Magnetic Energy Constants of Dipolar Lattices

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In this paper, calculations are presented for the determination of the magnetic energy, assuming dipole-dipole interaction, of a macroscopic crystal possessing paramagnetic ions situated on a definite lattice structure. Parallel and antiparallel configurations are considered as well as specimens of different shapes and lattice structures of various types. It is shown that the configuration of lowest energy cannot be strictly defined but is dependent upon the shape of the specimen. This configuration is an antiparallel one for a sphere but changes to a parallel one for a long slender specimen. The transition between the two configurations appears to take place at a certain critical value of the demagnetization factor. For specimens above this value the theory accounts qualitatively for the low values of the magnetization found experimentally and for the apparent constancy of the Curie point with changes of shape. Below the critical value the theory implies a pure ferromagnetic state, which is not in agreement with experiment. Probable reasons for the discrepancy are given.

IN attempting to give a theoretical explanation of the anomalous experimental results of Kurti and Simon[1] on paramagnetic salts at low temperatures, the author found it desirable to first make a definite determination of the configuration of lowest energy. This paper is devoted to that end. The model used is a three-dimensional lattice of freely suspended magnetic dipoles, each of which is assumed to possess two orientations, either parallel or antiparallel to some given direction.

To compute the configurational energy, the exact method of attack would be to calculate by wave-mechanical means the energy levels of the assembly as a whole, considering the crystal as one large molecule. Owing, however, to the complexity of the wave equation when interaction between particles is considered, this method is prohibitive. Therefore we resort to a purely classical determination of the magnetic energy of the given three-dimensional configurations, assuming different possible arrangements of the paramagnetic ions. From spectroscopic analysis, as carried out by Beevers and Lipson,[2] the structure of such paramagnetic salts as iron alum is now well known. The unit cell is about 12 angstroms in length and the metal atoms are placed on a face-centered structure. It is due to these comparatively large distances apart that the exchange forces, which fall off exponentially with the distance, probably do not matter; whereas the magnetic forces, varying only as the inverse third power of the distance, become of prime importance.

The dependence of the energy upon the magnetic forces rather than the exchange forces between atoms makes the calculations much more complex as the magnetic interaction between two magnets, considering only dipole moments, depends on their orientation relative to the connecting line as well as on their distance apart. The classical expression for the interaction energy is

$$(\mathfrak{y}_i\cdot\mathfrak{y}_j)r_{ij}^{-3}-3(\mathfrak{y}_i\cdot\mathbf{r}_{ij})(\mathfrak{y}_j\cdot\mathbf{r}_{ij})r_{ij}^{-5}, \qquad (1)$$

where $\mathfrak{y}_i$ and $\mathfrak{y}_j$ are the strength of the magnetic dipoles and $\mathbf{r}_{ij}$ is the distance between the two. If the dipoles have the same direction as well as strength, the expression simplifies to $\mu^2r^{-3}(1-3\cos^2\theta)$ where θ is the angle between the dipole direction and the line joining the two dipoles.

For a single row of dipoles the lowest energy is obtained when they are all parallel to one another and directed along the line joining them. For a double row or a two-dimensional set-up, this is no longer true. Here a direct evaluation of Eq. (1), summed over all dipoles, shows that the antiparallel alignment—one string pointing to the right, the next nearest string to the left, and so on gives the deepest energy.

For the three-dimensional solid, with magnetic dipoles situated at all lattice points and all

* The major part of this paper was written while the author was at Cambridge University, England.

[1] Kurti, Laine and Simon, Comptes rendus **204**, 675, 754 (1937).

[2] C. A. Beevers and H. Lipson, Proc. Roy. Soc. **148**, 664 (1935).

pointing in the same direction, the magnetic energy is given by

$$W=-\sum_i \sum_{l,m,n} \frac{\mu_i^2}{r^3} \frac{2l^2-m^2-n^2}{(l^2+m^2+n^2)^{5/2}}$$

$$=-\tfrac{1}{2}N^2\mu^2 \sum_{l,m,n} \frac{2l^2-m^2-n^2}{(l^2+m^2+n^2)^{5/2}}, \quad (2)$$

