On the Adiabatic Demagnetization of Caesium Titanium Alum

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Titanium salts should behave more simply than most materials under magnetic cooling, since the ground level of the paramagnetic ion is here inherently doubly degenerate and so unaffected by crystalline fields. De Haas and Wiersma show that as long as the magnetic moment remains constant during adiabatic demagnetization, the temperature is a linear function of a field strength, a most valuable fact since it permits the establishment of a thermodynamic temperature scale. The present paper computes when deviation of the moment from constancy should commence because of the perturbing effect of second-order terms (the first nonvanishing order) in the dipole-dipole coupling energy. The calculated moment does not remain constant to as low field strengths as reported experimentally. The discrepancy cannot be ascribed to a counterbalancing effect of exchange coupling but may be due to the neglect of third and higher order dipole terms. Because of these large dipole perturbations, the status of the experimental temperature scale in titanium alum becomes rather uncertain. The present stage of the theory may be tested more accurately by using much lower initial fields than in the existing Leiden experiments.

INTRODUCTION

THE production of very low temperatures by the method of adiabatic demagnetization is a subject already classic. However, the great difficulty is the determination of the thermodynamic temperature. This is usually estimated by assuming Curie's law. The latter, however, cannot be accurate, as it would require zero specific heat in the absence of an applied magnetic field, and so allows no heat capacity to prevent the substance from cooling clear down to the absolute zero!

A neat way out of the difficulty, though of somewhat limited applicability, has been proposed by de Haas and Wiersma,[1] who suggest and try the following procedure. As the field is diminished adiabatically from the high value which produced the initial decrease of entropy at helium temperatures, there is a certain interval during which the moment retains the same value as at the original temperature and field strength. It is purely a matter of thermodynamics to show, as they do, that as long as this is the case, the thermodynamic temperature is a linear function of field strength, so that

$$T = aH + b. \tag{1}$$

The constants a and b in general involve the intensity of magnetization M as a parameter, and can be determined by finding two known

pairs of values of H, T in the helium range which yield the same given value of M. Once a and b have been fixed, (1) can be used to yield T in terms of H at low temperatures where T cannot be measured by ordinary means. If the field is reduced below a certain critical point, however, the moment deviates from its original value, in general decreasing. Below this point, Eq. (1) ceases to apply.

To illustrate, de Haas and Wiersma find that caesium titanium alum has the same moment when demagnetized to 105 gauss as under the initial conditions of 1.20°K and 24,075 gauss. They thus conclude that the temperature associated with 105 gauss is $1.20 \times (105/24,075)$ or 0.0052°K. Below 105 gauss the moment decreases rapidly, and at 1.05 gauss has less than 1/50 of its initial value.

In selecting a material to be measured, it is important to find one which comes as close as possible to an "ideal" behavior, i.e., to zero specific heat when $H = 0$. When $H \neq 0$ there is a finite, socalled magnetic specific heat even for an ideal substance. It is when H is reduced so far that the heat capacity due to other causes begins to be comparable with this magnetic specific heat that (1) starts to lose validity.

De Haas and Wiersma's choice of caesium titanium alum was an exceedingly wise one. In the first place it is magnetically dilute. Secondly, it has a spin of $S = \frac{1}{2}$ and susceptibility measurements show that it is in a nondegenerate orbital state, at least below hydrogen temperatures or

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so. On superposing both spin and orbit, one thus sees that the Ti^{+++} ion is in a doubly degenerate state. Now a fundamental theorem of Kramers[2] tells us that no crystalline field whatsoever is capable of separating the levels in a doubly degenerate state with an odd number of electrons. Hence there is no Stark splitting to create deviations from Curie's law. The only apparent cause of deviation from an ideal behavior is therefore the magnetic dipole-dipole coupling, and possibly a little exchange interaction, between the widely spaced paramagnetic ions. In the present paper we calculate when these effects should begin to enter.

