

DIPOLE INTERACTIONS IN CRYSTALS

by

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## I Introduction

Various problems in theory of solids lead to the consideration of interactions among dipoles. Typical examples are the dielectric and thermal behavior of certain crystals containing polar molecules and of most of the substances used in experiments on adiabatic demagnetization. The paramagnetic substances which are suitable for these experiments must contain magnetic moments whose freedom of orientation is practically unhampered by interactions. This requirement is satisfied by magnetic ions which contain an odd number of electrons. In fact, there is a theorem, due to Kramers<sup>1</sup>, which states that magnetic ions, consisting of an odd number of electrons, maintain a double degeneracy in any electrostatic field. Therefore, in this case, the usually important Stark effect is ineffective. Nernst's theorem requires, however, that some mechanism should exist which will split the degeneracy. This splitting will actually take place by means of the direct magnetic (dipole-dipole) forces between ions, or through exchange forces. The latter, although electrostatic in origin, are not purely electrostatic in nature and it is not in conflict with Kramer's theorem to have these forces removing the degeneracy. Of these two forces, it is almost certain that the dipole coupling is more important in the paramagnetic salts usually used. Moreover, in contrast to most types of interaction, the dipole coupling contains no unknown constants which refer to the atomic or crystalline structure of the substance. Thus, the calculation of the magnetic interaction energies and of the partition is of added interest because there is the possibility of it being carried completely

through.

At present, the theory of dipole interactions in crystals is in a rather unsatisfactory state. The simplest approach is that of the Lorentz local field but this method leads to very serious difficulties.<sup>2</sup> We will not enter into a discussion of this field, or of its consequences, but only mention in passing that it predicts a great many substances should behave ferroelectrically. In reality, such behavior is never observed. Another approach to the problem has been made by Onsager.<sup>3</sup> The model is again a local field one (i.e. the effect of each of the dipoles on a single dipole is replaced by an average field at the dipole) and although it removes some of the difficulties of the Lorentz field, it is by no means a satisfactory theory. While the Lorentz field predicts too many transition points, the Onsager field predicts too few. (In fact, it will never produce a transition because the local field is always taken parallel to the dipole in question and can, therefore, have no orienting effect upon it.) For a critical discussion of this method, we refer the reader once more to the article of Van Vleck.<sup>2</sup>

The first rigorous treatment of the problem seems to be due to Waller.<sup>4</sup> This method was also independently developed by Van Vleck.<sup>2</sup> The idea here is to expand the partition function in inverse powers of the temperature, the coefficients of the first few terms being fairly simple to evaluate. The method is a rigorous quantum mechanical one and is certainly valid at high

temperatures ( $kT \gg$  dipole interaction energy.) However, the region of principal interest is low temperatures and it is precisely here that the method fails utterly. This is due to poor convergence of the series in question. That this is so is seen most clearly in a paper by Van Vleck on Cs-Tl alum,<sup>5</sup> where he shows that retaining the first few terms of the expansion leads to completely absurd results, i.e. a negative specific heat.

Other attempts<sup>6</sup> have been made to develop a theory valid for arbitrary temperature and field strength with no satisfactory results. In general, one would expect any "nearest neighbor" method to fail, not only because of the long range of the dipole forces, but also because of their peculiar directive nature. The latter would tend to make averaging over direction a poor approximation.

An entirely different sort of calculation has been performed by Sauer.<sup>7</sup> He computed the energies of certain intuitively selected dipole arrays by direct summation of the dipole interaction energies. It is clearly evident from his calculations that the energy of an array is not a function of its magnetization only (as would be predicted by the Lorentz local field) as he found that different arrays of polarization may have widely different energies.

The purpose of the present paper is to develop a new method of attacking the problem of dipole interaction in crystals. In Section II, we shall develop a simple and rigorous "normal coordinate" method of calculating the energies of

dipole arrays. The fact that the dipole moments of the individual ions enter the formula for the interaction energy quadratically enables us to reduce the entire problem to the diagonalization of a certain quadratic form, i.e. to an eigenvalue problem. Here, group theory may be employed to advantage in determining the eigenvectors of the characteristic matrix. We shall then apply it to the determination of the minimum energy arrays with and without external magnetic field. This is made possible by superposition theorems for the arrays which allow us to "add" arrays as vectors in a vector space, the energies also being additive. The method is demonstrated by the complete solution for a very symmetrical class of simple cubic (S.C.) arrays and the results are then extended to the body centered (B.C.) cubic and face centered (F.C.) cubic. Detailed numerical calculations are also given for the above three cases.

In Section III, we discuss the quantum mechanics of the model given above. Here a general theorem is proven relating quantum mechanical expectations and classical values. By means of simple examples, the nature of the quantum mechanical problem is investigated.

In Section IV, we discuss the statistical mechanics of a dipole array. Here, an approximate method is developed for treating the problem. It is applicable only in the region where deviations from the completely ordered case are small. This does not necessarily mean low temperatures but implies that the ratio of acting field, whether internal or external, to temperature is large. This calculation is given classically and "half" quantum mechanically, the quantum procedure being

that given previously by Kramers and Heller<sup>8</sup> for a problem in ferromagnetism. The problem falls naturally into two parts; first, when the external field is large compared to the interactions and second, when it is small. These problems are treated separately. All the calculations of this section refer to simple cubic arrays only.

Finally, in Section V, we discuss the possible application of our results to experiment. In particular, we consider the experiments of DeHaas and Wiersma<sup>9</sup> on the adiabatic demagnetization of Cs-Ti alum in the light of our theory.

## II ENERGY CONSIDERATIONS

### 1) The Energy of a General Dipole Array

Let us first consider S.C. dipole arrays obtained from S.C. lattices by placing a dipole of definite moment and direction at every lattice point (l.p.). Dimensionless quantities will be used throughout this paper. Dipole moments will be measured in terms of an arbitrary dipole moment  $\mu$ , length in terms of the lattice constant  $a$ . All magnetic (or electric) fields will be expressed in units of  $\mu/a^3$  and energies per unit volume in terms of  $N\mu^2$ , where  $N$  is the number of dipoles per unit volume. (In the S.C., B.C. and F.C. cases one has  $N = 1/a^3, 2/a^3, 4/a^3$ , respectively.)

In terms of these units, the energy  $\mathcal{H}$  of any array may be written:

$$\mathcal{H} = \frac{1}{2} \sum'_{m,n} \frac{\mathcal{L}^2(\mu_m \cdot \mu_n) - 3(\mathcal{L} \cdot \mu_m)(\mathcal{L} \cdot \mu_n)}{\mathcal{L}^5} \quad (1)$$

where  $\sum'_{m,n}$  means a summation over all integral values of  $m = (m_1, m_2, m_3)$  and  $n = (n_1, n_2, n_3)$  such that  $m \neq n$ .  $\mathcal{L}$  is the distance between the points  $m$  and  $n$ , i.e.  $\mathcal{L} = (m_1 - n_1, m_2 - n_2, m_3 - n_3) \equiv (\mathcal{L}_1, \mathcal{L}_2, \mathcal{L}_3)$  and  $\mu_m = (\mu_m^1, \mu_m^2, \mu_m^3)$  is a unit vector in the direction of the  $m^{\text{th}}$  dipole.

We may write equation (1) in the form

$$\mathcal{H} = \sum_{m,n} \mu_m^i \mathcal{H}_{mn}^{ij} \mu_n^j \quad (2)$$

$i, j = 1, 2, 3$

where  $\mathcal{H}_{mn}^{ij}$  defines a matrix whose elements are given by:

$$H_{mm}^{ij} = 0 \quad \text{for all } m$$

$$H_{mn}^{ij} = \frac{l^2 \delta_{ij} - 3l_i l_j}{2l^5} \quad \text{for } m \neq n \quad (3)$$

From the definition (3), it immediately follows that

$$H_{mn}^{ij} = H_{nm}^{ji} \quad (4)$$

Now, if we regard the set of numbers  $\mu_m^i$  as forming a column vector  $\underline{\mu}$ , we have (by (2)) that the energy  $H$  is a quadratic form <sup>10</sup> in the components of  $\underline{\mu}$ . If we denote the matrix  $H_{mn}^{ij}$  by  $\underline{W}$ , we may write (2) in the form

$$H = \underline{\tilde{\mu}} \underline{W} \underline{\mu} \quad (5)$$

the indicated multiplications being matrix multiplications and  $\underline{\tilde{\mu}}$  representing the transpose of  $\underline{\mu}$ . To diagonalize this quadratic form, we make the following substitution

$$\underline{\mu} = \sum_{n,j} \xi_n^j \underline{\psi}_n^j \quad (6)$$

where  $\underline{\psi}_n^j$  is the  $(j,n)^{\text{th}}$  eigenvector of the matrix  $\underline{W}$ .

That we may expand an arbitrary vector  $\underline{\mu}$  in the eigenvectors of  $\underline{W}$  follows from well known theorems since  $\underline{W}$  is a real, symmetric matrix. Substitution of (6) into (5) yields

$$\begin{aligned} H &= \left( \sum_{n,j} \xi_n^j \underline{\tilde{\psi}}_n^j \right) \underline{W} \left( \sum_{i,m} \xi_m^i \underline{\psi}_m^i \right) \\ &= \sum_{\substack{m,n \\ i,j}} \xi_m^i \xi_n^j \left( \underline{\tilde{\psi}}_n^j \underline{W} \underline{\psi}_m^i \right) \end{aligned}$$

but by definition of  $\underline{\psi}_m^i$ , we have

$$\underline{W} \underline{\psi}_m^i = \lambda_m^i \underline{\psi}_m^i \quad * \quad (7)$$

Further, we may always choose the  $\underline{\psi}_m^i$  so that they are orthogonal and normalized, i.e. so that

$$\underline{\tilde{\psi}}_m^i \underline{\psi}_{m'}^{j'} = \delta_{jj'} \delta_{mm'} \quad (8)$$

Substituting these in our expression for  $\mathcal{H}$  we obtain

$$\begin{aligned} \mathcal{H} &= \sum_{\substack{m, n \\ i, j}} \xi_m^i \xi_n^j \underline{\tilde{\psi}}_m^i \lambda_n^j \underline{\psi}_n^j \\ &= \sum_{j, m} \lambda_m^j (\xi_m^j)^2 \end{aligned} \quad (9)$$

That is, if we consider our new variables  $\xi_m^j$  as the independent variables, we have reduced the energy expression to a sum of squares. If now the  $\lambda_m^j$  and  $\underline{\psi}_m^j$  were known, we could calculate the energy of any dipole array immediately from (9). The

$\xi_m^j$  would be given in the usual way, i.e. multiplying (6) by  $\underline{\tilde{\psi}}_m^i$  we get

$$\xi_m^j = \underline{\tilde{\psi}}_m^j \underline{\mu}$$

---

\* The  $\lambda_m^j$  are the eigenvalues of  $\underline{W}$ .

and (9) becomes

$$H = \sum_{j,n} \lambda_n^j (\tilde{\Psi}_n^j \underline{\mu}) \quad (10)$$

(10) is an explicit formula for the energy of any dipole array requiring only the knowledge of the eigenvectors and eigenvalues of a certain matrix  $\underline{W}$ .

To find these, let us consider the eigenvalue equation

$$\underline{W} \underline{\chi} = \lambda \underline{\chi}$$

Written out in components, this takes the form

$$\sum_{j,n} H_{mn}^{ij} \chi_n^j = \lambda \chi_m^i \quad (11)$$

$\chi_m^i$  being the  $(j,n)^{\text{th}}$  component of  $\underline{\chi}$ . Now it follows from group theory or simply from substitution <sup>12</sup> that since  $H_{mn}^{ij}$  is a function only of  $|m-n|^2$ , the eigenvectors must have the form

$$\chi_m^j = \eta^j(\sigma) e^{\frac{2\pi i}{G}(\sigma \cdot m)} \quad (12)$$

where  $\sigma = (\sigma_1, \sigma_2, \sigma_3)$ ,  $G$  is the length of the sample along any one of the crystallographic directions and  $\eta^j(\sigma)$  are a set of numbers independent of  $m$ . Periodic boundary conditions now require that  $\sigma_i$  is an integer. In order to obtain the proper number of solutions, we restrict  $\sigma_i$  to the values  $0 \leq \sigma_i \leq G-1$ .

Substitution of (12) into (11) now gives:

$$\lambda \eta^i(\sigma) e^{\frac{2\pi i}{G}(\sigma \cdot m)} = \sum_{n,j} H_{mn}^{ij} \eta^j(\sigma) e^{\frac{2\pi i}{G}(\sigma \cdot m)}$$

or 
$$\lambda \eta^i(\sigma) = \sum_{m,j} H_{mn}^{ij} \eta^j(\sigma) e^{\frac{2\pi i}{G}(\sigma \cdot (m-n))}$$

or 
$$\lambda \eta^i(\sigma) = \sum_{j=1,2,3} Q^{ij}(\sigma) \eta^j(\sigma) \tag{13}$$

where

$$\begin{aligned} Q^{ij}(\sigma) &= \sum_n H_{mn}^{ij} e^{-\frac{2\pi i}{G}(\sigma \cdot (m-n))} \\ &= \sum_{\substack{n \\ n+m}} \frac{l^2 \delta_{ij} - 3l_i l_j}{2l^5} e^{-\frac{2\pi i}{G} \sigma \cdot l} \\ &= \sum_{\substack{n \\ n \neq 0}} \frac{m^2 \delta_{ij} - 3m_i m_j}{2m^5} e^{-\frac{2\pi i}{G} m \cdot \sigma} \end{aligned} \tag{14}$$

if we neglect surface effects. Since (14) is independent of  $m$  or  $n$ , we have reduced the problem of finding the eigenvalue of  $\underline{W}$  to that of finding the eigenvalues of  $Q^{ij}(\sigma)$ . The latter is only a three by three matrix and therefore, the problem is (in principle) solved. The eigenvalues will be given as roots of the secular equation  $|Q^{ij}(\sigma) - \lambda \delta_{ij}| = 0$  from which we may determine the  $\eta^j(\sigma)$ . The  $\eta^j(\sigma)$  will fall into three sets  $\eta_k^j(\sigma)$  ( $k = 1, 2, 3$ ), which we choose orthogonal and normalized so that the total eigenvector is normalized to 1. If we label the eigenvector by  $(k, \sigma)$ , we have for the  $(j, n)^{th}$  component

$$\chi_{\sigma n}^{kj} = \eta_k^j(\sigma) e^{\frac{2\pi i}{G} n \cdot \sigma} \tag{15}$$

---

\* The three eigenvectors which correspond to a given  $\sigma$  may be thought of as corresponding to the three different polarizations of a sound wave in a solid. Since the forces in this case are anisotropic, one cannot simply break these waves up into transverse and longitudinal ones, but one must work with superpositions as the proper modes.

From these eigenvectors, it would be possible to form a set which are real. This is equivalent to the transition from the Fourier series in complex form to the ordinary Fourier series in sine and cosine. However, for simplicity's sake, we leave the result in the form (15.)

Unfortunately, the general relationships just given are rather hard to deal with. To obtain concrete results, we shall have to specialize them. The cases we shall study are those arrays for which  $\sigma_i = 0 \sim \frac{G}{2}$ . In the S.C. case, there are 24 such arrays which we shall name  $\Gamma^2$  basic arrays (B.A.)

These arrays have the property of being left invariant by any translation of the lattice by two lattice spacings.\* Because of the great simplicity of this special case, we shall develop for it a special formalism rather than derive the properties from the general equations given above.

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\*

There are good reasons to believe that the configurations of lowest (and highest) energy are of the class  $\Gamma^2$ . All previously calculated arrays (for example, by Sauer) are of this class. No rigorous proof of this statement seems to be possible however before a thorough investigation of the matrix elements  $Q^i(\kappa)$  is made. The series which represent them may be transformed into  $\mathcal{V}$ -functions (this has been independently noticed by H. Primakoff-private communication to Dr. C. Kittel in another connection) but as yet we have not been able to utilize this transformation in establishing the result above.

