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Influence of the Dipole-Dipole Coupling on the Specific Heat of Cesium Titanium Alum

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To find the influence of the magnetic dipole-dipole coupling on the specific heat in a fcc lattice, the Hamiltonian was computed in a straightforward way. If one omits the nonring diagrams, the successive terms in $1/kT$ can be obtained from the Fourier transform. We found that the third-order term was different from the results quoted in the literature, both in sign and in magnitude. Some discussion is devoted to the question of what magnetic state will be realized below the critical temperature.

I. INTRODUCTION

Ever since adiabatic cooling was used to obtain lower temperatures, the question about the influence of dipole-dipole coupling has been of interest. This type of interaction is well defined, but its consequences are tedious to evaluate. The problem cannot be sidestepped by considering nearest neighbors only, as was often the custom. The long-range nature of the interaction and its angular dependence make it hard to replace it by some simple approximation. In the 1930's Van Vleck[1] courageously set out to calculate algebraically a number of terms for various cubic lattices. In this calculation he made some simplifications, which although understandable at that time, are no longer necessary. The second-order term in $1/kT$ is relatively simple, but the third- and fourth-order terms required a considerable amount of work. In order to facilitate the computation, the arrangement of dipoles he considered was simple cubic, rather than fcc, for the last two terms. We have made calculations elsewhere[2] for c/a values (c and a are defined in Fig. 1) different from $\sqrt{6}$ (fcc), and found a clear-cut dependence on this parameter. (The simple cubic lattice corresponds to $c/a = \sqrt{\frac{3}{2}}$.) Hence it was considered worth while to repeat the calculations.

To discuss a few more of the technical details of Van Vleck's calculation let me first point out the other simplifications used. In the "triple-bar" terms (compare Fig. 2, diagram 3-2) the sum was taken over the nearest neighbors only, which is indeed a good approximation; moreover, the whole term is of no importance as long as the exchange interaction is small. In the triangular term (diagram 3-1), only isosceles right triangles were used. In the fourth-order calculation, Van Vleck left out the " square" term, since he used nearest neighbors only. We believe that this term gives an important contribution. This term is extremely difficult to obtain algebraically beyond the nearest-neighbor approximation since one is dealing with a ninefold summation: three positions in three dimensions. In our numerical work this difficulty is avoided by using the Fourier transform inside the Brillouin zone.

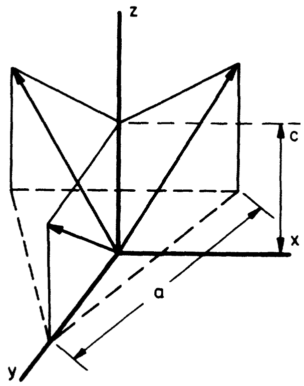

FIG. 1. Choice of primitive lattice vectors $(c/a)^2 = 6$.

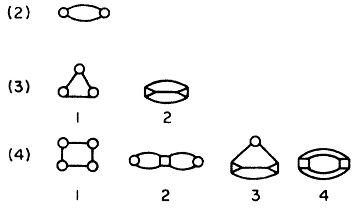

FIG. 2. Terms of order 2, 3, and 4 in $(1/kT)$ represented by diagrams.

TABLE I. Coefficients C_n' for $n=2$, 3, 4 in the expansion of Eq. (1).

	$g=2$	
n	Calculated	Hebb and Purcell (Ref. 3)
2	2.390	2.40
3	−4.41	−4.35
4	23.44	−13.5

II. METHOD

As described elsewhere[2] in detail, the contributions of the ring diagrams 2, 3-1 and 4-1 (Fig. 2) can be found most conveniently via a Fourier transformation $P(\vec{k})$ of the dipole sum. This method has the advantage that the summation over the spin components can be done at the same time, via a Kramers-Wannier transformation.

For comparison we also calculated diagrams 2 and 3 directly. A further check on the Fourier transform is the integral over $P(\vec{k})$ to the first order which has to be equal to zero since it corresponds to the contribution of the origin, which is absent in the sum. The cancellation of the three eigenvalues was better than one per thousand.

III. RESULTS OF COMPUTATION

We restrict our consideration to the case of cesium titanium alum, a salt with effective spin moment $S=\frac{1}{2}$, uncomplicated by crystal field effects. The undiluted salt is, magnetically speaking, rather dilute so that exchange interaction might be expected to be small.

We made two runs: One run used $g_\perp = g_\parallel = 2$ in order to compare our results with those of Hebb and Purcell[3]; the other used the actual measured values for the two g values, which were not known at the time that the Van Vleck, Hebb and Purcell papers were written.

