Spin-Wave Contribution to the Heat Capacity of Magnetite

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The dispersion curve recently found by Milford and Glasser for the acoustical branch of the spin-wave spectrum of magnetite is used in a numerical calculation of the heat capacity. The results obtained are compared to the fit found by Kouvel for his low-temperature experimental data. It is found that the use of a more precise dispersion curve does not remove the disagreement between low-temperature heat-capacity determinations of the exchange constant and determinations based on measurement of the Curie temperature, but that it does destroy the apparent agreement between the low- and high-temperature measurements of the Debye temperature.

INTRODUCTION

RECENTLY, Milford and Glasser[1] derived, under the approximation of the linear spin-wave theory with nearest-neighbor interactions, otherwise exact dispersion relations for spin waves in ordered magnetite (Fe_3O_4). In the case where the A (tetrahedral) and the B (octahedral) sites do not interact among themselves ($J_{AA}=J_{BB}=0$, $J_{AB}\neq0$), good agreement was found between the theory and the experimental dispersion curves of Watanabe and Brockhouse[2] for a value of J_{AB} of about 2.4×10^{-3} eV. Insertion of a small negative exchange interaction between B sites gave even better agreement[3] with the same value of J_{AB} but with $J_{BB}=-J_{AB}/10$. Furthermore, it was found that the usual quadratic approximation to the acoustic branch was valid only for a very small range of k.

It is well known[4] that the values of the exchange constant derived from low-temperature specific-heat measurements do not agree with high-temperature measurements of Curie temperature for a number of ferrites. In order to test the possibility that this discrepancy is caused by the rapid deviation of the correct dispersion relations from quadratic k dependence, and in order to see in detail what effect this deviation has on the dependence of the heat capacity on temperature, we have undertaken a numerical calculation of the heat capacity of magnetite. The results of this computation are presented in a dimensionless form and are compared to the least-squares fit to a function of the form $AT^{3/2}+BT^3$ found by Kouvel[5] for his experimental data.

HEAT-CAPACITY CALCULATION

The heat capacity of a system of independent harmonic oscillators is easily obtained from the appropriate partition function. In the particular case of spin waves the details have been given in several places.[6,7]

For the purpose of calculating the spin-wave heat capacity using the dispersion curves derived earlier[1] the following expression is convenient:

$$\frac{a^3}{V\kappa}C_v=\int d^3\xi\left(\frac{\tau U(\xi)}{\sinh\frac{1}{2}\tau U(\xi)}\right)^2,\qquad(1)$$

where $\tau=J/\kappa T$, $J=J_{AB}$ is the exchange integral, κ is Boltzmann's constant, T is the absolute temperature in °K, $\xi=ka/2\pi$, k is a vector in the reciprocal lattice, a is the lattice spacing parameter, V is the volume of the crystal, C_v is the total heat capacity at constant volume, and $U(\xi)$ is defined by

$$U(\xi)=\hbar\omega(\xi)/J.\qquad(2)$$

In all calculations the contribution due to optical modes has been neglected. This is justified if τ is larger than unity as is the case for the experimental situation considered here. The integral extends over the first Brillouin zone. The symmetry of the dispersion curves[3] allows us to integrate over one-fourth of the zone (shown in Fig. 1) and take four times the result. The integral (1) was evaluated using a three-fold application of the Legendre-Gauss quadratures formula with the tabulated roots and weights given by Lowan, Davids, and Levenson[8] for a Legendre polynomial of order 10. In order to take account of the strong damping, which causes the integrand to be very small over most of the zone, a subprogram was included which, for a given
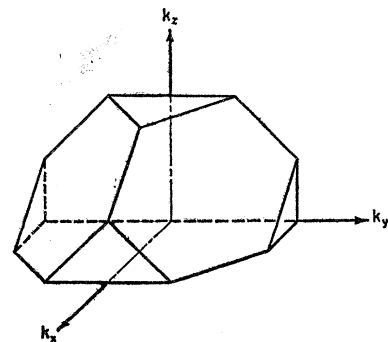

FIG. 1. One quarter on the Brillouin zone for magnetite. The intercepts on the k_x, k_y, k_z axes are at $\pm\pi/a$, π/a, π/a, where a is the dimension of the unit cell in the direct lattice.