2) Vector Space Representations of  $\Gamma^2$  Dipole Arrays

Let  $\Gamma$  be the group of cubic translations

$l_1 \underline{i} + l_2 \underline{j} + l_3 \underline{k}$  ( $l_1, l_2, l_3$  are integers,  $\underline{i}, \underline{j}, \underline{k}$  are unit vectors in the x,y,z directions respectively.)

The most completely symmetrical arrays are invariant under the same group, i.e. all their dipoles are equal and parallel. (This situation corresponds to  $\sigma_1 = \sigma_2 = \sigma_3 = 0$  in our former notation.) These arrays are of importance in building up others and will be called S arrays. The dipole interaction energy of an S array is  $-1/2 (4\pi/3 - \ell)$ , where  $\ell$  is the demagnetization coefficient. For a spherical sample  $\ell = 4\pi/3$  and the energy vanishes. A more general class of arrays is obtained if invariance is required only under the subgroup  $\Gamma^2$  of  $\Gamma$  consisting of the translations of the form  $l_1 (2\underline{i}) + l_2 (2\underline{j}) + l_3 (2\underline{k})$ . These are the  $\Gamma^2$  arrays and will be the only ones considered in this paper. They correspond as mentioned above to  $\sigma_1 = 0$  or  $\frac{4}{2}$ .

To generate such arrays, we have to specify 8 dipoles  $p^\nu$  ( $\nu = 1, 2, \dots, 8$ ), where  $\nu$  is associated in some definite manner with corners of the unit cube having the coordinates  $l_1, l_2, l_3 = 0, 1$ . The whole array is constructed by the translations  $\Gamma^2$ .

The resulting array may be considered as a superposition of eight arrays each of which consists of parallel dipoles. These arrays are geometrically similar to the S arrays previously introduced but have a lattice constant two (in units of a). These shall also be called S arrays; in case of ambiguity, the

lattice constant will be specified. This point of view will be useful for the numerical calculations of 3.)

It is seen that every array of class  $\Gamma^2$  can be specified by a set of 24 numbers, e.g., the three rectangular components of the 8 dipole moments  $p_x^\nu, p_y^\nu, p_z^\nu$   $\nu=1,2,\dots,8$ . Also, in a more concise notation  $p_i, i=1,2,\dots,24$ .

In the cases of practical interest, the dipoles placed at the 8 cube corners will have moments of the same absolute value which will be denoted by  $p$ . For such an array, the 24 numbers satisfy the 8 conditions

$$(p_x^\nu)^2 + (p_y^\nu)^2 + (p_z^\nu)^2 = p^2 \quad \nu = 1, 2, \dots, 8 \quad (16)$$

It will, however, prove advantageous to temporarily disregard these conditions and admit arrays of unequal dipole moments into the class  $\Gamma^2$ . In this case, every set of 24 real numbers defines a  $\Gamma^2$  array and there is a one to one correspondence between these arrays and the points of a 24-dimensional vector space  $\mathcal{R}$ . The arrays satisfying the conditions (16) will be called arrays of constant (dipole) strength  $p$ . The corresponding points form a 16-dimensional hypersurface in  $\mathcal{R}$ . This will be frequently used in what follows and will be briefly called the "constant dipole surface."

\*

The dipole strength of our array should be distinguished from its resultant dipole moment. The latter is proportional to the vector sum of the moments of the 8 cube corners.

The operations of addition multiplication with a scalar and taking the scalar product are defined in the usual manner.\*

$$\begin{aligned}
 (a) \quad \vec{P} + \vec{Q} &= \{ \vec{p}^{\nu} + \vec{q}^{\nu} \} \\
 (b) \quad c\vec{P} &= \{ c\vec{p}^{\nu} \} \\
 (c) \quad \vec{P} \cdot \vec{Q} &= \sum_{\nu=1}^8 \vec{p}^{\nu} \cdot \vec{q}^{\nu}
 \end{aligned}
 \tag{17}$$

The square of the norm of an array  $P$  is defined as

$$\vec{P} \cdot \vec{P} = \sum_{\nu=1}^8 (\vec{p}^{\nu})^2
 \tag{18}$$

If the array  $\vec{P}$  is of constant strength  $p$ , its norm is  $8^{\frac{1}{2}}p$ .

In order to compute the energy of an array  $\vec{P}$ , it is necessary to know the field generated by  $\vec{P}$  at all the lattice points. Obviously, the field will have the same symmetry ( $r^2$ ) as the array. Hence, the set of vectors representing the field at the lattice points will again correspond to a vector in the space  $\mathcal{R}$ , and will be denoted by  $\vec{F}$ .

The operation leading from any array  $\vec{P}$  to its field  $\vec{F}$  can be regarded as a mapping of the space  $\mathcal{R}$  on itself. One may write symbolically

$$\vec{F} = \mathcal{J} \vec{P}
 \tag{19}$$

where  $\mathcal{J}$  is the "field operator." It is linear, as follows at once from the well-known expression for the field  $\vec{f}$  of a dipole  $\vec{p}$  at a point  $\vec{r}$ :

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\* Boldfaced small letters will denote ordinary 3-dimensional vectors and boldfaced capital letters vectors in the 24-dimensional vector space.

$$\vec{f} = (3\vec{r}(\vec{p} \cdot \vec{r}) - \vec{p}r^2)/r^5 \quad (20)$$

The dipole interaction energy per unit volume is \*

$$U = -1/16 \vec{P} \cdot \vec{F} = -(1/16) \vec{P} \cdot \mathcal{F} \vec{P} \quad (21)$$

Equation (21) is an invariant relation independent of the choice of coordinate system. If, as above, we choose a coordinate system in which the array is represented by the rectangular components of the 8 dipole moments then one may rewrite Eq.(21) in matrix form:

$$U = -\frac{1}{16} \sum_{\mu, \nu} \sum_{x, y} \mathcal{F}_{\mu\nu}^{xy} p_x^\mu p_y^\nu \quad (22)$$

The matrix  $\mathcal{F}_{\mu\nu}^{xy}$  satisfies the symmetry relation

$$\mathcal{F}_{\mu\nu}^{xy} = \mathcal{F}_{\nu\mu}^{yx} \quad (23)$$

This is a direct consequence of the existence of a potential energy for two dipoles; the energy can be considered as scalar product of the first dipole moment with the field due to the second or vice versa. (Cf. equation (19) above.)

It is sometimes convenient to write (22) and (23) in a more concise form by replacing the index couple  $(\mu, x)$  by a single index  $i$  running from 1 to 24.

One has \*\*

$$U = -\frac{1}{16} \sum_{i, j=1}^{24} \mathcal{F}_{ij} p^i p^j \quad (22a)$$

\* The numerical factor in this expression is explained as follows: the energy per unit volume is in our units the energy of one dipole while (6) involves 8 dipoles. The additional factor  $\frac{1}{2}$  corrects in the usual manner the fact that the interaction of every pair of dipoles is counted twice.

\*\* In case of vectors in the space  $\mathcal{R}$  superscripts describe components and subscripts distinguish between different vectors.

The quadratic form (22) can be transformed into a sum of squares by means of an orthogonal transformation of the coordinate system in  $\mathcal{R}$  which leaves (18) invariant (rotation).  
 The new coordinate system will be given by an orthogonal set of vectors  $\vec{A}_i, i = 1, 2, \dots, 24$ , which will be called basic arrays (B.A.). These are closely analogous to the normal coordinates introduced for the description of vibrating systems. The calculation of the energy of an arbitrary array can then be reduced to finding the characteristic values of the operator  $\mathcal{J}$ . This problem is greatly facilitated by group theoretical methods, based on the remark that the operator  $\mathcal{J}$  is invariant under the group  $\Gamma$ .

$$\Gamma \mathcal{J} = \mathcal{J} \Gamma \tag{24}$$

This relation is intuitively evident, as it is immaterial whether a translation  $\Gamma$  is carried out on a field  $\vec{F}$ , or on a corresponding array  $\vec{P}$  and the mapping leading to the field is carried out afterwards.

It follows from (24) by standard methods used in case of other linear operators (Schroedinger operator, vibrating systems) that the eigenvectors can be so chosen as to transform according to irreducible representations of the group  $\Gamma$ .

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\* This represents but a small modification of the procedure given in 1).  
 \*\* In fact, it is invariant also under the group including the cubic rotations. However, this will be of no importance in the special case considered in the present paper.

It may be remarked that so far no essential use has been made of the fact that the arrays  $\vec{P}$  are of the class  $\Gamma^2$ . If instead of  $\Gamma^2$  another sub-group of  $\Gamma$  had been chosen, the only difference in the above considerations would be that the number of dimensions of the space  $\mathcal{R}$  would be larger than 24.

The actual solution of the eigenvalue problem is considerably simpler, however, for the class  $\Gamma^2$  than for the general classes.

A  $\Gamma^2$  array consisting of dipoles all pointing in, say, the  $x$  direction gives rise to fields at the l.p. pointing in the same direction, i.e.

$$J_{\mu\nu}^{xy} = 0 \text{ unless } x=y \quad (25)$$

This is caused by the fact that a  $\Gamma^2$  array is invariant under a mirroring  $y \rightarrow -y$ , while the expression of the  $y$  component of the field consists of terms proportional to  $xy$  and thus changes sign.

In addition, because of the cubic rotational symmetry

$$J_{\mu\nu}^{xx} = J_{\mu\nu}^{yy} = J_{\mu\nu}^{zz} \quad (26)$$

Thus, the 24-dimensional matrix is reduced to three identical  $8 \times 8$  matrices.

It is well known that the representations of the group  $\Gamma$  are the roots of unity. In the case of  $\Gamma^2$  arrays the relevant roots are the square roots  $+1$  and  $-1$ . One is thus led uniquely to a definition of the B.A. which will be

given now. The fact that they are B.A., i.e. characteristic vectors of the operator  $\mathcal{J}$  can be easily verified without any reference to group theory.

Corresponding to the reduction of the matrix  $\mathcal{J}$  into 3 identical 8 row matrices, the 24 B.A. fall into 3 groups  $\vec{X}_i, \vec{Y}_i, \vec{Z}_i$ ,  $i = 1, 2, \dots, 8$  consisting of dipoles pointing in the x, y, z directions, respectively.

The 8 non-vanishing components of the  $\vec{Z}_i$  arrays are given by

$$\vec{Z}_i = (-)^{\alpha_i l_1 + \beta_i l_2 + \gamma_i l_3} \quad i = 1, 2, \dots, 8 \quad (27)$$

where  $\alpha_i, \beta_i, \gamma_i = 0, 1$ . It may be recalled that the superscripts are associated with the 8 cube corners  $l_1, l_2, l_3 = 0, 1$ . One has the following 8 possibilities:

	$\alpha$	$\beta$	$\gamma$		$\alpha$	$\beta$	$\gamma$
$\vec{Z}_1$	0	0	0	$\vec{Z}_5$	1	1	0
$\vec{Z}_2$	0	0	1	$\vec{Z}_6$	0	1	1
$\vec{Z}_3$	1	0	0	$\vec{Z}_7$	1	0	1
$\vec{Z}_4$	0	1	0	$\vec{Z}_8$	1	1	1

These arrays are explicitly given in Fig. 1.  $\vec{X}_i$  and  $\vec{Y}_i$  are obtained from  $\vec{Z}_i$  through cubic rotations, so that identical subscripts refer to identical geometric arrangements. Being basic arrays the  $\vec{Z}_1 \dots \vec{Z}_8$  are orthogonal. They obey the relations:

$$\vec{Z}_i \cdot \vec{Z}_j = 8 \delta_{ij} \quad (28)$$

and similarly the  $\vec{X}_i$  and  $\vec{Y}_i$ .

Equation (28) can be verified either by means of Fig. 1 or algebraically as follows:

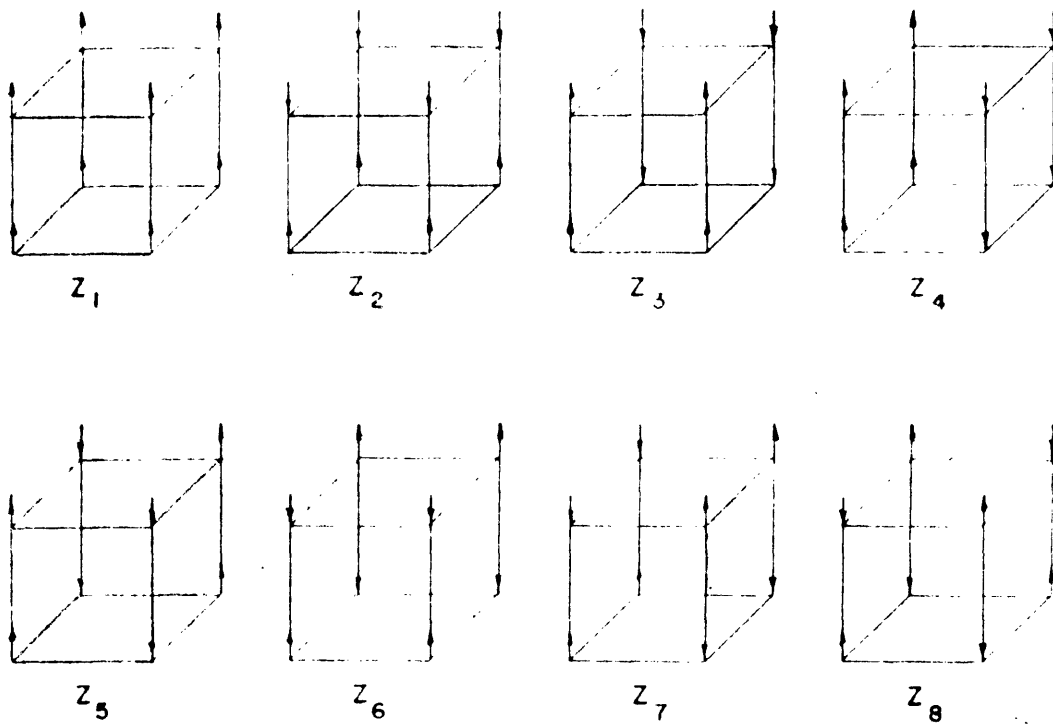


FIG. 1. The eight basic arrays. Interchange the labels  $Z_3$  and  $Z_4$ .

$$\begin{aligned} \vec{Z}_i \cdot \vec{Z}_j &= \sum_{\nu=1}^8 z_i^\nu z_j^\nu \\ &= \sum_{l_1, l_2, l_3=0,1} (-1)^{(\alpha_i + \alpha_j)l_1 + (\beta_i + \beta_j)l_2 + (\gamma_i + \gamma_j)l_3} \end{aligned}$$

If  $i \neq j$ , then at least one of the inequalities holds:  $\alpha_i \neq \alpha_j$ ,  $\beta_i \neq \beta_j$ ,  $\gamma_i \neq \gamma_j$ . Say  $\alpha_i \neq \alpha_j$ , then  $\alpha_i + \alpha_j = 1$  and  $\vec{Z}_i \cdot \vec{Z}_j = 0$  because of the summation over  $l_1$ .