where N is the number of ions per cc and l, m, and n are integers running from $-\infty$ to ∞. This is an infinite summation of the type $1/r^3$ in three dimensions. It cannot be definitely evaluated as the series is logarithmically divergent. This is equivalent to saying that the value of the interaction energy will depend on the shape. For a spherical or cubic specimen, symmetry requirements show directly that W will be zero. For a specimen of any other shape it becomes necessary to resort to the Lorentz approximation. Lorentz considers a small sphere surrounding the dipole in question and assumes that the summation over all dipoles can be expressed as a summation within the sphere and an integration outside. The summation contributes nothing to the field at the center, provided the dipoles are arranged in symmetrical fashion. There will, however be a contribution for unsymmetrical arrangements. This point has been considered by Sauer and Temperly,[3] who show that the internal field may be taken as proportional to the degree of order of the dipole arrangement. The value of the integration over all the dipoles outside the small sphere is determined by considering the effect of the surface charge produced by these outside magnets. On the surface of the small sphere itself there exists a charge density which contributes to the field at the center a factor of $(4\pi/3)I$, where I is the intensity of magnetization per unit volume; the additional field due to the surface charge on the external boundary of the specimen is brought in by what is commonly referred to as the demagnetization factor. For a sphere the demagnetization factor of $-(4\pi/3)$ exactly annuls the local field factor of $+(4\pi/3)$ so that the energy is given correctly by the Lorentz approximation.

For parallel alignment of the elementary dipoles the magnetic interaction energy, using the Lorentz approximation, can be obtained for any external shape of specimen provided the appropriate demagnetization factor is given or can be determined. But for other alignment configurations such as the antiparallel one, the Lorentz method fails and it becomes necessary, in order to get a reasonable approximation to the correct magnetic energy, to take a direct sum result over a large number of dipoles. All direct sum results hereinafter given will be determined by taking into account the effect of all dipoles within a small cube surrounding the dipole in question and containing approximately 125 atoms. Careful attention must be paid to algebraic signs in carrying out this summation as antiparallel dipoles give an interaction energy of opposite sign to that of parallel dipoles. For purposes of direct summation the equation for W can conveniently be written as

$$W=-\tfrac{1}{2}N^2\mu^2 \sum_\gamma \sum_l (2l^2-\gamma^2)/(l^2+\gamma^2)^{5/2}. \quad (3)$$

Here γ is the right-angle distance from the center dipole to whichever string is being considered. Thus if we were determining the energy for an antiparallel arrangement in a simple cubic crystal, γ would take the values 1, $\sqrt{5}$, $\cdots$ for the antiparallel dipoles, $\sqrt{2}$, 2, $\sqrt{8}$, $\cdots$ for the parallel dipoles, while W has the sign given by Eq. (3) for the parallel rows and changes sign for the antiparallel.

Although the paramagnetic ions are located on a face-centered lattice, it appears worth while for reference purposes to include the energy calculations for the simple cubic structure and the body-centered structure as well. In the case of the body- and face-centered structures, it is possible that a deeper energy might be obtained by assuming the magnets directed along the body or face diagonal rather than along the axis of the unit cell. Such indeed proves to be the case. We also distinguish between two different possible types of antiparallel alignment which we shall refer to as "A" and "B." In arrangement "A" the rows closest to one another are alternately directed. For example, in the body-centered cubic lattice the corner dipoles would all point forward and the body-centered dipoles would point backward. In arrangement "B," the nearest dipoles situated on a plane perpendicular to the

[3] J. A. Sauer and H. N. V. Temperly, Proc. Roy. Soc. (in print).

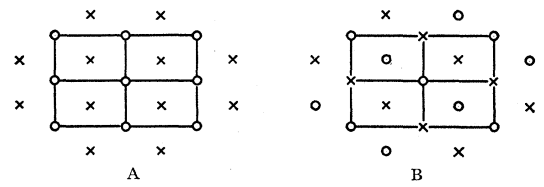

FIG. 1. Showing sections taken at right angles to direction of dipoles.

axis are alternately directed; in the example given above, this means that the corner dipoles are themselves arranged in antiparallel fashion and similarly for the body-centered ones. Any possible ambiguity arising from these definitions will be compensated by illustrating, wherever necessary, the difference between the two arrangements. The magnetic interaction energy for each of three alignments, parallel, antiparallel "A," and antiparallel "B" will now be obtained for different shaped specimens.

INTERACTION ENERGY FOR A SPHERICAL SPECIMEN

(*1*) *Parallel Alignment:* The magnetic energy for a simple cubic lattice structure is found to be zero whether the determination is made directly from Eq. (2) or by means of the Lorentz method. This result still holds good for the body-centered and face-centered lattices, as they consist, respectively, of two and four interlocked cubic lattices.

(*2*) *Antiparallel "A" and "B":* It is necessary here to consider each one of the three lattice structures separately.

Simple Cubic Structure: Evaluation of Eq. (3), taking into account the interaction of the nearest 125 dipoles, leads to an energy value of $W=-2.7N^2\mu^2$.

