the resulting dipole-dipole specific heat. The latter is, of course, quite different from that obtained with dipole coupling between free atoms, as the interaction is materially modified because the moments tend to be suppressed by the crystalline field as the temperature is lowered. In fact, Hebb and Purcell find that the dipole-dipole specific heat can become negative under certain conditions. This at first seems contrary to one's physical intuition, as one always thinks of a specific heat as necessarily being positive. However, this statement applies only to the total specific heat, i.e., both terms of (75), which is indeed always positive, but there is no reason why a partial specific heat, represented by the second term alone, cannot be negative. The physical reason is that at high temperatures the energy of dipole-dipole interaction is negative. As the temperature is lowered, the susceptibility is at least partially quenched by the crystalline field, and the energy of dipole-dipole interaction hence decreased in absolute magnitude or in other words raised towards zero. Such a rise in energy means a negative specific heat. We have verified that when the crystalline field is removed, (75) reduces to the portion of (35) of comparable approximation (i.e., τ^2), as should of course be the case. We shall omit details of the proof, which is based largely on a method of pairing terms given elsewhere by the author.[25]

Calculation of the susceptibility.—The leading coefficient A^0 in (66) was found to vanish because of (73). However, $A^{(2)}$ does not equal zero, as only the x and y parts of (73) are valid when $H_0 \neq 0$ (i.e., the zero superscripts can be removed only for $q = x, y$). Even use of the x, y portions of (73) is permissible only if the field is applied parallel to one of the principal axes of magnetic susceptibility, which we suppose to be the case.[26] Then

$$\sum_{j>i}(w_{ij})_{Av} = \sum_{j>i} r_{ij}^{-3}[1 + v_{ij} - 3\cos^2(z, r_{ij})](\mu_{zi})_{Av}(\mu_{zj})_{Av}, \tag{76}$$

with

$$(\mu_{zi})_{Av} = d_i \sum_{m_i} \mu_{zi}(m_i; m_i) \exp[-W_i(m_i)/kT]. \tag{77}$$

We shall now suppose that if there are several types of atoms, the "inner" or "local" field in a classical calculation is the same for each type of atom, so that we can take

$$\sum_j r_{ij}^{-3}[1 + v_{ij} - 3\cos^2(z, r_{ij})](\mu_{zj})_{Av} = (-N\Phi + Nvz')(\mu_z)_{Av}, \tag{78}$$

where Φ is defined as in (43), and where $(\mu_z)_{Av}$ is the mean of μ_{zi} over all the different types of atoms, weighted in accordance with their relative abundance. The approximation (78) will be warranted not merely in case the atoms are all alike, but, if we neglect exchange, also in case the paramagnetic neighbors of a given atom are spaced with cubic or spherical symmetry. Then the contributions to (78) will cancel for any sphere taken wholly inside the test body, and there will be a local field only in virtue of the nonspherical shape of the boundary. However, the noncancelling contributions come from regions so far from i that we can neglect the difference in the value of r_{ij}^{-3} contributed by the different species, and (77) is valid. Hence (66) becomes

$$A = -\sum_{j>i}(w_{ij})_{Av}/kT = -\tfrac{1}{2}k^{-1}T^{-1}N(-N\Phi + Nvz')[(\mu_z)_{Av}]^2. \tag{79}$$

Now $(\mu_z)_{Av}$ is the same as the moment M_0/N per atom at infinite magnetic dilution, i.e. the susceptibility in a system composed of atoms devoid of dipole-dipole coupling, but subject to crystalline fields. As already mentioned, the determination of M_0/N is a one-atom problem. By (3), (64), and

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[24] If various classes of atoms are present, we must, of course, prorate the first term in (75), also the N-triple product in (65), among the various types.

[25] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, p. 161.

[26] If there are various types of atoms there is the possibility that different classes have different principal axes. Consideration of such an unpleasant complication is, however, not worthwhile until crystalline fields are known much more precisely than at present.