$\vec{X}_i, \vec{Y}_i, \vec{Z}_i$  form a complete set of 24 orthogonal vectors and are the only ones which have the correct transformation properties. Hence, they solve the eigenvalue problem:\*

$$f \vec{X}_i = f_i \vec{X}_i, \quad f \vec{Y}_i = f_i \vec{Y}_i, \quad f \vec{Z}_i = f_i \vec{Z}_i \tag{29}$$

Because of the completeness, every  $\Gamma^2$  array  $\vec{P}$  can be represented as

$$\vec{P} = \sum_{i=1}^8 (a_i \vec{X}_i + b_i \vec{Y}_i + c_i \vec{Z}_i)$$

with  $a_i = \frac{1}{8} \vec{P} \cdot \vec{X}_i$ ,  $b_i = \frac{1}{8} \vec{P} \cdot \vec{Y}_i$ ,  $c_i = \frac{1}{8} \vec{P} \cdot \vec{Z}_i$ . The square of the norm of  $\vec{P}$  is obtained in terms of the new coordinates from (18) and (30) and the orthogonality relations:

$$\vec{P} \cdot \vec{P} = 8 \sum_{i=1}^8 (a_i^2 + b_i^2 + c_i^2) \tag{31}$$

The factor 8 arises because the B.A. are normalized to have the dipole strength unity, and hence, have the norm  $8^{\frac{1}{2}}$ . The

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\* Equation (29) could be easily verified directly using the explicit expressions to be given in 3).

field corresponding to  $\vec{P}$  is

$$\vec{F} = \sum_{i=1}^8 (a_i f_i \vec{X}_i + b_i f_i \vec{Y}_i + c_i f_i \vec{Z}_i) \quad (32)$$

and the energy per unit volume

$$\begin{aligned} U &= -\frac{1}{2} \sum_{i=1}^8 (a_i^2 + b_i^2 + c_i^2) f_i \\ &= \sum_{i=1}^8 (a_i^2 + b_i^2 + c_i^2) U_i \end{aligned} \quad (33)$$

where  $U_i = -f_i/2$ .

It is seen that the computation of the energy of any  $\Gamma^2$  array is reduced to the knowledge of the characteristic values  $f_i$ . These have been computed by a method outlined in the next section and the values are to be found in Table II.

From the point of view of practical application, there is also a somewhat different problem to be considered: given a S. C. crystal with dipoles of constant moment (taken as unity), but undetermined orientation, what is the  $\Gamma^2$  array of lowest energy? Or, in the terminology introduced above: find the minimum value of the energy (33) for arrays lying on a given constant dipole surface. These arrays satisfy the 8 auxiliary conditions (16) which can be rewritten in terms of B.A. as follows:

$$\left( \sum_{i=1}^8 a_i x_i^v \right)^2 + \left( \sum_{i=1}^8 b_i y_i^v \right)^2 + \left( \sum_{i=1}^8 c_i z_i^v \right)^2 = 1$$

$v = 1, 2, \dots, 8$  (34)

TABLE I. Values of the fields. The values given for  $Z_1$  are valid for spherical samples. Otherwise  $((4\pi/3)-l)Z_1$  should be added to every term in the first line.  $l$  is the demagnetization coefficient. The numerical values of  $f_i$ ,  $g$ ,  $h_i$  are to be found in Table II.

Array	Field at	Field at	Fields at F.C.		
	l.p.	B.C.	XY Face	YZ Face	ZX Face
$Z_1$	0	0	$-2h_1Z_1$	$h_1Z_1$	$h_1Z_1$
$Z_2$	$f_2Z_2$	0	$-2h_2Z_2$	0	0
$Z_3$	$f_3Z_3$	0	0	$h_2Z_3$	0
$Z_4$	$f_4Z_4$	0	0	0	$h_2Z_4$
$Z_5$	$f_3Z_5$	0	0	0	0
$Z_6$	$f_6Z_6$	$gY_7$	0	$h_3Y_7$	0
$Z_7$	$f_7Z_7$	$gX_6$	0	0	$h_3X_6$
$Z_8$	0	0	0	$h_4Y_8$	$h_4X_8$

TABLE II. Characteristic values  $f$ ,  $g$ , and  $h$ .

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$f_2 =$	$-\frac{1}{2} [S_z(0, \frac{1}{2}, \frac{1}{2}) - S_z(\frac{1}{2}, 0, 0)] =$	$-9.687$
$f_3 =$	$-\frac{1}{4} [S_z(0, \frac{1}{2}, \frac{1}{2}) - S_z(\frac{1}{2}, 0, 0)] =$	$4.844$
$f_4 =$	$-\frac{1}{4} [S_z(0, \frac{1}{2}, \frac{1}{2}) - S_z(\frac{1}{2}, 0, 0)] =$	$4.844$
$f_5 =$	$-\frac{1}{2} [S_z(0, \frac{1}{2}, \frac{1}{2}) + S_z(\frac{1}{2}, 0, 0)] =$	$5.351$
$f_6 =$	$\frac{1}{4} [S_z(0, \frac{1}{2}, \frac{1}{2}) + S_z(\frac{1}{2}, 0, 0)] =$	$-2.676$
$f_7 =$	$\frac{1}{4} [S_z(0, \frac{1}{2}, \frac{1}{2}) + S_z(\frac{1}{2}, 0, 0)] =$	$-2.676$
$g =$	$S_y(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}) =$	$10.620$
$h_1 =$	$S_z(0, \frac{1}{2}, \frac{1}{2}) =$	$4.334$
$h_2 =$	$S_z(0, \frac{1}{4}, \frac{1}{4}) - S_z(0, \frac{1}{2}, \frac{1}{2}) =$	$7.992$
$h_3 =$	$\frac{1}{2} [S_y(0, \frac{1}{4}, \frac{1}{4}) + S_y(\frac{1}{2}, \frac{1}{4}, \frac{1}{4})] =$	$17.065$
$h_4 =$	$\frac{1}{2} [S_y(0, \frac{1}{4}, \frac{1}{4}) - S_y(\frac{1}{2}, \frac{1}{4}, \frac{1}{4})] =$	$14.461$

---

The standard procedure of accounting for the auxiliary conditions by the method of Lagrange multipliers proves to be very cumbersome. The following artifice yields the desired result without any further calculation, not only in the simple case considered here, but also in some of the more complicated cases discussed later: The condition of constant dipole strength unity implies that the norm of the array is  $8^{\frac{1}{2}}$ , or using (31)

$$\sum_{i=1}^8 (a_i^2 + b_i^2 + c_i^2) = 1 \quad (35)$$

The conditions (34) imply (35), but not vice versa. Therefore, they will be called briefly the strong and the weak conditions, respectively.

The procedure consists in minimizing the energy (33) under the weak condition alone. This can be done at once by means of the well known extremum property of the characteristic values.<sup>10</sup>

The lowest value of the energy is  $-f_m/2$  where  $f_m$  is the greatest characteristic value of the operator. The array is a linear combination of the B.A. corresponding to  $f_m$ . If some of these linear combinations satisfy the strong conditions, then the original problem is solved.

It is seen from Table II that the lowest energy for the S.C. lattice is  $-f_5/2 = -2.676$ . The corresponding array is  $a_5 \vec{X}_5 + b_5 \vec{Y}_5 + c_5 \vec{Z}_5$  with  $a_5^2 + b_5^2 + c_5^2 = 1$ . It is easily seen that this array satisfies the strong condition and represents the correct solution of the problem.

### 3) Calculation of the Fields

The object of this section is the computation of the characteristic values  $f_i$  defined in the preceding section. According to its definition,  $f_i$  is the value of the field of the  $i$ th B.A., say  $\vec{Z}_i$ , at a lattice point. It was pointed out at the beginning of 2) that any  $\square^2$  array (and thus in particular  $\vec{Z}_i$ ) can be considered as a superposition of eight S arrays of lattice constant two. Hence, the field at any point of a B.A. will be known as soon as the field of an S array is known at every point. We shall denote the field of a  $z$  directed S array as  $^* \vec{S}(\vec{r})$ ,  $\vec{r}$  being the location of the point in question.

Using the expression (5) for the field of a dipole, we arrive at the following equations for the x, y, and z components

$$\begin{aligned}
 S_x(\vec{r}) &= \sum_{l_1, l_2, l_3} \frac{3(l_1 - x)(l_3 - z)}{[(l_1 - x)^2 + (l_2 - y)^2 + (l_3 - z)^2]^{5/2}} \\
 S_y(\vec{r}) &= \sum_{l_1, l_2, l_3} \frac{3(l_2 - y)(l_3 - z)}{[(l_1 - x)^2 + (l_2 - y)^2 + (l_3 - z)^2]^{5/2}} \\
 S_z(\vec{r}) &= \sum_{l_1, l_2, l_3} \frac{2(l_3 - z)^2 - (l_1 - x)^2 - (l_2 - y)^2}{[(l_1 - x)^2 + (l_2 - y)^2 + (l_3 - z)^2]^{5/2}}
 \end{aligned} \tag{36}$$

---

\*  $S(r)$  is a spatial vector point function of the points  $r$  within the unit cell, and should not be confused with the 24 dimensional vectors representing the field at the lattice points.

Using the function  $S(r)$  (which we shall call the "characteristic function"), we may write the field  $\vec{H}_i$  at any point  $\vec{r}$  of  $\vec{Z}_i$  explicitly as

$$\vec{H}_i(\vec{r}) = \frac{1}{8} \sum_{l_1, l_2, l_3=0,1} (-1)^{\alpha_i l_1 + \beta_i l_2 + \gamma_i l_3} \vec{S}\left(\frac{l_1-x}{2}, \frac{l_2-y}{2}, \frac{l_3-z}{2}\right) \quad (37)$$

where  $\alpha_i, \beta_i, \gamma_i$  correspond to the B.A.  $\vec{Z}_i$ . The  $\frac{1}{2}$  in the argument of the characteristic function and the  $\frac{1}{8}$  multiplying the entire expression arise from the fact that the characteristic function is defined for an S array with lattice constant unity, while the component S arrays of a B.A. have lattice constant equal to two. Thus, the question of finding the characteristic values is reduced to the knowledge of the values of the function S at the points with coordinates having half integral values.

It will be seen in the next section that the solution of the characteristic value problem for the B.C. and F.C. lattices necessitates the knowledge of the field in the body centers and face centers. These may also be obtained provided a few more values of the function  $\vec{S}(\vec{r})$  are computed.

In the actual computation of the fields full use is made of symmetry considerations, which show that at many points the field is zero, or is simply related to the field at other points. As a typical example, we shall show that the field of  $\vec{Z}_6$  at a lattice point is minus one-half the field of  $\vec{Z}_5$  at a lattice point. From the expression for the dipole interaction (20) and the definition of the basic arrays, one easily finds

$$H_{52}(000) = \sum' \frac{2l_3^2 - l_1^2 - l_2^2}{(l_1^2 + l_2^2 + l_3^2)^{5/2}} (-1)^{l_1 + l_2} \quad (38)$$

$$H_{62}(1000) = \sum' \frac{(2l_3^2 - l_1^2 - l_2^2)}{(l_1^2 + l_2^2 + l_3^2)^{5/2}} (-1)^{l_2 + l_3} \quad (39)$$

noticing that  $l_1$  and  $l_2$  enter into (38) in the same manner, we get

$$H_{52} = 2 \sum' \frac{l_3^2 - l_2^2}{(l_1^2 + l_2^2 + l_3^2)^{5/2}} (-1)^{l_1 + l_2}$$

Interchanging\*  $l_1$  and  $l_3$  in (39) we get

$$\begin{aligned} H_{62} &= \sum' \frac{(2l_1^2 - l_3^2 - l_2^2)}{(l_1^2 + l_2^2 + l_3^2)^{5/2}} (-1)^{l_1 + l_2} \\ &= \sum' \frac{l_2^2 - l_3^2}{(l_1^2 + l_2^2 + l_3^2)^{5/2}} (-1)^{l_1 + l_2} = -\frac{1}{2} H_{52} \end{aligned}$$

which is the required result.

Many other relationships exist, connecting the different fields at the body centers with each other, connecting different lattice point fields, different face-center fields, etc. By means of these relationships, it is possible to calculate the fields at the lattice points, body centers and face centers of a B.A. by computing only six different values of the characteristic

\* Such procedures may be justified by transforming these series to absolutely convergent ones by means of the Ewald method. For details see J. Bouman, Archives Neerlandaises [3A], 13, 1-28 (1931)

function  $\vec{S}(\vec{r})$ . These are  $S_z(\frac{1}{2}, 0, 0)$ ,  $S_z(0, \frac{1}{2}, \frac{1}{2})$ ,  $S_y(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ ,  $S_z(0, \frac{1}{4}, \frac{1}{4})$ ,  $S_y(0, \frac{1}{4}, \frac{1}{4})$ ,  $S_y(\frac{1}{2}, \frac{1}{4}, \frac{1}{4})$ . It is clear that others could have been chosen, but these turn out to be convenient. Tabel I gives all the fields expressed in terms of these fields. The numerical values of the first three have been taken from a paper of McKeehan<sup>13</sup> while the others have been calculated using the Ewald<sup>14</sup> method. A check on our values may be obtained from McKeehan since it is possible to evaluate  $S_y(0, \frac{1}{4}, \frac{1}{4}) - S_y(\frac{1}{2}, \frac{1}{4}, \frac{1}{4})$  from his tables. The agreement is excellent. The values of these fields are

$$S_z(\frac{1}{2}, 0, 0) = -15.040, \quad S_z(0, \frac{1}{4}, \frac{1}{4}) = 12.329$$

$$S_z(0, \frac{1}{2}, \frac{1}{2}) = 4.334, \quad S_y(0, \frac{1}{4}, \frac{1}{4}) = 31.521$$

$$S_y(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}) = 10.620, \quad S_y(\frac{1}{2}, \frac{1}{4}, \frac{1}{4}) = 2.599$$

Tables I and II give the resulting values of all the fields.

#### 4) Body Centered and Face Centered Arrays

It is convenient to consider the B.C. and F.C. arrays as consisting of two and four S.C. arrays respectively, which can be resolved into B.A. In this representation, the field matrix contains diagonal elements corresponding to the energies of the constituent S.C. arrays and off-diagonal elements giving the interaction of B.A. at different points. The interaction terms are listed in Tables I and II. It is apparent that most of the off-diagonal terms vanish and the energy of any B.C. or F.C. array can be readily computed. As an example, we have

considered a set of arrays previously computed by Sauer<sup>7</sup>. Table III compares the energies resulting from the decomposition into B.A. with the values obtained by Sauer through direct summation.

This representation does not lead in any systematic way to the minimum energy configuration of an array of given dipole strength. The latter problem can be solved by completing the diagonalization of the field matrix and introducing B.A. in the 48- and 96-dimensional vector spaces corresponding to B.C. and F.C. arrays respectively. Since most of the off-diagonal terms vanished in the above representation, this can be easily carried out. The procedure will be explained in detail for the B.C. case.

It is seen from Table II that if one of the B.A.  $\vec{X}_i, \vec{Y}_i, \vec{Z}_i$  ( $i \neq 6,7$ ) is placed at the lattice points, it gives rise to no field at the body center. Similarly, one of these arrays placed at the body centers will give rise to no field at the lattice points, as the lattice points and the body centers are interchangeable. Thus, by placing  $\vec{X}_i$  at the lattice points and nothing at the body centers, we obtain a B. A. and similarly placing  $\vec{X}_i$  at the body centers and nothing at the lattice points will also give B.A. We now introduce the notation  $[\vec{P}, \vec{Q}]$  to denote a B.C. array with  $\vec{P}$  at the lattice points and  $\vec{Q}$  at the body centers. The above B.A. will then be written as  $[\vec{X}_i, 0]$  and  $[0, \vec{X}_i]$ , respectively. Using the same process on  $\vec{Y}_i, \vec{Z}_i$ , we obtain four more B.A.  $[\vec{Y}_i, 0], [0, \vec{Y}_i], [\vec{Z}_i, 0], [0, \vec{Z}_i]$ . These six

TABLE III. Arrays calculated by Sauer. (Sauer's symbols are in the first column.)