The computation of the influence of the dipole-dipole coupling involves no unknown constants, as the lattice spacing is known. We find that when terms of the second order (the first non-vanishing order) in this coupling are included, the moment at 105 gauss should be about 18 percent lower than the value associated with the initial field 24,000 gauss. Experimentally, the moments are the same at these two field strengths to within the experimental error, estimated by de Haas and Wiersma as five percent. Conceivably the discrepancy arises from the neglect of third and higher order dipole terms, but in any event the existence of such large dipole perturbations casts serious doubts on the propriety of using (1), without further investigation, to determine temperatures as low as 0.0052°K, the value yielded by (1) at 105 gauss. Quite irrespective of quantitative estimates, simple qualitative considerations show that one should expect ideal conditions probably not to persist down to 0.0052°K. Namely, the dipole-dipole perturbations should be appreciable when the temperature ceases to be high compared with the characteristic temperature[3] $\tau = 3N\beta^2/k$ associated with dipole-dipole interaction. Here N is the number of atoms/cc, and β is the Bohr magneton $he/4\pi mc$. Now caesium titanium alum has $\tau = 0.0038°K$ and so one would a priori expect the dipole corrections to be appreciable at temperatures considerably above 0.0052°K.

MATHEMATICAL DETAILS

It is necessary to have formulas for the entropy and magnetic moment of an ensemble of coupled atoms. Practically all the requisite calculations have been made in a previous paper by the writer,[4] henceforth called l.c., in which the partition function was computed in Eqs. (21), (23), (27) to the second approximation in the coupling parameters, with arbitrarily large external applied fields. As the demagnetization measurements are made on a powder, the anisotropic term proportional to Ω_4 in Eq. (21) of l.c. can be omitted, since it averages to zero. The effective field H is now to be taken as identical with the applied field, rather than as primarily an inner Weiss field such as was used in the previous application of the calculations to ferromagnetism.

Once the partition function Z has thus been determined, it is a matter of simple differentiation to find the entropy S and magnetic moment M, viz.,

$$S = -\partial F/\partial T, \quad M = -\partial F/\partial H, \quad F = -kT \log Z.$$

Thus it is found that

$$S/kN = \log 2 + \log \cosh (g\beta H/2kT) - (g\beta H/2kT) \tanh (g\beta H/2kT)$$
$$+ (\tau/T)f_S' + (\tau/T)^2(f_S'' + F_S + G_S), \quad (2)$$

$$M/g\beta N = B_1 + (\tau/T)f_M' + (\tau/T)^2(f_M'' + F_M + G_M), \quad (3)$$

where $B_1, f_S \cdots G_M$ are functions only of the argument $x = g\beta H/2kT$ and are defined as follows:

[2] H. A. Kramers, Proc. Amsterdam Acad. **33**, 959 (1930).

[3] Cf. J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937); M. H. Hebb and E. M. Purcell, ibid., p. 338.

[4] J. H. Van Vleck, Phys. Rev. **52**, 1189 (1937). The following errata may be noted in this paper. In the first line of Eq. (21), read 4 in place of y. In the third relation of Eq. (27), Q should read Q_0 and in the formula for $z'v$ on the first line of p. 1193, N should read N^{-1}. Because we are usually dealing with measuring fields large enough to produce saturation, it is necessary to use the calculations of this article rather than the treatment appropriate to weak final fields given in reference 3. Hebb and Purcell (reference 3) have already discussed calorimetric measurements on the field-free specific heat of caesium titanium alum.

$B_1 = \frac{1}{2} \tanh(g\beta H/2kT)$, $\quad f_S' = \frac{1}{3}(\Phi - vz')(-g\beta H/kT)(1 - 4B_1^2)B_1$,

$9f_S'' = (\Phi - vz')^2[8B_1^4 - 2B_1^2 - (g\beta H/kT)(1 - 4B_1^2)(B_1 - 8B_1^3)]$,

$9F_S = -(z''v^2)[4B_1^4 + \frac{3}{2} - 4B_1^2 + (g\beta H/kT)(4B_1^3 - 2B_1)(1 - 4B_1^2)]$,

$9G_S = -Q_0[\frac{1}{4} - B_1^2][3 - 16B_1^2 + \frac{1}{5}(g\beta H/kT)(10B_1 - 32B_1^3)]$,

$f_M' = \frac{1}{3}(\Phi - z'v)(1 - 4B_1^2)B_1$, $\quad 9f_M'' = (\Phi - z'v)^2(1 - 4B_1^2)(B_1 - 8B_1^3)$, $\quad 9F_M = z''v^2(1 - 4B_1^2)(4B_1^3 - 2B_1)$,

$9G_M = Q_0[\frac{1}{5}(kT/g\beta H)^2(24B_1^3 - 12B_1)] + Q_0(4 - 16B_1^2)[-\frac{1}{8}B_1 + \frac{2}{5}B_1^3 + \frac{3}{5}(kT/g\beta H)(\frac{1}{4} - \frac{3}{2}B_1^2)]$.

