LBL-858
Preprint

HEAT CAPACITY OF $Tm_2(SO_4)_3 \cdot 8H_2O$ BETWEEN 0.08 AND 20 K

T. E. Katila, N. W. Phillips, M. C. Veuro,
and B. B. Triplett

May 1972

AEC Contract No. W-7405-eng-48

For Reference

Not to be taken from this room

LBL-858

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

0 0 0 0 5 8 0 1 0 1 9

Heat Capacity of $Tm_2(SO_4)_3 \cdot 8H_2O$ Between 0.08 and 20 K *

T. E. Katila, N. E. Phillips,† and M. C. Veuro,
Department of Technical Physics,
Technical University of Helsinki,
Otaniemi (Helsinki), Finland

and

B. B. Triplett,‡
Lawrence Berkeley Laboratory and
Department of Chemistry,
University of California
Berkeley, California 94720, U.S.A.

Abstract

The heat capacity of $Tm_2(SO_4)_3 \cdot 8H_2O$ 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 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 exchange interaction exceeds a critical value,[2] and the associated heat capacity has been calculated[3] 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 $Tm_2(SO_4)_3 \cdot 8H_2O$ 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 measurements[5] 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 $Tm_2(SO_4)_3 \cdot 8H_2O$ 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 $Tm_2(SO_4)_3 \cdot 8H_2O$ sample was purified by two recrystalizations, 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 measured 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, 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 $Tm_2(SO_4)_3 \cdot 8H_2O$ 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 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

$$\mathcal{H} = \sum_i V_{ci} - \sum_{i \neq j} \mathcal{J}_{ij} \underline{J}_i \cdot \underline{J}_j + \mathcal{A} \sum_i \underline{I}_i \cdot \underline{J}_i \qquad (1)$$

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 $\underline{J}_i$ and $\underline{J}_j$, $\mathcal{A}$ is the magnetic hyperfine interaction constant, and $\underline{I}_i$ is a nuclear spin. Since I is $\frac{1}{2}$ for ^{169}Tm, the only naturally occuring isotope, no quadrupole hyperfine interaction is present. Wang and Cooper[3] 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 $-\mathcal{J}(0) < J > \sum_i J_{zi}$ where $\mathcal{J}(0) \equiv \sum_i \mathcal{J}_{ij}$, and a z axis has been chosen in such a way[8] that only one component, $\alpha \equiv \langle 0 | J_z | 1 \rangle$, of $\langle 0 | \underline{J} | 1 \rangle$ is nonzero. The eigenvalues of the Hamiltonian are

$$E_{A,m} = -E_{B,m} = -\left[\frac{\Delta^2}{4} + \left(\frac{A < J > \Delta}{2\alpha} - \mathcal{A}\, m\alpha\right)^2\right]^{1/2} \qquad (2)$$

where $A = 4\mathcal{J}(0)\,\alpha^2/\Delta$ and $m(=\pm\frac{1}{2})$ is the z component of $\underline{I}$. $\langle J \rangle$ is determined by the self-consistent 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 $\mathcal{A} = 0$, 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

$$\tanh \frac{\Delta}{2T_c} = \frac{1}{A} \quad . \tag{3}$$

Curves representing the temperature dependence of $\langle J \rangle/\alpha$ for $\mathcal{A} = 0$ and for $\mathcal{A}$ = 18 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 measurements[5] in the paramagnetic region and the pseudo-quadrupolar part of Eq.(2); Δ = 0.88 K was taken from EPR data;[4] 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 $\mathcal{A}$ = 18 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. 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 calculation[3] for $A = 1.0499$. 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 $Tm_2(SO_4)_3 \cdot 8H_2O$. The MFA calculation gives a hyperfine field that is only approximately one half of that observed (at $T \lesssim 0.1$ 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 $Tm_2(SO_4)_3 \cdot 8H_2O$ 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.

We wish to thank Dr. S. Stenholm, Dr. R. A. Fisher, and Mr. E. Seidel for helpful discussions and suggestions, Mrs. U. Zahn for the preparation of the sample, and Dr. M. Linkoaho and Mr. E. Rantavuori for X-ray analysis of the sample. One of us (N.E.P.) is also grateful to the NSF for the award of a fellowship that led to the collaboration of the Otaniemi and Berkeley groups, and to the Otaniemi group for its hospitality.

References

* Work supported in part by the U.S. Atomic Energy Commission.

† NSF Senior Postdoctoral Fellow, on leave from University of California, Berkeley, 1970-71

‡ Present address: Department of Physics, Stanford University, Stanford, California 94305.

