decaying. In the above experiment 12 percent of the mesons should be transformed into neutrettos before being stopped. Of the remaining 88 percent half should be captured leaving 44 percent decaying into electrons.

The experiments are not accurate enough to decide whether the number of decay electrons is actually appreciably less than 50 percent. The actual percentage should depend on the thickness of the absorber.

VIII. CONCLUSIONS

On the whole the theory was seen to give a satisfactory account of all the chief cosmic-ray phenomena. Although a number of points, especially the cascade production of mesons (cf. Section II), the east-west effect of the soft component and the penetrating showers, must await further investigation, it is probable that this theory is fundamentally correct. The conclusions that can be drawn from our results are twofold: (i) The theory of damping used as a basis for all our calculations will be a correct part of future quantum electrodynamics or at least a good approximation. (ii) Cosmic-ray mesons are in fact identical with the quanta predicted by Yukawa which are responsible for the nuclear fields. It may perhaps be too early to say that the special form of the meson theory used in this paper (the one suggested by Møller and Rosenfeld) is the correct form of the meson theory. We have carried out all the calculations also with a different form of the theory (assuming that only charged mesons exist) and found the agreement with cosmic-ray experiments less good, though this form of the theory cannot be wholly excluded. (The energy loss of fast protons would be three times smaller.) It is satisfactory that the form of the meson theory which gives the best account of the nuclear forces also agrees best with cosmic-ray facts. Especially, the assumption of both pseudoscalar and transverse mesons is strongly supported by the fact that all components of cosmic radiation can be explained as owing their origin to one kind of primary particles, i.e., protons.

We are very much indebted to Dr. L. Janossy for a most useful comment on this paper and also for communicating some of his experimental results to us before publication.

PHYSICAL REVIEW VOLUME 64, NUMBERS 3 AND 4 AUGUST 1 AND 15, 1943

On the Adiabatic Demagnetization of Iron Alum

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(Received April 26, 1943)

The behavior of iron alum during adiabatic demagnetization to temperatures near the absolute zero is of particular theoretical interest because of the deviations from Curie's law that arise from the perturbing actions of crystalline field and magnetic dipole-dipole coupling. The effect of these perturbations on the magnetic moment and the entropy is calculated exactly to second-order terms in the magnetic coupling and to third-order terms in the crystalline potential. The calculations are presented for crystalline fields of either cubic or axial symmetry and are valid for the case of large applied fields in which saturation effects become important. Theoretical values of the adiabatic moment are found to be in satisfactory agreement with the experimental values determined by Casimir and de Haas. A true thermodynamic scale is established that enables the temperature to be calculated at any value of the magnetic field during demagnetization. The relationship of this scale to the temperatures determined by the magnetic method of de Haas and Wiersma is discussed.

PART I: DESCRIPTIVE ANALYSIS

I. Introduction

ONE of the greatest difficulties encountered in the production of low temperatures by the method of adiabatic demagnetization is the determination of the thermodynamic temperature. Until recently, it has been the general practice of experimenters to set up a "magnetic" temperature scale based on the validity of Curie's law. Deviations from this law, however, will be

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produced both by the magnetic interaction between the paramagnetic ions of the alum and by the Stark splitting due to the crystalline electric field. These effects become progressively more important as the temperature is lowered so that there may exist an appreciable difference between the "magnetic" or "reciprocal susceptibility" temperature T^* and the true Kelvin temperature T.

To overcome this uncertainty in temperature measurement, various procedures have been proposed, most of which base their determination of the true thermodynamic temperature on calorimetric measurements. De Haas and Wiersma,[1] however, have proposed a method of determining the Kelvin temperature entirely from magnetic measurements. Their procedure is based essentially on the experimental fact that when certain alums are subject to an adiabatic demagnetization process, the magnetic moment is found to remain constant, within the limits of experimental error, as the field is decreased from its initial high value to some much lower value. When this is the case, one can show purely from the laws of thermodynamics that the true temperature T is a function of the field strength H and is given by an expression of the form

$$T-T_0=c(H-H_0), \tag{1}$$

where c is a parameter depending on the value of the initial magnetization, and T_0 and H_0 denote values of temperature and field, respectively, at the beginning of demagnetization. This equation was applied by de Haas and Wiersma to the particular case of caesium titanium alum as this material experimentally showed no change in the value of the magnetic moment in the range from 24,000 gauss to 100 gauss.

Similar experiments on a powdered specimen of iron alum by Casimir and de Haas[2] indicate that the magnetic moment during adiabatic demagnetization does not remain constant over any appreciable interval, but varies with the applied field strength H_a in the following manner:

$$M=M_0(1-b/H_a^2). \tag{2}$$

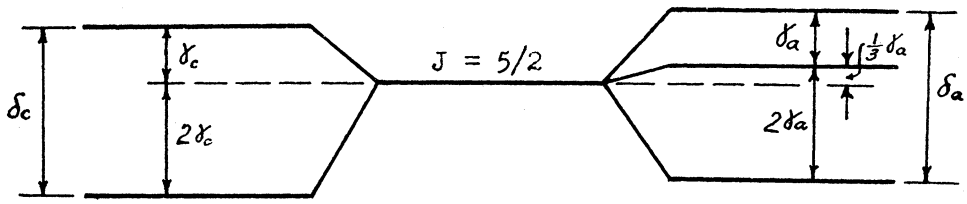
Here M_0 is the original magnetic moment due to an initial magnetic field H_0 of 18,100 gauss, and b is a constant whose experimental value is 1.7×10^5. From this value of b it is readily seen from Eq. (2) that for sufficiently large values of the field strength ($H_a>10{,}000$) the term in $1/H_a^2$ is negligible compared to unity. Hence for values of the field strength above this magnitude the method of de Haas and Wiersma for determining the true Kelvin temperature is clearly applicable. For fields between 10,000 gauss and 5000 gauss, the existence of the second term in Eq. (2) above will cause a small error to be made in the temperature determination, while for fields less than 5000 gauss the error becomes appreciable.

It is not surprising that the magnetic moment of iron alum fails to remain constant during the process of adiabatic demagnetization. Rather the reverse would be the case as even a simple theoretical treatment shows the existence of a $1/H^2$ term in the expression for the adiabatic moment. Such a treatment has been given by Casimir and de Haas[2] who show that for low values of the initial field, the coefficient of the $1/H^2$ term [i.e., b in Eq. (2)] is some function of the original magnetization and hence of the original field strength, but does not depend on the value of the final field. They were unable to evaluate this function for the general case, but for the special case of low initial fields that do not produce saturation, they found b to be 1.3×10^5 as compared to the experimental value of 1.7×10^5. The discrepancy between the computed and the experimental value is probably due to neglect of saturation effects. The magnetic fields used in their experiment were quite large (18,000 gauss) and for fields of this order of magnitude one would normally expect saturation effects—neglected in their treatment of the problem—to be very important. That such is the case will be demonstrated in this article for, contrary to the opinion of Casimir and de Haas, it *is* possible to make an exact theoretical determination of the adiabatic moment for high fields. The method of solution is described in Part I of this paper but the mathematical details associated with the determination are placed in Part II.

Once the necessary theoretical treatment has been developed, it can be used not only for the determination of the adiabatic magnetic moment

[1] W. J. de Haas and E. C. Wiersma, Physica **3**, 491 (1936).

[2] H. B. G. Casimir and W. J. de Haas, Physica **7**, 72 (1940). The symbol capital B in this paper is the same as our small b.



a. Cubic field b. Axial field

FIG. 1. Splitting of $J=5/2$ level by a crystalline field. In notation of Penney and Schlapp (reference 7) $\delta_c=3\gamma_c=72Dq$, $\delta_a=3\gamma_a=18Aa$.

but also becomes immediately available for use in two other connections. First, it enables us to calculate the true thermodynamic temperature and to estimate the error that will arise if the temperature is determined by the simple magnetic method of de Haas and Wiersma, i.e., by use of Eq. (1). Secondly, by comparing the theoretical expression of M with the experimental, we obtain information in regard to the nature of the crystalline field that acts on the paramagnetic ions of the alum.

II. Method of Approach

The procedure adopted is based upon a method of attack originally developed by Van Vleck[3] and used by him to study theoretically the adiabatic demagnetization of caesium titanium alum ($CsTi(SO_4)_2\cdot 12H_2O$). The indicated mathematical treatment is applicable for the case of iron alum ($NH_4Fe(SO_4)_2\cdot 12H_2O$) as well, but there are some significant differences in treatment due to basic differences in the structure of the two materials. In caesium alum the Ti^{+++} ion has a spin $S=\frac{1}{2}$ and lies in a doubly degenerate ground state and hence, according to a fundamental theorem of Kramers,[4] is unaffected by a surrounding crystalline field of any type of symmetry. The free orientation of the paramagnetic ions is thereby hindered only through the agency of the magnetic coupling, and possibly a little exchange coupling, between spins. In iron alum, on the other hand, the paramagnetic Fe^{+++} ion has a spin $S=5/2$ and lies in a sixfold degenerate ground state. This sixfold level is subject to Stark splitting by the electric fields of the crystal as has been shown by Bethe,[5] Kramers,[4] and Van Vleck and Penney.[6] A field of axial symmetry splits the sixfold degenerate level of the ground state into three separate doubly degenerate levels, while a crystalline field of cubic symmetry separates the sixfold level into a fourfold and a twofold one. This is illustrated in Fig. 1 (see Penney and Schlapp[7]).