Body-centered Structure: We consider two different possibilities of dipole direction, along edge of unit cell or along body diagonal. For each of these chosen directions, the magnetic energy is calculated for both types of antiparallel alignment. The two configurations "A" and "B" are shown in Fig. 1, the circles indicating parallel dipoles and the crosses antiparallel ones. The interaction energy for the (001) direction and with arrangement "A" is zero, while with arrangement "B," the result is -1.35. For the diagonal direction, W is -1.75 for "A" and "B."

Face-centered Structure: Fig. 1 may again be used for noting the essential difference between the two types of alternating alignment. The approximate values of the energy are 2.2 for arrangement "A" and dipole direction along cube edge, and -1.1 for the same direction with "B." With face-diagonal direction of the magnets, W decreases to -1.1 for "A" and -1.8 for "B."

INTERACTION ENERGY FOR AN ELLIPSOIDAL SPECIMEN

(*1*) *Parallel Alignment:* For this case the energy may be expressed as

$$W=-0.5\sum\mu[(4\pi/3)-(\text{D.F.})]I \qquad (4)$$

where by D.F. is meant the demagnetization factor. The values obtained will differ from the energies in the case of the sphere by having the proper demagnetizing factor, depending on the axis ratio of the ellipsoid, inserted in place of the $4\pi/3$ of the sphere. For example, a specimen with an axis ratio of $r=3$ possesses a demagnetization factor of 1.37 and gives rise to an interaction energy of 1.9. As the axis ratio approaches infinity, D.F. approaches zero and W is then given by $0.5\sum\mu\cdot(4\pi/3)N\mu=2.1N^2\mu^2=2.1$ in units of $N^2\mu^2$. The results are the same for all three types of crystal lattice structure.

(*2*) *Alternating Arrangements:* The energy values as given above for a spherical specimen are true here as well. This is so because in the alternating arrangement of dipoles there exists no charge density on the surface and hence the shape of the boundary does not matter.

For simplicity of reference and comparison, the foregoing results, together with some other energy values as yet unmentioned, have been assembled in Table I. Some of these magnetic energy values have already been given by Van Vleck,[4] but as no details of the calculation and also no explicit values for the possible diagonal directions appeared in his paper, it was thought desirable to collect all the values in one Table. In addition to the energies for the parallel configuration, the antiparallel "A," and the antiparallel "B," Table I includes the magnetic energy for a rather special configuration, pictured in Fig. 2. This arrangement of dipoles might be

[4] J. H. Van Vleck, J. Chem. Phys. **5**, 556 (1937).

termed a nonmagnetic, disordered state of the crystal as compared to the parallel arrangement, which is a magnetic, ordered state and the antiparallel arrangement, which is also ordered but nonmagnetic. This particular disordered state is only one of a number of possible disordered arrays, yet it is of interest to compare its energy values with those of the ordered arrangements.

Examination of Table I allows us to draw the following conclusions:

(1) The parallel alignment gives an energy independent of the type of lattice structure but dependent upon the shape of the specimen. That is, for a given shape, the energy is the same whether the dipoles are arranged on a body-centered, face-centered, or simple cubic lattice yet a change in specimen shape from a sphere to a long slender specimen changes the energy from the value zero to -2.1.

(2) Conversely, the antiparallel configurational energy is dependent upon the type of lattice structure but independent of the shape. For example, the energy changes in value from -2.7 to 1.1 in going from a simple cubic lattice to a face-centered one, while a change in the external boundary leaves the values unaltered. Comparing the two types of antiparallel alignment, we see that the lower energy is in general associated with type "B" rather than "A."

(3) Dipoles set along the direction of the face diagonal for the face-centered lattice and along the direction of the body-diagonal for the body-centered lattice, lead to deeper energy values than when directed along the cube axis. This is what we should expect for changing direction from cube axis to body or face diagonal reduces the distance between adjacent dipoles of a parallel string and hence causes an increase in the magnetic energy.

(4) For parallel alignment dipoles tend to set themselves in such a direction that the demagnetizing factor is a minimum. In other words, in an ellipsoidal specimen, the dipoles would prefer to align along the long axis rather than the short.

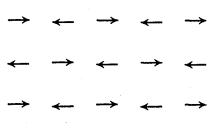

FIG. 2.