Type	Resolution into basic arrays	Energy constants	
		Sauer	Present paper
"A"			
<i>a</i>	$Z_5$	-2.7	-2.676
<i>b</i>	$Z_1$ at l.p., $-Z_1$ at b.c.	0	0
<i>c</i>	$Z_5 + X_7 + Y_6$ at l.p. and b.c.	-1.75	-1.770
<i>d</i>	$Z_1$ at l.p. and $XY$ f.c. $-Z_1$ at $YZ$ and $ZX$ f.c.	2.2	2.167
<i>e</i>	$Z_1 + Y_1$ at l.p. and $YZ$ f.c. $-Z_1 - Y_1$ at $XY$ and $XZ$ f.c.	-1.1	-1.084
"B"			
<i>a</i>	$Z_5$	-2.7	-2.676
<i>b</i>	$Z_5$ at l.p., $-Z_5$ at b.c.	-1.35	-1.338
<i>c</i>	$Z_5 + X_7 + Y_6$ at l.p. and b.c.	-1.75	-1.770
<i>d</i>	$Z_1$ at l.p. and $YZ$ f.c. $-Z_1$ at $XY$ and $XZ$ f.c.	-1.1	-1.084
<i>e</i>	$Z_8 + Y_8$ at l.p., $XY$ and $YZ$ f.c. $-Z_8 - Y_8$ at $ZX$ f.c.	-1.8	-1.808
<i>a</i>	is S.C., dipole direction 001		
<i>b</i>	is B.C., dipole direction 001		
<i>c</i>	is B.C., dipole direction 111		
<i>d</i>	is F.C., dipole direction 001		
<i>e</i>	is F.C., dipole direction 011		
"A"	is an array which has nearest neighbor strings of antiparallel dipoles		
"B"	is an array which has nearest neighbor strings of antiparallel dipoles if the dipoles are contained in a plane perpendicular to the dipole direction, and passing through the dipole.		

TABLE IV. Characteristic values and typical basic arrays in the B.C. case. Valid for spherical sample, otherwise, cf. Table I.

Characteristic value of $\mathfrak{F}$	Degree of degeneracy	At lattice points	Typical B.A.	At body centers
$f_1 = f_8 = 0$	6	$Z_1$		$Z_1$
	6	$Z_8$		$Z_8$
$f_2 = -9.687$	6	$Z_2$		$Z_2$
$f_3 = f_4 = 4.844$	12	$Z_3$		$Z_3$
$f_5 = 5.351$	6	$Z_5$		$Z_5$
$f_6 + g = 7.944$	6	$Z_6$		$Y_7$
$f_6 - g = -13.296$	6	$Z_6$		$-Y_7$

TABLE V. Characteristic values and typical basic arrays in the F.C. case.  
Valid for spherical samples, otherwise, cf. Table I.

Characteristic value of $\mathfrak{F}$	Degree of degeneracy	At l.p.	Typical B.A. with this characteristic value	
			At XY face	At YZ face
0	3	$Z_1$	$Z_1$	$Z_1$
$-4h_1 = -17.336$	3	$Z_1$	$Z_1$	$-Z_1$
$2h_1 = 8.668$	6	$Z_1$	$-Z_1$	$Z_1$
$f_2 - 2h_2 = -25.671$	6	$Z_2$	$Z_2$	$Z_2$
$f_2 + 2h_2 = 6.297$	6	$Z_2$	$-Z_2$	$-Z_2$
$f_3 + h_3 = 12.836$	12	$Z_3$	$Z_3$	$Z_3$
$f_3 - h_3 = -3.148$	12	$Z_3$	$Z_3$	$-Z_3$
$f_6 = 5.351$	12	$Z_6$	$Z_6$	$Z_6$
$f_6 + h_6 = 14.389$	12	$Z_6$	$Z_6$	$Y_7$
$f_6 - h_6 = -19.741$	12	$Z_6$	$Z_6$	$-Y_7$
$h_4 = 14.461$	4	$Z_8$	$Z_8$	$-Y_8$
$h_4 = 14.461$	4	$2X_8 + Y_8 - Z_8$	$2X_8 + Y_8 - Z_8$	$2X_8 - Y_8 + Z_8$
$-2h_4 = -28.922$	4	$X_8 - Y_8 - Z_8$	$X_8 - Y_8 + Z_8$	$X_8 + Y_8 - Z_8$

B.A. all correspond to the same characteristic value  $f_1$  of the field operators  $\mathcal{F}$ , therefore any set of six orthogonal linear combinations of these B.A. will also be B.A. In view of the considerations at the end of 2), it is convenient to choose B.A. having constant dipole strength. Such a choice would be  $[\vec{Z}_1, \vec{Z}_1]$  and  $[\vec{Z}_1, -\vec{Z}_1]$  and similarly for  $\vec{X}_1, \vec{Y}_1$ .

The number 6 and 7 arrays require special consideration as they give rise to off-diagonal terms in the field matrix. In other words, there is an interaction between, for example, a  $\vec{Z}_6$  array at the lattice points and a  $\vec{Y}_7$  array at the body centers. The diagonalization is easily completed by choosing  $[\vec{Z}_6, \vec{Y}_7]$  and  $[\vec{Z}_6, -\vec{Y}_7]$  as B. A. The corresponding characteristic values are  $f_5+g$  and  $f_6-g$ . Similar B.A. are constructed from the other 6 and 7 arrays.

These results are summed up in Table IV.

The F.C. case can be discussed in exactly the same manner. The treatment is somewhat more complicated because of the presence of many more interaction terms. Only the results are given (Table V). In order to obtain the energy values in units of  $N^2 \mu^2$ , one has to multiply the characteristic values of  $\mathcal{F}$  by  $(-\frac{1}{4})$  in the B.C. case and  $(-\frac{1}{8})$  in the F.C. case.

Since all the B.A. are defined so as to have a constant dipole strength, the minimum energy configurations are simply obtained by choosing the highest characteristic values from Tables IV and V. Hence, the minimum energy for

the B.C. case is  $-\frac{1}{4}(g+f_6)N^2\mu^2 = 1.986N^2\mu^2$  and for the F.C. case  $-(h_4/8)N^2\mu^2 = -1.808N^2\mu^2$ .

It may be noted that Sauer correctly guessed one of the minimum energy arrays in the S.C. and F.C. case, but not in the B.C. case.

Finally, the possibility of "ferromagnetism" for these arrays should be discussed. Summing up our results, we notice that in all cases the minimum energy configuration has been non-polarized. This result, however, is true only for spherical samples. Otherwise one has to add a term  $-\frac{1}{2}(4\pi/3-l)N^2\mu^2$  to the energy of the polarized number 1 arrays, for all three cubic types. In the extreme case of a very long thin needle  $l=0$ , and the energy constant becomes  $-2\pi/3 = -2.094$ , while the energy constants of the lowest non-polarized arrays are for S.C.  $-2.675$ , for B.C.  $-1.986$  and for F.C.  $-1.808$ . Thus, the S.C. array is always non-ferromagnetic, while the other cases should exhibit ferromagnetism for long thin needles. In the case of a F.C. lattice cut in the form of a prolate spheroid, the ferromagnetic state is favored above an axis ratio of 6:1. This result has been found before by Sauer<sup>7</sup>. Whether this ferromagnetic state has a physical reality is, however, subject to some doubt.

##### 5) $\Gamma^2$ Arrays in a Magnetic Field

The energy of a given  $\Gamma^2$  array in a magnetic field is easily calculated. Considering first the S.C. case, one has:

$$U = -\frac{1}{2} \sum_{i=1}^8 f_i (a_i^2 + b_i^2 + c_i^2) - (a_1 H_x + b_1 H_y + c_1 H_z) - \left(\frac{4\pi}{3} - \mathcal{L}\right) (a_1^2 + b_1^2 + c_1^2) / 2 \quad (40)$$

since only the number 1 arrays have a resultant magnetic moment. Let us introduce the notation  $a_1^2 + b_1^2 + c_1^2 = q^2$ ,  $q$  being the magnetization of the array in units of  $N\mu$ . Denoting the angle between magnetization and external field by  $\psi$ , (40) becomes

$$U = -\frac{1}{2} \sum_{i=1}^8 f_i (a_i^2 + b_i^2 + c_i^2) - q \cos \psi - \left(\frac{4\pi}{3} - \mathcal{L}\right) q^2 / 2 \quad (41)$$

This expression should be minimized under the strong condition (34), which we again replace temporarily by the weak condition (35). In our present notation (35) takes the form:

$$\sum_{i=2}^8 (a_i^2 + b_i^2 + c_i^2) + q^2 = 1 \quad (42)$$

We now minimize the energy at fixed  $q$ . From (41) we see that  $\cos \psi = 1$ , i.e. the magnetization is parallel to the magnetic field. The minimization of the first term is exactly the problem solved at the end of 2) since  $f_1 = 0$ . The solution is

$$\vec{P} = a_1 \vec{X}_1 + b_1 \vec{Y}_1 + c_1 \vec{Z}_1 + a_5 \vec{X}_5 + b_5 \vec{Y}_5 + c_5 \vec{Z}_5, \quad (43)$$

with  $a_5^2 + b_5^2 + c_5^2 = 1 - q^2$ .

The energy becomes

$$U = -\frac{1}{2}(1 - q^2)f_5 - qH - (4\pi/3 - \mathcal{L})q^2/2 \quad (44)$$

Equation (44) may now be minimized with respect to  $q: \partial U / \partial q = 0$  leads to

$$g = \frac{H}{f_s - \left(\frac{4\pi}{3} - f_s\right)}$$

Defining a critical field  $H_c$  as

$$H_c = f_s - \left(\frac{4\pi}{3} - 1\right) \tag{45}$$

and remembering that  $q \leq 1$ , we have

$$g = \begin{cases} H/H_c & \text{for } H \leq H_c \\ 1 & \text{for } H \geq H_c \end{cases} \tag{46}$$

In other words, there exists a magnetic field  $H_c$  above which the magnetization is constant (saturation) and below which it drops to zero linearly with the field. It is recalled that the magnetization is given in units of  $N \mu$ .

Whether or not (43) is the correct solution is still dependent on whether it satisfies the strong conditions. This is generally not the case for an arbitrary direction of the magnetic field ( $a_1 \neq 0, b_1 \neq 0, c_1 \neq 0$ ). If, however, the magnetic field is along one of the cubic axis or in one of cubic planes, then the resulting array can be chosen to have constant dipole strength. For example, if the field is along the cubic axis, say in the Z direction, then the array

$$\vec{P} = a_5 \vec{X}_5 + b_5 \vec{Y}_5 + c_1 \vec{Z}_1$$

satisfies all the requirements.

Since in the general case, the simple artifice of first ignoring the strong conditions does not work, one has to introduce (34) at the outset. This can be done by the method of Lagrange multipliers, but the resulting equations are very complicated and have not been solved. The case of physical interest is the F.C. array (paramagnetic alums), and here the

simple method works once more.

The above considerations may be repeated for the F.C. case. Equations (40) through (46) are maintained provided the characteristic values and B.A. defined for the S.C. case for the space  $\mathcal{R}$  are replaced by the corresponding quantities in the 96-dimensional space. In particular, the energy constant  $-f_5/2$  should be replaced by  $-h_4/8$ . The minimum energy array under the weak condition is a superposition of the polarized B.A. and those belonging to the characteristic value  $h_4$ . Here, however, the formal identity ceases. Actually, the situation is more favorable than in the S.C. case as the strong conditions may now be satisfied for an arbitrary magnetic field. The array which satisfies the strong conditions is a superposition of the polarized arrays and those arrays belonging to the second class of  $h_4$  arrays given in Table V.

#### 6) The Effect of Larmor Precession

We now discuss briefly the effect of Larmor precession on the results of the previous sections. We shall show two things:

(1) Under the influence of Larmor precession, an array does not change its energy. This is clear from general principles of energy conservation and is also a simple consequence of the formalism given above.

(2) If an array initially satisfies the strong conditions (34), then it will always satisfy them.

The combination of (1) and (2) implies that our minimum energy considerations are in no way affected by the Larmor

effect. We need only imagine that initially the proper configuration obtains, and it will then always be the case.

To prove (2), we make use of the expression for the torque on a dipole in a field. If the field at the  $l^{\text{th}}$  dipole is  $\vec{H}^l$  and its moment  $\vec{\mu}^l$ , then the torque is

$\vec{\mu}^l \times \vec{H}^l$ , and the equations of motion are

$$\dot{\vec{J}}^l = \vec{\mu}^l \times \vec{H}^l \quad (47)$$

where  $\vec{J}^l$  is the angular momentum associated with  $\vec{\mu}^l$ .

But, in general,  $\vec{J}^l = \frac{1}{\gamma} \vec{\mu}^l$  where  $\gamma$  is a constant depending on the gyromagnetic ratio. Therefore

$$\dot{\vec{\mu}}^l = \gamma \vec{\mu}^l \times \vec{H}^l \quad (48)$$

Taking the dot product of (48) with  $\vec{\mu}^l$  gives  $\dot{\vec{\mu}}^l \cdot \vec{\mu}^l = 0$  since the triple scalar product vanishes. This means that

$$\frac{d}{dt} (\vec{\mu}^l)^2 = 0 \quad \text{or} \quad \vec{\mu}^l = \text{const} \quad (49)$$

(49) is true in the presence of an external as well as internal field (since we made no assumptions about  $\vec{H}^l$ ) and is just the mathematical statement of (2) above.

III QUANTUM MECHANICAL CONSIDERATIONS

1) General

In this section, we shall discuss the quantum mechanics of the model given in Section II. The quantum mechanical problem which we need to solve may be formulated in a completely general fashion. We ask, "What are the eigenvalues of the operator obtained when we replace each  $\vec{\mu}_m$  of equation (1) by a corresponding Pauli spin matrix?" That is, what are the eigenvalues of the operator

$$H = \frac{1}{2} \sum_{m,\mu} \frac{l^2(\sigma_m \cdot \sigma_m) - 3(l \cdot \sigma_m)(l \cdot \sigma_m)}{l^5} \quad (50)$$

This problem seems at present insoluble. In attempting to obtain any information from (50), one immediately runs into the full difficulty of the quantum mechanical many body problem. Indeed, it has not yet been found possible to obtain a single exact eigenfunction or eigenvalue of (50). Even the usual simplifications that enable reasonable approximations to be made in the case of ferromagnetism, (i.e. nearest neighbor interaction, isotropy of interaction) break down here. Further (50) does not commute with the total angular momentum  $\sum_m \sigma_m^z$  of the system, and therefore does not represent a system which conserves angular momentum. This means that it is impossible to specify states with a definite total spin and therefore, that simple states, such as those discussed in the previous section, can have no exact quantum analogue. They must exist in some approximate sense, however, for it is clear that for a macroscopic sample,

one must be able to speak of a magnetization.

In one dimension, the situation is not so bad as in three. Here  $\mathcal{H}$  takes the form

$$\mathcal{H} = \frac{1}{2} \sum_{l,k} \frac{\sigma_l \cdot \sigma_k - 3\sigma_l^z \sigma_k^z}{|l-k|^3} \quad (51)$$

This commutes with  $\sum_m \sigma_m^z$  (as it clearly must from the rotational symmetry of the problem) and therefore states of definite multiplicity do exist. One may solve the spin wave problem for such an array (this is done in appendix 1.) for example. The form of (51) is actually not too different from that corresponding Hamiltonian for the ferromagnetic linear chain. (The  $\sigma_l \cdot \sigma_k$  being in exact correspondence, and the  $\sigma_l^z \sigma_k^z$  term adding nothing to the complexity as it is already diagonalized in the representation one would use.) One would, therefore, expect that the method of Bethe<sup>15</sup> (which gives the complete solution of the eigenvalue problem in the one dimensional ferromagnetic case) might be applicable here. The long range of the dipole forces, however, sufficiently complicates an already extremely complicated procedure, so as to render the problem practically (if no longer in principle) insoluble.

We will therefore abandon the exact eigenvalue problem and attempt to get information by less direct means.