Hamiltonian Function

The first step in our theoretical treatment must be to set up an expression for the Hamiltonian that will correctly represent the conditions to which the paramagnetic alum is subject during the adiabatic demagnetization process. In addition to the applied magnetic field acting on the paramagnetic ions of the alum, there is a magnetic coupling of the three-dimensional array of dipoles and an electrostatic interaction between the various paramagnetic ions and their surrounding crystalline fields. The Hamiltonian may therefore be written

$$\mathcal{H}=-g\beta H\sum_i S_{z_i}+\sum_{j>i} w_{ij}+\sum_i V_i, \quad (3)$$

where g is the Lande splitting factor, β the Bohr magneton, and S the spin of the Fe^{+++} ion. The first term thus represents the Zeeman energy due to a field H supposedly directed along the z axis. The second and third terms respectively represent the magnetic dipole-dipole coupling and the crystalline field interaction. The exchange interaction between the paramagnetic ions has been neglected in Eq. (3) because, in iron alum, the ions are known to be spaced relatively far apart.[8]

[3] J. H. Van Vleck, J. Chem. Phys. **6**, 81 (1938). One typographical error should be noted. In the expression for G_s on p. 83 the sign before the $(g\beta H/kT)$ term should be reversed.

[4] H. A. Kramers, Proc. Kon. Akad. Amst. **33**, 953 (1930); **34**, 965 (1931).

[5] H. A. Bethe, Ann. d. Physik **3**, 133 (1929).

[6] J. H. Van Vleck and W. G. Penney, Phil. Mag. **17**, 961 (1934).

[7] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932); **42**, 666 (1932).

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

In the mathematical treatment that follows, the Zeeman term of Eq. (3) is taken as the unperturbed part of the Hamiltonian, and the other two terms are considered as small perturbations causing slight shifts in the unperturbed energy levels.

The first of the perturbing influences, namely the magnetic dipole-dipole coupling, is explicitly introduced into the analysis by writing for w_{ij} the expression[9]

$$w_{ij}=g^2\beta^2 r_{ij}^{-3}\{(\mathbf{s}_i\cdot\mathbf{s}_j)-3(\mathbf{s}_i\cdot\mathbf{r}_{ij})(\mathbf{s}_j\cdot\mathbf{r}_{ij})r_{ij}^{-2}\}$$

where $\mathbf{s}_i$ is the spin angular momentum vector in units of $h/2\pi$ of atom i, $\mathbf{r}_{ij}$ is the radius vector connecting atoms i and j, and r_{ij} is its modulus. As the lattice spacing is known, there are no unknown constants in this expression, and hence the computation of the influence of this term, though lengthy, is straightforward.

On the other hand, when the crystalline field potential is considered, either one or more unknown constants are introduced depending on the nature of the crystalline field assumed. From x-ray analysis by Beevers and Lipson,[8] it is known that the field surrounding the paramagnetic ion possesses trigonal symmetry. The most general potential of this type is[10]

$$V_t=F_2(r)T_2^0+F_4(r)T_4^0+F_4'(r)(T_4^3+T_4^{-3}), \quad (4)$$

where the F's are coefficients depending only on r, the T_l^m's are spherical harmonics of the form $T_l^m=P_l^m(\cos\theta)\exp(im\varphi)$, and the P_l^m's are Legendre polynomials. In these expressions $\theta=0$ corresponds to the trigonal axis, which coincides with one of the four-body diagonals of the cubic lattice. If the fourth-order terms of Eq. (4) are neglected then the crystalline field is one of axial symmetry and that part independent of r can be expressed by

$$V_a=A(x'^2+y'^2-2z'^2), \quad (4a)$$

where A is an arbitrary constant associated with the strength of the field, and the primed coordinates are rectangular coordinates in which the trigonal axis coincides with the z' axis. This is the only type of second-order term compatible with trigonal symmetry. Probably the most important fourth-order terms in (4) are those having cubic symmetry. In terms of rectangular coordinates referred to the cubic axes, these terms are given by

$$V_c=D(x^4+y^4+z^4-\tfrac{3}{5}r^4), \quad (4b)$$

where D is an arbitrary constant measuring the strength of the field, and the $\frac{3}{5}r^4$ term is included in order to have V_c satisfy La Place's equation.

The Hamiltonian of Eq. (3) is used as the basis for a rigorous calculation of the partition function Z. Once this is established, the magnetic moment and the entropy, both of which are required in order to get the adiabatic moment, are obtained by simple differentiation. In the calculation of Z, we assume the dipole-dipole coupling and the crystalline field potential are both small compared to the energy of thermal agitation. As the partition function is expanded in powers of the ratio of the perturbing influences to kT, the convergence of this expansion will be rapid as long as our original assumption is valid. Fortunately, the ratio is small except at sufficiently low temperatures where the interactions become comparable to kT. The unperturbed energies arising from the first term in the Hamiltonian are not assumed small compared to kT as it is the form of M for *large* values of H that is desired.

The perturbing influences are taken explicitly into account by using the well-known quantum-mechanical expressions from perturbation theory,[11] and then calculating the matrix elements of the perturbing part of the Hamiltonian. The calculation of the matrix elements and also of the partition function is greatly facilitated by use of the methods of group theory. These methods are particularly applicable to our problem where the experimental use of a powdered specimen instead of a single crystal necessitates the writing of the crystalline field and dipole-dipole contribution to the partition function in terms of generalized coordinates over which an average must be taken before the final expressions for the magnetic moment and the entropy can be obtained. It is precisely in the carrying out of this averaging process—otherwise a long-winded and tedious job—that the group theory method affords such a great saving.

[9] J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937).
[10] A. Siegert, Physica **3**, 85 (1936).
[11] E. C. Kemble, *Fundamental Principles of Quantum Mechanics* (McGraw-Hill, New York, 1938).

III. Adiabatic Moment to Second Order in Perturbing Influences

The development of the partition function is carried out in Sections 6 and 8 of Part II. The expressions for the magnetic moment and the entropy, given by Eqs. (21) and (22) of Section 9, are functions of both T and H. To find the adiabatic magnetic moment, the procedure is to eliminate T between the two equations, and then since S is constant during the course of an adiabatic demagnetization experiment, one has an equation for the adiabatic magnetic moment that depends only on the field strength. In Section 10, this expression is shown to be

$$M=M_0(1-b/H^2), \tag{5}$$

where b represents a function of the initial field and initial magnetization given by Eq. (29) of Section 10. Equation (5) is of the same form as the experimental relation as regards dependence of M upon H. It should be noted, however, that in the theoretical expression H is to be interpreted as the true field acting on the paramagnetic ions and not as the experimentally applied field.

To find the numerical value of the theoretically derived expression for b the unknown parameter or parameters that entered into the crystalline field potentials must be evaluated. This evaluation is made by comparing the theoretical expression for the specific heat in zero applied field with the experimental. Both are of the form $C_v=A'/T^2$, where the coefficient A' includes the contribution of both the dipole-dipole coupling and the crystalline field interaction. If the trigonal field acting on the paramagnetic ion is taken as purely cubic or purely axial in character, then only a single unknown parameter enters into the expression for A' and the constant is directly evaluated by comparison with the known experimental value of this constant for iron alum. This evaluation is made in Section 10 of Part II. The experimental value of A' has been determined by several investigators, some of whom used entirely different methods of attack. Considering this, it is remarkable how well they agree.[12]

After these unknown crystalline field constants have been evaluated, one can calculate the numerical value of the coefficient of $1/H^2$ and thereby obtain the final expression for M correct to the second order in the two perturbing influences. In Section 10, this expression is shown to be

$$M=M_0(1-9.4\times10^4/H^2). \tag{5a}$$

The numerical value of 9.4 is calculated on the assumption that the trigonal field acting on the paramagnetic ion is predominantly cubic. This value should be changed to 11.5 if an axial field is assumed. In either case, however, a comparison with the experimental values of Casimir and de Haas shows that the theoretical values of M obtained from (5a) are too high. Part of this discrepancy is accounted for by the fact that, because of demagnetization corrections, the true field H appearing in Eq. (5a) is somewhat less than the applied field H_a entering into Eq. (2). It is shown in Section 10 of Part II that this accounts for only a minor part of the difference between the theoretical values for M and the experimental and leaves the major part of the discrepancy still to be explained.

Two possible reasons for the existence of the discrepancy present themselves. The first of these is the neglect of third and higher order terms in the expansion of the partition function and the second is the restriction that the crystalline field acting on the paramagnetic Fe^{+++} ion is trigonal in character. Of these two, the former seems to be the more likely as the trigonal nature of the field is attested by the experimental x-ray methods of Beevers and Lipson.[8] Still, from a theoretical standpoint, the possibility of the existence of a more general field should not be excluded and hence we shall first consider how the removal of the trigonal restriction would affect the results.

[12] H. B. G. Casimir, W. J. de Haas, and D. de Klerk, Physica **6**, 241 (1939); F. K. du Pre, Physica **7**, 79 (1940); P. Teunissen and C. J. Gorter, Physica **7**, 33 (1940); C. Starr, Phys. Rev. **60**, 241 (1941); F. Simon, private correspondence to J. H. Van Vleck (1940). Casimir, de Haas, and de Klerk determined the specific heat constant by direct magnetic measurements on pure crystals. They find A' to be 2200 ± 40. Du Pre records a value of 2300 ± 50 determined by experiments on paramagnetic relaxation. Indirect measurements by Teunissen and Gorter, from experiments on paramagnetic dispersion, tend to lower this value slightly while similar indirect measurements by Starr tend to raise it by about the same amount. Private correspondence from Simon indicates a value of the splitting distance of 0.193 determined from direct magnetic measurements. This corresponds to a specific heat constant of 2350. All values whether determined by direct or indirect measurements thus approximate 2300 and this we take as the correct magnitude.

TABLE I. Comparison of theoretical and experimental values of adiabatic moment of iron alum.