TABLE I. *Energy constants. All direct sum values (antiparallel ones) given to within 0.05. a—simple cubic, dipole direction along (001); b—body-centered, dipole direction along (001); c—body-centered, dipole direction along (111); d—face-centered, dipole direction along (001); e—face-centered, dipole direction along (011).*

DIPOLE ARRANGEMENTS	LATTICE STRUCTURE	AXIS RATIOS	ENERGY CONSTANT
Parallel	*a, b, c, d, e*	$\frac{1}{3}$	1.91
		1	0.0
		3	-1.41
		4	-1.62
		5	-1.75
		6	-1.83
		∞	-2.1
Antiparallel "A"	*a*	any	-2.7
	b		0.0
	c		-1.75
	d		2.2
	e		-1.1
Antiparallel "B"	*a*	any	-2.7
	b		-1.35
	c		-1.75
	d		-1.1
	e		-1.8
Disordered	*a*		0.0

(5) The actual configuration of minimum energy is not strictly defined but is dependent upon the shape. For a sphere or an ellipse with low axis ratio, the antiparallel arrangement is definitely the lower. For a long slender specimen or an ellipse with high axis ratio ($r>6$ for the face-centered lattice) the parallel configuration becomes the more stable.

(6) A comparison of the values from Table I for the parallel and the disordered configurations indicates that a spherical specimen, in the absence of any external field, has equal energies in the completely ordered state and in the completely disordered state. This, perhaps, may not be an expected relation; yet when it is recalled that for a spherical specimen the Lorentz and the demagnetizing terms cancel, thus causing the magnetic interaction energy to vanish, the correlation appears more natural. The recorded energy value for the disordered array was calculated only for a simple cubic lattice but it appears likely that the same result would be obtained for the other lattice types.

The three-dimensional model studied in this paper appears to eliminate the chance of a spherical specimen becoming spontaneously magnetized as a result of pure dipole-dipole coupling. The ferromagnetic state would be possible,

though, for a long slender specimen. Now it is well known that the usual Ising model, to which our model roughly corresponds, will never give ferromagnetism. This result, however, holds only in the case of a linear chain. Peierls[5] has generalized Ising's model to include the two- and three-dimensional cases and he finds that ferromagnetism is possible. It is not correct though to assume, in our model, that even a long slender specimen will necessarily be ferromagnetic. For even if the lowest energy level of the crystal does correspond to the parallel state, there may exist other nonparallel states of only slightly higher energy values; and the greater number of complexions of these nonparallel states might easily be sufficient to overcome the energy advantage of the parallel level.

By taking the antiparallel configuration as the stable one at low temperatures, and by using the energy values given in Table I, it is possible to determine the Curie points. This is done in a paper by Sauer and Temperly[3] who show that the Curie point, for all specimens in which the antiparallel state is the stable one, i.e., for ellipsoidal shapes with r less than 6, the critical temperature is independent of the shape. This appears to be in confirmation with the experimental results as Dr. Simon has reported that for a sphere as well as long samples, there is very little change in the Curie point.

In view of our results, the Curie point for a sphere is now to be interpreted as the temperature at which a transition takes place between a disordered state and the ordered antiparallel state. Heretofore, it has usually been taken as an indication of a conversion from the disordered state to the ordered parallel one; because of this interpretation, one expected the measured magnetization to be in the neighborhood of its saturation value. All experiments, however, show it to be very much smaller. This has always been considered one of the very puzzling features of the experimental results but the mystery is readily removed when we recognize that the ordered state below the Curie point is not magnetic but essentially nonmagnetic.

For an ellipsoidal specimen with $r>6$ the reason for a low value of the magnetization is not so apparent, as here the Curie point should correspond as usual to the transition to the parallel saturated state, provided, of course, that our simple treatment is adequate. Before definite conclusions can be drawn there is a great need for more experimental evidence, especially in the region of $r>6$. The low value of the magnetization is inferred, at present but from a single experimental value on iron alum with an r ratio of 6. Still there does appear to be a definite discrepancy between theory and experiment. The probable reason for this discrepancy is the too definite postulation of the existence of the parallel state as the stable one on the simple evidence that its energy value is slightly less than that of the antiparallel state. In a rigorous treatment the effect of the greater statistical weight of the nonparallel states must needs be considered.

It requires very little change to convert the energy constants of Table I to conform to the case of electrical dipole-dipole interaction instead of magnetic. Nothing in the electrical case corresponds to the demagnetization factor in the magnetic, hence the D.F. term of Eq. (4) must vanish. This converts all the different energy constants for parallel alignment to the single value -2.1. The antiparallel configurational energies remain the same. A comparison now leads to the conclusion that, for the simple cubic lattice, the antiparallel arrangement still gives the deeper energy. For the face-centered and body-centered lattices, however, the electric dipole coupling leads to different results than the magnetic. It indicates that, of the various arrangements considered, the parallel state is always the most stable regardless of the shape of the specimen. This does not imply electric saturation for the same reasons as given above for the magnetic case.

I wish to express my gratitude to Professor Fowler for suggesting this problem and for his generous assistance. I am also indebted to Mr. A. H. Wilson and Professor Van Vleck for helpful discussions.

[5] R. Peierls, Proc. Camb. Phil. Soc. **32**, 471 (1936).