Here $\qquad\qquad g = 2, \quad Q_0 = 14.4, \quad z = 12, \quad \tau = 3N\beta^2/k = 0.0038°\text{K},$ $\qquad\qquad$ (4)

$\qquad\quad \beta = he/4\pi mc, \quad v = -2\sqrt{2}J/g^2\beta^2N, \quad z' = 6\sqrt{2}, \quad z'' = r^{-6}N^{-2}z = 6,$ $\qquad\qquad$ (5)

where J is the usual exchange integral between adjacent atoms. Exchange coupling between the atoms is included as a possibility in order to examine whether this can sometimes fortuitously neutralize the perturbing effect of the dipole-dipole forces. In (4), (5) we give the values of various expressions appropriate to caesium titanium alum, i.e., a face-centered lattice with practically all the magnetism arising from spin. For increased generality in connection with possible future uses, we mention that (2), (3) still apply to other types of cubic lattices provided the definitions (4), (5) of the symbols are replaced by more general ones given in l.c.[3, 4]

The G terms in (2) and (3) are the perturbations due to dipole-dipole interaction, which enter only in the second order (τ^2). The terms f' and $f'' + F$ give respectively the first and second-order effect of the exchange (v) as well as demagnetization (Φ) corrections. The significance of the demagnetization plus Lorentz factor Φ is explained in l.c. and earlier papers,[3, 4] and need not be elaborated here. Anyway, Φ vanishes for a sphere, the shape of the test body used in the Leiden experiments.

If we omit all the correction terms of the various types f, F, G, Eqs. (2), (3) reduce to

$$M/g\beta N = \frac{1}{2}\tanh x, \qquad (6)$$

$$S/kN = \log 2 + \log \cosh x - x \tanh x, \qquad (7)$$

where $x = g\beta H/2kT$. Then (1) clearly applies with $b = 0$. We show below in fine print that (6), (7) are also valid when the f terms are retained, provided the argument is taken as

$$x = g\beta[H + (\Phi - z'v)M]/2kT. \qquad (8)$$

In this case (1) is still correct, with now

$$b/a = (\Phi - z'v)M. \qquad (9)$$

One way to prove (6), (7), (8) is to expand (6), (7) as Taylor's series in $(\Phi - z'v)$, using successively more accurate values of M on the right side. Then (2), (3) and (6), (7) agree to terms in $(\Phi - v'z)^2$ inclusive, provided $F = G = 0$. Another way of establishing the result is to utilize the well-known fact that the demagnetization plus Lorentz or Φ corrections are equivalent to use of an effective local field $H + \Phi M$ in the formula for the moment. If the v as well as Φ terms are included, it is clear that the effective field is $H + (\Phi - z'v)M$, since Φ and $-z'v$ enter in a simple additive fashion in f. One immediately suspects that as far as the entropy is concerned, the f terms are also incorporated by employing a field of this character. An analytical proof that (6, 8) imply (7), except for an easily determined function of T alone, is furnished by the thermodynamic relation

$$(\partial M/\partial T)_H = (\partial S/\partial H)_T$$

inasmuch as by (6) and (8)

$$(\partial x/\partial T)_H / (\partial x/\partial H)_T = -(\partial H/\partial T)_x$$
$$= -(\partial H/\partial T)_M = -2kx/g\beta.$$

In view of the foregoing, we can drop the f terms in (2), (3), as they do not affect the constancy of the moment, or the validity of (1). We henceforth interpret H not as the applied field H_a but rather as the local field $H_a + (\Phi - z'v)M$. Our proof of the equivalence of the f terms to this effective field ceases to apply with complete rigor when the F and G corrections are superposed, but the resulting error is unimportant for our purposes, as to a sufficient approximation the various contributions may be considered additive.

Since S is constant under adiabatic conditions, Eq. (2) determines T as a function of H. The procedure is to solve (2) for T in terms of H, or more simply, for T in terms of $x = g\beta H/2kT$. The resulting pairs of values of T, H (or T, x) are then substituted in (3) and in this way the course of the moment during the adiabatic demagnetization can be calculated.

In computing the influence of the F and G terms, it is often possible to make one of two simplifications appropriate to different limiting conditions.

TABLE I.

