PHYSICAL REVIEW VOLUME 162, NUMBER 2 10 OCTOBER 1967

Specific Heat of $Cu(NH_3)_4(NO_3)_2$†

R. N. Rogers*

Sandia Laboratory, Albuquerque, New Mexico and *Wesleyan University, Middletown, Connecticut*

AND

C. W. Dempesy

Amherst College, Amherst, Massachusetts

(Received 17 May 1967)

The specific heat of $Cu(NH_3)_4(NO_3)_2$ has been studied over the temperature range 1.2–16°K. The results show a broad maximum similar to that reported in other substances that magnetically order in linear chains. By comparing with the calculations of Bonner and Fisher, it is determined that the substance forms antiferromagnetic linear chains with a nearest-neighbor Heisenberg interaction constant of $J/k=(3.70\pm0.04)$ °K.

I. INTRODUCTION

THE theoretical understanding of magnetic interactions in insulators has advanced rapidly during the past few years. Considerable insight has been derived through the study of specially constructed models having particularly tractable calculational properties. One such model often discussed is that of the one-dimensional spin lattice—the infinite linear chain. In 1964 Bonner and Fisher,[1] and independently, Griffiths,[2] were able to make exact calculations of the thermodynamic properties of short closed magnetic linear chains and to approximate the infinite-chain case by extrapolation. Conclusive evidence for the existence of physical systems approximating the linear-chain model was given by Griffiths who showed that the experimental specific-heat and magnetic-susceptibility data in the literature for $Cu(NH_3)_4SO_4\cdot H_2O$ (copper tetrammine sulfate monohydrate, herein denoted as CTS) closely fit the linear-chain results.[3] The reported x-ray analysis for CTS indeed shows a likely linear structure consisting of water molecules shared by tetramminecopper (II) complexes to form a Cu-O-CU-O chain.[4]

Unpublished electron-paramagnetic-resonance studies of exchange narrowing by one of the present authors (RNR) indicated that a similar tetrammine compound $Cu(NH_3)_4(NO_3)_2$ (copper tetrammine nitrate, herein CTN) possesses magnetic properties closely resembling those of CTS, and suggested the possibility of another compound characterized by magnetic linear chains. In this paper, the results of specific-heat measurements made upon CTN are reported which do indeed confirm the presence of magnetic linear chains.

II. EXPERIMENTAL

Crystals of CTN may be conveniently obtained from an ammoniated aqueous solution of cupric nitrate by the addition of alcohol with the rate of crystal growth being determined by the rate at which the alcohol is added. For these experiments, a fine slurry was prepared by the rapid addition of a large quantity of alcohol. The solution was immediately filtered, and the CTN crystalline precipitate was quickly washed and dried with successive rinses of methanol and ether. Examination under a microscope revealed the resultant powder to be made up of well-formed pyramidal crystals with no indications of mother liquor inclusions; the absence of water in the crystals was confirmed by uv absorption analysis.

For the specific-heat measurements, the CTN powder was mixed with approximately an equal weight of "Castolite X,"[5] a cold setting plastic used here as a binder, and a cylindrical sample was formed. A small copper rod was also cast in the sample to aid thermometry. At the time this sample was prepared, a second cylinder of pure Castolite X was also prepared to be used in measuring the Castolite X contribution to the specific heat of the CTN sample. The specific-heat measurements were made following standard procedures, and utilized an exchange-gas type of adiabatic calorimeter. An initial run was made. Later analysis revealed that the thermometry above ~4.0°K was unacceptable, and further, that the Castolite X contribution increased more rapidly with temperature than had been anticipated. Accordingly, the same samples were measured again about a year later. This later run concentrated on the higher-temperature range and used calibrated Ge resistance thermometers for temperature measurement in place of the carbon resistors used originally.

To protect the sample from decomposition (tetrammine compounds tend to revert to hydrated forms

---

† This work was supported by the U.S. Atomic Energy Commission and the National Science Foundation.

* Present address: Department of Physics and Astrophysics, University of Colorado, Boulder, Colorado.

[1] J. C. Bonner and M. E. Fisher, Phys. Rev. **135**, A640 (1964).

[2] R. B. Griffiths, thesis, Stanford University, 1962 (unpublished).

[3] R. B. Griffiths, Phys. Rev. **135**, A659 (1964).

[4] F. Mazzi, Acta Cryst. **8**, 137 (1955).

[5] Castolite X Liquid Setting Plastic, manufactured by The Castolite Company, Woodstock, Illinois.