(79) the moment is

$$M = kT\partial \log Z_0/\partial H_0 + M_0(\partial M_0/\partial H_0)(\Phi - vz') = M_0 + M_0(\partial M_0/\partial H_0)(\Phi - vz'), \tag{80}$$

provided we neglect B in (64), i.e., provided we disregard squares and higher powers of the dipole-dipole interaction. The reader should be careful to distinguish between M and M_0. Namely M is the actual moment, while M_0 is the moment which would result were dipole-dipole and exchange coupling neglected. Now, except for the exchange term v, (80) is exactly the moment which would be obtained by the Lorentz method of the local field, provided we disregard second and higher powers of Φ. Namely in the method of local fields

$$M = M_0(H_0 + \Phi M) = M_0(H) + (\partial M_0/\partial H_0)\Phi M_0 \quad \text{to first powers of } \Phi. \tag{81}$$

We thus see that the local field is correct in the first approximation. Our demonstration has been very general, in that we have used quantum mechanics rather than classical theory to describe the interaction of the various dipoles or magnetic moments and have used a perfectly arbitrary atomic model subject to an arbitrary crystalline field. Furthermore, unlike the calculation in Section 4, our proof has included saturation, as it has not been necessary to stop with quadratic terms in H_0 in the expansions (66–67), the complete expressions being used instead.

Second or Gaussian approximation.—When squares of the dipole-dipole interaction are included, the formula for the moment becomes

$$M = \chi_0 H/[1 - (\Phi - vz')\chi_0 + (Q\chi_0{}^2 - 2\alpha^{(2)}\chi_0{}^{-1}kT)], \tag{82}$$

where $\alpha^{(2)}$, Q are defined as in (72), (18) and $\chi_0 = M_0/H$ is the susceptibility at infinite magnetic dilution, i.e., exclusive of dipole-dipole interaction but inclusive of the crystalline field. Here for simplicity we have neglected saturation, and assumed that the atoms are all alike. Eq. (82) is derived from (64–72) in much the same manner as (56) from (46), and the two formulas represent comparable approximations in their respective cases. Thus (82) represents an accuracy comparable with assuming a Gaussian distribution of energies, as explained in Section 5. The portion $2\alpha^{(2)}\chi_0{}^{-1}kT$ of (82) comes from the last or third term in the formula for B in (68). The first term in this formula does not contribute until fourth powers of the field strength (incipient saturation) are considered. The second term is, as in (51), conveniently handled by adding and subtracting the excluded members; the subtracted part gives rise to $Q\chi_0{}^2$ in (82). Even without exchange corrections v, (82) is not the same as the formula given by the usual local field theory. The latter has

$$M = \chi_0(H_0 + \Phi M), \quad \text{i.e.,} \quad M = \chi_0 H_0/(1 - \chi_0\Phi). \tag{83}$$

We have verified that (82) reduces to (56) for free atoms. In general, however, with even the simplest crystalline fields present, the explicit numerical formulas for $\alpha^{(2)}$ prove to be exceedingly cumbersome and laborious to obtain, so that (82) would not be useful even were the Gaussian approximation a good one. An exception to this statement arises if the crystalline potential has cubic symmetry, and the temperature is so low that only the lowest cubic level need be considered. If $2D+1$ be the degeneracy of this level, and if its Zeeman components be $W - W^0 = -H_0 g'\beta D$, $-H_0 g'\beta(D-1), \cdots, Hg'\beta D$, then the behavior is mathematically similar to that for free atoms, and so can be handled by the theory of Sections 3–4, provided J be replaced by D and g by g'.[27] This correspondence is established by noting the similarity in the Zeeman patterns and in the elementary magnetic moment matrices.

The above observations enable one to devise a simple approximate interpolation formula for $\alpha^{(2)}$ in (82) in the intermediate temperature region in which the temperature dependence of χ_0 deviates from the simple Curie form because of the crystalline field of dominantly cubic symmetry. Suppose that we have an atom whose angular momentum (spin only in the iron group, total in the rare earths) can be regarded as free at room temperatures, but which at low temperatures has its susceptibility so quenched that only a cubic level of degeneracy $2D+1$ is

[27] We use the notation g' rather than g because with crystalline fields the proportionality factor in the Zeeman formula is no longer necessarily the same as the gyromagnetic ratio g.

inhabited. The considerations of the preceding paragraph and Eq. (56) show that the asymptotic values of $2\alpha^{(2)}kT/\chi_0{}^3$ for low and high (room temperatures) are, respectively, $-Q(x_D-1)$ and $-Q(x_J-1)$. Here x_J is the value of x obtained by using in (55) the true inner (or in iron group, spin) quantum number J of the atom, while x_D denotes the expression (55) with D substituted for J. Presumably $\alpha^{(2)}/\chi_0{}^3$ varies monotonically between its limiting values. Moreover, the variation in x is not large; its range is a maximum in the case $D=\frac{1}{2}$, $J=\infty$, where $x_D=3/2$, $x_J=1$ if we neglect exchange. Also the effect of the last term in the denominator of (82) is either subordinate, or else (82) is only a rough approximation because of the poor convergence of the development of the partition function. So not much harm will be done if we use almost any interpolation formula for $\alpha^{(2)}/\chi_0{}^3$. The simplest is

$$-2\alpha^{(2)}kT/\chi_0{}^3Q=x_D-1$$
$$+[(x_J-x_D)(T\chi_0-C_2)/(C_1-C_2)], \quad (84)$$

where C_1 and C_2 are, respectively, the asymptotic values of $\chi_0 T$ characteristic of high and low temperatures.