H_a	H	M(exp.)	M(calc.) Cubic field 2nd ord.	3rd ord.	M(calc.) Axial field 2nd ord.
18,100	18,000	—	4.70	4.70	4.70
11,170	11,040	4.77	4.70	4.70	4.70
5,550	5,420	4.66	4.69	4.68	4.68
3,130	3,000	4.61	4.65	4.64	4.64
1,352	1,230	4.25	4.41	4.33	4.34
912	807	3.7	4.02	3.75	3.87
494	412	2.9	2.10	0.10	1.53

Note: Values of M expressed in units of $N\beta$.

Failure of Arbitrary Crystalline Field to Improve Agreement

Let us replace the trigonal expression for the crystalline field given by Eq. (4) by the more general expression

$$V_a = \sum_{s=-4}^{4} a_{4s} T_4^s + \sum_{r=-2}^{2} b_{2r} T_2^r, \qquad (6)$$

where the a's and b's are arbitrary coefficients. If the coefficients of this general field are so selected as to retain unrestricted trigonal symmetry, it should be noted that (6) still represents an increase in generality over the cubic and axial fields thus far considered. It would be useless to include terms in T_3 and T_1 as matrix elements for odd order potentials must vanish in virtue of the LaPorte rule. The matrix elements have already been computed for the T_4 and T_2 term and hence it is an easy matter to set up the partition function for any combination of these terms with arbitrary coefficients. The contribution of this type of field to the specific heat and to the adiabatic magnetic moment is given by Eqs. (33) and (32), respectively, of Part II. Examination of these two equations discloses that, at least as far as the second-order terms are concerned, *no assigned values of the arbitrary parameters can bring the theoretical and experimental results in closer agreement than already found under the assumption of a trigonal field of axial symmetry.* Hence the failure of the theoretical results to give closer agreement with the experimental data is definitely not due to any restriction on the nature of the crystalline field.

IV. Beneficial Effect of Higher Order Terms

The most likely reason for the discrepancy between the theoretical values of M and the experimental values is the neglect of third and higher order terms in the expansion process employed in the calculation of the partition function. Fortunately, it is possible to save much of the labor associated with the calculation of higher order terms by making use of some previous theoretical work on iron alum by Kronig and Bouwkamp.[13] For large fields and for arbitrary direction of the magnetic field relative to the crystal axes—just the required conditions necessarily imposed on us by experiment—they have calculated the energy levels of iron alum to the third order in the crystalline field parameter. Their calculations were made for a crystalline field of cubic symmetry and do not take into account the effect of the magnetic dipole-dipole coupling. This is not a serious drawback, however, as the neglect of the third-order term in the dipole-dipole coupling will not appreciably change the final result. This is so because the contribution of the crystalline field terms to the magnetic moment is about eight times as large as the dipole-dipole contribution.

Once the energy levels are known, it is a straightforward process to determine the partition function, the entropy, and the magnetic moment. The details of this treatment are given in Section 11. The effect of inclusion of the third-order crystalline field terms is to add a new term in $1/H^3$ to the adiabatic moment. The complete expression for the magnetization then becomes

$$M = M_0(1 - bH^{-2} - b'H^{-3}), \qquad (7)$$

where b' is independent of the final field but depends upon the initial conditions. For the experimental conditions of de Haas and Wiersma b' takes the numerical value of 30×10^6 while b itself has the value previously stated, *vis.*, 9.4×10^4. If M is expressed in the form of Eq. (2), the correction to b due to introduction of the third-order term in the cubic crystalline field interaction is a factor $(1+320/H)$. This factor becomes increasingly important as the field is lowered. The effect of the additional term in the expansion has thus been to increase the value of the coefficient of the H^{-2} term and hence its inclusion has tended to lower the value of the adiabatic magnetic moment in the proper direc-

[13] R. de L. Kronig and C. J. Bouwkamp, Physica **6**, 290 (1939).

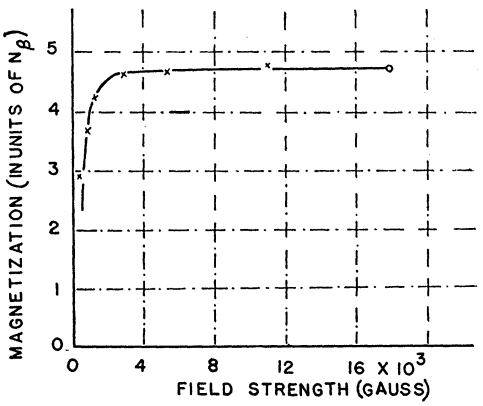


FIG. 2.

tion in order to give better agreement with experimental data.

The theoretical values of M based on Eq. (7) and Eq. (5) are compared with the experimental data in Table I. From this table it is readily seen that the agreement between the third-order theoretical and the experimental values of M is now quite satisfactory. One exception is the last row in the table, but here the true field strength is less than 500 gauss and for a field as low as that, the temperature obtained by assuming the law of de Haas and Wiersma to apply is already below the characteristic magnetic coupling temperature. When this is the case, the convergence of the expansion breaks down completely.

The relation between the magnetic moment and the final field strength is graphically shown by Fig. 2, where the actual experimental points are indicated by the small crosses. No experimental value of M is recorded by de Haas and Wiersma in the neighborhood of the original field, and no mention is made of the order of accuracy of their experimental data. We are no doubt safe in assuming that the experimental error is of the order of 3 percent. For all values of the field above 900 gauss the greatest difference between the theoretical and the experimental value of M is less than this amount. Hence it does not appear worth while at present to carry out any further calculations on the effect of still higher order terms.

Nature of Crystalline Field Present in Iron Alum

It was thought likely when the theoretical calculations were first started that a comparison between the experimental values of the adiabatic moment and the theoretical values, as computed on the assumption of crystalline fields of varying types, would enable us to determine the proper symmetry characteristics of the crystalline field present in iron alum. On the basis of second-order calculations alone, it would appear from Table I that a trigonal field of axial symmetry leads to slightly better agreement with experiment than a crystalline field of predominantly cubic symmetry. However, when third-order terms in the cubic field are taken explicitly into account in the calculations, the agreement between theory and experiment is found to be much improved.

Further examination of Table I might lead one to suspect that had third-order terms also been calculated for the crystalline field of axial symmetry, the theoretical values of M might be drawn still closer to the experimental values. To take this statement as evidence in support of a trigonal field of axial symmetry in preference to one of cubic symmetry would, however, be definitely misleading since the difference between the two cases is probably less than the experimental error involved in making the measurements. Furthermore, it is now quite possible that a more general trigonal field consisting of a combination of the axial and cubic terms would also fit the facts, but as long as the agreement is so close as indicated in Table I there is no means of deciding on the exact form this arbitrary field should take. The one definite conclusion that can be drawn from the evidence presented is that values of M calculated to the third order in the cubic field perturbation are in somewhat closer agreement with experiment than values based

TABLE II. Temperatures and corresponding field strengths.

H_a	H	T(calc.)	T [From Eq. (1)]	% difference
18,100	18,000	1.18	1.18	—
15,330	15,200	1.00	1.00	—
12,330	12,200	.800	.803	0.37
9,270	9,140	.600	.604	0.67
6,210	6,080	.400	.405	1.25
3,170	3,040	.200	.206	3.00
2,400	2,275	.150	.156	4.00
1,630	1,510	.100	.106	6.00
1,305	1,190	.080	.085	6.25
1,140	1,030	.070	.074	6.25

only on second-order calculations with an axial field assumption.

Determination of True Temperature

To find the true temperature appropriate to any value of the field strength after the beginning of adiabatic demagnetization, the procedure is to solve the entropy equation [(22) plus (40) of Part II] for T in terms of H. Since the entropy retains a constant value during the process of demagnetization, the resulting equation immediately enables us to find T for any H or H for any T, provided only that the temperatures are not so low that the expansion process employed in the calculation of the adiabatic moment breaks down. In Table II are shown the values of the temperatures appropriate to a number of different fields.[14]

In column 4 of Table II appear the temperature values one would obtain by using the simple de Haas-Wiersma procedure discussed in the Introduction of this paper. In principle their procedure is never applicable to iron alum, but it is clear from inspection of the table that the temperature estimated by use of the de Haas-Wiersma equation [Eq. (1)] differs very little from the exact temperature for all values of the field down to about 7000 gauss. Between 7000 and 1000 gauss, the percentage error incurred by use of Eq. (1) rises from about 1 percent to about 6 percent. For fields less than 1000 g the expansion process employed in the determination of the entropy, and hence of the exact relation between T and H, is no longer valid.

On the basis purely of the experimental relation between the adiabatic moment and the field strength, Casimir and de Haas[2] have noted that for fields down to 2500 gauss the error in temperature measurement caused by use of Eq. (1) is probably less than 0.01°K. Our calculations show an error in temperature measurement at 2500 g of 0.006°K. This appears to be the maximum absolute error involved at all values of the field for which Table II and our method of calculation are valid.

PART II: MATHEMATICAL ANALYSIS

V. Preliminary Details

We require expressions for the magnetic moment and the entropy of an assembly of atomic magnets subject both to an applied magnetic field and a crystalline electrical field and coupled together magnetically. These are most easily obtained from the partition function by means of the equations

$$M=kT\frac{\partial}{\partial H}(\log Z), \quad S=\frac{\partial}{\partial T}(kT\log Z). \tag{8}$$

The partition function is given by

$$Z=\sum_\lambda \exp\,(-W_\lambda/kT), \tag{9}$$

where the summation is over all states of the entire crystal considering the crystal as a giant molecule. Since we are dealing with the partition function instead of the individual energy levels of each atom, we are concerned only with the energy W_λ of the crystal as a whole.