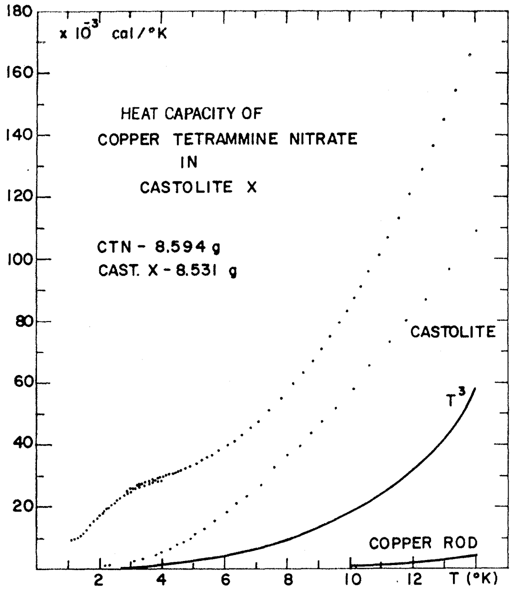

FIG. 1. Heat capacity of $Cu(NH_3)_4(NO_3)_2$ in Castolite X. The figure indicates the relative magnitude of the contributions from the Castolite X binder, the copper rod, and the T^3 term obtained from fitting. Not all the experimental specific-heat points are shown.

through the replacement of ammonia ligands) it was stored in a sealed dry container and refrigerated at −20°C. The pure Castolite X sample was also stored in the same manner so that hopefully any aging effects in the Castolite X portion of the CTN sample would be compensated for by corresponding changes in the pure Castolite X sample.

III. RESULTS AND DISCUSSION

The total measured heat capacity of the (CTN+Castolite) sample is shown in Fig. 1, as is the calculated contribution of the Castolite X and the copper rod. In order to successfully fit the net CTN specific heat to the Heisenberg antiferromagnetic linear-chain results of Bonner and Fisher it was found necessary to subtract a T^3 lattice term. The fitting was performed both graphically and with the aid of a computer program utilizing a least-squares fitting routine developed by Powell.[6] The measured net CTN specific heat is shown in Fig. 2 and the CTN less the T^3 term is compared with the Bonner-Fisher curve based on the best-fitting value of J in Fig. 3. It is seen that the agreement between experiment and theory is quite good. If the specific heat of the CTN is expressed as

$$C = C_{\mathrm{B-F}}(kT/J) + aT^3, \qquad (1)$$

where J is defined by the Heisenberg Hamiltonian

$$\mathcal{H} = -2J\sum_{i=1}^{N} S_i S_{i+1}, \qquad (2)$$

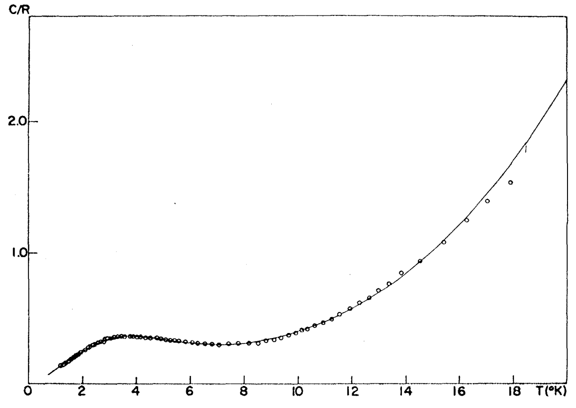

FIG. 2. Specific heat of $Cu(NH_3)_4(NO_3)_2$. The contributions to the measured specific heat of the Castolite X and the copper rod have been subtracted. The line is the curve calculated from the sum of the Bonner-Fisher theoretical curve plus the T^3 lattice contribution.

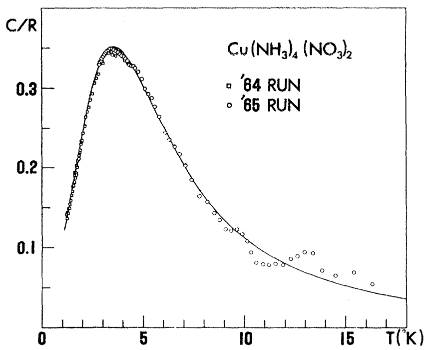

FIG. 3. Net magnetic specific heat of $Cu(NH_3)_4(NO_3)_2$. The T^3 term obtained from fitting has been subtracted from the results shown in Fig. 2. The solid line is that calculated using the results of Bonner and Fisher with $|J|/kT = 3.70$°K.

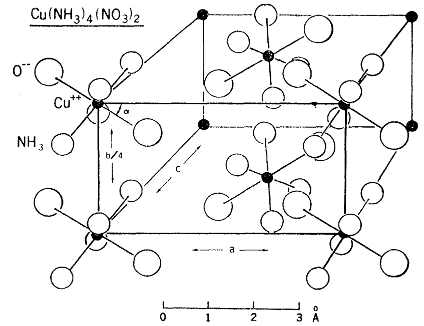

FIG. 4. Unit cell of $Cu(NH_3)_4(NO_3)_2$ (after Morosin). One-quarter of the orthorhombic cell is shown. The lattice constants are $a = 10.840(2)$, $b = 23.693(3)$, and $c = 6.902(2)$. The tetragonal symmetry axes of the tetramminecopper (II) complex lie nearly in the ab plane and make an angle $\alpha = 32°22'$ with the a axis. The oxygen atoms shown are associated with the nitrate groups (not shown) which also lie approximately in the ab plane.

