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Specific Heat of Three Magnetic Linear-Chain Antiferromagnets*

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The specific heat of $Cu[NH_2(CH_2)_3NH_2]_2SO_4\cdot H_2O$ ("$CPDS\cdot H_2O$") and of a mixed sample of $Cu(NH_3)_4SeO_4$ ("CTSel") and $Cu(NH_3)_4SeO_4\cdot H_2O$ ("$CTSel\cdot H_2O$") have been measured from 2 to 20 K, and excellent agreement has been obtained with the Bonner-Fisher theory for infinite magnetic linear chains of spin $\frac{1}{2}$, with an isotropic Heisenberg interaction between nearest neighbors. From the fit between experiment and theory, the following exchange constants J are obtained: $CPDS\cdot H_2O$, $(1.09_{-0.08}^{+0.04})$ K; CTSel, $(0.24_5 \pm 0.03)$ K; and $CTSel\cdot H_2O$, (2.36 ± 0.03) K. A preliminary description of the crystal structures of these compounds is also given. $CTSel\cdot H_2O$ is isomorphous with $Cu(NH_3)_4SO_4\cdot H_2O$; in addition, a close structural relationship is found between these salts and $CPDS\cdot H_2O$. Thus, the variation of J with interionic separation r may be estimated for these simple linear systems. This estimate gives $N=10.9$ where $J=ar^{-n}$.

I. INTRODUCTION

FINITE and infinite one-dimensional chains and rings of ferro- or antiferromagnetically coupled $S=\frac{1}{2}$ spins have been the subject of several theoretical and experimental studies during the past few years. Recent theoretical studies[1–3] have concentrated on the problem of calculating the energy levels of a system of a finite number of spins, the partition function, and hence such thermodynamic properties as the specific heat and magnetic susceptibility. In all of these calculations, the magnetic part of the Hamiltonian has been represented by the usual term appropriate to many magnetic insulators: a term representing bilinear interactions between pairs of localized spins $\mathbf{S}_i$. The most general and exhaustive calculations—those of Bonner and Fisher—used the anisotropic "intermediate" Hamiltonian (for a chain or ring of N spins)

$$\mathcal{H}=-2J\sum_{i=1}^{N}[\gamma\mathbf{S}_i\cdot\mathbf{S}_{i+1}+(1-\nu)S_i{}^zS^z{}_{i+1}] -g\beta\sum_{i=1}^{N}\mathbf{H}_i\cdot\mathbf{S}_i, \quad (1)$$

which reduces to the completely anisotropic Ising Hamiltonian for $\gamma=0$, and to the isotropic "pure Heisenberg" Hamiltonian for $\gamma=1$. Since exact closed form expressions have not been found for the finite-temperature behavior of infinite linear chains with Heisenberg or "intermediate γ" Hamiltonians, it has been necessary to demonstrate that the limiting behavior for infinite $(N\rightarrow\infty)$ linear chains can be obtained by extrapolation of the results for a finite number of spins. Bonner and Fisher have used their exact numerical results for $N=2$–11 to show that good extrapolations can be made for $kT/|J|\geq 0.5$, and have accurately evaluated the shape of broad maxima in the specific heat and magnetic susceptibility (which occur near $T=|J|/k$) in terms of the two parameters J and γ. In their treatment, the actual exchange (or superexchange) interaction is described entirely phenomenologically through the nearest-neighbor exchange constant J and the anisotropy parameter γ; the calculations deal only with the statistical mechanics of a spin system with the coupling specified by J and γ.

The possibility of observing experimental behavior, which would substantiate the one-dimensional calculations, depends upon finding natural systems possessing a preferred direction for magnetic interactions. Since superexchange effects are usually dominant in insulators, a linear magnetic chain is likely to be found associated with structures exhibiting electronic bonding primarily in one direction. Griffiths,[4] using the data of Haseda and Miedema,[5] was the first to demonstrate conclusively the existence of a crystal, $Cu(NH_3)_4SO_4\cdot H_2O$ (copper tetrammine sulfate monohydrate, known hereafter as $CTS\cdot H_2O$), whose magnetic susceptibility and specific heat matched the broad maxima predicted for an infinite isotropically coupled $(\gamma=1)$ antiferromagnetic linear chain. In reporting their specific-heat results, Haseda and Miedema had earlier noted the existence of structural infinite linear chains of tetrammine copper complexes linked by water molecules, to form a Cu-O-Cu-O-$\cdots$-Cu chain, as indicated by x-ray studies.[6] Recently, another crystal containing the copper tetrammine complex [$Cu(NH_3)_4(NO_3)_2$, copper tetrammine nitrate, hereafter CTN] was shown by the

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† Based in part on the thesis submitted by D. H. L. in fulfillment of the requirements of the Ph.D. degree at the University of Colorado. Present address: Department of Physics, University of Sussex, Falmer, Brighton, Sussex, England.