## 2) A Mean Value Theorem

We shall now show that the expectation value of the energy in any "Hartree approximation" will be exactly what was

to be expected classically. By "Hartree approximation" we simply mean one in which the wave function is theorem as a simple product of single spin wave functions. Now the most general spin function ( $\gamma$ ) is given by<sup>16</sup>

$$\gamma = (\cos \theta) \alpha + (\sin \theta e^{i\varphi}) \beta \quad (52)$$

$\alpha$  representing a spin function with the spin in the plus  $z$  direction,  $\beta$  a spin function with the spin in the minus  $z$  direction. This function  $\gamma$  represents a spin quantized in the positive  $\theta, \varphi$  direction. Let us take as our general Hartree function

$$\psi = \prod_{k''} \gamma_k \quad (53)$$

$\gamma_k$  being determined by  $\theta_k$  and  $\varphi_k$ ; the product being over all the dipoles in the crystal. We consider the expectation value of the energy, i.e.

$$\bar{H} = (\psi, H \psi) \quad (54)$$

If we write  $\gamma_k = a_k \alpha_k + b_k \beta_k$  and substitute (53) and (50), we find

$$\begin{aligned} H \psi = \frac{1}{2} \sum_{m,n} \prod_k \frac{\gamma_k}{L^3} & \left\{ a_m a_n [(1-3z^2) \alpha_m \alpha_n + 3(y-ix) \beta_m \beta_n + 3z(x+iy)(\alpha_m \beta_n + \beta_m \alpha_n)] \right. \\ & + b_m b_n [3(y+ix) \alpha_m \alpha_n + (1-3z^2) \beta_m \beta_n + 3z(x-iy)(\alpha_m \beta_n + \alpha_n \beta_m)] \\ & \left. + (a_m b_n + a_n b_m) [-3z(x-iy) \alpha_m \alpha_n + 3z(x+iy) \beta_m \beta_n - (1-3z^2)(\alpha_m \beta_n + \alpha_n \beta_m)] \right\} \end{aligned} \quad (55)$$

where we have put  $(\frac{l_1}{l}, \frac{l_2}{l}, \frac{l_3}{l}) \equiv (x, y, z)$ . Taking the scalar product of (55) with  $\psi$ , we find

$$\begin{aligned} \bar{H} = (\psi, H\psi) &= \frac{1}{2} \sum_{m,m'} \frac{1}{l^3} \left\{ \cos \theta_m \cos \theta_{m'} + \sin \theta_m \sin \theta_{m'} \cos(\varphi_m - \varphi_{m'}) \right. \\ &\quad - 3(x^2 \sin \theta_m \sin \theta_{m'} \cos \varphi_m \cos \varphi_{m'} + y^2 \sin \theta_m \sin \theta_{m'} \sin \varphi_m \sin \varphi_{m'} + z^2 \cos \theta_m \cos \theta_{m'}) \\ &\quad - 3(xy \cos \theta_m \cos \theta_{m'} \sin(\varphi_m + \varphi_{m'}) + yz(\cos \theta_m \sin \theta_{m'} \sin \varphi_m + \cos \theta_{m'} \sin \theta_m \sin \varphi_{m'}) \\ &\quad \left. + xz(\cos \theta_m \sin \theta_{m'} \cos \varphi_m + \cos \theta_{m'} \sin \theta_m \cos \varphi_{m'}) \right\} \end{aligned}$$

A little algebraic manipulation now shows this to be exactly the same as (1) if we make the substitution

$$\mu_m^1 = \sin \theta_m \cos \varphi_m$$

$$\mu_m^2 = \sin \theta_m \sin \varphi_m$$

$$\mu_m^3 = \cos \theta_m$$

The theorem is actually more generally valid (no very specific use of the dipole-dipole nature of the forces having been made) but we shall only use it in the simple form given above.

We may view the above theorem in another light. By the variational formulation of the fundamental problem of quantum mechanics, we know that  $H = (\psi, H\psi)$  is always greater than or equal to the lowest energy of the system. Since, if we take a product eigenfunction which represents a (say)  $\vec{Z}_5$  array, we get (for the S.C. case) the lowest possible classical energy, we know immediately that the lowest quantum mechanical level is at least as deep as the lowest classical one. We cannot, however,

conclude that there is really a lower level quantum mechanically. The results of this section, in connection with those of the first, do seem to make this reasonable.

### 3) Special Examples

In attempting to get some information about the nature of the exact solutions of the eigenvalue problem, we have solved a number of simple examples. These are:

- a) Two dipoles on a line.
- b) Two dipoles in a magnetic field not directed along the line joining them.
- c) Three dipoles along a line.
- d) Four dipoles along a line.

a) is quite simple and may be solved in a variety of ways.

The Hamiltonian is

$$H = \sigma_1 \cdot \sigma_2 - 3 \sigma_1^z \sigma_2^z \quad (56)$$

where we have chosen the line of centers to be the  $z$  axis, and the dipole to be at a unit distance. Perhaps the most elegant solution of the problem is to notice that (56) is invariant to rotations about the  $z$  axis and to permutation of the two particles. This uniquely determines the eigenfunctions to be  $\alpha_1 \alpha_2, \beta_1 \beta_2, \alpha_1 \beta_2 + \beta_1 \alpha_2, \alpha_1 \beta_2 - \beta_1 \alpha_2$ . The corresponding eigenvalues are  $-2, -2, 4, 0$ . The classical energies corresponding to this situation would be a continuum stretching from  $-2$  to  $2$ . It is seen that the lowest level is unaffected, but that the higher ones are.

(b) Even this quite simple problem is difficult algebraically and contains some features of the general problem. The Hamiltonian is

$$\begin{aligned} \mathcal{H} = & -H (\sigma_x + \sigma_x') \alpha + (\sigma_y + \sigma_y') \beta + (\sigma_z + \sigma_z') \gamma \\ & + \sigma_x \sigma_x' + \sigma_y \sigma_y' - 2 \sigma_z \sigma_z' \end{aligned} \quad (57)$$

$(\alpha, \beta, \gamma)$  being the direction of  $H$ . We expand a general  $\psi$  as  $\psi = \sum_{i=1}^4 a_i \psi_i$  where  $\psi_1 = \alpha\alpha'$ ,  $\psi_2 = \beta\beta'$ ,  $\psi_3 = \alpha\beta' + \beta\alpha'$ ,  $\psi_4 = \alpha\beta' - \beta\alpha'$ . The form of the latter is chosen so that they are eigenfunctions of the permutation operator of the two particles. Substituting into  $\mathcal{H}\psi = E\psi$  and equating coefficients, we find one eigenvalue to be  $E = 0$  (belonging to  $\psi_4$ ) and the other eigenvalues determined by

$$\begin{vmatrix} 2(C-1) - E & 0 & 2(A-iB) \\ 0 & -2(C+1) - E & 2(A+iB) \\ (A+iB) & (A-iB) & 4-E \end{vmatrix} = 0$$

$$A = -H\alpha, \quad B = -H\beta, \quad C = -H\gamma.$$

Expansion of this equation yields

$$E^3 - 4E(C^2 + 3 - A^2 - B^2) + 8(2(C-1) - A^2 - B^2) = 0 \quad (58)$$

If the field were along the  $Z$  axis,  $A=B=0$  and  $E = 4, -2(1 \pm C)$ , as might be expected. An exact solution of (58) may be given, but the results are very complicated and throw no particular light on the main problem. Perhaps the only conclusion one may draw from the above example is that as soon as there ceases to be one preferred direction in the dipole problems, they become enormously more complicated.

The problems c) and d) were investigated in an attempt to get information about the changing energy spectrum as one increases the length of the chain of dipoles. It was also hoped that it might be possible to learn enough from the solution of these comparatively simple problems to develop a technique applicable to the general case. The latter did not develop however. The formal solution of the above problems may be accomplished rather simply using permutation and rotation operators as constants of the motion, or by using the fact that the structure in question is invariant under the group  $D_{2v}^{17}$ . The eigenvalues in the three dipole cases turn out to be  $-\frac{17}{4}, 0, 2 \pm \frac{177}{4}$  each of which is doubly degenerate. In the four dipole case, the eigenvalues are rather complicated (though they may be given explicitly) and will not be entered here. The pertinent conclusion however, is that in all three cases, the lowest quantum level coincides with the lowest classical level--a result which seems generally valid for any one dimensional array.

#### IV STATISTICAL CONSIDERATIONS

##### 1) General

The considerations of the previous sections would be applicable to the discussion of dipole arrays which were completely ordered, i.e. those in which temperature effects were not present or negligible. In this section, we shall develop an approximative method which enables one to take into account a very small quantity of disorder in the array.

One would at first imagine that the problem could be dealt with by a suitable generalization of the usual Bloch-Slater theory of ferromagnetism. Closer investigation, however, shows this to be impossible, or at least impractical. There are several reasons: the long range of the dipole-dipole forces (in contrast to the short range of exchange forces), their strong directional dependence, and the fact that the dipole situation is, if anything, more analogous to anti-ferromagnetism than to ferromagnetism. The latter is particularly serious because, as far as the writer knows, no rigorous theory of anti-ferromagnetism has ever been given. Van Vleck<sup>18</sup> and Bitter<sup>19</sup> have given treatments analogous to the usual Weiss-Heisenberg theory of ferromagnetism. These methods, while satisfactory for the problems they consider, do not seem to be generalizable to the problem of dipole interaction.

On the other hand, there exists a method of treating ferromagnetism due to Kramers and Heller<sup>20</sup> (which has been generalized to anti-ferromagnetism by Hulthen<sup>21</sup>) This method (under

certain suitable assumptions to be given later) turns out to be of use in our problem. This scheme permits us to take full advantage of our information about the ordered states of the system, and also permits a quantization of our results (in a sense to be given in the subsequent discussion.) We have applied this method to the case of strong and weak fields, i.e. fields much greater than the internal field produced by the dipoles and fields less than this internal field, respectively.

## 2) Dipole Arrays in a Strong Field

Let us consider the energy ( $\mathcal{H}$ ) of an array of dipoles on a S.C. lattice in the presence of an external magnetic field  $H$  in the  $z$  direction (taken to be one of the crystallographic axes):

$$\mathcal{H} = -\mu H \sum_m z_m + \gamma \sum_{m,n} \frac{(\mu_m \cdot \mu_n) r^2 - 3(\mu_m \cdot r)(\mu_n \cdot r)}{r^5} \quad (59)$$

$\mu$  is the dipole moment of the dipoles in question,  $\gamma = \mu^2 / 2a^3$ ,  $a$  is the lattice spacing,  $\mu_m = (x_m, y_m, z_m)$  the direction cosines of the  $m^{\text{th}}$  dipole. Other quantities are defined as in equation (1). Now, if the external field is very strong, most of the dipoles will be pointed in the  $z$  direction. Or to phrase it slightly differently, the average deviation of a dipole from the  $z$  direction will be small. Therefore,  $x_m, y_m \ll z_m$ . Since  $z_m = \sqrt{1 - x_m^2 - y_m^2}$ , we may write approximately

$$z_m = 1 - \frac{1}{2} (x_m^2 + y_m^2) \quad (60)$$

If we substitute this into (59) we would obtain for  $\mathcal{H}$  a constant (representing the energy if there were no thermal agitation) plus a quadratic form in  $x_m, y_m$ . We write

$$\mathcal{H} = -\mu H N + \frac{\mu H}{2} \sum_m (x_m^2 + y_m^2) + \gamma \sum_{\substack{m, n \\ \text{Nearest} \\ \text{Neighbors}}} \{x_m x_n (1-3l_3^2) + y_m y_n (1-3l_3^2)\} \quad (61)$$

$N$  being the number of dipoles present. This expression contains several further assumptions. Firstly, we have assumed that in this quadratic form we need only consider nearest neighbor interactions. This is not as severe an approximation as might be thought at first, because the whole term itself is assumed small. Further, the effect of non-nearest neighbors would only amount to about 20 % (dipole forces falling off inversely as the cube of the distance) if it were completely additive. This is not the case, however, since the deviations  $x_m$  and  $y_m$  are chaotic (at least to a first approximation) and it is well known that the dipole forces give zero interaction for a chaotic arrangement of dipoles. The second assumption

is that the sample is spherical which allows us to place the term  $\sum z_m z_m (1-3l_3^2) = \sum (1-\frac{1}{2}(x_m^2 + x_n^2 + y_m^2 + y_n^2))(1-3l_3^2)$   
 $= -\frac{1}{2} \sum (x_m^2 + x_n^2 + y_m^2 + y_n^2)(1-3l_3^2) = 0.$

We now make a canonical change of variables in the energy expression (61). We can consider as canonical variables of a single spin the two independent coordinates necessary to specify it. Call these  $S_m, \phi_m$ , where  $S_m$  measures the  $z$  component of  $\mu_m$  and  $\phi_m$  the angle the projection of  $\mu_m$  on the

xy plane makes with the x axis.  $S_m$  will be proportional to  $z_m$ , but to give  $S_m \phi_m$  the dimensions of  $\hbar$ , we must multiply by a constant having the dimensions of  $h$ . We choose  $S_m = \frac{n\hbar}{2} z_m$  where  $n$  is the number of spins belonging to the dipole moment. The reason for this choice will become apparent when we "quantize" our model in the next section, for there we shall see that this choice gives correct limiting values for the magnetization and entropy. Now, if we consider small deviations from the z axis, it is clear that  $x_m$  and  $y_m$  are approximately rectangular coordinates for specifying  $\mu_m$ , and therefore are approximately canonical variables. Choosing new variables  $X_m = \frac{n\hbar}{2} x_m, Y_m = y_m$

we may write (61) as

$$\begin{aligned} \mathcal{H} = & -\mu NH + \left(\frac{1}{\frac{n\hbar}{2}}\right)^2 \sum_{\substack{m,m \\ NN}} \left( \frac{\mu H}{2} \delta_{mn} + \gamma(1-\delta_{mn})(1-3\ell_1^2) \right) X_m X_n \\ & + \sum_{\substack{m,m \\ NN}} \left( \frac{\mu H}{2} \delta_{mn} + \gamma(1-\delta_{mn})(1-3\ell_2^2) \right) Y_m Y_n \end{aligned} \quad (62)$$

The summation  $\sum_{\substack{m,m \\ NN}}$  means we sum over each dipole and its six nearest neighbors. Now any unitary transformation on the  $X_m$  and  $Y_m$  change canonical variables into canonical variables. In particular, if we choose linear transformations into new variables  $p_{\mathbf{x}}$  and  $q_{\mathbf{x}}$  such that (62) will be a sum of squares of  $p_{\mathbf{x}}$  and  $q_{\mathbf{x}}$ , these new variables will also be canonical. It is well known<sup>10</sup> that if a quadratic form is transformed to a sum of squares, then the new coefficients are the eigenvalues of the matrix of the old coefficients. Call these new coefficients  $a(\mathbf{x})$  and  $b(\mathbf{x})$ , respectively. Then we have

$$\mathcal{H} = -\mu H + \sum_{\mathbf{x}} \left( a(\mathbf{x}) \left( \frac{1}{m\hbar} \right)^2 P_{\mathbf{x}}^2 + b(\mathbf{x}) q_{\mathbf{x}}^2 \right) \quad (63)$$

and it only remains to find the eigenvalues  $a(\mathbf{x})$ ,  $b(\mathbf{x})$ .