$H_0 = 24,000$ gauss, $T_0 = 1.17°K$ $(x_0 = 1.37)$				
H	430	250	105	1.05
$(T/\tau)_{calc}$	5.50	3.15	1.20	1.61
$(x_0/x)_{calc}$	.993	.972	.89	120
$(M/M_0)_{calc}$	.99	.97	.82	.001
$(M/M_0)_{obs}$			1.00	.016

$H_c = 12,000$ gauss, $T_0 = 1.25°$ $(x_0 = 0.64)$				
H	200	115	64	5.23
$(T/\tau)_{calc}$	5.7	3.60	2.81	2.68
$(x_0/x)_{calc}$	1.04	1.14	1.60	18.8
$(M/M_0)_{calc}$	.93	.79	.51	.040
$(M/M_0)_{obs}$				.050

$H_0 = 7000$ gauss, $T_0 = 1.17°$ $(x_0 = 0.4)$				
H	145	95	50	5.23
$(T/\tau)_{calc}$	7.20	5.5	4.4	4.02
$(x_0/x)_{calc}$	1.14 •	1.33	2.00	17.4
$(M/M_0)_{calc}$	.85	.71	.47	.052

Down to fields of about 200 gauss one can usually with fair approximation assume that the argument of the F and G terms, which are perturbations, has the same value x_0 as at the initial helium temperature, while the leading terms in S and M, i.e. those of structure (6), (7) can be developed as a Taylor's series in $x - x_0$, and only terms through the first order retained. On remembering that S remains constant, it is thus found that

$$x - x_0 = [(F_S^0 + G_S^0)/x_0(1 - 4B_1^{02})](\tau/T_0)^2(H_0/H)^2 \quad (10)$$

$$M - M^0 = g\beta N[\tfrac{1}{2}(F_S^0 + G_S^0)x_0^{-1} + F_M^0 + G_M^0](\tau/T_0)^2(H_0/H)^2 \quad (11)$$

where H_0, T are the original helium values of H, T, and where F^0 means that F is to be evaluated with the argument $x = x_0$, etc.

At very low field strengths (x about 0.3 or lower), a Taylor's development in ascending powers of H can be made, viz.

$$S/kN = \log 2 - \tfrac{1}{2}x^2 - \tfrac{1}{3}(\tau/2T)^2(Q_0 + z''v^2) + \tfrac{1}{3}(\tau/2T)^2x^2(3Q_0 + 4z''v^2), \quad (12)$$

$$M/g\beta N = \tfrac{1}{2}x - (\tau/3T)^2x(\tfrac{3}{2}Q_0 + z''v^2) - \tfrac{1}{6}x^3 + x^3Q_0(97\tau^2/675T^2) + x^3z''v^2(11\tau^2/54T^2). \quad (13)$$

Eq. (12) is readily solved for $(\tau/T)^2$, and the result substituted in (13).

EFFECT OF EXCHANGE COUPLING

The F terms in (10), (11), or v terms in (12), (13) represent the part of the exchange corrections which cannot be incorporated by the artifice of a local field proportional to M. The expression $\tfrac{1}{2}F_S^0x^{-1} + F_M^0$ in (11) is easily seen to

be always negative. Hence exchange effects tend to decrease the moment in adiabatic demagnetization, regardless of the sign of v, i.e., of the exchange integral. The constancy of the moment reported in the Leiden experiments thus cannot be attributed to a fortuitous cancelation of exchange and dipole-dipole corrections, a hypothesis which looked hopeful before the requisite mathematical calculations were made. We henceforth omit the exchange terms F, as they do not help matters any. It is, of course, reasonable that the exchange integrals should be very small, because of the large spacing between paramagnetic ions. The most important effect of any possible exchange coupling is to give rise to a nonvanishing constant b in (1), since b is by (9) of the first rather than second order in the exchange integral. Such a b term, of course, does not affect the constancy of the moment, but might prove troublesome in calculating the temperature, inasmuch as b is negligible compared with aH at helium temperatures and so cannot be detected by calibration experiments made there, but may be appreciable at the final low temperatures, where aH is small.

EFFECT OF DIPOLE-DIPOLE COUPLING

Table I illustrates the effect of dipole-dipole forces as calculated from Eqs. (2), (3). The values of H given in the table often are not round numbers because x_0/x_0 rather than H is conveniently taken as the independent variable in numerical solution. The ratio $x_0/x = (TH_0/HT_0)$ is the same as the factor by which the temperature deviates from the "ideal" value (1).

