

ment. Further rotation of the powder was inhibited because of the tight packing due to settling. Since no magnetization data were taken, there was no opportunity for the powder to realign.

The importance of alignment with the field has been discussed in detail by Rohrer and Thomas,¹⁴ but the main point to be stressed here is that without reasonably precise axis alignment along a field, spin flopping could be missed entirely. Such may be the case for the results shown.

SUMMARY

Ideally, a single crystal should be used for experimentally determining magnetic phase diagrams. However, this may not always be possible. The

results of this study show that it is possible to obtain the "phase" diagram from the adiabatic magnetization of powdered samples. Data obtained for a powdered sample of $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ are in general agreement with reported single-crystal results. We are planning further studies of magnetic materials using adiabatic magnetizations of a powdered sample to verify the results reported here.

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Heat Capacity of $\text{Tm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ between 0.08 and 20 K[†]

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The heat capacity of $\text{Tm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ shows a sharp peak, characteristic of a cooperative transition, superimposed on the low-temperature side of the anomaly associated with the singlet ground and first excited states. The data are in qualitative agreement with theory for exchange-induced magnetization in a singlet-crystal-field-ground-state system.

Several developments in recent years have renewed interest in the magnetism of singlet-ground-state systems. If a magnetic moment appears only in the presence of an external field the substance

may be useful for hyperfine-enhanced nuclear magnetic cooling.¹ On the other hand, it has been recognized that ordered magnetic moments can appear in zero external field if the ratio of exchange inter-

action to crystal field splitting exceeds a critical value,² and the associated heat capacity has been calculated³ on the basis of several different approximations. For certain values of the parameters two overlapping heat-capacity peaks, associated with the crystal field and exchange interactions, have been predicted.³ No experimental data have been available for comparison with the theory, but recent measurements indicate that the relevant parameters for $\text{Tm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ may be within the range for which interesting heat-capacity effects have been predicted.³ In this salt the crystal field completely removes the degeneracy of the 3H_6 ground state of the free Tm^{+3} ion. Optical Zeeman and EPR studies have shown that the singlet ground and first excited states are separated from each other by approximately 1 K and from all other levels by much higher energies.⁴ Furthermore, Mössbauer measurements⁵ have shown the appearance of magnetic hyperfine structure at ~ 0.31 K, suggesting a transition to an ordered magnetic state.⁶ From the point of view of comparison with theory, it is also an advantage that $\text{Tm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ is a dielectric because the role of conduction electrons in exchange interactions is complicated. Our heat-capacity measurements cover the entire range of temperature of interest in connection with the two lowest crystal field states and the exchange interaction. They confirm the occurrence of a cooperative transition at 0.31 K, and are in qualitative agreement with theoretical predictions.

The $\text{Tm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ sample was purified by two recrystallizations, powdered, and mixed with grease to provide thermal contact to a copper calorimeter. The thermal relaxation times were less than a few seconds except below 0.1 K where the hyperfine heat capacity is the major contribution and the longer relaxation times may have been associated with nuclear spin-lattice relaxation. The heat capacity of the grease plus calorimeter amounted to approximately 30% of the total heat capacity above 3 K, less than 1% below 1 K, and to intermediate percentages between 1 and 3 K. Measurements between 0.08 and 1 K were made in an adiabatic demagnetization cryostat and between 0.4 and 20 K in a He^3 cryostat.⁷ In both cryostats germanium thermometers that had been calibrated against single-crystal CMN ($\text{Ce}_2\text{Mg}_3(\text{SO}_4)_{12} \cdot 24\text{H}_2\text{O}$), He^4 vapor pressure, and a gas thermometer were used. The same thermometers give generally accepted values for the heat capacity of copper throughout the temperature range.⁷

The heat capacity of $\text{Tm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ is shown in Fig. 1. The broad peak, which has a maximum near 0.5 K, corresponds approximately to the heat-capacity anomaly that would be expected to be associated with the two lowest crystal field states. The narrower peak, which has a maximum

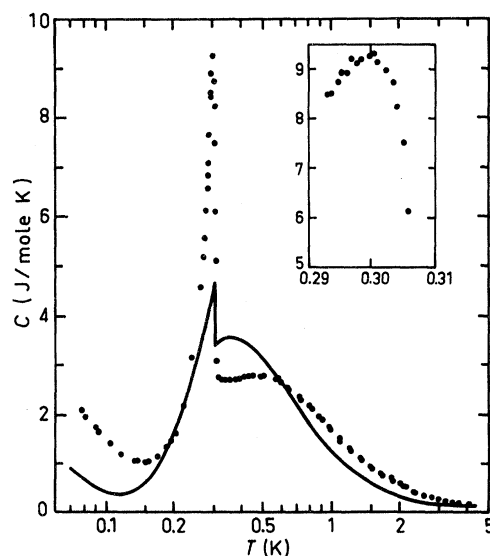


FIG. 1. The heat capacity of $\text{Tm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ per mole of Tm^{+3} . The inset shows points taken with $\Delta T \approx 1$ mK. The solid curve represents a molecular-field calculation (see text for description).