Let us consider first  $a(\mathbf{x})$  ( $b(\mathbf{x})$  will be obtained in exactly the same fashion.) The matrix of the coefficients is given by

$$M_{mn} = \frac{\mu H}{2} \delta_{mn} + \gamma (1 - \delta_{mn}) / (1 - 3l_i^2) \quad \text{if } m, n \text{ represent nearest neighbors} \quad (64)$$

$$M_{mn} = 0 \quad \text{if } m, n \text{ represent non nearest neighbors}$$

If we take an arbitrary vector to be  $\{\psi_m\}$ , the eigenvalues will be given by

$$\sum_m M_{mn} \psi_m = \lambda \psi_n \quad (65)$$

Since  $M_{mn}$  depends only on  $\ell$  (or  $(m-n)$ ), we immediately try the substitution

$$\psi_n = e^{i(\alpha_1 n_1 + \alpha_2 n_2 + \alpha_3 n_3)} \quad (66)$$

Substituting (66) into (65) we find

$$\lambda = \frac{\mu H}{2} + 2\gamma (-2 \cos \alpha_1 + \cos \alpha_2 + \cos \alpha_3) \quad (67)$$

Now the periodic boundary conditions (which we assume here) assert that if we increase  $n$  in  $\psi_n$  by  $G$  ( $G$  being the size of the sample in any crystallographic direction,  $G^3=N$ ) in any direction we must get the same value. In order for this

to be so, we must have  $\chi_i = \frac{2\pi\sigma_i}{G}$  where  $\sigma_i$  is an integer. In order to obtain all the eigenvalues, we must take all  $\sigma$ 's in the range  $0 \leq \sigma_i \leq G-1$ . We then have that

$$Q(x) = \frac{\mu H}{2} + 2\gamma(-2\cos\chi_1 + \cos\chi_2 + \cos\chi_3)$$

and similarly

$$b(x) = \frac{\mu H}{2} + 2\gamma(\cos\chi_1 - 2\cos\chi_2 + \cos\chi_3) \quad (68)$$

The partition function  $Q$  will be given by

$$\begin{aligned} Q &= \int \dots \int e^{-\frac{H(x,y)}{kT}} dX_1 \dots dY_N \\ &= \int \dots \int e^{-\frac{H(p,q)}{kT}} dq_1 \dots dp_N \end{aligned}$$

(69)

since the transformation from  $(X,Y)$  to  $(p,q)$  is canonical. Substituting (63) in (69), one obtains

$$\begin{aligned} Q &= e^{\mu NH/kT} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \frac{\pi}{x} e^{-\left(\frac{a(x)}{(\frac{m\pi}{2})^2 kT}\right) p_x^2} dp_x e^{-\frac{b(x)}{kT} q_x^2} dq_x \\ &= e^{\mu NH/kT} \frac{\pi}{x} \sqrt{\frac{\pi}{a(x)/(\frac{m\pi}{2})^2 kT}} \sqrt{\frac{\pi}{b(x)/kT}} \\ &= \left(\frac{\pi kT \hbar m}{2}\right)^N \frac{\pi}{x} \frac{1}{\sqrt{a(x)b(x)}} e^{\mu NH/kT} \end{aligned} \quad (70)$$

The free energy ( $A$ ) will be given by

$$\begin{aligned} A &= -kT \log Q \\ &= -kT \log \left(\frac{\pi kT \hbar m}{2}\right)^N \frac{\pi}{x} \frac{1}{\sqrt{a(x)b(x)}} e^{-\frac{\mu NH}{kT}} \\ &= -\mu NH - NkT \log \left(\frac{\pi kT \hbar m}{2}\right) + \frac{kT}{2} \sum_x \log \{a(x)b(x)\} \end{aligned} \quad (71)$$

---

\* In reality the limits should be small, but since the contributions from large  $p$  and  $q$  are small, we can extend them to  $\infty$  in either direction.

Now  $a(\chi)$  and  $b(\chi)$  are practically continuous functions of  $\chi$  and therefore we may replace the sum in (71) by an integral according to the rule

$$\sum_{\chi} f(\chi) = \frac{G^3}{(2\pi)^3} \iiint_0^{2\pi} f(\chi) d\chi_1 d\chi_2 d\chi_3$$

Using this, (71) becomes

$$A = -\mu NH - NkT \log \frac{\pi kT \hbar \mu}{2} + \frac{NkT}{2(2\pi)^3} \iiint_0^{2\pi} \log(a(\chi) b(\chi)) d\chi_1 d\chi_2 d\chi_3$$

(72)

To obtain the magnetization (M) and the entropy (S) of our sample, we make use of the well known results

$$M = -\frac{\partial A}{\partial H}$$

$$S = -\frac{\partial A}{\partial T}$$

$$M = N\mu - \frac{N\mu kT}{4(2\pi)^3} \iiint_0^{2\pi} \left[ \frac{1}{a(\chi)} + \frac{1}{b(\chi)} \right] d\chi_1 d\chi_2 d\chi_3$$

$$S = Nk \log \frac{\pi kT \hbar \mu}{2} - \frac{1}{2} \frac{Nk}{(2\pi)^3} \iiint_0^{2\pi} \log(a(\chi) b(\chi)) d\chi_1 d\chi_2 d\chi_3$$

(73)

We may now write the expression (73) for M as

$$M = N\mu \left( 1 - \frac{kT}{(2\pi)^3 \mu H} \iiint_0^{2\pi} \left[ 1 - \frac{2\gamma}{\mu H} (-2c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3) + \left( \frac{2\gamma}{\mu H} \right)^2 (-2c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3)^2 + \dots \right] d\chi_1 d\chi_2 d\chi_3 \right)$$

Here we have assumed that  $\frac{2\gamma}{\mu H} \ll 1$  \* so that we could make

---

\* i.e. that the internal field is much less than the external field.

the expansion. The resulting integrals are very easy to evaluate and we find

$$M = N\mu \left[ 1 - \frac{kT}{\mu H} \left( 1 - 3 \left( \frac{4\gamma}{\mu H} \right)^2 + \frac{81}{9} \left( \frac{4\gamma}{\mu H} \right)^4 + \dots \right) \right] \quad (74)$$

Similar expansions for the integral appearing in S yield

$$S = Nk \left[ 1 + \log \frac{\hbar n \pi k T}{\mu H} + \frac{3}{2} \left( \frac{4\gamma}{\mu H} \right)^2 + \frac{81}{16} \left( \frac{4\gamma}{\mu H} \right)^4 + \dots \right] \quad (75)$$

When H is so large that we may completely neglect  $(4\gamma/\mu H)^2$ , we obtain

$$M = N\mu \left[ 1 - \frac{kT}{\mu H} \right]$$

$$S = Nk \left[ 1 + \log \frac{\hbar n \pi k T}{\mu H} \right]$$

These formula are exactly the same (except for a trivial additive constant in the entropy) as the asymptotic form of the usual Langevin expressions for completely free dipoles.

### 3) Quantization in a Strong Field

It is clear that in order for the above results to have any use they must be "quantized" in some sense. For at these low temperatures, the interaction of a dipole with an external field must be treated as a quantum effect. If the dipoles were completely free, we would obtain the Brillouin function<sup>22</sup> instead of the Langevin function (for the magnetization) The difference is very striking if we consider the fields and temperatures which occur in adiabatic demagnetization experiments. For example, if the spin is  $\frac{1}{2}$ , the field

30,000 G and temperature  $1^{\circ}\text{K}$ , the Brillouin function gives 96 % saturation, the Langevin function 54 % . We therefore look for some reasonable way of quantizing our results. Such a process has already been given by Kramers and Heller<sup>18</sup>, who justified it on the basis of the fact that it gave Bloch's  $T^{3/2}$  law for ferromagnetics. We shall also use this process and justify it on the grounds that it yields the asymptotic form of the Brillouin function for negligible internal interactions.

Let us go back to expression (63) for the energy

$$\mathcal{H} = -\mu NH + \sum_{\kappa} \left( a(\kappa) \left( \frac{1}{m\hbar} \right)^2 p_{\kappa}^2 + b(\kappa) q_{\kappa}^2 \right) \quad (63)$$

We may regard (63) as the energy of a set of harmonic oscillators (one for each  $\kappa$  ). The quantization of the energy of these oscillators is then the desired result. Now, the frequency which corresponds to an oscillator whose Hamiltonian is  $A p^2 + B q^2$  is easily seen to be  $2\sqrt{AB}$  and therefore the frequency associated with the  $\kappa$ 'th oscillator is

$$\omega_{\kappa} = 2 \sqrt{\left( \frac{1}{m\hbar} \right)^2 a(\kappa) b(\kappa)} = \frac{4}{m\hbar} \sqrt{a(\kappa) b(\kappa)} \quad (76)$$

The energy associated with the system if the  $\kappa^{\text{th}}$  oscillator is in the  $n_{\kappa}^{\text{th}}$  state is \*

$$E = -\mu NH + \sum_{\kappa} \hbar \omega_{\kappa} n_{\kappa} \quad (77)$$

\* Here we have dropped the zero point energy  $\frac{1}{2} \hbar \sum \omega_{\kappa}$  following Kramers and Heller. If one carries it along, it is impossible to get an agreement with the correct asymptotic form of the Brillouin function.

The partition function is then given by

$$Q = e^{\frac{N\mu H}{kT}} \sum_{m_1, \dots, m_N} e^{-\sum \frac{\hbar \omega_x m_x}{kT}} = e^{\frac{N\mu H}{kT}} \prod_x \frac{1}{1 - e^{-\hbar \omega_x / kT}} \quad (78)$$

The free energy becomes

$$\begin{aligned} A &= -kT \log Q = -N\mu H + kT \sum_x \log(1 - e^{-\frac{\hbar \omega_x}{kT}}) \\ &= -N\mu H + \frac{NkT}{(2\pi)^3} \iiint \log(1 - e^{-\frac{\hbar \omega_x}{kT}}) dx_1 dx_2 dx_3 \\ &= -N\mu H + \frac{NkT}{(2\pi)^3} \mathcal{K} \end{aligned} \quad (79)$$

where

$$\mathcal{K} = \iiint_0^{2\pi} \log(1 - e^{-\frac{\hbar \omega_x}{kT}}) dx_1 dx_2 dx_3 \quad (80)$$

Let us consider  $\log(1 - e^{-\frac{\hbar \omega_x}{kT}})$ . If we put

$$\lambda^1 = -2 \cos x_1 + \cos x_2 + \cos x_3, \quad \lambda^2 = \cos x_1 - 2 \cos x_2 + \cos x_3$$

we may write for  $(\frac{\hbar \omega_x}{kT})$

$$\begin{aligned} \frac{\hbar \omega_x}{kT} &= \frac{2\mu H}{m kT} \sqrt{(1 + \delta \lambda^1)(1 + \delta \lambda^2)} & \delta &= \frac{4\gamma}{\mu H} \ll 1 \\ &= \frac{2\mu H}{m kT} \left(1 + \frac{1}{2} \delta (\lambda^1 + \lambda^2) + \dots\right) \end{aligned}$$

since we have assumed  $\mu H > kT$  (neighborhood of saturation)

Therefore  $e^{-\frac{\hbar \omega_x}{kT}} \ll 1$  and  $\log(1 - e^{-\frac{\hbar \omega_x}{kT}}) \cong e^{-\frac{\hbar \omega_x}{kT}} \cong e^{-\frac{\gamma}{2} (1 + \delta/2 (\lambda^1 + \lambda^2))}$

where  $\frac{\gamma}{2} = \frac{2\mu H}{m kT}$ . Substitution of this and

$\lambda^1 + \lambda^2 = -\cos x_1 - \cos x_2 + 2 \cos x_3$  into (80) yields

$$\mathcal{K} = -e^{-\frac{\gamma}{2}} \iiint_0^{2\pi} e^{-\tau (2 \cos x_3 - \cos x_1 - \cos x_2)} dx_1 dx_2 dx_3 \quad (81)$$

where  $\tau = \frac{4\gamma}{m kT}$

$$\mathcal{K} = -e^{-\frac{\gamma}{2}} (2\pi)^3 I_0(2\tau) I_0^2(\tau) \quad (82)$$

$I_0(\tau) = J_0(it)$  where  $J_0(z)$  is the ordinary Bessel function of zero th order. Substituting this into (79), we find

$$A = -N\mu H - NkT e^{-\xi} I_0(2\tau) I_0^2(\tau) \quad (83)$$

Differentiation will give  $M$  and  $S$ , i.e.

$$M = N\mu \left( 1 - \frac{2}{n} e^{-\xi} I_0(2\tau) I_0^2(\tau) \right)$$

$$S = Nk \left( I_0(2\tau) I_0(\tau) (1+\xi) - 2\tau I_0(\tau) (I_1(\tau) I_0(2\tau) + I_0(\tau) I_1(2\tau)) \right) e^{-\xi}$$

$$I_1(\tau) \equiv -i J_1(i\tau) \quad (84)$$

These are our final formulas for the magnetization and entropy in the strong field case. We notice that when the interaction is so weak that it can be neglected against  $kT$ ,  $\tau = 0$  and

$$M = N\mu \left( 1 - \frac{2}{n} e^{-\xi} \right)$$

$$S = Nk (1 + \xi) e^{-\xi}$$

which are exactly the asymptotic expressions for the Brillouin function.

When  $\tau$  is small but not zero (internal interactions weak compared to  $kT$ ) we can expand the expressions (84) with respect to  $\tau$ . It is then possible to show that the magnetization decreases with decreasing field (as it should), but that the effect is quite small. The relative change in magnetization is of the order of  $\tau^2 e^{-\xi}$ . We omit the tedious expansions which lead to this conclusion.

4) Weak External Fields

If the external field is less than  $H_c$  (cf.5) Section II) and the entropy zero, then, we would expect a mixture of number 5 basic arrays and S arrays. (Throughout this section, we deal only with the S.C. case.) The presence of a small amount of disorder gives rise to small deviations from this "equilibrium" condition. The procedure here shall be just as in the previous two sections, i.e. we shall perform an expansion about the "equilibrium" condition, dropping terms of higher than second order. The original Hamiltonian will be the same as (59) above

$$H = -\mu H \sum_m z_m + \gamma \sum_{m_1, m_2} \frac{(\mu_{m_1} \mu_{m_2}) l^2 - 3(\mu_{m_1} l)(\mu_{m_2} l)}{l^5} \quad (59)$$

We assume the equilibrium state is given by

$$\begin{aligned} z_m &= q \\ x_m &= (-)^{m_2+m_3} \epsilon \equiv S(m) \epsilon \\ y_m &= 0 \end{aligned} \quad (85)$$

where  $q = H/H_c$  as before and  $\epsilon = \sqrt{1-q^2}$ . For small deviations from equilibrium (85) will take the form

$$\begin{aligned} z_m &= q + \zeta_m \\ x_m &= S(m) \sqrt{1-z_m^2} \cos \phi_m \\ y_m &= S(m) \sqrt{1-z_m^2} \sin \phi_m \end{aligned} \quad (86)$$

$\phi_m, \zeta_m$  are small, and  $\frac{\hbar \mu}{2} \zeta_m, \phi_m$  are the canonical coordinates of the  $m^{\text{th}}$  dipole.

We have

$$\sqrt{1-z_m^2} = \sqrt{1-(q+\zeta_m)^2} \approx \epsilon \left( 1 - \frac{q\zeta_m}{\epsilon^2} - \frac{\zeta_m^2}{2\epsilon^4} \right) \quad (87)$$

as long as  $q$  is not too close to 1. We shall make the same nearest neighbor approximation as in section 2. Then, using (87) and (86), we obtain for the Hamiltonian (to second order)

$$\begin{aligned} \mathcal{H} = & -\mu N H q - \gamma \epsilon^2 N f_s + 8\gamma \sum_m \left( \frac{\zeta_m^2}{\epsilon^2} + \epsilon^2 \phi_m^2 \right) \\ & + \gamma \sum_{\substack{m,n \\ NN}} \left\{ (1-3l_3^2) + \frac{q^2}{\epsilon^2} S(m)S(n)(1-3l_1^2) \right\} \zeta_m \zeta_n \\ & + \gamma \sum_{\substack{m,n \\ NN}} \left\{ \epsilon^2 S(m)S(n)(1-3l_2^2) \phi_m \phi_n \right\}^* \end{aligned} \quad (88)$$

If we let  $\frac{\zeta_m}{\epsilon} = R_m$  and  $\phi_m \epsilon = \psi_m$ , then  $R_m, \psi_m$  are also canonical, (88) takes the form

$$\begin{aligned} \mathcal{H} = & E_0 + 8\gamma \sum_m (R_m^2 + \psi_m^2) + 8\gamma \sum_{\substack{m,n \\ NN}} \left\{ \epsilon^2(1-3l_3^2) + q^2(1-3l_1^2) \right\} S(m)S(n) R_m R_n \\ & + \gamma \sum_{\substack{m,n \\ NN}} \left\{ S(m)S(n)(1-3l_2^2) \right\} \psi_m \psi_n \end{aligned} \quad (89)$$

$$E_0 = -\mu N H q - \gamma \epsilon^2 N f_s$$

To write (89) as a sum of squares, we introduce a linear transformation on  $\left( \frac{\kappa m}{2} R_m, \psi_m \right)$ . Calling the eigenvalues of the matrix of the coefficients of the  $R_m$  terms  $A(\kappa)$ , and those of the  $\psi_m$  terms  $B(\kappa)$ , we obtain

$$\mathcal{H} = E_0 + \gamma \sum_{\kappa} \left\{ A(\kappa) \left( \frac{\kappa m}{2} \right)^2 P_{\kappa}^2 + B(\kappa) q_{\kappa}^2 \right\}$$

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\* The letters NN under the summation imply summation over nearest neighbors only.