Generalized Onsager formula.—Instead of using (82, 84) it is usually more satisfactory to employ a generalization of Onsager's formula obtained by defining ψ as $4\pi\chi_0$ in (58). He derived the result (58) only for free permanent dipoles, where $\chi_0=N\mu^2/3kT=\tau/3T$. That actually his formula can be used for such dipoles even in a crystalline field, provided we take $\psi=4\pi\chi_0$, can be seen from the following argument. Onsager's[21] local field is

$$\mathbf{F}=[3\kappa/(2\kappa+1)]\mathbf{H}_i+\tfrac{1}{3}N[8\pi(\kappa-1)/(2\kappa+1)]\mathbf{u},$$
$$(85)$$

where κ is the permeability $1+4\pi M/H$ and where $\mathbf{u}$ is the dipole moment vector of the given atom or molecule. The corresponding terms added to the potential function per atom[28] are

$$\Delta V=-[3\kappa/(2\kappa+1)]\mathbf{u}\cdot\mathbf{H}_i$$
$$-\tfrac{1}{3}N[4\pi(\kappa-1)/(2\kappa+1)]\mathbf{u}^2. \quad (86)$$

Now as long as the molecule has a permanent dipole moment, $\mathbf{u}^2$ will have an invariant constant value μ^2 for all stationary states. This will be the case if only one multiplet component is effective, (Eq. (6)), regardless of how complicated the splitting of this component due to the

crystalline Stark field may be. Consequently the second part of (85), which Onsager calls the reaction field (cf. Fig. 1), merely introduces an additive constant term in the energy, and one need retain only the first part of (85) or (86) in dealing with the susceptibility.[29] Then

$$M=\chi_0F=3\kappa\chi_0H/(2\kappa+1). \quad (87)$$

Also by definition

$$\kappa=1+4\pi M/H. \quad (88)$$

Elimination of κ between (87) and (88) shows that (58) applies with $\psi=4\pi\chi_0$.

Specific heat by Onsager's method.—Though the second member of (86) is unimportant for susceptibility if μ^2 is permanent, this portion of (86) persists even when $H=0$ and so gives rise to a field-free specific heat c_v. As kindly pointed out to me by Dr. Hebb, the Onsager procedure is clearly preferable in this respect to that of Lorentz, which furnishes no c_v at all. Now according to classical statistical mechanics the susceptibility χ_0 at infinite magnetic dilution is $N(\mathbf{u}^2)_{Av}/3kT$, where the average is a Boltzmann one over the various molecules.[30] It is to be emphasized that this relation, though seldom given is quite general, not being confined to the case of a permanent dipole moment, where the average is clearly unnecessary. (For example, with harmonic oscillators, the mean square amplitude, and hence the average of $\mathbf{u}^2$, is propor-

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[28] The easiest way to establish (86) is to note that the external force acting on a dipole may be written as $\mathbf{u}\cdot\nabla\mathbf{F}$. The result (86) then follows since force is the negative gradient of the potential and since, except for an unimportant diamagnetic correction, $\mathbf{u}=\Sigma e_i[\mathbf{r}_i\times\mathbf{P}_i]/2m_ic$ or (in the electric case) $\mathbf{u}=\Sigma e_i\mathbf{r}_i$.

[29] When crystalline fields are present, it is probably a better approximation to replace $\mathbf{u}^2$ by $3kT\chi_0/N$ in the second member of (86). This change is suggested because in quantum mechanics the square of only the "low frequency" part of the moment makes an important contribution to the susceptibilities, whereas the Onsager model, being classical, gives weight to the square of the entire moment. Since with a crystalline potential χ_0 varies from state to state, the second part of (86), thus modified, can no longer be regarded as an additive constant in computing the susceptibility, and has the effect of displacing the field-free energy levels. At the present state of our knowledge this alteration is of no particular consequence, because the crystalline potential contains enough unknown parameters so that the positions of the energy levels may be considered arbitrary. It does not enter in classical theory inasmuch as with the latter μ^2 and $3kT\chi_0/N$ are identical for permanent dipoles in crystalline fields provided only there is a center of symmetry (cf. Stoner, *Magnetism and Atomic Structure*, p. 176). Thus for permanent dipoles, (91) is the same as (92) at low densities in classical theory even with a crystalline potential, but in quantum mechanics only without the latter. With the potential, (91) is required rather than (92) in quantum theory, because the mode of derivation of (91) implicitly includes the modifications proposed in the present footnote.