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

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

[3] W. Duffy and K. P. Barr, Phys. Rev. **165**, 647 (1968).

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

[5] T. Haseda and A. R. Miedema, Physica **27**, 1102 (1961).

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

same sort of analysis (fit to the Bonner-Fisher theory) to also contain linear chains of antiferromagnetically coupled spins.[7] In this case, however, preliminary x-ray analysis did not show the presence of a molecular bond-linked linear chain.

The copper tetrammine compounds mentioned above and to be reported here show behavior which is in extremely good agreement with the theoretical predictions for infinite linear chains. The properties of a number of other compounds have also been interpreted as exhibiting more or less linear chain characteristics. Among these are $CuSO_4 \cdot 5H_2O$ and $CuSeO_4 \cdot 5H_2O$ whose magnetic properties have been interpreted in the light of a model whereby there are two separate spin systems, one of which is paramagnetic down to lowest temperatures and the other of which is antiferromagnet linear-chain coupled ($J \sim 1.5$ K and ~ 0.8 K, respectively).[8] The work on several Cu-containing coordination polymers suggests the existence of finite chains having 5–20 members,[9] and results in $KCuF_3$ likewise indicate finite ($N \sim 15$) chains.[10] Other measurements have been interpreted as indicating linear chains in the presence of anisotropic *intra*chain interactions [$K_3Fe(CN)_6$],[11] Ising-like exchange interactions ($CoCl_2 \cdot 2H_2O$),[12] a spin-$\frac{5}{2}$ system ($CsMnCl_3 \cdot 2H_2O$),[13] or competitive *inter*chain interactions ($CuCl_2$,[14] $CrCl_2$,[14] and $CuBr_2$[15,16]).

Recent x-ray structural studies by one of the authors[17] have indicated that several additional copper tetrammine compounds also contain structural linear chains of Cu^{++} ions. Since the primary copper tetrammine complex ion remains relatively unchanged in these compounds, we hoped that further information concerning the systematics of linear-chain magnetic interactions could be obtained by specific-heat studies of these compounds. Accordingly, samples were prepared and x-ray studies made. In this paper, we report the results of specific-heat measurements on $Cu[NH_2(CH_2)_3NH_2]_2SO_4 \cdot H_2O$ [bis(1,3-propanediamine) copper sulfate monohydrate, hereafter $CPDS \cdot H_2O$] and on a mixed sample of $Cu(NH_3)_4SeO_4$ and $Cu(NH_3)_4SeO_4 \cdot H_2O$ (copper tetrammine selenate and its monohydrate, hereafter CTSel and $CTSel \cdot H_2O$).

The measurements are interpreted with the Bonner-Fisher calculations to indicate that linear chains are indeed present. Using the results for $CTSel \cdot H_2O$ and $CPDS \cdot H_2O$ with the earlier data on $CTS \cdot H_2O$ compounds, we are able to suggest a power-law dependence for the variation of the exchange interaction with distance between copper ions, and also to support the supposition that the magnetic linear chains in these materials indeed follow the linear path indicated by the crystallographic structure.

II. EXPERIMENTAL

A. Sample Preparation and Structure Determination

Crystals of CTSel were grown at room temperature by adding methanol to an ammoniated aqueous solution of cupric selenate. The crystalline growth rate is determined by the rate at which methanol is added: For these experiments, a powdered sample was sufficient (as is described below), and so a fine slurry was precipitated from solution by the rapid addition of a large amount of methanol. After filtering the solution, the CTSel crystals were rinsed with methanol and dried with ether. The same procedure was repeated several times, using the same batch of crystals, until the precipitate attained a uniform deep purple color. Examination of the crystals with a low-power microscope showed no obvious presence of the mother liquor, but the crystals did react (by losing mass) when exposed to air. It is known that tetrammine compounds tend to revert to hydrated forms by the replacement of ammonia ligands with water; hence, care was taken in the storage and handling of the samples to keep them in a closed, dry atmosphere.