The determination of  $A(\chi)$  and  $B(\chi)$  goes just as before--  
we only quote the result:

$$\begin{aligned} A(\chi) &= [8 + \lambda'_\chi] \\ B(\chi) &= [8 + \lambda''_\chi] \end{aligned} \quad (90)$$

$$\lambda'_\chi = 2 \left( (\epsilon^2 - 2g^2) \cos \chi_1 + (\epsilon^2 - g^2) \cos \chi_2 - (2\epsilon^2 + g^2) \cos \chi_3 \right)$$

$$\lambda''_\chi = 2 \left( \cos \chi_1 + 2 \cos \chi_2 - \cos \chi_3 \right)$$

and

$$\chi_i = \frac{2\pi\sigma_i}{6} \quad 0 \leq \sigma_i \leq 6-1$$

To obtain the classical partition function, we use

$$Q = \int_{-\infty}^{\infty} \cdots \int e^{-\frac{H(p, q)}{kT}} dp_1 \cdots dq_n$$

yielding (analogously to (70), (71) and (72))

$$A = E_0 + NkT \log \frac{2\gamma}{\pi kT h n} + \frac{1}{2} \frac{NkT}{(2\pi)^3} \iiint_0^{2\pi} \log (A(\chi) B(\chi)) d\chi_1 d\chi_2 d\chi_3$$

(91)

It is possible to give an approximate treatment of the integral appearing in (91) for different limiting cases but as we are really only interested in the quantum mechanical formula, we shall not enter into this discussion.

### 5) Quantization in a Weak External Field

The process here is exactly analogous to that used in Section 3), the only difference being that we have a different formula for the characteristic frequencies. The free energy will be given by

$$A = E_0 + \frac{NkT}{(2\pi)^3} \iiint_0^{2\pi} \log \left( 1 - e^{-\frac{\hbar\omega_\chi}{kT}} \right) d\chi_1 d\chi_2 d\chi_3 \quad (92)$$

with

$$\begin{aligned} \omega_n &= 2 \sqrt{\frac{\gamma^2}{(\frac{n\pi}{2})^2} A(x) B(x)} \\ &= \frac{8\gamma}{\hbar n} \sqrt{(4 + (c^2 - 2g^2) \cos x_1 + (c^2 - g^2) \cos x_2 - (2c^2 + g^2) \cos x_3) (4 + \cos x_1 + 2 \cos x_2 - \cos x_3)} \\ &\equiv \frac{8\gamma}{\hbar n} \sqrt{g(x)} \end{aligned}$$

Substituting, we obtain

$$\begin{aligned} A &= E_0 + \frac{NkT}{(2\pi)^3} \iiint_0^{2\pi} \log(1 - e^{-\frac{8\gamma}{\hbar n k T} \sqrt{g(x)}}) dx_1 dx_2 dx_3 \\ &= E_0 + \frac{NkT}{(2\pi)^3} K \\ K &= \iiint_0^{2\pi} \log(1 - e^{-\frac{8\gamma}{\hbar n k T} \sqrt{g(x)}}) dx_1 dx_2 dx_3 \end{aligned}$$

We can evaluate K in two limiting cases. These are:

1)  $\frac{8\gamma}{\hbar n k T} \ll 1$  . This is easily seen to reduce to the classical result (91) and will not be further discussed.

2)  $\frac{8\gamma}{\hbar n k T} \gg 1$  . In this case, the chief contribution to the integral comes from the region where  $g(x) \cong 0$ .

We therefore expand  $g(x)$  about this point (there is only one such point.) We put

$$\begin{aligned} \cos x_1 &= -1 + \frac{(x_1')^2}{2} & x_1' &= \pi - x_1 \\ \cos x_2 &= -1 + \frac{(x_2')^2}{2} & x_2' &= \pi - x_2 \\ \cos x_3 &= 1 - \frac{(x_3')^2}{2} & x_3' &= x_3 \end{aligned}$$

resulting in

$$g(x) = \frac{1}{4} (x_1'^2 + 2x_2'^2 + x_3'^2) (12g^2 + (1-3g^2)x_1'^2 + (1-2g^2)x_2'^2 + (2-g^2)x_3'^2)$$

$$\cong 3g^2(x_1'^2 + 2x_2'^2 + x_3'^2)$$

neglecting fourth order terms in the  $x$ 's. This assumes, however, that  $q^2$  is much greater than range of  $x$ 's which contribute to the integral. Substitution gives for  $K$ \*

$$\begin{aligned} \underline{K} &= \iiint_{-\infty}^{\infty} \log \left( 1 - e^{-\frac{8\sqrt{3}\gamma q}{nkT} (x_1'^2 + 2x_2'^2 + x_3'^2)^{1/2}} \right) dx_1 dx_2 dx_3 \\ &= \frac{1}{\sqrt{2}} \iiint_{-\infty}^{\infty} \log \left( 1 - e^{-\frac{8\sqrt{3}\gamma q}{nkT} (x_1'^2 + 2x_2'^2 + x_3'^2)^{1/2}} \right) dx_1 dx_2 dx_3 \\ &= \frac{4\pi}{\sqrt{2}} \int_0^{\infty} \log \left( 1 - e^{-\frac{8\sqrt{3}\gamma q}{nkT} r} \right) r^2 dr \\ &= \frac{4\pi}{\sqrt{2}} \left( \int_0^{\infty} \log(1 - e^{-p}) p^2 dp \right) \left( \frac{nkT}{8\sqrt{3}\gamma q} \right)^3 \\ &= -\frac{4\pi^5}{45\sqrt{2}} \left( \frac{nkT}{8\sqrt{3}\gamma q} \right)^3 \end{aligned}$$

Therefore

$$A = E_0 - \frac{NkT}{90\sqrt{2}} \pi^2 \left( \frac{nkT}{8\sqrt{3}\gamma q} \right)^3$$

or

$$A = E_0 - \frac{\pi^2}{90\sqrt{2}} Nk \left( \frac{nk}{8\sqrt{3}\gamma} \right)^3 \frac{T^4}{q^3} \quad (93)$$

yielding

$$M = -\frac{\partial A}{\partial H} = \nu \mu q - \frac{\pi^2}{30\sqrt{2}} \frac{Nk}{Hc} \left( \frac{nk}{8\sqrt{3}\gamma} \right)^3 \frac{T^4}{q^4}$$

$$S = -\frac{\partial A}{\partial T} = \frac{2\pi^2}{45\sqrt{2}} Nk \left( \frac{nk}{8\sqrt{3}\gamma} \right)^3 \frac{T^3}{q^3} \quad (94)$$

\* We have extended the limits to infinity since we assume that only the contributions from the neighborhood of the origin are significant.

We may eliminate  $T$  from equation (90) and obtain

$$M = N\mu g - 6\sqrt{3} \left( \frac{45\sqrt{2}}{2\pi^2} \right)^{1/3} \frac{N\gamma}{m\hbar c} \left( \frac{S}{Nk} \right)^{2/3} \quad (95)$$

This gives us the magnetization as a function of field strength for an adiabatic process.

When  $q^2$  is actually extremely small (very weak fields) we must resort to another method of evaluating the integral  $K$ . Since  $K$  is a function of  $q^2$  only ( $g(\kappa)$  being a function of  $q^2$  only) we may expand, i.e.

$$K = K_0 + K_1 q^2 \quad (96)$$

where

$$K_0 = K \Big|_{q^2=0}$$

$$K_1 = \frac{\partial K}{\partial (q^2)} \Big|_{q^2=0}$$

As above, we may write  $g(\kappa)$  in the form

$$g(\kappa) = \frac{1}{4} (\kappa_1^2 + 2\kappa_2^2 + \kappa_3^2) (12q^2 + \kappa_1^2 + \kappa_2^2 + 2\kappa_3^2 - q^2(3\kappa_1^2 + 2\kappa_2^2 + \kappa_3^2))$$

Since throughout this discussion we are regarding  $\kappa_1, \kappa_2, \kappa_3$  small, we may neglect the term  $q^2(3\kappa_1^2 + 2\kappa_2^2 + \kappa_3^2)$  relative to  $12q^2$ . This gives

$$g(\kappa) \approx \frac{1}{4} (\kappa_1^2 + 2\kappa_2^2 + \kappa_3^2) (\kappa_1^2 + \kappa_2^2 + 2\kappa_3^2 + 12q^2)$$

and therefore

$$K = \iiint_{-\infty}^{\infty} \log(1 - e^{-\tau \sqrt{(\kappa_1^2 + 2\kappa_2^2 + \kappa_3^2)(\kappa_1^2 + \kappa_2^2 + 2\kappa_3^2 + 12q^2)}}) d\kappa_1 d\kappa_2 d\kappa_3$$

We have put  $\frac{4}{nkt} = \tau$ , as before

$$\begin{aligned} E_0 &= \iiint_{-\infty}^{\infty} \log \left( 1 - e^{-\tau \sqrt{(x_1^2 + 2x_2^2 + x_3^2)(x_1^2 + x_2^2 + 2x_3^2)}} \right) dx_1 dx_2 dx_3 \\ &= \frac{1}{\tau^{3/2}} \iiint_{-\infty}^{\infty} \log \left( 1 - e^{-\sqrt{(u^2 + 2v^2 + w^2)(u^2 + v^2 + 2w^2)}} \right) du dv dw \\ &\equiv -C/\tau^{-3/2} \end{aligned} \tag{97}$$

$$\begin{aligned} E_1 &= \left. \frac{\partial E}{\partial q} \right|_{q=0} = 6\tau \iiint_{-\infty}^{\infty} \frac{e^{-\tau \sqrt{(x_1^2 + 2x_2^2 + x_3^2)(x_1^2 + x_2^2 + 2x_3^2)}} \sqrt{\frac{x_1^2 + 2x_2^2 + x_3^2}{x_1^2 + x_2^2 + 2x_3^2}}}{e^{\sqrt{(u^2 + 2v^2 + w^2)(u^2 + v^2 + 2w^2)}} - 1} dx_1 dx_2 dx_3 \\ &= 6\tau^{-1/2} \iiint_{-\infty}^{\infty} \frac{\sqrt{(u^2 + 2v^2 + w^2)/(u^2 + v^2 + 2w^2)}}{e^{\sqrt{(u^2 + 2v^2 + w^2)(u^2 + v^2 + 2w^2)}} - 1} du dv dw \equiv a/\tau^{1/2} \end{aligned} \tag{98}$$

In these expressions, we have made the substitutions  $x_1 = \frac{1}{\sqrt{2}} u$ ,  $x_2 = \frac{1}{\sqrt{2}} v$ ,  $x_3 = \frac{1}{\sqrt{2}} w$ . The integrals  $a$  and  $c$  appearing in (97) and (98) are pure numbers. They may be evaluated numerically, and yield

$$a = 60.3$$

$$c = 6.10$$

The free energy now becomes

$$\begin{aligned} A &= E_0 + \frac{NkT}{(2\pi)^3} \left( -\frac{c}{\tau^{3/2}} + \frac{a}{\tau^{1/2}} g^2 \right) \\ &= E_0 + \frac{4\pi N}{n(2\pi)^3} \left( -c \frac{1}{\tau^{3/2}} + \frac{a}{\tau^{1/2}} g^2 \right) \end{aligned} \tag{99}$$

Differentiation of (99) with respect to  $H$  and  $T$  (or  $g$  and  $\tau$ ) gives the magnetization and entropy of the sample:

$$M = -\frac{\partial A}{\partial H} = N\mu g \left( 1 - \frac{g\tau a}{n\mu H c} \frac{1}{(2\pi)^3} \frac{1}{\tau^{3/2}} \right) \tag{100}$$

$$S = -\frac{\partial A}{\partial T} = \frac{Nk}{2(2\pi)^3} (5c \tau^{-3/2} - 3a \tau^{-1/2} g^2) \tag{101}$$

To get the adiabatic magnetization curve for very small  $q$ , we eliminate  $\tau$  from (100) and (101). To a first approximation, we may put (using (101))

$$\tau^{-3/2} \cong \frac{2(2\pi)^3}{5c} \left( \frac{S}{Nk} \right)$$

and therefore

$$M \cong N\mu g \left( 1 - \frac{8\gamma a}{n\mu H_c} \left( \frac{1}{2\pi} \right)^3 \frac{2(2\pi)^3}{5c} \left( \frac{S}{Nk} \right) \right)$$

or

$$M = N\mu g \left( 1 - \frac{16\gamma}{n\mu H_c} \left( \frac{a}{5c} \right) \left( \frac{S}{Nk} \right) \right) \quad (102)$$

(102) shows that the initial slope of the magnetization curve is less than it would be if the system were completely ordered (i.e.  $S=0$ .) This conclusion is consistent with the solution for larger  $q$ , and permits us to draw a smooth curve for the entire region of weak fields.

Formulas (84), (95) and (102) form the main results of this section. They give (except for certain regions into which we may extrapolate) a description of the adiabatic magnetization of a paramagnetic substance throughout the entire range of external field.

## V DISCUSSION OF RESULTS

In this section, we shall discuss the possible application of our results to experiment. For this purpose, one would have to find a substance which is magnetically dilute (so as to minimize interaction and rule out exchange effects) and in which the levels are unaffected by Stark splitting. Such a "magnetically ideal" substance is Cs-Ti alum<sup>23</sup>--indeed, at present, it seems to be the only one. Unfortunately, almost nothing is known about its magnetic properties. For example, the saturation magnetization has never been measured absolutely, and consequently the magneton number of the substance is not known. On the other hand, the crystal structure has been worked out by Lipson and Beevers,<sup>24</sup> who find the magnetic ions to be on a face centered cubic structure, the number per c.c. being  $2.08 \times 10^{21}$ . In the following, we shall assume this data of Lipson and Beevers, and we shall also assume that the Ti ion carries one Bohr magneton.

To investigate the validity of our formulas, one would recommend a procedure something like this: First, measure the saturation moment of Cs-Ti alum so that  $\mu$  is definitely known. Then perform adiabatic demagnetization experiments from very high initial fields (about  $4 \times 10^4$  g) and low initial temperature (about 1°K.) In this case, the entropy of the sample would be so small that the non-statistical theory of section III could be applied with complete confidence. Should there fail to be an agreement with

experiment, we could attribute it definitely to quantum mechanical effects. Indeed, these experiments should give us information about the lowest energy level of the system. Then by lowering the initial field (or increasing the initial temperature) one could see clearly the statistical effects.