The Hamiltonian function has already been described in Section II. We choose a system of representation which diagonalizes the first (or Zeeman) term of $\mathfrak{H}$ and then consider the spin-spin coupling and the crystalline field potential as small perturbations. The unperturbed energies are given by

$$W_\lambda{}^0=-g\beta H\sum_i M_i, \tag{10}$$

where the M_i are the characteristic values of S_{zi} and the letter λ is used to represent the totality of quantum numbers for a given state of the entire crystal. The crystalline energies W_λ are given in

[14] Values of H in Table II are not whole numbers, as it was found simpler to assume values of T and then determine corresponding values of H.

terms of the unperturbed energies by the expression

$$W_\lambda = W_\lambda^0 + W_1 + W_2, \tag{11}$$

where W_1 and W_2 are the first- and second-order energy corrections corresponding to the perturbing potentials. If now we replace these latter two terms by the well-known quantum mechanical expressions from perturbation theory, substitute Eq. (10) into Eq. (11), and Eq. (11) into Eq. (9), expand the perturbing terms of the partition function in powers of kT, and retain terms to the second order in the perturbing potentials, we find the partition function to be

$$Z = Z_0(1 + \boldsymbol{A} + \boldsymbol{B} + \cdots), \tag{12}$$

with

$$\boldsymbol{A} = -(1/kTZ_0)\sum_\lambda \mathfrak{IC}^{(1)}(\lambda;\lambda)\exp(-W_\lambda^0/kT), \tag{12a}$$

$$\boldsymbol{B} = (1/2k^2T^2Z_0)\sum\nolimits^{=}_{\lambda\lambda'} \mathfrak{IC}^{(1)}(\lambda;\lambda')\mathfrak{IC}^{(1)}(\lambda';\lambda)\exp(-W_\lambda^0/kT) + (1/kTZ_0)\sum\nolimits'_{\lambda\lambda'}\{\mathfrak{IC}^{(1)}(\lambda;\lambda')\mathfrak{IC}^{(1)}(\lambda';\lambda)/(W_{\lambda'} - W_\lambda)\}\exp(-W_\lambda^0/kT), \tag{12b}$$

and

$$Z_0 = \sum_\lambda \exp(-W_\lambda^0/kT) = [\sum_{M_i}\exp\{-W_i(M_i)/kT\}]^N. \tag{12c}$$

In these expressions Z_0 represents the partition function in the absence of the perturbing potentials and $\mathfrak{IC}^{(1)}(\lambda;\lambda)$, which represents the perturbing part of the Hamiltonian, includes both the dipole-dipole coupling $\sum_{j>i} w_{ij}(\lambda;\lambda)$ and the crystalline field potential $\sum_i V_i(\lambda;\lambda)$. The equality and prime signs on the summations are in accordance with the notation of Van Vleck.[9] The equality sign indicates that only those values of λ' for which $W_{\lambda'} = W_\lambda$, or in the later Eq. (13b) those $M_i'M_j'$ for which $W_i(M_i) + W_j(M_j) = W_i(M_i') + W_j(M_j')$, are to be included in the summation; the prime sign means that just these values are to be excluded.

Now let

$$\sum_{j>i}(w_{ij})_{\text{Av}} = \sum_{j>i} d_i d_j \sum_{M_iM_j} w_{ij}(M_iM_j;\, M_iM_j)\exp[-(W_i(M_i) + W_j(M_j))/kT],$$

$$\sum_i (V_i)_{\text{Av}} = \sum_i d_i \sum_{M_i} V_i(M_i;\, M_i)\exp[-W_i(M_i)/kT],$$

where

$$d_i = (\sum_{M_i}\exp[-W_i(M_i)/kT])^{-1}.$$

Then the $\boldsymbol{A}$ part of the partition function becomes

$$\boldsymbol{A} = -(1/kT)\mathfrak{IC}_{\text{Av}}^{(1)} = -(1/kT)\{\sum_{j>i}(w_{ij})_{\text{Av}} + \sum_i (V_i)_{\text{Av}}\}, \tag{13a}$$

while the $\boldsymbol{B}$ part is

$$\boldsymbol{B} = \tfrac{1}{2}k^{-2}T^{-2}\{\sum_{ijkl}(w_{ij})_{\text{Av}}(w_{kl})_{\text{Av}} + \sum_{ijk}(w_{ij}w_{jk})_{\text{Av}} + \sum_{ik}(V_i)_{\text{Av}}(V_k)_{\text{Av}}\}_{j>i,\, l>k,\, (i,j\neq k,\, l)} + \boldsymbol{\alpha}, \tag{13b}$$

where

$$(w_{ij}w_{jk})_{\text{Av}} = d_id_jd_k\sum_{M_iM_jM_k}\{2kT\sum\nolimits'_{M_j'} w_{ij}(M_iM_j;\, M_iM_j')w_{jk}(M_j'M_k;\, M_jM_k)/[W_i(M_i) - W_j(M_j)] + w_{ij}(M_iM_j;\, M_iM_j)w_{jk}(M_jM_k;\, M_jM_k)\}\exp[-(W_i(M_i) + W_j(M_j) + W_k(M_k))/kT]$$

and

$$\boldsymbol{\alpha} = \tfrac{1}{2}k^{-2}T^{-2}\{\sum_{j>i} d_id_j\sum\nolimits^{=}_{M_iM_jM_i'M_j'} |w_{ij}(M_iM_j;\, M_i'M_j')|^2\exp[-(W_i(M_i) + W_j(M_j))/kT] + \sum_i d_i\sum\nolimits^{=}_{M_iM_i'}|V_i(M_i;M_i')|^2\exp[-W_i(M_i)/kT]\}$$
$$+k^{-1}T^{-1}\{\{\sum_{j>i} d_id_j\sum\nolimits'_{M_iM_jM_i'M_j'}\{|W_{ij}(M_iM_j;\, M_i'M_j')|^2/(W_i(M_i') + W_j(M_j') - W_i(M_i) - W_j(M_j))\}\exp[-(W_i(M_i) + W_j(M_j))/kT] + \sum_i d_i\sum\nolimits'_{M_iM_i'}\{|V_i(M_i;\, M_i')|^2/(W_i(M_i') - W_i(M_i))\}\exp[-W_i(M_i)/kT]\}\}.$$

Equations (13a) and (13b) are more general than the corresponding equations given by Van Vleck[9] as provision is here made to take account of a cystalline field contribution to the partition function

as well as of a contribution from the magnetic dipole-dipole coupling. It may be noticed that only terms linear or quadratic in each interaction appear in these last equations whereas one would expect the operations of Eq. (12) to lead also to cross terms, i.e., terms containing a product of the two perturbing potentials. Such terms do arise but have been omitted from Eqs. (13) as it can be shown[15] that for our application their contribution to the magnetic moment vanishes. This being so, the complete contributions of the two perturbing potentials to the partition function are directly additive and may be considered separately.

VI. Partition Function to Second Order in Dipole-Dipole Coupling

In order to determine the contribution of the dipole-dipole parts of Eqs. (13a) and (13b) to the partition function, the matrix elements of this coupling must first be evaluated. This evaluation has already been carried out in a paper by Van Vleck,[16] henceforth called l.c., in which the partition function is calculated to the second order in the magnetic coupling for the case of arbitrarily large applied fields and for arbitrary direction of field relative to cubic axes. We have[17]

$$\begin{aligned} Z/Z_0 = 1 &- \tfrac{1}{2}Nk^{-1}T^{-1}B_1{}^2\Omega_0 + \tfrac{1}{8}Nk^{-2}T^{-2}\Omega_0{}^2[B_1{}^4(N-4)+4B_1{}^2B_2] \\ &+ \tfrac{1}{5}Nk^{-2}T^{-2}\Omega_1[\tfrac{1}{4}B_1{}^4 - \tfrac{1}{2}B_1{}^2B_2 + \tfrac{1}{4}B_2{}^2 + \tfrac{1}{16}(S^2+S-B_2)^2 - \tfrac{1}{16}B_1{}^2 + \tfrac{1}{8}B_1(S^2+S-B_2)(kT/g\beta H)] \\ &+ \tfrac{1}{5}Nk^{-2}T^{-2}\Omega_2[\tfrac{1}{4}B_1(S^2+S-B_2) - B_1{}^3 + B_1B_2](kT/g\beta H) \\ &+ \tfrac{1}{5}Nk^{-2}T^{-2}\Omega_3[\tfrac{1}{16}(S^2+S-B_2)^2 - \tfrac{1}{16}B_1{}^2 - \tfrac{1}{8}(S^2+S-B_2)B_1(kT/g\beta H)], \end{aligned} \tag{14}$$

where the Ω's are functions of the coefficients of the product terms $S_{qi}S_{qj}(q=xyz)$ that appear in the expression for the dipole-dipole coupling referred to a set of axes fixed relative to the crystal instead of to the magnetic field direction. It has been shown in l.c. that the Ω's can be expressed as[18]

$$\Omega_0 = -Ng^2\beta^2\Phi, \quad \Omega_1 = 2N^2g^4\beta^4Q_0, \quad \Omega_2 = \tfrac{3}{2}N^2g^4\beta^4Q_0, \quad \Omega_3 = -N^2g^4\beta^4Q_0, \tag{14a}$$

where $Q_0 = 2N^{-2}\sum r_{ij}^{-6}$. This summation, varying as the inverse sixth power of the atomic distance, converges rapidly. The value of Q_0 for a face-centered lattice such as that occupied by the paramagnetic ions in iron alum is 14.4. The quantity Φ is defined as the sum of the Lorentz local field factor $(4\pi/3)$ and the demagnetization factor (η). It takes account of the fact that the H of Eq. (14) which represents the applied field, differs from the true field acting on the paramagnetic ions.