1. K. Andres and E. Bucher, Phys. Rev. Letters 21, 1221 (1968); 22, 600 (1969); 24, 1181 (1970), and references cited therein.
2. G. T. Trammell, J. Appl. Phys. 31, 3625 (1960); Phys. Rev. 131, 932 (1963).
3. Y.-L. Wang and B. R. Cooper, Phys. Rev. 185, 696 (1969).
4. J. B. Gruber, E. A. Karlow, D. N. Olsen, and U. Ranon, Phys. Rev. B2, 49 (1970).
5. T. E. Katila, E. R. Seidel, G. Wortmann, and R. L. Mössbauer, Solid State Commun. 8, 1025 (1970).
6. Other Tm salts have been investigated by this technique to 0.05 K, but no other examples of magnetic ordering have been found. T. E. Katila, V. K. Typpi, and E. R. Seidel, in Proceedings of the 12th International Conference on Low Temperature Physics, Kyoto, 1970.
7. B. B. Triplett, Ph.D. thesis, University of California, Berkeley, 1970.
8. J. S. Griffith, Phys. Rev. 132, 316 (1963).

Figure Captions

Fig. 1 The heat capacity of $Tm_2(SO_4)_3 \cdot 8H_2O$ 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).

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

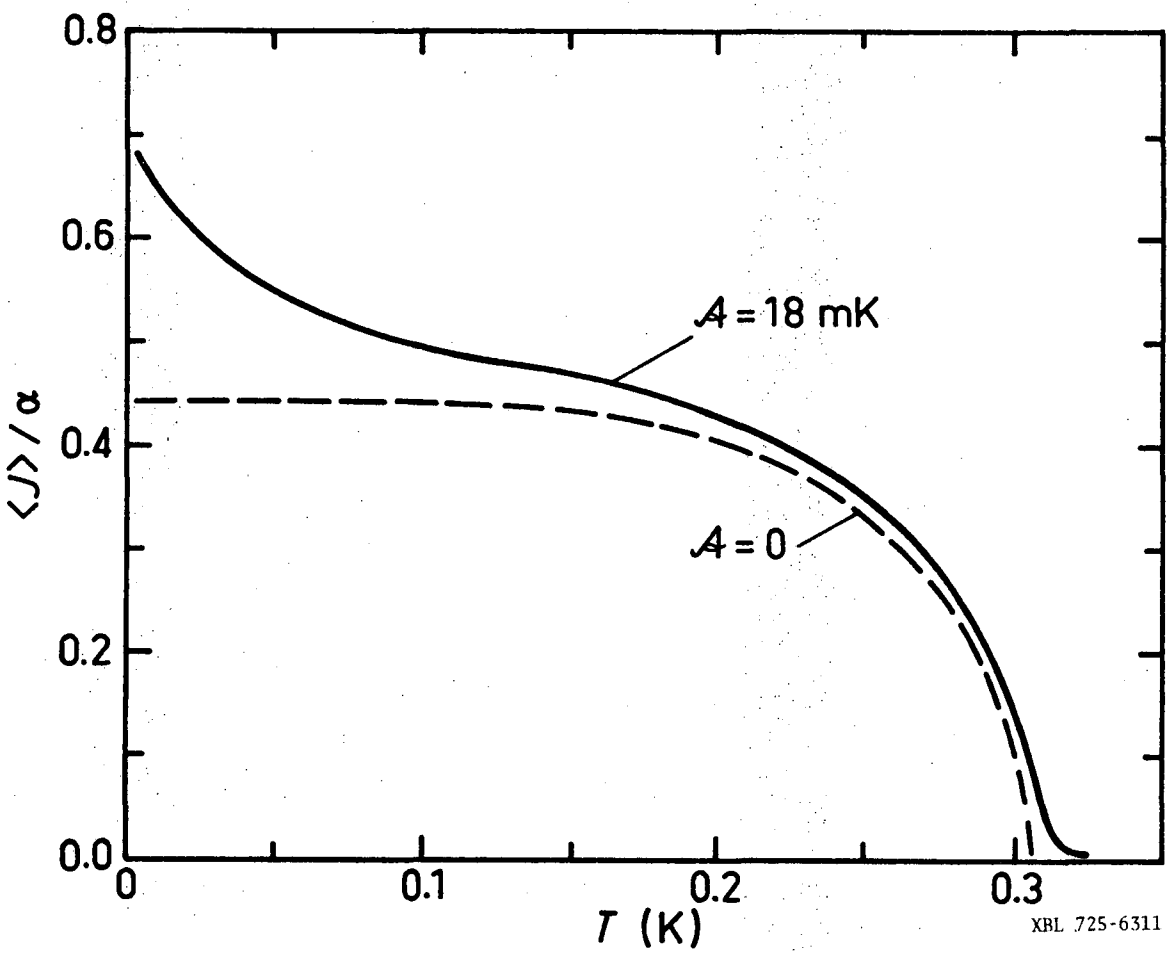

Fig. 1.