An x-ray analysis of (powdered) crystals taken from the same batch as our CTSel sample revealed that the crystals we had grown consisted of two distinct phases. As estimated from the intensities of the powder lines, approximately 80% of the sample was CTSel, while approximately 20% was identified as $CTSel \cdot H_2O$ on the basis of the similarity of the powder patterns of this phase to those obtained from $CTS \cdot H_2O$. The detailed crystal structure of CTSel and of $CTS \cdot H_2O$ are shown in Figs. 1 and 2, respectively.[18]

$CPDS \cdot H_2O$ crystals were prepared from copper sulfate and a stoichiometric quantity of 1,3-propanediamine, following the procedure described above. All starting materials for the preparation of both CTSel and $CPDS \cdot H_2O$ were of analytical reagent grade. Published x-ray data for $CPDS \cdot H_2O$ show that the unit cell is orthorhombic with a similar space group to that

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[10] S. Kadota, I. Yamada, S. Yoneyama, and K. Hirakawa, J. Phys. Soc. Japan **23**, 751 (1967).

[11] W. Duffy, Jr., J. Lubbers, H. van Kempen, T. Haseda, and A. Miedema, in *Proceedings of the Eighth International Conference on Low-Temperature Physics, London*, 1962, edited by R. O. Davies (Butterworths Scientific Publications, Ltd., London, 1963).

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[18] B. Morosin, Acta Cryst. **B25**, 19 (1969).

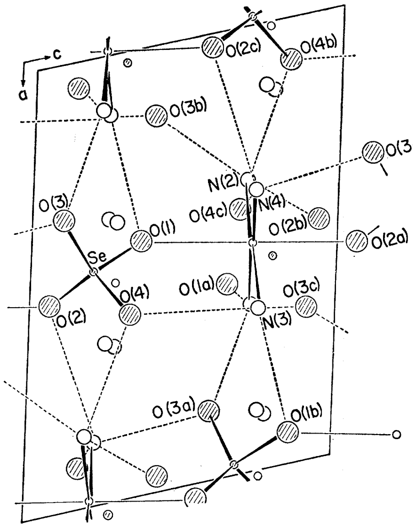

FIG. 1. Crystal structure of $Cu(NH_3)_4SeO_4$ viewed along the *b* axis. Solid lines indicating chemical bonding and dashed lines indicating hydrogen bonding are included only for atoms situated in the upper half of the unit cell. In this structure, the selenate ions are part of the chemical chain, running parallel to *c* which connects the copper ions.

of CTS·H_2O[19]; however, our preliminary x-ray structural analysis indicates that the structure is not isomorphous though the gross structures are very similar. By comparing Figs. 2 and 3, it can be seen that the adjacent chains (those located on the right side of the unit cell) and anion are translated $\frac{1}{4}$ along *a* in the CPDS ·H_2O when compared with the CTS·H_2O structure. The lattice constants listed in Table I indicate that the presence of the additional carbon atoms in the chelate groups results in a greater separation of these adjacent chains in the *b* direction compared with those in CTS ·H_2O (~7.9 Å versus 6.0 Å).

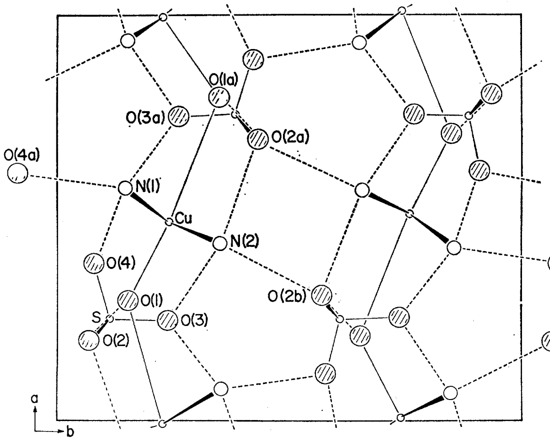

FIG. 2. Crystal structure of $Cu(NH_3)_4SO_4 \cdot H_2O$ viewed along the *c* axis. The chemically linked chains, which lie on symmetry planes (mirrors) at $\frac{1}{4}$ and $\frac{3}{4}$ along *c*, parallel to the *b* direction in this structure. Hydrogen bonding is indicated by dashed lines. The structure of CTSel·H_2O is isomorphous with this one.