---

[6] M. J. D. Powell, Comp. J. **7**, 303 (1965).

the results of the fit yield

$$J/k = (3.70 \pm 0.04)°K \qquad (3)$$

and

$$a = (2.85 \pm 0.10) \times 10^{-4} \text{ per deg}^3, \qquad (4)$$

where the errors quoted represent estimated confidence limits on the data and fit.

These results apply to the temperature range 1-16°K as indicated in Fig. 3. Above this range, the net magnetic CTN contribution to the total measured specific heat becomes too small to allow its separate determination. Thus in the region of the magnetic peak, the net magnetic contribution is 80% of the measured specific heat, but by 16°K the contribution has dropped to 2% and is diminishing rapidly.

As can be noted in the region just below the peak of the magnetic contribution, there appears to be a slight discrepancy between the data of the two runs, which from the fairly good agreement of the Castolite data for the two runs, would appear to be either instrumental or possibly an aging effect of the CTN. The discrepancy is small enough, however, that its effect is included in the error range quoted for the value of J.

By comparison with the results in CTS, our results are seen to be quite reasonable. The T^3 lattice-coefficient value agrees exactly (to within experimental error) with that quoted by Eisenstein for the CTS data of Fritz and Pinch.[7] The value of J found is also comparable to the CTS result $J/k = 3.15°K$,[3] and, like CTS, is somewhat larger than that found in hydrated copper salts of similar lattice dimensions, e.g., $J/k = 1.3°K$ for the linear chain-connected sites of $CuSO_4 \cdot 5H_2O$.[8] The fact that the experimental results agree with the linear-chain theory down to the lowest temperatures measured is an indication that any interchain interaction is extremely small. It is to be expected that, as in the case of CTS, a cooperative transition spike in the specific heat will occur at some lower temperature T_N when the interchain interactions (denoted here by J') produce relative ordering of the antiferromagnetic chains. In reference to the CTS case, Oguchi has examined the relation of $|J'|/|J|$ for values of $kT_N/|J|$ in such systems.[9] From his results and the measurements here it is found that for CTN, $|J'|/|J| < 0.03$.

From the consistent similarity between the properties of CTN and CTS, it might be expected that the structures would be similar, and that CTN would possess structural linear chains. Recent preliminary results of an x-ray structural analysis of CTN by Morosin, however, indicate that this is not the case.[10] In Fig. 4, the positions and orientation of the copper complexes are shown, based on Morosin's results. It is seen that the copper positions approximate a B-centered lattice. As is commonly found, the Cu(II) is coordinated by a tetragonally distorted octahedron. The sites along the lattice edge are related to the centered sites by a mirror reflection in the ac plane. Of most interest here, however, is the fact that there is no direct structural linkage connecting complexes, as there was in the case of CTS. Furthermore, the lattice dimensions do not isolate any particular direction as most likely for the chain direction, i.e., the distance between nearest neighbors is only 3% less than the next-nearest-neighbor distance. It would seem that on the structural basis, there is no clearly preferred possible superexchange linkage. Possible paths then might be via the overlap of the ammine ligands along either the a or c directions thus connecting like sites, or via a path connecting the corner sites to the centered sites through the associated nitrate group of one site and a hydrogen bond bridge to an ammine of the other site.

IV. CONCLUSION

The material studied, $Cu(NH_3)_4(NO_3)_2$, possesses magnetic properties consistent with linear antiferromagnetic Heisenberg chains having an interaction constant of 3.70°K. The agreement with the calculations of Bonner and Fisher would seem to validate their approximations for the infinite-linear-chain case.

ACKNOWLEDGMENTS

We wish to thank Professor R. B. Griffiths for supplying us with details concerning his results and those of Bonner and Fisher, and Professor J. Gordon, Professor R. Romer, and L. Amstat for their assistance in the collection of data. We are grateful to Dr. Bruno Morosin for communication of his preliminary experimental results and for helpful discussions.

---

[7] J. C. Eisenstein, J. Chem. Phys. **28**, 323 (1958); J. J. Fritz and H. L. Pinch, J. Am. Chem. Soc. **79**, 3644 (1957).

[8] S. Wittekoek, N. J. Poulis, and A. R. Miedema, Physica **30**, 1051 (1964).

[9] T. Oguchi, Phys. Rev. **133**, A1098 (1964).

[10] B. Morosin (private communication).