One immediately speculates as to the cause of the rather glaring discrepancy between the observed and calculated behavior in the case of the demagnetization from 24,000 gauss. As far as we can see, the only possibility is to attribute it to neglect of third and higher powers of the dipole-dipole interaction, as Eqs. (2), (3) are correct only to the second power, the first nonvanishing order, in this coupling. The effect of each successive power is dimensionally of the order τ/T compared with the preceding. Unfortunately the ratio τ/T is not very small, and so the convergence of the development of the partition function is notoriously bad in problems of the present sort.

The ultimate inadequacy of Eqs. (2), (3) can be seen in a particularly striking way by the graphical construction given in Fig. 1. If we plot S against $1/H^2$, Eq. (2) shows that the curves of constant $x = g\beta H/2kT$ are straight lines of slope $\tau(k^2x^2/\beta^2)G_S$, as illustrated in Fig. 1. Since the entropy retains a constant value S_0 during demagnetization, the magnitude of x and hence of the temperature appropriate to the final field strength H can be found by locating the point in Fig. 1 whose ordinate is S_0 and whose abscissa is $1/H^2$, and then finding which line passes through this point. Fig. 1 shows that often the lines cross, so that many points yield more than one value of x. Such a situation is impossible, as it would require that the temperature be a two-valued function of the field strength, an absurdity. Also, if the curves crossed, to the right of the crossing we would have higher S correlated with higher x, and hence $(\partial S/\partial T)_H < 0$, i.e., a negative specific heat, something obviously impossible physically, and also impossible mathematically because of the exponential character of the partition function. Hence the lines of large x which start with positive slope doubtless ultimately tend to curve downwards when the neglected higher powers of the dipole-dipole interaction are included, as we have indicated schematically by the dashed lines in Fig. 1, whose exact position is, of course, only conjectural. The lines corresponding to small x are reliable further to the right than those of large x because the former correspond to smaller values of τ/T for given H.

To the extreme left of Fig. 1, the effect of the neglected higher members is unimportant and the lines are reliable. Consequently Fig. 1 shows that for x_0 greater than about 0.9, the ratio of temperature to field strength actually decreases for a while during adiabatic demagnetization. (This is reflected by some values of x_0/x being less than unity in the table for $x = 1.37$.) In the vicinity of $x = .9$, there is a line of zero initial slope, and for this particular field strength, Eq. (1) is valid even when second order terms in the dipole-dipole interaction are included.

The table for $x = 1.37$ shows actually a lower temperature for $H = 105$ gauss than for $H = 1.05$. This absurd situation is because x has been determined from a rising line for $H = 105$, the only choice available here (as $S_0/kN = 0.22$), while a descending line has been employed for $H = 1.05$. The values of τ/T are here so high that obviously no quantitative significance can be attached to our calculations with straight lines.

Of course the mere fact that Fig. 1, or general considerations, show that third and higher order dipole terms cannot really be neglected, by no means makes it clear that the neglected members will just cancel the included second-order effects, so that the moment has the same value at 105 and 24,000 gauss. Indeed, the substitution of the dashed curves for the solid lines in Fig. 1 raises the temperature, and so accentuates the falling off of the moment, unless there is a counter-balancing upward bending of the curves of

constant x in the $M - (1/H^2)$ plane. (According to (3) these curves are straight lines with downward slope for all x.) If there is an actual near equality of moments at these two field strengths, the question immediately arises as to whether the moment remains constant at intervening fields, or instead passes through a maximum somewhere between 105 and 24,000 gauss. It would obviously be desirable to have measurements at intermediate fields. Unfortunately such measurements are not available and do not appear very feasible with de Haas and Wiersma's apparatus since at low temperatures, a weak solenoid capable of producing only low "measuring fields" is employed, while the very large magnet used at helium temperatures is only fit for high fields. So the gap in data apparently cannot be closed. However, even a small increase in the measuring field above 105 gauss would be illuminating. If there is an intervening maximum, which we rather doubt, Eq. (1) obviously cannot be used to determine the thermodynamic temperature, since its derivation requires that the moment remain constant over an interval rather than be merely fortuitously equal at two field strengths. If, however, the high temperature
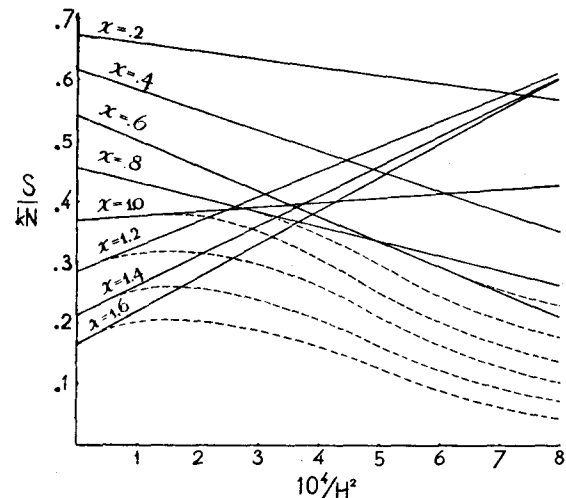