The B functions of Eq. (14) are Brillouin functions defined by

$$B_n = (1/Q)(\partial^n Q/\partial\theta^n), \tag{15}$$

where

$$Q = \sum_{M=-S}^{S} \exp(M\theta) \quad \text{and} \quad \theta = (g\beta H/kT).$$

VII. Matrix Elements of Crystalline Field

For simplicity we consider first the matrix elements for a trigonal field containing only second-order terms, i.e., a crystalline field of axial symmetry. Such a field is represented by Eq. (4a) of

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[15] J. A. Sauer, Doctoral Dissertation, University of Cambridge (1941). The cross terms are found to drop out regardless of the shape of the specimen. Essentially the reason is that these terms are linear in the representation coefficient and hence vanish when the spatial averaging is performed.

[16] J. H. Van Vleck, Phys. Rev. **52**, 1178 (1937), henceforth l.c.

[17] Our Eq. (14) differs from Eq. (21) of l.c. only in the absence of a term in Ω_4. This term was needed in the study of anisotropy but for our application to demagnetization experiments performed on a powdered specimen this term can be omitted as it vanishes when averages over all directions are included.

[18] In the Ω's as defined by Eq. (27) of l.c., there also appear terms in the exchange integral. These have been omitted from our Eq. (14a) as exchange effects can be neglected in our treatment because of the known magnetic diluteness of iron alum.

TABLE III. Matrix elements of crystalline field of axial symmetry.

M_J	5/2	3/2	1/2	−1/2	−3/2	−5/2
5/2	$D_2^{00}/\sqrt{6}$	$-D_2^{10}/\sqrt{5}$	$D_2^{20}/\sqrt{10}$	0	0	0
3/2	$D_2^{-10}/\sqrt{5}$	$-\frac{1}{5}D_2^{00}/\sqrt{6}$	$-\frac{2}{5}D_2^{10}/\sqrt{2}$	$\frac{3}{5}D_2^{20}/\sqrt{2}$	0	0
1/2	$D_2^{-20}/\sqrt{10}$	$\frac{2}{5}D_2^{-10}/\sqrt{2}$	$-\frac{4}{5}D_2^{00}/\sqrt{6}$	0	$\frac{3}{5}D_2^{20}/\sqrt{2}$	0
−1/2	0	$\frac{3}{5}D_2^{-20}/\sqrt{2}$	0	$-\frac{4}{5}D_2^{00}/\sqrt{6}$	$\frac{2}{5}D_2^{10}/\sqrt{2}$	$D_2^{20}/\sqrt{10}$
−3/2	0	0	$\frac{3}{5}D_2^{-20}/\sqrt{2}$	$-\frac{2}{5}D_2^{-10}/\sqrt{2}$	$-\frac{1}{5}D_2^{00}/\sqrt{6}$	$D_2^{10}/\sqrt{5}$
−5/2	0	0	0	$D_2^{-20}/\sqrt{10}$	$-D_2^{-10}/\sqrt{5}$	$D_2^{00}/\sqrt{6}$

Note: All matrix elements to be multiplied by $\frac{2}{5}I_2A\sqrt{10}$ or, in the notation of Penney and Schlapp, by $10Aa\sqrt{6}$.

Section II or by the equivalent expressions

$$V_a = Ar^2(1-3\cos^2\theta) = -Ar^2\frac{2\sqrt{10}}{5}T_2^0, \tag{16}$$

where T_2^0 is a spherical harmonic of the second order normalized to unity. Since the experiments of Casimir and de Haas were performed on a powdered specimen in which all directions of magnetic field relative to the cubic axes are equally probable, it is necessary to transform from the x, y, z system relative to fixed axes over to a new coordinate X, Y, Z system relative to the arbitrary magnetic field direction. Under this transformation the Tesseral harmonic of order two will transform into a sum of other Tesseral harmonics of the same order. In particular, $T_2^0 = \sum_{m'} D_2^{m',0}T_2^{m'}$ where the $D_l^{mm'}$'s are the so-called representation coefficients of order l. The desired matrix elements are now found by use of the Kramers symbolic method[4,19] or by direct computation from the fundamental quadrature. The matrix representing V_a in the "M" system of representation is given in Table III. The symbol I_2 multiplying the matrix elements is given by $I_2 = c_J\int r^2R^2dr$, where c_J is an undetermined parameter that enters in the Kramers group-theory method of calculation of the matrix elements and R is the radial wave function. The value of I_2 may be determined by comparing the diagonal element for $M=5/2$ with the corresponding matrix element determined by Penney and Schlapp.[7] Their value is applicable only for a pure crystal in which the magnetic field is directed along the z axis. Taking this restriction into account and comparing, we find that our expression $\frac{2}{5}I_2A\sqrt{10}$ is the same as $10Aa\sqrt{6}$ in the notation of Penney and Schlapp.

If the second-degree terms of the trigonal crystalline field are omitted and only the fourth-degree cubic terms considered, that part of the crystalline potential independent of r can be written

$$V_c = \frac{2}{15}\sqrt{2}T_4^0 + \frac{2}{105}(35)^{\frac{1}{2}}T_4^4 + \frac{2}{105}(35)^{\frac{1}{2}}T_4^{-4}, \tag{17}$$

where the T_4^m's are fourth-order harmonics normalized to unity. In this expression $\theta=0$ refers to a direction along one of the cubic axes. In transforming over to a new coordinate system with polar axis in direction of magnetic field, the T_l^m's transform like representation coefficients of the rotation group of dimensionality $2l+1$ so that

$$T_4^m = \sum_{m'} D_4^{m'm}T_4^{m'}.$$

The matrix table for any one of the fourth-order Tesseral harmonics is now obtained by use of the Kramers symbolic method. The matrix elements for that combination of spherical harmonics given by the cubic crystalline field of Eq. (17) are given in Table IV. In this table, the symbol D_4^m stands

[19] H. C. Brinkman, Doctoral Dissertation, University of Utrecht (1932).

TABLE IV. Matrix elements of crystalline field of cubic symmetry.

M_J	5/2	3/2	1/2	−1/2	−3/2	−5/2
5/2	$D_4^0/\sqrt{70}$	$-2D_4^1/\sqrt{70}$	$3D_4^2/\sqrt{70}$	$-D_4^3/\sqrt{5}$	$D_4^4/\sqrt{5}$	0
3/2	$2D_4^{-1}/\sqrt{70}$	$-3D_4^0/\sqrt{70}$	$D_4^1/\sqrt{7}$	$-D_4^2/\sqrt{14}$	0	$D_4^4/\sqrt{5}$
1/2	$3D_4^{-2}/\sqrt{70}$	$-D_4^{-1}/\sqrt{7}$	$2D_4^0/\sqrt{70}$	0	$-D_4^2/\sqrt{14}$	$D_4^3/\sqrt{5}$
−1/2	$D_4^{-3}/\sqrt{5}$	$-D_4^{-2}/\sqrt{14}$	0	$2D_4^0/\sqrt{70}$	$-D_4^1/\sqrt{7}$	$3D_4^2/\sqrt{70}$
−3/2	$D_4^{-4}/\sqrt{5}$	0	$-D_4^{-2}/\sqrt{14}$	$D_4^{-1}/\sqrt{7}$	$-3D_4^0/\sqrt{70}$	$2D_4^1/\sqrt{70}$
−5/2	0	$D_4^{-4}/\sqrt{5}$	$-D_4^{-3}/\sqrt{5}$	$3D_4^{-2}/\sqrt{70}$	$-2D_4^{-1}/\sqrt{70}$	$D_4^0/\sqrt{70}$

Note: All matrix elements to be multiplied by $\frac{2}{105}(35)^{\frac{1}{2}}DI_4$ or, in the notation of Penney and Schlapp, by $60Dq$.

for the following combination of representation coefficients:

$$D_4^m=(14/5)^{\frac{1}{2}}D_4^{m0}+D_4^{m4}+D_4^{m,-4} \quad \text{and} \quad I_4=c_J\int r^4R^2dr.$$

The switch to the Penney and Schlapp notation is carried out in the same manner as indicated above.

Numerical Checks: One check on the numerical accuracy of both matrix tables that we have verified is that those elements which arise due only to even values of m in T_2^m or T_4^m must agree with values previously calculated by Van Vleck and Hebb[20] in connection with a different problem.

Secondly, since the diagonal terms of the cubic field matrix were used to change from our notation to that of Penney and Schlapp, a comparison of the off-diagonal terms in the two cases can be used as a check. All that is necessary is to give the representation coefficients their specific numerical value for the special case considered by Penney and Schlapp, and when this is done and the comparison made, the two expressions are found to be alike.

VIII. Partition Function to Second Order in Crystalline Field Interaction

The partition function for the crystalline field terms is now obtained by substituting the matrix elements from Table III or IV into Eqs. (13a) and (13b). The resultant expressions are functions of the $D_l^{mm'}$'s that appear in the matrix elements. These representation coefficients, however, can be eliminated by performing the spatial averaging required in virtue of the powdered form of the test samples.[21] The averaging is easily carried out by using the group theory relationship

$$\int\int\int D_l^{mn}D_{l'}^{pq}d\Omega \Big/ \int\int\int d\Omega=\delta_{mp}\delta_{nq}\delta_{ll'}/\nu. \tag{18}$$

Here δ is the Dirac delta function and ν is the dimensionality of the representation given by $2l+1$.

After carrying out the indicated procedure, we find the contribution of the axial crystalline field to log Z to be

$$(N/45)\gamma_a^2T^{-2}\{-2Q^{-2}(5\cosh 5x-\cosh 3x-4\cosh x)^2+Q^{-1}(25\cosh 5x+\cosh 3x+16\cosh x) +3Q^{-1}(kT/g\beta H)(25\sinh 5x-3\sinh 3x-4\sinh x)\}. \tag{19}$$

For the crystalline field of cubic symmetry, the contribution to log Z is

$$(N\gamma_c^2/21T^2)\{-2Q^{-2}(\cosh 5x-3\cosh 3x+2\cosh x)^2+Q^{-1}(\cosh 5x+9\cosh 3x+4\cosh x) +4Q^{-1}(kT/3g\beta H)(25\sinh 5x+18\sinh 3x-11\sinh x)\}. \tag{20}$$

[20] J. H. Van Vleck and M. H. Hebb, Phys. Rev. **46**, 17 (1934).