[30] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Section 13.

tional to T, and so χ_0 is independent of temperature.) Thus when $H=0$ we have

$$(\Delta V)_{\mathrm{Av}} = -kT[4\pi(\kappa-1)/(2\kappa+1)]\chi_0. \quad (89)$$

The corresponding value of the free energy is

$$F = -4\pi NkT \int_0^{\chi_0} [(\kappa-1)/(2\kappa+1)]d\chi_0. \quad (90)$$

The reader is referred to Fowler's *Statistical Mechanics*[31] for a detailed discussion of the rather delicate arguments involved in the derivation of (90) from (89). His presentation is primarily in connection with the Debye-Hückel theory, but can be immediately adapted to our problem. In fact, the Onsager model shows considerable resemblance to the Debye-Hückel one, with of course the difference that the force centers are dipoles rather than ions, and are uniformly rather than statistically distributed in space. In particular, to get (90), the quantity χ_0 can be taken as proportional to Fowler's parameter σ whose growth corresponds to the step-by-step assembly of the system. In (90), κ is then to be regarded as a function of χ_0 obtained by elimination of M between (87) and (88). The specific heat is (cf. Eqs. (1)–(2))

$$c_v = -\frac{d}{dT}\left[T^2\frac{d(F/T)}{dT}\right]$$

$$= 4\pi Nk\frac{d}{dT}\left[T^2\frac{(\kappa-1)}{(2\kappa+1)}\frac{d\chi_0}{dT}\right]. \quad (91)$$

At sufficiently high temperatures or low magnetic densities we may replace $(\kappa-1)/(2\kappa+1)$ by $\frac{1}{3}4\pi\chi_0$. In the case of free dipoles, where $\chi_0 = N\mu^2/3kT$, Eq. (91) then becomes

$$c_v = 16\pi^2 N^3\mu^4/27kT^2 = Nk(16\pi^2\tau^2/27T^2). \quad (92)$$

This expression is the same as the first term in the formula (35) for c_v obtained by the method of partition functions, provided one uses the value (60) of Q corresponding to a continuum. (In this connection one recalls that μ^2 is the same as $g^2\beta^2 J(J+1)$ and that with an arbitrary model the factor 2.8 in (35) is replaced by $\frac{1}{6}Q$ as remarked after Eq. (35)). Thus again there is a

[31] R. H. Fowler, *Statistical Mechanics*, second edition, pp. 267–9.

gratifying agreement between the Onsager procedure and the exact treatment in the early stages of approximation. This agreement incidentally, is not confined to the case of permanent dipoles, as it can be shown that a general calculation with classical statistics, made by combining the methods of Section 3 and reference 30, yields a formula which is the same as (91) at low densities. For instance, with harmonics oscillators, where $d\chi_0/dT=0$, Eq. (91) yields $c_v=0$, as should be. Eq. (91) ceases to have so exact a basis when quantum mechanics are substituted for classical, but detailed examination of this question shows that any inaccuracy in (91) due to this cause is usually subordinate to the error inherent in the use of any model such as Onsager's. So (91) can be regarded as a convenient formula for c_v. In particular, (91) possesses the satisfactory property of yielding a finite specific heat at $T=0$ even for permanent dipoles, whereas (35) or (92) do not. Also under proper conditions, Eq. (91) can yield a negative dipole-dipole specific heat, which sometimes occurs as mentioned after Eq. (75). If a crystalline field is present, Eq. (91), but not (92), still gives the dipole-dipole contribution to c_v; the first term of (75) must, however, be added to include the part of c_v due to the ordinary action of the field on individual atoms.

It must be cautioned that both for susceptibility and specific heat the initial agreement between the Onsager and kinetic methods is secured only by the rather artificial assumption that the cavity volume equals the mean atomic volume. As a matter of fact, the value (60) of Q is over twice those (20) furnished by actual discrete arrangements. The specific heat formulas are easily, though somewhat arbitrarily, adapted to lower values of Q simply by reducing the expressions (89–92) by a factor $9Q/32\pi^2$. The corresponding patching of the susceptibility formulas is a little more complicated and will be given in a later paper on dielectric constants (after its Eq. (7)).