The $g=2$ values for the dipole-dipole sums were compared with the values previously published by introducing a factor τ defined by

$$\tau = (g^2\mu_B^2/k)NS(S+1) \quad .$$

The origin of the value of N is not quite clear in the Hebb and Purcell paper. We used

$$N=\sqrt{3}/a^3 \quad ,$$

the inverse of the volume of the translational unit cell. Here, a is the distance indicated in Ref. 2 as the side of the triangle. The value of $c/a=\sqrt{6}$ in this system of reference. The length a is $1/\sqrt{2}$ times the length of the cube edge of the fcc lattice, which is 12.17 Å for cesium titanium alum. With $S=\frac{1}{2}$ and μ_B and k the usual values, we find $\tau = 4.140\ 10^{-3}$ K. Hebb and Purcell[3] quote 3.8×10^{-3} K based on their assumption for N. For the purpose of comparison we use our τ values, since the ratios of the nth order coefficients over τ^n should be independent of a (and so of N), and hence we are internally consistent. If we write the high-temperature specific-heat series as

$$C(T) = R \sum_{n=2} C_n' \left(\frac{\tau}{T}\right)^n \quad , \tag{1}$$

we find the values of the C_n' tabulated in Table I. In comparison with Hebb and Purcell's values, the first is in excellent agreement; the second is 10% off; the third we find twice as big and of the opposite sign. It is likely that the sign in Ref. 3 is an error.

The results of the runs with the actually measured g values are displayed in Tables II and III. Table II gives the results for the ring diagrams. Since they were obtained via a Fourier transform, there is an overcount for $n \geq 4$. This is illustrated in Fig. 3. One can show that the second diagram in Fig. 3 gives the same contribution as diagram 4-2 in Fig. 2 (see the Appendix).

The results in Table III are for comparison with, and correction to, the results in Table II. In the third order, the influence of 3-2 is of no importance. In the fourth order, the influence of 4-2 (which can be calculated by using diagram 2 squared minus diagram 4-4) is of importance, but already incorporated in the Fourier transform. The influence of 4-3 is minor, that of 4-4 the same. The corrections to the fifth- and sixth-order terms

TABLE II. FT is the Fourier transform of g^2P, the lattice sum incorporating the g factors in units $a=1$. Values used are $g_\perp=1.140$; $g_\parallel=1.250$; and $(c/a)^2=6$. ΔS is the entropy correction in mK^n, using $\sqrt{2}\ a=12.17$ Å. ΔS is the difference between S/R and ln2.

n	FT	ΔS
2	165.434	−2.4697
3	917.942	4.4648
4	1.89425×10^4	−25.3534
5	2.0401×10^5	71.105
6	3.2194×10^6	−285.63

TABLE III. Two- and three-point direct summations for g^2P and ΔS. Same parameters as in Table II.

Vertices	Bonds	Label	g^2P	ΔS
2	2	2	167.04	-2.4937
2	3	3-2	-17.047	$+8.291\times10^{-2}$
2	4	4-4	424.03	-5.675×10^{-1}
3	3	3-1	905.18	4.399
3	4	4-3	406.67	0.5441

are not yet available. Hence, the first three terms of Table II form the actual result of the calculation.

IV. COMPARISON WITH EXPERIMENT

The first experiments were done by de Haas and Wiersma.[4] Experiments by Kurti and Simon are quoted in Ref. 3 and they resulted in the work by Van Vleck and Hebb and Purcell. Since these calculations were done before the start of paramagnetic resonance, g factors were unknown and taken equal to 2. Bijl[5] and later Bleaney *et al.*[6] measured the g factors. Benzie and Cooke[7] measured the susceptibility and specific heat (as well as the relaxation time, which is outside the scope of this paper). Measuring the susceptibility, they determined that $g_{\parallel}=1.40$, and $g_{\perp}=0.96$ from their average g value of the powdered sample, using Bleaney's equations and the spin-orbit coupling constant. For the specific heat C they obtained a separate value for the nuclear contribution ($CT^2/R=0.4\times10^{-5}$) from measurements on samples of various dilutions. This left for the electron-spin contribution

$$CT^2/R=3.5\times10^{-5}\,\mathrm{K}^2\quad .$$

Benzie and Cooke used Van Vleck's dipolar equation for isotropic g factor with their rms g value to compute the dipolar contribution, obtaining

$$CT^2/R=2.9\times10^{-6}\,\mathrm{K}^2\qquad(g_{\mathrm{rms}}=1.12).\qquad(2)$$

Then they assigned the remainder to exchange interaction.

That their procedure is wrong is probably known to them, since the dipolar sums $\sum P_{ij}^{\alpha\beta}(\alpha,\beta=x,y,z)$ do not all contribute the same amount. (Remember that $\parallel$ and $\perp$ refer to the crystalline c axis and not to the edges of the fcc lattice.) Second, their g factors were incorrect, being deduced indirectly from the susceptibility, which is a poor method since the result depends on the values of other parameters.