[21] The averaging should be carried out not on Z itself but on log Z. The reason why Z can't be used is clear when we recall that log $(1+x)$ where x is small compared to unity is equal to $x-\frac{1}{2}x^2$ to the second order. Hence, if average was taken on Z itself instead of log Z, we would be dealing with $\langle x\rangle_{\text{Av}}^2$ instead of with $\langle x^2\rangle_{\text{Av}}$ and these are by no means equivalent.

In these expressions $x=(g\beta H/2kT)$ and γ_a and γ_c have taken the place, respectively, of the crystalline field constants $6Aa$ and $24D_q$. The γ symbols may be considered as characteristic temperatures associated with the crystalline field splitting pattern. If we set up and solve the secular equation for the one atom problem, we find that the γ's of Eqs. (19) and (20) are exactly $\frac{1}{3}$ the δ's of Fig. 1.

IX. Magnetic Moment and Entropy to Second Order in Perturbing Potentials

Expressions for the magnetic moment and entropy correct to the second order in the perturbing potentials are now found by substituting Eqs. (12c), (14), and either (19) or (20) into Eq. (12) and using Eq. (8). We obtain:

$$(M/Ng\beta)=B_1+(\tau/T)f_{M'}+(\tau/T)^2(f_{M''}+G_M)+(\gamma/T)^2v, \tag{21}$$

$$S/Nk=\log Q-(g\beta H/kT)B_1+(\tau/T)f_{s'}+(\tau/T)^2(f_{s''}+G_s)+(\gamma/T)^2u. \tag{22}$$

Here τ is a characteristic temperature associated with the dipole-dipole coupling and for iron alum with $S=5/2$ it takes the value

$$\tau=Ng^2\beta^2S(S+1)/k=0.0472°.$$

The f' and f'' terms of Eqs. (21) and (22) are the first- and second-order effects of the local field plus demagnetization corrections while the G terms, entering only in the second order, represent the perturbations due to the dipole-dipole interaction that are not included in the Φ terms. They are defined by

$$f_{M'}=\Phi S^{-1}(S+1)^{-1}B_1(B_2-B_1^2), \tag{21a}$$

$$f_{M''}=\Phi^2S^{-2}(S+1)^{-2}\{B_1(B_2-2B_1^2)(B_2-B_1^2)+\tfrac{1}{2}B_1^2(B_3-B_1B_2)\}, \tag{21b}$$

$$\begin{aligned}G_M=\tfrac{1}{5}Q_0S^{-2}(S+1)^{-2}\{&(B_3-B_1B_2)[-B_1^2+B_2-\tfrac{1}{8}(S^2+S-B_2)+\tfrac{3}{4}(kT/g\beta H)B_1]\\&+(B_2-B_1^2)[2B_1^3-2B_1B_2-\tfrac{1}{8}B_1+\tfrac{3}{4}(kT/g\beta H)(S^2+S+B_2-6B_1^2)]\\&+(kT/g\beta H)^2[-\tfrac{3}{4}B_1(S^2+S-B_2)-\tfrac{3}{2}B_1B_2+\tfrac{3}{2}B_1^3]\}.\end{aligned} \tag{21c}$$

$$f_{s'}=-\Phi S^{-1}(S+1)^{-1}(g\beta H/kT)B_1(B_2-B_1^2), \tag{22a}$$

$$\begin{aligned}f_{s''}=\tfrac{1}{2}\Phi^2S^{-2}(S+1)^{-2}\{&B_1^4-B_1^2B_2-(g\beta H/kT)B_1^2(B_3-B_1B_2)\\&-(g\beta H/kT)2B_1(B_2-2B_1^2)(B_2-B_1^2)\},\end{aligned} \tag{22b}$$

$$\begin{aligned}G_s=-(Q_0/10)S^{-2}(S+1)^{-2}\{&B_1^4-2B_1^2B_2+B_2^2+\tfrac{1}{8}(S^2+S-B_2)^2-\tfrac{1}{8}B_1^2+\tfrac{3}{2}B_1(B_3-B_1B_2)\\&+\tfrac{3}{2}(B_2-B_1^2)[(S^2+S-B_2)-6B_1^2+2B_2]+(g\beta H/kT)[(B_2-B_1^2)(4B_1^3-4B_1B_2-\tfrac{1}{4}B_1)\\&+(B_3-B_1B_2)(2B_2-2B_1^2-\tfrac{1}{4}(S^2+S-B_2))]\}.\end{aligned} \tag{22c}$$

These equations are true for any value of the spin S, but a convenient check on the correctness of the algebraic manipulations involved in the derivation of the above equations can be had by restricting the atomic spin to the value $\frac{1}{2}$ and then comparing these expressions with the corresponding ones given by Van Vleck.[3] After making the required restriction, we find complete agreement.

The v and u terms of Eqs. (21) and (22) represent the perturbations due to the crystalline field. Consider first the field of axial symmetry and let

$$\mathbf{C}^n(a,b,c)=Q^{-n}(a\cosh 5x+b\cosh 3x+c\cosh x)^n,$$

$$\mathbf{S}^n(a,b,c)=Q^{-n}(a\sinh 5x+b\sinh 3x+c\sinh x)^n$$

with

$$Q=2(\cosh 5x+\cosh 3x+\cosh x).$$

Then

$$45v_a=4B_1\mathbf{C}^2(5,-1,-4)-2\mathbf{C}(5,-1,-4)\mathbf{S}(25,-3,-4)-B_1\mathbf{C}(25,1,16)+\tfrac{1}{2}\mathbf{S}(125,3,16)$$
$$+\tfrac{3}{2}(kT/g\beta H)[\mathbf{C}(125,-9,-4)-2B_1\mathbf{S}(25,-3,-4)-2(kT/g\beta H)\mathbf{S}(25,-3,-4)], \quad (21d)$$

$$45u_a=2\mathbf{C}^2(5,-1,-4)-\mathbf{C}(25,1,16)-\tfrac{3}{2}\mathbf{C}(125,-9,-4)+3B_1\mathbf{S}(25,-3,-4)$$
$$+(g\beta H/kT)[-4B_1\mathbf{C}^2(5,-1,-4)+B_1\mathbf{C}(25,1,16)-\tfrac{1}{2}\mathbf{S}(125,3,16)$$
$$+2\mathbf{C}(5,-1,-4)\mathbf{S}(25,-3,-4)]. \quad (22d)$$

For a trigonal field of cubic symmetry, the v and u symbols are given by[22]

$$21v_c=4B_1\mathbf{C}^2(1,-3,2)-2\mathbf{C}(1,-3,2)\mathbf{S}(5,-9,2)-B_1\mathbf{C}(1,9,4)+\tfrac{1}{2}\mathbf{S}(5,27,4)$$
$$+\tfrac{2}{3}(kT/g\beta H)[\mathbf{C}(125,54,-11)-2B_1\mathbf{S}(25,18,-11)-2(kT/g\beta H)\mathbf{S}(25,18,-11)], \quad (21e)$$

$$21u_c=2\mathbf{C}^2(1,-3,2)-\mathbf{C}(1,9,4)+\tfrac{4}{3}B_1\mathbf{S}(25,18,-11)-\tfrac{2}{3}\mathbf{C}(125,54,-11)$$
$$-(g\beta H/kT)[4B_1\mathbf{C}^2(1,-3,2)+\tfrac{1}{2}\mathbf{S}(5,27,4)-B_1\mathbf{C}(1,9,4)-2\mathbf{C}(1,-3,2)\mathbf{S}(5,-9,2)]. \quad (22e)$$

If one neglects the correction terms in Eqs. (21) and (22) arising from the dipole-dipole and crystalline field interactions, the expressions for M and S reduce to

$$M=Ng\beta B_1, \quad (23)$$

$$S=Nk(\log Q-\theta B_1). \quad (24)$$

Since S remains constant during an adiabatic demagnetization process, it can readily be seen from the above equations, remembering that $\theta=(g\beta H/kT)$, that the temperature is a linear function of the field of the form $T=C_1H+C_2$ with C_2 zero. The procedure of de Haas and Wiersma for determining the true thermodynamic temperature now clearly applies. It has been shown by Van Vleck[3] that even if the correction terms in f' and f'' are retained Eqs. (23) and (24) are still valid provided only that the magnetic field H be no longer interpreted as the applied field but as the true local field $H+\Phi M$. The linear equation between T and H still holds, but the coefficients now satisfy the relation $C_2/C_1=\Phi M$.

Thus, even for specimens of non-spherical shape—for spherical specimens the Φ terms are always zero—the f terms may now be omitted from Eqs. (21) and (22) though care must be taken when comparing the results of theory with experiment first to convert the applied field over into the true local field by introducing the proper demagnetization corrections for the shape in question.

X. Determination of Adiabatic Magnetic Moment

To derive an expression for the magnetic moment valid throughout the entire demagnetization process, one needs only to solve Eq. (22) for T in terms of H and then substitute this function in Eq. (21). In this manner one obtains an equation involving only M, M_0, and H. We are primarily interested in the form of M for large initial fields and therefore assume, as a comparable approximation to those previously made, that the primary terms in M and S in Eqs. (21) and (22) can be expanded as a Taylor's series in $\theta-\theta^0$ and only first-order terms retained. Furthermore, it is assumed that the argument of the v, u, and G terms, which are all small perturbations, has the same value as at the initial helium temperatures. This means that θ can be everywhere replaced in these terms by θ^0.