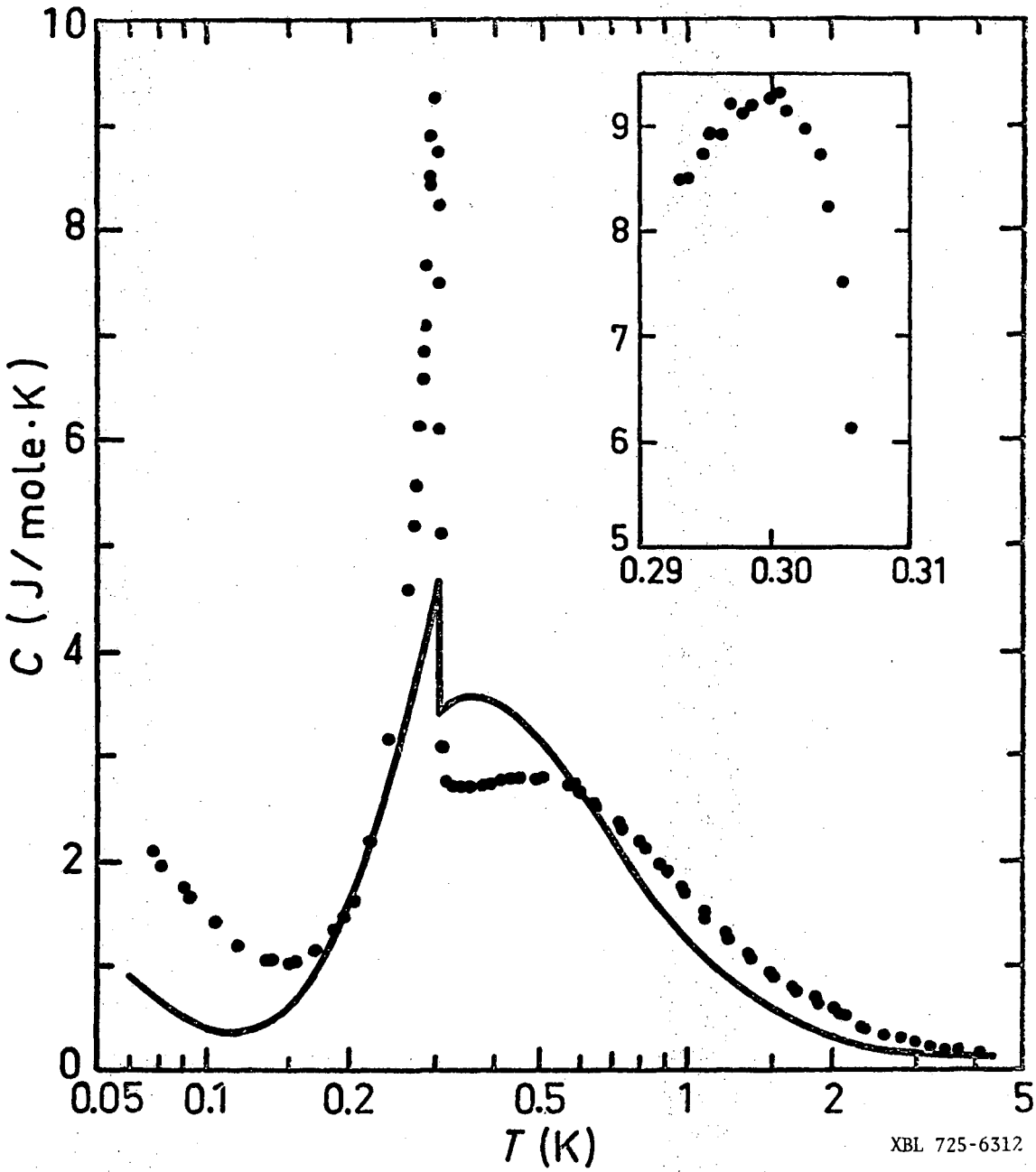
10
8
6
4
2
0
C (J/mole·K)
0.05
0.1
0.2
0.5
1
2
5
T (K)
9
8
7
6
5
0.29
0.30
0.31
XBL 725-6312

Fig. 2.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720