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[7] J. S. Kouvel, Tech. Rept. 210, Cruft Laboratory, Harvard University, Cambridge, Massachusetts, 1955 (unpublished).

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TABLE I. The computed values of the heat capacity per unit cell for several values of the dimensionless coordinate τ. Also tabulated are the corresponding values of $(\tau)^{-3/2}$ and $(\tau)^{3/2}$ times the heat capacity per cell. J is the exchange integral $(J>0)$ and κ is Boltzmann's constant.

$\tau^{-3/2}$ $(\kappa T/J)^{3/2}$	τ $(J/\kappa T)$	$100~C_v/\kappa$ (per cell)	$100~C_v\tau^{3/2}/\kappa$ (per cell)
0.05	7.38	0.0778	1.560
0.10	4.63	0.1611	1.605
0.15	3.54	0.2466	1.643
0.20	2.92	0.3362	1.677
0.25	2.53	0.4280	1.709
0.30	2.23	0.5226	1.741
0.35	2.02	0.6190	1.769
0.40	1.84	0.7194	1.799
0.45	1.71	0.8210	1.831
0.50	1.59	0.9237	1.854
0.55	1.51	1.061	1.881
0.60	1.41	1.144	1.907

value of τ, calculated the value of ζ for which the integrand, with $\xi = (0,0,\zeta)$, became less than 10^{-4}. This value of ζ was then used to define a "Brillouin zone" concentric with the actual zone but much smaller in volume, over which the integral was actually performed. The error committed here is small because, while it is not quadratic in ξ, the dispersion relation is nearly spherical. Several heat capacities were calculated with the cutoff at a value of the integrand equal to 10^{-5}. In all cases, the change in C_v was less than 0.06%. (The integrand was also set equal to zero whenever $U/2$ became larger than 12, corresponding to a contribution to the integral of the order of 10^{-6}.) The computation was carried out on the Bendix G-20 computer at Battelle Memorial Institute.

RESULTS OF THE COMPUTATION

The computed values of the heat capacity per unit cell are tabulated in Table I. Also tabulated there are
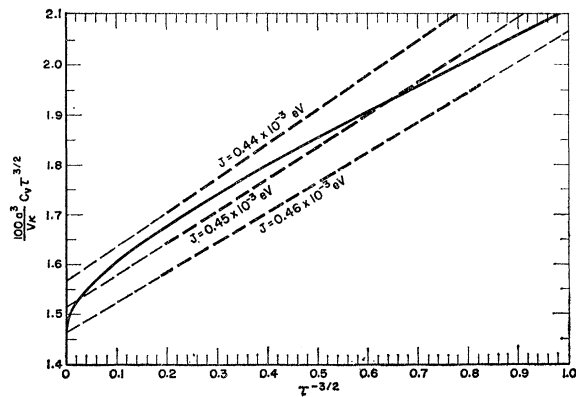

FIG. 2. Comparison of Kouvel's data (broken line) with the computed heat capacity (solid line). Dimensionless coordinates are used, with $\tau = J/\kappa T$, where J is the exchange integral, κ is Boltzmann's constant, and T is the absolute temperature. The straight lines are derived from Kouvel's least-squares fit of his experimental data; Kouvel's data line in the heavier portion of the dashed curves.

the corresponding values of $\tau^{-3/2}$ and $\tau^{3/2}$ times the heat capacity/cell, which are useful for comparison with experiment.

In Fig. 2 is displayed (solid curve) a graph of $\tau^{3/2}$ times the heat capacity/cell versus $\tau^{-3/2}$. The rounding of the curve for low temperatures is probably due to a small $T^{5/2}$ term which dominates the T^3 term at very low temperatures. The dashed lines in Fig. 2 are Kouvel's straight line fit to his experimental data,