[22] One helpful check on the algebraic accuracy of Eqs. (21) and (22) which has been useful is:
$$(\partial S/\partial H)_T=(\partial M/\partial T)_H.$$

After expanding the leading terms in M and S, we find

$$(S-S_0)/Nk=0=-\theta^0[B_2{}^0-(B_1{}^2)^0](\theta-\theta^0)+(\tau/T)^2G_s{}^0+(\gamma/T)^2u^0, \tag{25}$$

$$(M-M_0)/Ng\beta=[B_2{}^0-(B_1{}^2)^0](\theta-\theta^0)+(\tau/T)^2G_M{}^0+(\gamma/T)^2v^0, \tag{26}$$

where the superscript zero in the B_n, G, u, and v terms means that these are to be evaluated at $\theta=\theta^0=g\beta H_0/kT_0$. From Eqs. (25) and (26) we get

$$M-M_0=Ng\beta\left\{\left(\frac{\tau}{T_0}\right)^2\left(\frac{G_s{}^0}{\theta^0}+G_M{}^0\right)+\left(\frac{\gamma}{T_0}\right)^2\left(\frac{u^0}{\theta^0}+v^0\right)\right\}\left(\frac{H_0}{H}\right)^2. \tag{27}$$

In order that this equation apply for both axial and cubic crystalline fields, μ^0 and v^0 should be taken, respectively, as $u_a{}^0$, $v_a{}^0$ and $u_c{}^0$, $v_c{}^0$.

Equation (27) is the theoretical expression for the adiabatic magnetic moment correct to the second order in the perturbing potentials. For purposes of comparison with the experimental relation between M and H found by de Haas and Casimir, it can be put in the form

$$M=M_0(1-b/H^2), \tag{28}$$

where[23]

$$b=-\left(\frac{H_0{}^2}{B_1{}^0}\right)\left\{\left(\frac{\tau}{T_0}\right)^2\left(\frac{G_s{}^0}{\theta^0}+G_M{}^0\right)+\left(\frac{\gamma}{T_0}\right)^2\left(\frac{u^0}{\theta^0}+v^0\right)\right\}. \tag{29}$$

Another convenient check on our calculations is now available. De Haas and Casimir[2] have given a theoretical derivation for b that is accurate only for the case of low initial fields. Our analysis is valid for fields of any nature and hence our expression should reduce to theirs if we restrict H to low values only. The procedure is to expand the various correction terms G_s, u_a, etc., that appear in Eq. (29) in powers of θ and then retain only the lowest terms in the expansion. When this is done we find $b=3A'/2\tau$ and this is equivalent to the expression given by de Haas and Casimir.[24] The numerical value of $3A'/2\tau$ is 1.3×10^5. This should not be expected to agree with the experimental value of b of 1.7×10^5 since the demagnetization experiments were carried out at such high values of the initial field that saturation effects cannot be neglected.

For the more important case of high fields, the numerical value of b must be taken directly from Eq. (29). The characteristic magnetic coupling temperature τ has already been evaluated and numerical values of $G_s{}^0$ and $G_M{}^0$,[25] representing the effect of the magnetic coupling on the adiabatic moment, can be calculated directly from Eqs. (21c) and (22c) as these equations depend only on θ^0, Q_0, and S, whose respective numerical values are 2.04, 14.4, and 5/2. The v and u terms of Eq. (29) can also be directly evaluated[25] from their defining equations, but the complete crystalline field contribution to the adiabatic moment cannot yet be found as this contribution contains an unknown crystalline field parameter, *vis.*, γ_a or γ_c. Hence, it is first necessary to evaluate these parameters and this is done by calculating the theoretical expression for the specific heat in zero applied field and comparing it with the known experimental value.

Crystalline Field Constants for Specific Heat Data

The theoretical expression for the specific heat is obtained directly from the partition function by means of the equation

$$C_v=\frac{\partial}{\partial T}\left(kT^2\frac{\partial}{\partial T}\log Z\right). \tag{30}$$

[23] The bracketed part of Eq. (29) is always found to be negative; hence b itself is essentially positive.

[24] The expression actually given by de Haas and Casimir is $A/2a$ where small a is the coefficient of H/T in the ordinary formula for M when saturation is neglected. However, since in our notation this coefficient is $\tau/3$ and since our A' is identical with their A, the two expressions are equivalent.

[25] The calculated values of these various quantities are stated explicitly in reference 15.

We desire the specific heat in the absence of an applied field. Taking into account this condition and substituting Eqs. (14) and (19) into Eq. (30) we find

$$C_v = Nk\{2.4(\tau/T)^2 + 1.55(\gamma_a/T)^2\}, \tag{31}$$

where the first term represents the contribution of the dipole-dipole coupling and the second term that of an axial crystalline field. If the partition function derived for the case of a cubic crystalline field be substituted in Eq. (30), then $1.55\gamma_a^2$ should be replaced by $2.00\gamma_c^2$.

Equation (31) is of the form $A'T^{-2}$ as found experimentally by various observers.[12] Since the value of τ is known, this equation may be used for determining γ_a or γ_c by substituting for C_v on the left-hand side of the equation the accepted experimental value of $2300T^{-2}$. The crystalline field parameters now become $\gamma_c = 0.063$ and $\gamma_a = 0.072$ corresponding to splitting distances (see Fig. 1) of $\delta_c = 0.190$ and $\delta_a = 0.215$. Substituting these values and those of the other parameters into Eq. (29), we find $b = 9.4 \times 10^4$ for a field of cubic symmetry and $b = 11.5 \times 10^4$ for a field of axial symmetry.

Effect of Demagnetization Corrections on Adiabatic Moment

For either type of crystalline field, the calculated values of the coefficient b are found to be too low and hence the theoretical values of M are higher than the experimental. As mentioned in Part I, some of the discrepancy between the theoretical and the experimental values is due to the fact that the H of Eq. (28) is no longer the same as the applied field H_a of Eq. (2). To find the true local field H when H_a is known, it is first necessary to determine the proper demagnetization factor η for the shape of specimen used in the experiments. De Haas and Casimir used a powdered specimen of iron alum pressed in the form of a cylinder 90 mm long by 30 mm wide. Since the true demagnetization factor is calculable only for an ellipsoid, all one can do is to estimate this factor by assuming that the specimen can be adequately represented by an ellipsoid of revolution with an axes ratio of 3 : 1. The magnetic field was applied at right angles to the longitudinal axis of the ellipsoid. For this case $\Phi = (4/3)\pi - \eta$ becomes negative and hence the local field $H(=H_a + \Phi M)$ is less than the applied field H_a. This has a tendency to lower the theoretical values of M, thereby bringing them in somewhat closer relation to the experimental data. However, a direct evaluation shows that while a minor improvement has been made the major part of the discrepancy between the theoretical values of M and the experimental still exists.

Effect of a More General Crystalline Field

In Section III of Part I, the thought was raised that possibly a crystalline field of a more general nature than one of cubic or axial symmetry would lead to better agreement between theory and experiment. To examine this question more thoroughly, we calculate the contribution to the partition function and the magnetic moment of the arbitrary crystalline potential specified by Eq. (6) of Section III. We need the matrix elements of this potential and can easily obtain them from the calculations already made. The matrix elements of the T_2 terms of Eq. (6) can be obtained directly from the numerical values listed in Table II, and each of the T_4 terms of Eq. (6) leads to a matrix table similar to that of Table III. The only change that must be made in these tables is the replacement of the original coefficients of the T_l's that appear in Eqs. (16) and (17) by the new coefficients from Eq. (6). On substitution of the matrix elements into Eqs. (13) the contribution of the arbitrary crystalline potential to the log of the partition function is found to be the sum of Eqs. (19) and (20) with $\gamma_a^2/45$ replaced by

$$(\sum_{-2}^{2}{}_r (a_{2r})^2/750) \text{ and } \gamma_c^2/21 \text{ replaced by } (\sum_{-4}^{4}{}_s (a_{4s})^2/630).$$

The expressions for the magnetic moment and entropy previously given by Eqs. (21) and (22) can be made to apply to the general crystalline field, by replacing, respectively, the $\gamma^2 v$ and $\gamma^2 u$ terms of

these equations by the following expressions:

$$(v_c/30)\sum_{-4}^{4}{}_s\, a_{4s}^2+(3v_a/50)\sum_{-2}^{2}{}_r\, a_{2r}^2 \quad \text{and} \quad (u_c/30)\sum_{-4}^{4}{}_s\, a_{4s}^2+(3u_a/50)\sum_{-2}^{2}{}_r\, a_{2r}^2.$$

The adiabatic moment and the specific heat found in the same manner as previously indicated, are

$$M=M_0(1-b_g/H^2)$$

with

$$b_g=-(H_0^2/B_1^0)\left\{\left(\frac{\tau}{T_0}\right)^2\left(\frac{G_s^0}{\theta^0}+G_M{}^0\right)+\frac{\sum_s a_{4s}^2}{30T_0{}^2}\left(\frac{u_c{}^0}{\theta^0}+v_c{}^0\right)+\frac{3}{50}\frac{\sum_r a_{2r}^2}{T_0{}^2}\left(\frac{u_a{}^0}{\theta^0}+v_a{}^0\right)\right\} \tag{32}$$

and

$$C_v=NkT^{-2}\left\{2.4\tau^2+\frac{1}{15}\sum_s a_{4s}^2+\frac{7}{75}\sum_r a_{2r}^2\right\}. \tag{33}$$

These are the exact expressions correct to the second order in the perturbing influences which include both the magnetic dipole-dipole coupling and the arbitrary crystalline potential of Eq. (6). All the coefficients of this potential are at our disposal and the problem now is to give b_g and C_v their experimental values for iron alum and then determine whether a suitable choice of coefficients can be found that will lead to agreement in both equations. The results of this procedure have already been discussed in Section III of Part I.