at 0.30 K and a sharp drop at 0.307 K, clearly indicates a cooperative transition to an ordered state. In the presence of small magnetic fields the 0.3-K peak is broadened and shifted to lower temperatures, suggesting that the ordering is antiferromagnetic. At the lowest temperatures the heat capacity is dominated by a T^{-2} term that corresponds to a hyperfine field of 5.54 MOe, in good agreement with that derived from Mössbauer measurements.⁵

The Hamiltonian for the spin system is

$$\mathcal{H} = \sum_i V_{ci} - \sum_{i \neq j} \mathcal{J}_{ij} \vec{J}_i \cdot \vec{J}_j + \alpha \sum_i \vec{I}_i \cdot \vec{J}_i, \quad (1)$$

where V_c is the crystal potential which produces an energy gap Δ between the two singlet crystal-field states $|0\rangle$ and $|1\rangle$, \mathcal{J}_{ij} is the exchange constant coupling the angular momenta \vec{J}_i and \vec{J}_j , α is the magnetic-hyperfine-interaction constant, and \vec{I}_i is a nuclear spin. Since I is $\frac{1}{2}$ for ^{169}Tm , the only naturally occurring isotope, no quadrupole hyperfine interaction is present. Wang and Cooper³ have calculated the heat capacity associated with the crystal field and exchange terms of Eq. (1) in the molecular-field approximation (MFA), in the random-phase approximation (RPA), and, in the paramagnetic region, in the two-site-correlation approximation (TSCA). The solid curve in Fig. 1 represents an MFA calculation that has been generalized to include the hyperfine term in \mathcal{H} . In this calculation the exchange term has been taken as $-2\mathcal{J}(0)\langle J \rangle \sum_i J_{zi}$, where $\mathcal{J}(0) \equiv \sum_i \mathcal{J}_{ij}$, and a z axis has been chosen in such a way⁸ that

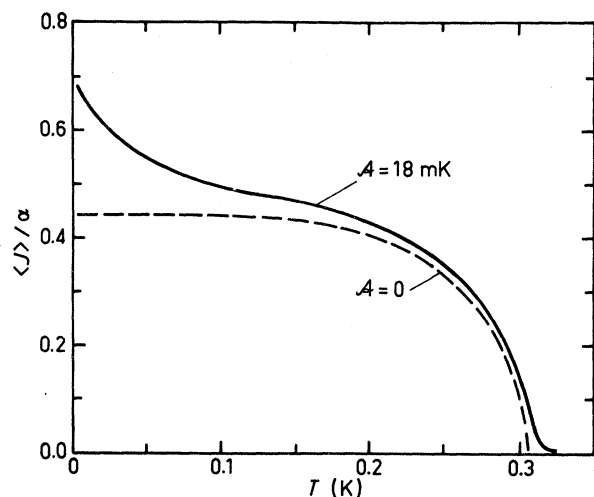


FIG. 2. Temperature dependence of $\langle J \rangle / \alpha$ as given by a molecular-field calculation for two values of hyperfine interaction (see text for complete description).

only one component, $\alpha \equiv \langle 0 | J_z | 1 \rangle$, of $\langle 0 | J | 1 \rangle$ is nonzero. The eigenvalues of the Hamiltonian are

$$E_{A,m} = -E_{B,m} = -\left[\frac{\Delta^2}{4} + \left(\frac{A\langle J \rangle \Delta}{2\alpha} - \alpha m \alpha \right)^2 \right]^{1/2}, \quad (2)$$

where $A = 4J(0)\alpha^2/\Delta$ and $m(\pm \frac{1}{2})$ is the z component of \vec{I} . $\langle J \rangle$ is determined by the solution of Eq. (2) and a standard expression from statistical mechanics for $\langle J \rangle$ as a function of $E_{A,m}$, $E_{B,m}$, and T . When $\alpha = 0$, the critical value of A for magnetic ordering at 0 K is $A = 1$. At higher values of A the transition temperature is given by

$$\tanh(\Delta/2T_c) = 1/A. \quad (3)$$

Curves representing the temperature dependence of $\langle J \rangle / \alpha$ for $\alpha = 0$ and for $\alpha = 18 \text{ mK}$, the value that corresponds to the observed hyperfine field, are shown in Fig. 2. For these curves α was taken to be 5.5, as estimated from Mössbauer measurements⁵ in the paramagnetic region and the pseudo-quadrupolar part of Eq. (2); $\Delta = 0.88 \text{ K}$ was taken from EPR data⁴; and $A = 1.115$ was chosen to give the observed transition temperature. The effect of the hyperfine interaction on the magnetization is clearly visible at the lowest temperatures, where nuclear polarization induces an enhanced magnetization, and near the transition between the ordered and paramagnetic states which is broadened and slightly shifted.