The parameters needed are the g values and the lattice constants. Both are known, but they occur in a rather high power; hence, much depends on their accuracy. The accuracy of the g factors is about 1% which gives a 4% inaccuracy in the coefficient of $(kT)^{-2}$.

If our parameters are sufficiently accurate, we deduce that the amount of dipole-dipole is about twice as large as that calculated by Benzie and Cooke [compare Table II with Eq. (2) and note that the specific heat coefficient is twice the entropy coefficient]. This does not, however, alter the earlier conclusion that the exchange contribution dominates the dipolar contribution.

This widely used method of attributing the remaining part to exchange is, of course, highly unsatisfactory, but since no data are yet available, there is little else one can do.

V. SPIN ARRANGEMENTS BELOW T_c

Below the critical temperature the spin system will go into a cooperative state. If the coupling were pure dipole-dipole the state might be antiferromagnetic, staggered, or helical. Moreover, there might be energetic factors that would require domains to be formed. In the literature there are arguments in favor of the antiferromagnetic state.[8] These calculations were actually meant for the ground state, which need not be the same as the state just below the critical temperature. It has also been suggested that the state will break up into domains.[9] It is difficult, if not impossible, to give a theory from first principles. It could be true, moreover, that the state is not associated with an array of simple regularity. For instance, Wannier[10] has shown that the ground state of a two-dimensional triangular antiferromagnetic Ising model could not be associated with any long-range order. Although the compound under consideration is fcc, the anisotropy of the g factor makes it look like a stack of two-dimensional triangular lattices, magnetically speaking.

In a previous paper,[2] we ventured the speculation that the magnetic structure would be determined by the largest negative component of the Fourier transform of the interaction. This disregards all possible domain formation. However, it is a less rigid assumption than the generally assumed antiferro-

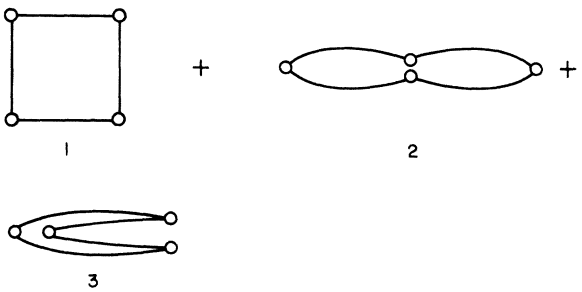

FIG. 3. Overcount in the four-step ring diagram by Fourier transform.

magnetic structure. (It is simple to show that ferromagnetism is definitely out of the question.) We determined again the value of the largest negative $P(\vec{k})$ components and the value of $\vec{k}$ for which the minimum occurs: $\vec{q}$. These are

$$g_\perp^2 P^{xx} = -7.9387 \text{ for } \vec{q} = (0.0,\ -9.069,\ 1.763) ,$$

$$g_\perp g_\parallel P^{xz} = -10.906 \text{ for } \vec{q} = (-1.571,\ 0.0,\ 1.44) .$$

The other diagonal and off-diagonal components have similar values. Unfortunately, the relation between $\vec{q}$ and the actual magnetization will be destroyed by the exchange interaction in cesium titanium alum, due to its magnitude.

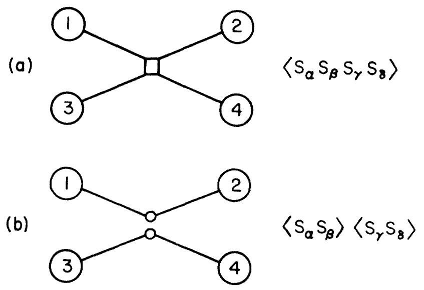

FIG. 4. Square vertex vs two circle-vertices (compare with the Appendix).

APPENDIX

The calculation of a square-vertex contraction $\langle S_\alpha S_\beta S_\gamma S_\delta \rangle$, versus two independent circular vertices $\langle S_\alpha S_\beta S_\gamma S_\delta \rangle$ on a given lattice site, gives the result provided the point is an articulation point in the lattice summation.

To show this we consider Fig. 4. We observe in both cases that the trace is zero unless either all Greek labels are equal, or they are equal pairwise. Moreover, it is clear that the first case is realized in more ways than the second. The additional options are

1	2	3	4
α	β	α	β
α	β	β	α
β	α	β	α
β	α	β	α

.

Here α and β represent, as before, x, y, and z. The numbers 1, 2, 3, 4 depict the pieces of diagram to which the vertex is connected. The extra options cancel if 1 and 3 or 2 and 4 can be interchanged. This is the case if the vertex is an articulation point in the lattice summation.

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