$$C_v/T^{3/2} = 0.255 + 0.0091 T^{3/2}, \tag{3}$$

reduced to dimensionless form for each of three different values of the exchange interaction. While the computed curve is not a straight line, the deviation from a straight line in the range of Kouvel's data $(2.5 \le T^{3/2} \le 9.5)$ is small. The extrapolation to zero temperature along a straight line is also seen to be invalid, but again the error committed will be only a few percent. The best fit occurs for $J = 0.45 \times 10^{-3}$ eV, in agreement with the
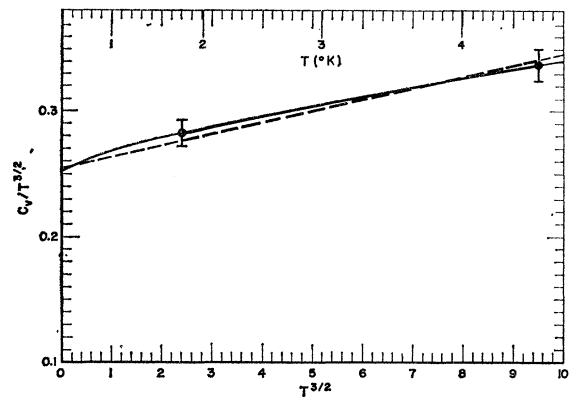

FIG. 3. Comparison of Kouvel's straight-line fit (broken line) to his experimental data with the computed heat capacity (solid line). The range of Kouvel's data is emphasized. The computed curve corresponds to $J = 0.45 \times 10^{-3}$ eV. The vertical bars indicate the ± 0.01 eV limits on the computed curve. The absolute temperature is indicated on the upper margin.

fit found by Kouvel using the quadratic approximation. Hence, the deviation from a quadratic dispersion law does not explain the disagreement between low- and high-temperature data. In Fig. 3 the same data are displayed in a slightly different form, namely using the scales established by Kouvel for his particular sample of magnetite. The fit to his data appears better here because the horizontal scale is expanded by a factor of about 12, while the vertical scale is compressed by about the same factor.

Figure 3 illustrates a second facet of the heat-capacity problem in ferrites. Almost all of the slope of Kouvel's data can be accounted for using the magnetic interaction alone. Over the range of his data, the slope from the spin-wave theory averages about 0.008 mJ/(°K)⁴. This leaves only about 0.001 mJ/(°K)⁴ for the Debye lattice heat, which increases the predicted Debye

temperature by about a factor of 2. This destroys the apparent agreement between the low- and high-temperature values of the Debye temperature.

DISCUSSION

The results of this and previous calculations may now be succinctly summarized by saying that the linearized spin-wave theory with only nearest-neighbor interactions is capable of accounting for the spin-wave dispersion curves observed above the ordering temperature and also of accounting for the spin-wave contribution to the heat capacity at low temperatures. These remarks must, however, be supplemented with the observation that in order to do this one requires values of the exchange integral which differ by a factor of about five. The possibility that this discrepancy can be attributed to the use of a quadratic approximation to the spin-wave spectrum has been excluded by this calculation. It seems, then, that barring experimental errors the exchange integral changes at the ordering temperature (or at least in the vicinity of the ordering temperature) in a dramatic way. On the basis of the crystallography this seems not unreasonable; however, a number of experiments may be suggested which would contribute a great deal towards understanding the phenomena.

Perhaps the most interesting experiments would be neutron inelastic scattering at low temperatures. Such experiments have the advantage of yielding quite direct information about the spin-wave spectrum which, as we have shown, may be interpreted readily in terms of linearized spin-wave theory. By doing such experiments as a function of temperature, especially in the region of the ordering temperature, one should be able to obtain the exchange integral as a function of temperature and this might supply some worthwhile clues about how ordering affects J.

Further measurements of the heat capacity also seem to be in order. At temperatures below 1.5°K, for example, one might see the $T^{5/2}$ contribution to the heat capacity. Such a term is to be expected on the basis of Dyson's analysis and of course would dominate a T^3 term due to a basic antiferromagnetic behavior at very low temperatures. At higher temperatures (but still below the ordering temperature) one might hope to identify better the lattice contribution to the specific heat. Here, however, a word of caution needs to be repeated; namely the calculation presented here takes account of only the lowest spin-wave mode. For magnetite at temperatures above about 5°K there is appreciable excitation of the lowest optical mode and this would need to be taken into account. Such calculations are not intrinsically more difficult than those which have already been done; however, the absence of experimental data with which to compare such calculations has led to the decision not to carry them out at this time.