The heat capacity corresponding to the $\langle J \rangle / \alpha$

curve for $\alpha = 18 \text{ mK}$ is shown as the solid curve in Fig. 1. Above the transition temperature, MFA gives just the Schottky curve for the two crystal-field levels, but the experimental data exhibit a lower and broader anomaly. A value $\Delta \approx 1 \text{ K}$ is obtained from the location of the anomaly. Furthermore, the observed heat-capacity peak at the transition temperature is higher and sharper than that given by the MFA calculation. In each of these respects the qualitative features of the experimental data are better represented by the results of an RPA calculation³ for $T_c/\Delta \lesssim 0.1$. In RPA, however, the transition becomes first order for a value of A that would give the observed transition temperature, whereas the observed transition is second order. (A first-order transition might well be somewhat broadened in a real crystal but it seems very improbable that it would be broadened to the width or to the unsymmetrical shape observed.) It seems possible that the nature of the transition in RPA might be affected by the inclusion of the hyperfine interaction, which is not negligible for $\text{Tm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. The MFA calculation gives a hyperfine field that is only approximately one-half of that observed (at $T \lesssim 0.1 \text{ K}$). Furthermore, the Mössbauer data show that the hyperfine field increases by only 10% between 275 and 75 mK.⁵ It follows that the saturation value of $\langle J \rangle$ is higher and is approached more rapidly with decreasing temperature than predicted by MFA.

In summary, the heat capacity of $\text{Tm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ shows a second-order transition to an ordered state superimposed on the low-temperature side of the anomaly associated with the singlet ground and first excited states. The data are in qualitative agreement with calculations for the case in which the exchange interaction exceeds the critical value for magnetic ordering. As might be expected, the general shape of the heat-capacity peaks is in better agreement with RPA calculations (for values of the parameters that give a second-order transition) than with MFA calculations. However, RPA predicts a first-order transition for values of the parameter that give the observed transition temperature.

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Resistivity and Magnetoresistance of Dilute Solutions of Cr in Cu-Ni Alloys

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The electrical resistivity from 1.3 to 100 K and the longitudinal magnetoresistance from 0 to 85 kOe at 4.2 K were measured on Cu-Ni (Cr) alloys with Ni concentrations of 0, 6, 13, and 23 at. % and Cr concentrations of 0, 125, 300, 600, and 1200 at. ppm. All Cr-bearing samples were observed to exhibit resistivity minima. The difference in resistivity between each Cu-Ni (Cr) alloy and its Cr-free equivalent did not depend linearly on $\log_{10} T$; the difference in magnetoresistance between these two alloys was found to be negative. The Cr impurity contribution to the resistivity and magnetoresistance showed a marked dependence on the Ni concentration and was proportional to the Cr concentration only in the alloys containing 23 at. % Ni. These results are discussed in terms of spin-flip-scattering processes, characteristic of the Kondo effect, subject to Cr-Cr interactions and the local Ni environment around a Cr cell.

I. INTRODUCTION

The first major breakthrough in the understanding of the resistance minimum exhibited by dilute magnetic alloys was Kondo's¹ paper. He assumed that localized magnetic moments resided on the impurity sites and would interact with the conduction electron via the *s-d* Hamiltonian. The success and the shortcomings of this second-Born-approximation calculation, along with the works of Daniel and Friedel² and Anderson³ on the description of localized magnetic states in metals, have stimulated much research in recent years. Excellent review articles covering the progress made up to the late 1960's have been given by Daybell and Steyert,⁴ Kondo,⁵ and Heeger.⁶ A more recent theoretical review has been provided by Fischer.⁷

The formation and magnitude of the local moment depends on the delicate interplay of three quantities: (i) the position of the Fermi level relative to the energy of the *d*-state resonance; (ii) the density of states of the host metal at the energy of the *d*-state resonance; and (iii) the strength of the exchange and correlation effects (these are responsible for Hund's rules for atoms)

which cause the spin splitting of the virtual bound state. It is well established that Fe, Mn, and Cr all exhibit local-moment behavior in Cu,⁴ as well as resistivity minima.⁸⁻¹⁰ In addition, all three systems show a negative magnetoresistance.^{8,10,11} Thus, this set of alloys provides an excellent opportunity to study how the altering of the Cu host in some continuous fashion affects the resistivity and magnetoresistance of these alloys.

The first work in this direction was done by Gärtner *et al.*^{12,13} on Cu-Ni(Fe) alloys with Ni concentrations of 6, 12, and 23 at. % and Fe concentrations up to 1100 at. ppm. For fixed Ni concentrations, they found that the impurity contribution to the resistivity was proportional to the Fe concentration. However, the slopes of the $\log_{10} T$ plots of the resistivity decreased with increasing Ni concentration. Concurrent work by Bennett *et al.*¹⁴ on the Mössbauer effect in Cu-Ni(Fe) alloys showed evidence for the existence of magnetic Fe-Ni clusters.

Harvey *et al.*¹⁵ continued the investigation by measuring the resistivity and magnetoresistance of Cu-Ni (Mn) alloys with concentrations comparable to those in Gärtner's study. They found that the impurity contributions to the resistivity