FIG. 1.

value of the moment is being approached asymptotically, (1) might be approximately correct. In this event, M would needs be slightly lower at 105 than at 24,000 gauss, but the deviation might conceivably be so much lower

than our estimate of 18 percent as to escape detection. Two other causes besides the neglected higher order members which might reduce the apparent discrepancy are (a) a g factor slightly less than 2, inasmuch as the second-order dipole perturbation is proportional to g^4, and (b) experimental errors in the relative calibrations of the magnets used at high and low temperatures. The error due to the latter cause might amount to 5 percent or so.

It is clear that additional theoretical and experimental work is much to be desired, because of the light it will shed on the mooted question of how far dipole-dipole interaction can be represented by an inner field of the Lorentz type. If the Lorentz hypothesis were strictly correct, then Eqs. (6), (7), (8) would always be fulfilled, and (1) would be valid at all temperatures. The latter is, of course, impossible, but the Lorentz assumption is to a certain extent the equivalent of the simplest form of the Heisenberg theory of magnetism, in which the constant of proportionality in the Weiss molecular field is independent of temperature, but which works much better than a second-order (so-called "Gaussian") perturbation calculation. All the same, it is impossible to have a power series in τ/T with nonvanishing coefficients always summing to zero, but this situation is what would be required if the perturbations of various orders are to neutralize each other so as to restore the accurate validity of (1).

It seemed worth while to publish the calculations in their present form, inclusive only of second order dipole effects, not merely because a third order computation would be quite long, but primarily because an experimental test of the second order corrections is possible by using much lower initial demagnetizing fields than 24,000 gauss. The lower this initial field H_0, the smaller the final value of τ/T and so by decreasing H_0 the ambiguity due to the neglected members becomes asymptotically small. Table I shows that the order of magnitude of the critical field strength H_c at which appreciable deviations of M/M_0 from unity first appear is not greatly influenced by the size of the initial field, so that experiments with lower H_0 remain feasible. The advantage is that H_c can be computed with increasing certainty, the smaller H_0. Unfortunately the only published measurement with $H_0 = 12,000$ gauss is for a very weak final field, 5.23 gauss. The discrepancy of about 25 percent between the observed and calculated value of M at this field is far from excessive for a possible influence of higher order members, since τ/T is still not small enough to make the series converge at all adequately,[5] and, after all, a deviation of 25 percent is small compared with the total reduction in moment by a factor 20. It would be of interest if measurements were available with still smaller initial fields, say 2000 to 7000 gauss.

It may be noted that in his most interesting experiments on paramagnetic relaxation, Gorter[6] finds that in caesium titanium alum the absorption per titanic ion does not increase greatly on dilution with nonmagnetic ingredients. This he interprets as showing that some other factor than coupling between paramagnetic ions interferes with the free orientation of the spin. Because of Kramers' theorem on double degeneracy,[2] and because no adequate disturbing nuclear moments can be invoked, it is hard to see what this mysterious factor can be. If it really exists, it perhaps modifies the present calculations for extremely low temperatures, in some unknown way.

The writer is much indebted to Dr. C. J. Gorter for valuable discussion.

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[5] That our neglected higher order terms are very important even in demagnetization from 12,000 gauss can be seen by integrating Hebb and Purcell's (reference 3) specific heat formula (13) so as to obtain an expression for the entropy. This formula is more special than our (2) in that it applies only to very weak fields, but it does include third and fourth as well as second order terms in the dipole interaction. The inclusion of these two extra orders makes the value of (T/τ) appropriate to zero field strength imaginary, an absurdity, rather than 2.68 as given in the table. The situation is reminiscent of that in the Heisenberg theory of ferromagnetism, where Opechowski shows that an imaginary Curie point is obtained if extra terms are included in place of stopping with the usual approximations (Physica **4**, 181 (1937)).

[6] Cf. C. J. Gorter and R. de L. Kronig, Physica **3**, 1018 (1936).