XI. Adiabatic Moment to Third Order in Crystalline Field Potential

The problem of the determination of the energy levels of iron alum supposed subject to a large applied magnetic field of arbitrary direction and to a crystalline electric field of cubic symmetry has been considered by Kronig and Bouwkamp.[13] They were able to calculate, correct to the third order in the cubic field splitting parameter, all six energy levels of the normally degenerate ground state. The six expressions are:[26]

$$\left.\begin{aligned} W_1\\ W_2\end{aligned}\right\}=\pm\tfrac{1}{2}g\beta H+p\gamma\pm\frac{2q_1\gamma^2}{g\beta H}+\frac{4r_1\gamma^3}{g^2\beta^2H^2}\pm\cdots,$$

$$\left.\begin{aligned} W_3\\ W_4\end{aligned}\right\}=\pm\tfrac{3}{2}g\beta H-\tfrac{3}{2}p\gamma\pm\frac{2q_2\gamma^2}{g\beta H}+\frac{4r_2\gamma^3}{g^2\beta^2H^2}\pm\cdots, \tag{34}$$

$$\left.\begin{aligned} W_5\\ W_6\end{aligned}\right\}=\pm\frac{5}{2}g\beta H+\tfrac{1}{2}p\gamma\pm\frac{2q_3\gamma^2}{g\beta H}+\frac{4r_3\gamma^3}{g^2\beta^2H^2}\pm\cdots,$$

where

$$p=1-5\varphi,\quad q_1=-\frac{5\varphi}{6}(7-25\varphi),\quad q_2=\frac{5}{32}+\frac{5}{32}\varphi(22-75\varphi),\quad q_3=\frac{5}{32}+\frac{5}{96}\varphi(50-113\varphi),$$

$$r_1=\frac{-5}{144}\varphi(196-1635\varphi+3125\varphi^2),\quad r_2=\frac{5}{128}+\frac{15}{128}\varphi(79-615\varphi+1125\varphi^2), \tag{35}$$

$$r_3=\frac{-5}{128}-\frac{25}{1152}\varphi(113-705\varphi+1075\varphi^2).$$

In these equations φ is a specific function of the direction cosines α_1, α_2, α_3 of H with respect to the

[26] Our symbol γ is the same quantity as that indicated by a in the Kronig-Bouwkamp paper.

cubic axes given by

$$\varphi=\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2+\alpha_1^2\alpha_2^2. \tag{36}$$

Let the six energy levels of Eq. (34) be substituted into the partition function

$$Z=[\textstyle\sum_M \exp(-W_M/kT)]^N.$$

Expanding the exponential and retaining terms only to the third order in the cubic field potential, we find

$$Z/Z_0=\left\{1-(\gamma/T)p\mathbf{C}(1,-3,2)+(\gamma/T)^2\left[\frac{1}{4}p^2\mathbf{C}(1,9,4)+4(kT/g\beta H)\mathbf{S}(q_3,q_2,q_1)\right]\right.$$
$$\left.-(\gamma/T)^3\left[\frac{1}{24}p^3\mathbf{C}(1,-27,8)+8(kT/g\beta H)^2\mathbf{C}(r_3,r_2,r_1)+2(kT/g\beta H)\mathbf{S}(pq_3,-3pq_2,2pq_1)\right]\right\}^N. \tag{37}$$

In order that our final results be applicable to a powdered specimen, it is necessary to calculate the average value of the various quantities p_1, r_2, q_3, etc., that depend on the direction cosines. Performing this averaging,[25] expanding log Z, and retaining terms only to the second power in γ, we obtain an expression for the log of Z that is identical with our previous Eq. (20) and thereby provides another check on the algebraic manipulation involved in its derivation. Since the effect on the magnetic moment and entropy of that part of the partition function given by Eq. (20) has already been considered, it is only necessary for us to consider now the third-order terms of Eq. (37). The contribution of these terms to the average value of $(1/N)$ log (Z/Z_0) is found to be

$$(1/3003)(\gamma/T)^3\{-6\mathbf{C}(1,-27,8)-48\mathbf{C}^3(1,-3,2)+36\mathbf{C}(1,-3,2)\mathbf{C}(1,9,4)$$
$$+(kT/g\beta H)[\mathbf{S}(125,453,-664)+2\mathbf{C}(1,-3,2)\mathbf{S}(-125,151,-332)]$$
$$+\tfrac{1}{6}(kT/g\beta H)^2\mathbf{C}(12295,9441,-2854)\}. \tag{38}$$

The additional term in the magnetic moment, due to inclusion of the above third-order term in the partition function, is found by differentiating Eq. (38) with respect to H and multiplying by kT. This term is

$$Ng\beta(\gamma/T)^3 w_M, \tag{39}$$

where

$$w_M=(1/7)w_M'+(1/3003)w_M''$$

with

$$w_M'=-(kT/g\beta H)\{(kT/g\beta H)\mathbf{S}(.268,1.05,1.55)+2(kT/g\beta H)^2\mathbf{C}(4.78,-3.67,1.04)$$
$$+B_1\mathbf{S}(.268,1.05,1.55)-\tfrac{1}{2}\mathbf{C}(1.34,3.15,1.55)$$
$$+B_1\mathbf{C}(4.78,-3.67,1.04)-\tfrac{1}{2}\mathbf{S}(23.9,-10.0,1.04)$$

and

$$w_M''=+6B_1\mathbf{C}(1,-27,8)-3\mathbf{S}(5,-81,8)-72\mathbf{C}^2(1,-3,2)\mathbf{S}(5,-9,2)+144B_1\mathbf{C}^3(1,-3,2)$$
$$-72B_1\mathbf{C}(1,-3,2)\mathbf{C}(1,9,4)+18\mathbf{S}(5,-9,2)\mathbf{C}(1,9,4)+18\mathbf{C}(1,-3,2)\mathbf{S}(5,27,4)$$
$$+(kT/g\beta H)\{-2(kT/g\beta H)\mathbf{C}(1,-3,2)\mathbf{S}(-125,151,-332)$$
$$-4B_1\mathbf{C}(1,-3,2)\mathbf{S}(-125,151,-332)+\mathbf{S}(5,-9,2)\mathbf{S}(-125,151,-332)$$
$$+\mathbf{C}(1,-3,2)\mathbf{C}(-625,453,-332)\}.$$

The contribution to the entropy of the third-order terms in the partition function is found to be

$$Nk(\gamma/T)^3 w_s, \tag{40}$$

where

$$w_s = (1/7)w_s' + (1/3003)w_s''$$

with

$$w_s' = +(kT/g\beta H)[-\mathbf{S}(.268, 1.05, 1.55) + \mathbf{C}(4.78, -3.67, 1.04) + \tfrac{1}{2}\mathbf{S}(23.9, -10.0, 1.04)] + B_1\mathbf{S}(.268, 1.05, 1.55) - \tfrac{1}{2}\mathbf{C}(1.34, 3.15, 1.55)$$

and

$$\begin{aligned} w_s'' = (g\beta H/kT)[&-6B_1\mathbf{C}(1, -27, 8) + 3\mathbf{S}(5, -81, 8) - 144B_1\mathbf{C}^3(1, -3, 2) \\ &+ 72\mathbf{C}^2(1, -3, 2)\mathbf{S}(5, -9, 2) + 72B_1\mathbf{C}(1, -3, 2)\mathbf{C}(1, 9, 4) - 18\mathbf{S}(5, -9, 2)\mathbf{C}(1, 9, 4) \\ &- 18\mathbf{C}(1, -3, 2)\mathbf{S}(5, 27, 4)] + 96\mathbf{C}^3(1, -3, 2) + 12\mathbf{C}(1, -27, 8) - 72\mathbf{C}(1, -3, 2)\mathbf{C}(1, 9, 4) \\ &+ 4B_1\mathbf{C}(1, -3, 2)\mathbf{S}(-125, 151, -332) - \mathbf{S}(5, -9, 2)\mathbf{S}(-125, 151, -332) \\ &- \mathbf{C}(1, -3, 2)\mathbf{C}(-625, 453, -332) - 2(kT/g\beta H)\mathbf{C}(1, -3, 2)\mathbf{S}(-125, 151, -332). \end{aligned}$$

Complete expressions for the magnetic moment and entropy to the third order in the crystalline field interaction and second order in the dipole-dipole coupling are obtained by adding Eqs. (39) and (40) to the previous Eqs. (21) and (22) developed in Section X. The adiabatic magnetization, found by solving the entropy equation for T as a function of H and substituting into the expression for the magnetic moment, is

$$M = M_0\left\{1 + \frac{H_0^2}{B_1^0 H^2}\left[\left(\frac{\tau}{T_0}\right)^2\left(\frac{G_s^0}{\theta^0} + G_M^0\right) + \left(\frac{\gamma}{T_0}\right)^2\left(\frac{u^0}{\theta^0} + v^0\right)\right] + \frac{H_0^3}{B_1^0 H^3}\left[\left(\frac{\gamma}{T_0}\right)^3\left(\frac{w_s^0}{\theta^0} + w_M^0\right)\right]\right\}, \tag{41}$$

where the sub- (or super-) script indicates that the quantities are to be evaluated at $\theta = \theta^0 = g\beta H_0/kT_0 = 2.04$. Placing numerical values of third-order correction terms—obtained directly from their defining equations—into Eq. (41) along with the proper values of the second-order correction terms and of the characteristic temperatures τ and γ, we finally obtain

$$M = M_0(1 - 9.4\times 10^4 H^{-2} - 30\times 10^6 H^{-3}). \tag{42}$$

This expression is exact to the second order in the dipole-dipole coupling and to the third order in the cubic crystalline field interaction. The agreement between it and experiment is discussed thoroughly in Section IV of Part I.

The writer wishes to thank Professor Van Vleck for suggesting this problem and for freely offering his assistance on many occasions