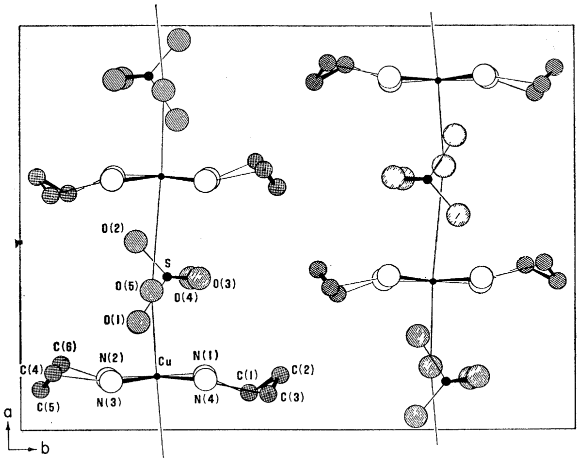

FIG. 3. Crystal structure of $Cu[NH_2(CH_2)_3NH_2]_2SO_4 \cdot H_2O$ viewed along the *c* axis. In this structure, the chains are not required to lie on mirror planes as in CTS·H_2O; the main difference between these structures is the translation of the adjacent chain ~$\frac{1}{4}$ along *a* as can be seen by comparing Figs. 2 and 3.

B. Physical Preparation of Samples

When making specific-heat measurements, one prefers to work with large single crystals or coarse polycrystals (rather than powders) because powders require longer times to reach thermal equilibrium after the application of a heat pulse. However, where the choice of a powder is dictated by the difficulty of preparing sufficiently large single crystals, it is customary to use an additional substance (or "thermal binder") to improve heat contact within the powder sample. Sealed containers filled with helium gas have been used, and so have cold-setting plastic resins[7]; our technique here was to use high-purity copper powder mixed with the sample as the binder. In practice, sample powders were mixed with an approximately equal volume of the fine copper powder.[20] The mixture was then loaded into a die

TABLE I. Lattice and exchange constants for copper tetrammine compounds.

Sample	*a* (Å)	*b* (Å)	*c* (Å)	*β* (Å)	*J*/*k* (K)
CTSel·H_2O	11.0	11.3	7.2		2.36
CPDS·H_2O	11.764	15.874	7.172		1.09
CTS·H_2O	10.651	11.986	7.069		3.15
CTSel[a]	10.313	10.759	7.405	104.43	0.24
CTN	10.840	23.6931	6.902		3.70

[a] Monoclinic; all others are orthorhombic.

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[19] R. Nasanen, E. Luukkonen, and I. Virtamo, Suomen Kemistilehti **B40**, 81 (1967).

[20] The copper powder used was Resistox 500RL (44-μ size), obtained from the Glidden Co., Metals Division, 1717 Summer St., Hammond, Ind. We wish to acknowledge helpful conversations with Dr. H. V. Culbert and Dr. J. G. Dash.

and piston arrangement[21] and compacted to a pressure of about 1000 kg/cm^2, using a standard hydraulic press. The final samples were cylinders approximately 3.8 cm long by 2.54 cm in diam. The CTSel sample was weighed and prepared in a dry nitrogen atmosphere, and the resultant sample was painted with a measured amount of GE 7031 varnish. These precautions were not observed for the CPDS$\cdot$H$_2$O, since the stronger chelating bonds of the propane-diammino ligand seem to prevent the type of decomposition observed in ordinary copper tetrammine compounds. The resultant pills prepared in the fashion described were uniform in appearance and strong enough to be machined and tapped. For these measurements, however, small OFHC copper anchors, drilled and tapped, were embedded at either end of the cylindrical pill for convenience in attaching to the sample holder.

The use of the pressed copper-powder technique employed here for the thermal binder seems preferable by far to the other techniques mentioned above. The copper has a higher thermal diffusivity (particularly at the low end of the temperature range) and contributes a well-behaved and very much smaller background specific heat, particularly at the higher temperatures.

Since the background heat capacity of the copper powder and the holder was less than 1% of that of the sample in the region of the magnetic peak, it was not necessary to measure the heat capacity of the holder; instead, its heat capacity was calculated. This calculation is believed to be quite reliable, particularly below 6 or 7 K, because of the good agreement between our data for Calorimetry Conference copper, obtained using this same holder, and the published data for this standard copper.[22]

III. APPARATUS

The calorimeter and cryostat are similar to those used by Finegold and Phillips,[23] by Senozan,[24] and by O'Neal and Phillips.[25] The major changes include the design of the mechanical heat switch and its operating mechanism, the method of suspending the sample and holder in the vacuum chamber, and the circuitry used to deliver heat pulses to the sample. Details of the apparatus are to be reported elsewhere,[26] although a few pertinent comments will be made below.