Possibly the only relevant experiment on Cs-Ti alum which has been thus far performed is that of DeHaas and Wiersma.<sup>23</sup> The salient feature of this experiment is that the magnetization stayed constant from  $H = 24,000$  gauss (which is about 90% saturation if one assumes a magnetic moment of a Bohr magneton) to a field of about 100 gauss. It then dropped to zero almost linearly with field. This behavior is in general agreement with the results of section III, where complete initial saturation was assumed. However, the calculation of the critical field (using above data) yields  $H_c = 69$  g. This is of the correct order of magnitude, but the deviation is serious. As mentioned above it could easily be due to quantum effects.

Since there is actually a small amount of disorder present, we should really use the results of section IV. However, the formulas there are only derived for the S.C. case, while the alum in question is F.C. Investigation of these formulas does seem to indicate that the strong field part of the curve would be practically unaffected, while the weak field part ( $H < H_c$  or  $q < 1$ ) would be slightly displaced. The fact that our formulas do tend to keep the magnetization near its initial value is in itself somewhat consoling as

Van Vleck's theory<sup>5</sup> indicates rapid dropping off of the magnetization with decreasing field strength. It is not surprising, however, that Van Vleck's results should not agree too well with experiment as the expansion he uses converges poorly (or not at all) in the critical region.

The magnetization could also be obtained on the basis of a theory of Sauer and Temperly<sup>6</sup>. This leads to a critical field below which the magnetization drops at once to zero. Such a result is an immediate consequence of their assumption that the spins are always parallel or antiparallel to the field. Hence, in this model there is no possibility of a state with vanishing entropy and having a magnetization intermediate between zero and the saturation value. Their coupling scheme corresponds to that used in the Paschen-Bach effect, while actually one is in the region of anomalous Zeeman effect.

In the case of alums containing magnetic ions with more than one electron the magnetization curve is very much influenced by the crystalline field and the present theory may not be used alone. The dipole interaction, however, should be the decisive factor for the state of the system at absolute zero if the number of electrons in the magnetic ions is odd. The question of main interest is whether or not the state will be polarized (ferromagnetism or anti-ferromagnetism). In III, it was shown that for spherical samples, the lowest state was always non-polarized, but that in the important F.C. case (to which the paramagnetic alums belong) a prolate spheroidal sample of axis ratio larger than 6, the polarized state will

have the lower energy. This is of interest in connection with the "ferromagnetism" observed by Kúrtil, Laine, and Simon<sup>25</sup> for iron ammonium alum at low temperatures. That a stable ferromagnetic state really exists is still open to some question. In the first place, the numerical values of the energy constants might be changed by the above mentioned quantum mechanical effects. In addition, it should be emphasized that pure energy considerations cannot completely decide questions of stability. The forces tending to polarize the crystal originate in distant parts of the sample, while the depolarization forces are due to relatively near neighbors. If the sample is cooled to a temperature below the Curie point by contact with a heat bath, rather than by adiabatic demagnetization, a ferromagnetic state would certainly not be established. This is not to be confused with the situation in true ferromagnetics, where the saturation moment is masked only by the domain structure. The question needs further study, both from the theoretical and the experimental point of view. It may certainly be said, however, that dipole ferromagnetism-if it exists-has a character essentially different from exchange ferromagnetism.

APPENDIX I

Spin Waves on a 1-dimensional Dipole Array

We assume a general familiarity with the Bloch treatment of spin waves<sup>26</sup> for ferromagnetism.

Let the Hamiltonian of the system be

$$H = \gamma \sum_{l,k} \frac{\sigma_l \cdot \sigma_k - 3\sigma_l^z \sigma_k^z}{|l-k|^3} \equiv \gamma \sum_{l,k} H_{lk} \quad (1)$$

We are interested in solutions of the eigenvalue problem for (1) which have all spins parallel except for a single one.

Let  $\psi_j$  be a wave function which has the spin of the atom down, all others up. Then our solution may be written in the form

$$\psi = \sum_j a_j \psi_j \quad (2)$$

Substituting in the eigenvalue problem

$$H \psi = E \psi \quad (3)$$

we obtain

$$E a_{j'} = \gamma \sum_{l,k} a_j (\psi_{j'}, H_{lk} \psi_j) \quad (4)$$

The matrix element in (4) is easily evaluated by making use of well known properties of the Pauli spin matrices. It is

$$(\psi_{j'}, H_{lk} \psi_j) = \frac{\gamma}{|l-k|^3} \left[ 2 \{ (1-\delta_{lk})(1-\delta_{j,l}) \delta_{j,j'} + \delta_{jk} \delta_{j',l} + \delta_{jl} \delta_{j',k} \} - \{ 1 + 3(1-2\delta_{lj}-2\delta_{kj}) \} \delta_{j,j'} \right]$$

Using this (4) becomes

$$E a_j = \gamma \sum_{l, k \neq j} a_l \frac{1}{|l-k|^3} \left[ 2 \{ (1-\delta_{ik})(1-\delta_{jl})\delta_{ij} + \delta_{jk}\delta_{j,l} + \delta_{jl}\delta_{j,k} \} - \{ 1+3(1-2\delta_{ij}-2\delta_{kj}) \} \delta_{jj} \right] \quad (5)$$

carrying out the summations indicated in (5), and making use

of the abbreviations  $a = \sum_{n=1}^{\infty} \frac{1}{n^3} \approx 1.202$   $\epsilon = E - E_0$   
 ( $E_0 = -4\alpha\gamma$ , the energy at no excitation) we find

$$(\epsilon - 16\gamma a) a_j = 4\gamma \sum_{k \neq j} a_k \frac{1}{|k-j|^3} \quad (6)$$

To solve equations (6), we make the usual substitution yielding

$$\epsilon - 16\gamma a = \sum_{\substack{k \\ k \neq j}} (4\gamma) \frac{e^{-i\chi(j-k)}}{|j-k|^3} = 8\gamma \sum_{n=1}^{\infty} \frac{\cos \chi n}{n^3} \quad (7)$$

$$\text{or } \epsilon = 16\gamma a + 8\gamma \sum_{n=1}^{\infty} \frac{\cos \chi n}{n^3}$$

Here  $\chi = \frac{2\pi\sigma}{N}$  ( $\sigma$  integer by periodic boundary conditions,

$0 \leq \sigma \leq N-1$ ). This gives us a band of levels centered

around  $E_x = 16\gamma a$ . For the spin wave investigation, one

is usually interested only in the lowest levels. These occur

in the neighborhood of  $\chi = \pi$ . We therefore investigate

$$f(\chi) = \sum_{n=1}^{\infty} \frac{\cos n\chi}{n^3}$$

in the neighborhood of  $\chi = \pi$ . Let us place  $\pi - \chi = \rho$ , then

if  $f(\chi) = g(\rho)$ , we obtain

$$g(\rho) = - \sum_{n=1}^{\infty} \frac{(-1)^{n+1} \cos \rho n}{n^3}$$

We now make use of a well known result in the theory of Fourier series<sup>27</sup>, i.e.

$$\begin{aligned} \sum_{n=1}^{\infty} \frac{(-1)^{n+1} \cos \rho n}{n} &= \log \left| 2 \cos \frac{\rho}{2} \right| \\ &= \log 2 \cos \frac{\rho}{2} \quad \text{if } 0 < \rho < \pi \end{aligned}$$

for small  $\rho$  this becomes  $\log 2 + \log (1 - \frac{\rho^2}{8})$

or 
$$\sum_1^{\infty} \frac{(-1)^{n+1} \cos \rho n}{n} \cong \log 2 - \frac{\rho^2}{8} \quad (8)$$

integration of (8) with respect to  $\rho$  from 0 to  $\rho$  yields

$$\sum_1^{\infty} (-1)^{n+1} \frac{\sin \rho n}{n^2} \cong \rho \log 2 - \frac{\rho^3}{24}$$

and another integration yields

$$g(\rho) \cong - \sum_1^{\infty} \frac{(-1)^{n+1}}{n^3} + \frac{\rho^2}{2} \log 2$$
$$\cong -.90 + .35 \rho^2 \quad (9)$$

One could now use this expression to obtain a low temperature partition function for this system. The analysis, however, is just as in the ferromagnetic case, and leads one to believe there is no dipole ferromagnetism in one dimension.

APPENDIX II

Some Results on the Statistical Mechanics of One Dimensional Systems

a) We shall first show that any finite ranged force in a one dimensional discrete system can never produce a phase transition. We assume here familiarity with the matrix method<sup>28</sup> of evaluating the partition function. Then it is clear, that in the matrix formulation, the problem will be solved as soon as we find the largest eigenvalue of a certain finite matrix. However, all we need know is that if the force is of finite range and the interacting elements only take on discrete states, then all the matrix elements are positive. There exists a theorem due to Frobenius,<sup>29</sup> which states that the largest eigenvalue of a finite matrix with positive elements is always non-degenerate.\* It is well known, however, that a phase transition can only occur if degeneracy is possible and therefore the above result is proved.

b) In this article, we shall demonstrate an infinite ranged force which does lead to a phase transition. We take as a model a set of  $N$  dipoles along a line each of which interacts with every other according to  $-J \mu_i \mu_j$ , where  $\mu_i = \pm 1$  (generalized Ising model.) The energy of the whole system is then

$$E(\mu_1, \mu_2, \dots, \mu_N) = -\frac{J}{2} \sum_{i,j} \mu_i \mu_j \quad (1)$$

---

\* It should be pointed out that if the forces have infinite range, or if the system is infinite in two directions, then we obtain an infinite matrix and the above proof breaks down.

and the partition function  $Q$  is given by

$$Q = \sum_{\{\mu_i\}} e^{H \sum_{ij} \mu_i \mu_j} \quad (2)$$

In (2)  $\sum_{\{\mu_i\}}$  means a summation over all possible configurations of the system and  $H = J/2kT$ . We may write (2) as

$$\begin{aligned} Q &= \sum_{\{\mu_i\}} e^{H(\sum_i \mu_i)^2 - H \sum_i \mu_i^2} \\ &= e^{-NH} \sum_{\{\mu_i\}} e^{H(\sum_i \mu_i)^2} \end{aligned}$$

Now, if we introduce  $K = \sum_i \mu_i$  and let  $W(K)$  represent the number of configurations of the system which has  $\sum_i \mu_i$  equal to a definite  $K$ , we may write  $Q$  as

$$Q = e^{-NH} \sum_K W(K) e^{HK^2} \quad (3)$$

To find  $W(K)$ , we proceed as follows: Let  $n$  be the number of positive spins. Then the number of negative spins is  $N-n$  and the total spin ( $K$ ) is given by  $K = n - (N-n) = 2n - N$  or  $n = \frac{K+N}{2}$ . Therefore, a fixed  $K$  implies a fixed  $n$ . Now the number of ways we can choose  $n$  spins up is  $N!/n! (N-n)!$  or

$$W(K) = \frac{N!}{\left(\frac{N+K}{2}\right)! \left(\frac{N-K}{2}\right)!} \quad (4)$$

$$Q = e^{-NH} \sum_K \frac{N!}{\left(\frac{N-K}{2}\right)! \left(\frac{N+K}{2}\right)!} e^{HK^2} \quad (5)$$

as is usual in such summations, we replace the sum by its maximum term. Call  $f(K) = e^{HK^2} / \left(\frac{N-K}{2}\right)! \left(\frac{N+K}{2}\right)!$

$$\log f(K) = HK^2 - \log \left(\frac{N-K}{2}\right)! - \log \left(\frac{N+K}{2}\right)!$$

using the Stirling approximation  $\log p! = p \log p - p$  we find

$$\begin{aligned} \log f(K) \approx HK^2 - \frac{N}{2} \left( \log \frac{N+K}{2} + \log \frac{N-K}{2} \right) \\ - \frac{K}{2} \left( \log \frac{N+K}{2} - \log \frac{N-K}{2} \right) \end{aligned}$$

The maximum is given by

$$\frac{\partial \log f(K)}{\partial K} = 0$$

$$4HK = \log \frac{N+K}{N-K}$$

or

or finally by

$$K = N \tanh 2HK \tag{6}$$

Now it is very easy to see (simply drawing the graph will show it) that one only has a  $K \neq 0$  solution of (6) when  $2H > \frac{1}{N}$  or when  $NJ > kT$ . If we define  $T_c$  by  $NJ = kT_c$ , then for  $T > T_c$   $K=0$  and there is no net magnetization. For  $T < T_c$ , we get a finite magnetization which is obtained by solving the above equation. That is,  $T_c$  is a curie point for the system.

It is not claimed that the above example is physically significant. It is merely given to indicate that somewhere between the extremes discussed in a) and b) lies a type of force which will give a one dimensional phase transition.

c) We conclude with a brief rigorous discussion of the linear classical ferromagnet. It is assumed that we have a set of spins arranged along a line, each pair of neighbors interacting with the energy  $-J \vec{\mu}_i \cdot \vec{\mu}_j$ , where  $\vec{\mu}_i$  is the dipole moment of the  $i^{\text{th}}$  atom and  $|\vec{\mu}_i| = 1$ , (Kramers<sup>8</sup> model of ferromagnetism)  $J$  is a constant. Since we have  $\vec{\mu}_i \cdot \vec{\mu}_j = \cos \theta_i \cos \theta_j + \sin \theta_i \sin \theta_j \cos(\varphi_i - \varphi_j)$  ( $(\theta_i, \varphi_i)$  being the polar angles of the  $i^{\text{th}}$  dipole) the partition function  $Q$  becomes

$$Q = \int \cdots \int_N e^{\sum_j H (\cos \theta_j \cos \theta_{j+1} + \sin \theta_j \sin \theta_{j+1} \cos(\varphi_j - \varphi_{j+1}))} d\Omega_1 \cdots d\Omega_N \quad (7)$$

$$j = i+1 \text{ and } d\Omega_i = \sin \theta_i d\theta_i d\varphi_i$$

Now, by the usual arguments of the matrix method, or simply by noticing that this can be written as an integral with an iterated kernel, we find

$$Q = \lambda_{\max}^N$$

where  $\lambda_{\max}$  is the largest eigenvalue of the integral equation

$$\iint_0^{2\pi} \int_0^\pi e^{H \cos \psi} \psi(\theta', \varphi') \sin \theta' d\theta' d\varphi' = \lambda \psi(\theta, \varphi) \quad (8)$$

$$\cos \psi = \cos \theta' \cos \theta + \sin \theta' \sin \theta \cos(\varphi' - \varphi) \quad \text{If we regard the integral}$$

in (8) as an integral operator, then we may write  $\mathcal{H}\psi = \lambda\psi$ .

But  $\mathcal{H}$  has rotational symmetry (since it only depends on the relative angle between the  $(\theta, \varphi)$  and  $(\theta', \varphi')$  directions) and therefore, we can choose <sup>the</sup>  $\psi$ 's to form an irreducible representation of the rotation group. But all the irreducible representations of the rotation group are given by the spherical

harmonics  $Y_l^m(\theta, \varphi)$  and therefore these are the required eigenfunctions of (8). To find the corresponding eigenvalues, we make use of the following formula from the theory of radiation<sup>30</sup>

$$f_m(kr) Y_l^m(\theta, \varphi) = \frac{1}{4\pi i^m} \int_0^{2\pi} \int_0^\pi e^{i kr \cos \gamma} Y_l^m(\theta', \varphi') \sin \theta' d\theta' d\varphi'$$

$f_m(z)$  being the spherical Bessel function of order  $m$ . Substitution of  $ikr = H$  yields just (8) above. Therefore, corresponding to  $\psi(\theta, \varphi) = Y_l^m(\theta, \varphi)$  we have the eigenvalue

$$\lambda_l^m = 4\pi i^l f_l(-iH) = 4\pi (-i)^l f_l(iH)$$

The largest of these (for all  $H$ ) is easily seen to be that for  $l=0$ , i.e.

$$\lambda_{max} = 4\pi f_0(iH) = 4\pi \frac{\sinh H}{H}$$

and we have an exact evaluation of the partition function,

$$Q = (4\pi)^N \frac{\sinh^N H}{H^N}$$

(9)

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### BIOGRAPHICAL NOTE

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