A. Sample Holder and Suspension

The samples were cylinders prepared as described above. The sample holder used in these experiments consisted of two thin flat copper disks which were screwed tightly against copper anchors embedded in the flat ends of the samples. Thermal contact between the sample and the holder was improved by a thin layer of Apiezon *T* grease of known mass and specific heat.[27] The germanium resistance thermometer was held snugly in a copper block soldered to the lower disk; again Apiezon *T* grease was used (between the thermometer and holder) to improve thermal contact. Typically, less than 20 mg of grease was used in all. The heater was noninductively wound on and varnished to a copper wire soldered to the top plate, using a nonsuperconducting (down to at least 0.1 K) solder.[28] Thermal and vibrational isolation of the sample was achieved by rigidly suspending the sample holder from two sets of three cotton threads. The other end of each thread was tied to a 5-cm-long brass screw (with a diameter hole drilled in its end) which was mounted in one of two brass rings attached (one above the sample, one below) to a cylindrical cage. The long brass screws, with locknuts, allow quick and convenient tightening of the sample suspension threads, and result in a suspension with a resonant frequency which is expected to be well above that of the low-frequency vibrations commonly present in a laboratory.[29]

B. Specific-Heat Measurements

The heat-pulse method of Nernst and Eucken[30] was used for these measurements. Heat was supplied to the sample holder as Joule heating by a noninductive Manganin wire heater wound on a copper rod attached to the upper sample-holding disk. Manganin is particularly useful for such applications, as well as for connections to the sample, because its small temperature coefficient of resistivity allows one to express the heater resistance analytically as

$$R(T)=a+bT+cT^2, \qquad (2)$$

with an absolute accuracy of better than 0.02% over the range 1–20 K. The heater current was supplied by a digitally programmed dc constant-current power supply and a high precision current shunt.[31]

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[21] The die and pistons were designed for pharmaceutical pill-making and were donated by Cherry-Burrell Corp., 603 Bridge St., Colton Plant, Elk Rapids, Mich. 49629.

[22] G. T. Furukawa, W. G. Saba, and M. L. Reilly, U. S. Government Printing Office, Washington, D. C., 1968, Publication No. NSRDS-NBS 18.

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[27] E. F. Westrum, Jr., C. Chou, D. W. Osborne, and H. E. Flotow, Cryogenics **7**, 43 (1967); J. G. Biddle Co., Plymouth Meeting, Pa.

[28] Easy-flo 45 (50% Ag, 18% Cd, 16.5% Zn, and 15.5% Cu) has been used down to 0.1 K by L. Finegold, Phys. Rev. Letters **13**, 233 (1964).

[29] I. Vigness, Phys. Today **18**, 42 (1965).

[30] A. Eucken, Z. Physik **10**, 586 (1909); W. Nernst, Preuss. Akad. Wiss. Berlin, Sitz. Ber. **12**, 262 (1910).

[31] Hewlett-Packard (Harrison Division) Berkeley Heights, N. J., Model 6181A (0–300 mA, 200-μsec rise time), controlled by Model 6931A digital programmer (0–100 kΩ). We are grateful to Dr. C. F. Jefferson of the National Bureau of Standards, Boulder, Colo., for the loan of this current supply.

As mentioned above, a germanium resistance thermometer[32] was used in these measurements. To avoid thermometer heating, the power dissipated in the germanium thermometer was kept to less than 2 nW. The reference temperature scales used for these measurements were the NBS 1965 provisional acoustic scale (T_{65}) above 2.3 K and the 1958 He^4 vapor-pressure scale (T_{58}) below 2.3 K.[33] The calibration of our thermometer is directly traceable to these standards through three transfers; our thermometer is thus a quaternary standard. As will be described in greater detail elsewhere,[26] the accuracy of our temperature scale as well as the basic consistency of the T_{65} and T_{58} temperature scales were further examined by the specific-heat measurement of a sample of the 1965 Calorimetry Conference Standard copper produced by Argonne National Laboratory and also a sample of extremely high electronic purity (residual resistivity ratio approximately 30 000) produced by the Cryogenics Division of the National Bureau of Standards in Boulder.[34] It was found that the copper results were in good agreement with previous results of other workers,[22] and that the resultant temperature scale was smooth to within 1 mK below 5 K, and to within a few mK elsewhere.

Temperature increments ΔT following the heat pulses were mostly of the order of $\Delta T \sim T/20$. The systematic error $\Delta C/C$ introduced in measurements of specific heat by taking finite temperature changes is approximately

$$\Delta C/C \sim [n(n-1)/24](\Delta T/T)^2$$

for $C \propto T^n$.[35] For the samples measured here, and even for n as high as 5, $\Delta C/C < 0.2\%$; in fact, no dependence of C upon ΔT was observable to within the precision of the measurements.

From a consideration of the total error, it is believed that the chief uncertainty in these measurements lies in the thermometer calibration and in the reference temperature scale itself.

IV. RESULTS AND DISCUSSION

A. $Cu(NH_3)_4SeO_4$ and $Cu(NH_3)_4SeO_4 \cdot H_2O$

The Bonner-Fisher calculation of the specific heat of a pure Heisenberg antiferromagnetic chain [$\gamma = 1$ in Eq. (1)] predicts a peak in the specific heat with a maximum height $C_{\max}/R \sim 0.35$ at a temperature $kT_{\max}/J \sim 0.962$. As the anisotropy of the exchange interaction is increased ($\gamma \rightarrow 0$), the peak becomes *narrower* and *higher*, the high-temperature tail of the peak becomes smaller, and the peak position shifts to a lower reduced temperature $kT_{\max}/J$. When our data for the net measured specific heat of CTSel were first plotted against temperature, we found a broad, low maximum centered just above 2 K, with a maximum height only about 19% of the 0.35 R maximum value for a pure Heisenberg chain (Fig. 4). As was described above, the sample used in these measurements consisted of two distinct phases; about 80% of the sample was CTSel, while the remainder was identified by x-ray measurements as CTSel$\cdot H_2O$. The amount of CTSel $\cdot H_2O$ present is thus just right to account for the height of the low-temperature peak that we observe, assuming a pure Heisenberg interaction ($\gamma = 1$) between linear chain-connected sites.

The net measured specific heat of the sample (1.4–20 K) was fitted to the equation

$$C/R = aC_{\mathrm{BF}}(kT/J) + b/T^2 + cT^3 + dT^5 + eT^7 \qquad (3)$$

using the computer program developed for the work of Ref. 7, where $C_{\mathrm{BF}}(kT/J)$ is the Bonner-Fisher specific-heat function for a pure Heisenberg ($\gamma = 1$) antiferromagnetic linear chain, and the terms in T^3, T^5, and T^7 represent the lattice contributions to the specific heat of the sample. The specific-heat data for this sample was originally fitted to Eq. (3) with the $1/T^2$ term omitted, and a relatively poor fit resulted. The $1/T^2$ term was then added on the physical basis that the high-temperature contribution for any unaccounted, weaker interaction would be expected to contribute a "tail" of this form to the specific heat. With the $1/T^2$ term added, an

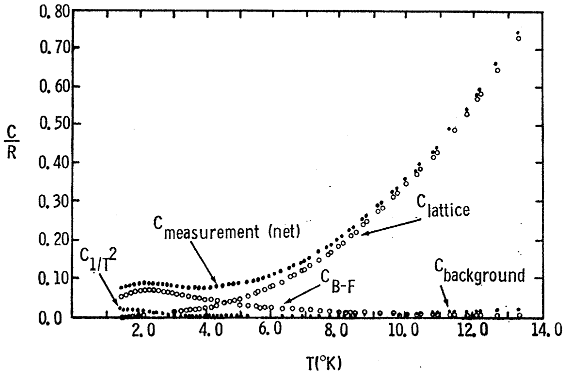

FIG. 4. Results of the least-squares fit to the net measured specific heat of the CTSel sample, 1–14 K. Results are shown for (1) $C_{\text{meas.(net)}}$, the measured net specific heat; (2) C_{lattice}, the lattice specific heat of the sample; (3) C_{BF}, the magnetic specific heat; (4) C_{1/T^2}, the contribution to the low-temperature specific heat proportional to $1/T^2$, which, for clarity, is not shown above 5 K; and (5) $C_{\text{background}}$, the calculated background heat capacity of the holder (plus copper powder), which is nearly negligible at most temperatures and, similarly, is not shown below 6 K.

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[32] Cryocal, Inc., Riviera Beach, Florida.

[33] H. Plumb and G. Cataland, Metrologia **2**, 127 (1966); Natl. Bur. Std. (U.S.) Monograph **10**.

[34] We are grateful to Argonne National Laboratory and to the Cryogenic Laboratories of the Institute for Basic Standards, National Bureau of Standards, Boulder, Colo., for these samples.

[35] F. E. Hoare, L. C. Jackson, and N. Kurti, *Experimental Cryophysics* (Butterworths Scientific Publications, Ltd., London, 1961). The result quoted on p. 272 is in error, apparently because of the neglect of third-order terms in T, in expanding T^{n+1}.

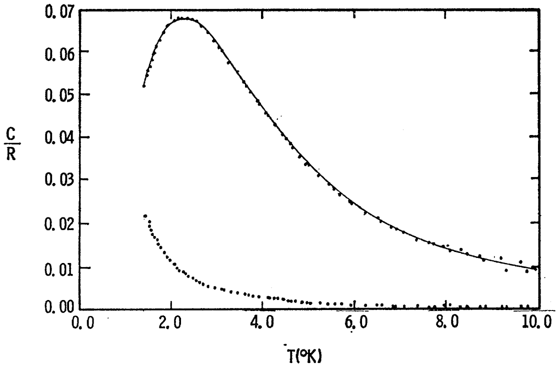

FIG. 5. Magnetic peak and $1/T^2$ contributions to the specific heat of the CTSel sample, 1–10 K. The full line is the best fit to the Bonner-Fisher function.

excellent fit resulted. While there are a number of possible sources for such a term, by far the most reasonable in view of the magnitudes of the various interactions in these materials is that this term is the high-temperature tail of the specific-heat anomaly arising from antiferromagnetic ordering in linear chains of the part of the sample (approximately 80%) which is CTSel. The results of this fit are shown individually in Fig. 4; Fig. 5 shows the magnetic specific heats consisting of the Bonner-Fisher peak and the $1/T^2$ contribution. At 10 K, the high-temperature tail of the Bonner-Fisher peak has dropped to only 2% of the net measured specific heat due to the rapid increase of the lattice contribution, so that above this temperature the magnetic part of the specific heat cannot be meaningfully measured.

The best fit to Eq. (3) gave the results

$$|J|/k = 2.36 \pm 0.03\ \text{K},$$

$$a = 0.194_3 \pm 0.001,$$

$$b = (4.38 \pm 0.1) \times 10^{-2}\ \text{K}^2,$$

$$c = (4.03_5{}^{+0.1}{}_{-0.2}) \times 10^{-4}\ \text{K}^{-3},$$

$$d = -6.06 \times 10^{-7}\ \text{K}^{-5},$$

and

$$e = 4.46 \times 10^{-10}\ \text{K}^{-7}.$$

(These results are quoted relative to the molecular weight 292.644 of CTSel·H_2O.) The errors quoted represent confidence limits based both on the data and on the degree to which a variation of one parameter in the fit affects the other parameters. Individual error limits are not quoted for the T^5 and T^7 term coefficients, since these terms are much smaller than the T^3 term; they simply represent the deviation of the lattice specific heat from the low-temperature T^3 behavior. In Fig. 5, the fit of the Bonner-Fisher function to the data is shown. It is observed that all data points lie within 1.5% of the fitted curve.

The main assumption in the analysis of our data has been that of an antiferromagnetic pure Heisenberg form of interaction between the linear chain-connected sites. This assumption is dictated by past experience with these materials, while the high quality of our fit gives it strong support. If we extend this assumption to say that the $1/T^2$ tail we observe is likewise due to an isotropic Heisenberg antiferromagnetic interaction between copper sites in CTSel, we can also determine the magnitude of J for this material. From the amplitude of the $1/T^2$ tail of the Bonner-Fisher function, we find $J/k = 0.24_5 \pm 0.03$ K for CTSel, assuming 80.6% CTSel, 19.4% CTSel·H_2O as determined by the fit of the peak height to the Bonner-Fisher function.

Since our data for CTSel·H_2O show no cooperative transition down to 1.4 K, we can put an upper limit on the magnitude of interchain interactions. Following the original experimental work on CTS·H_2O, Oguchi[36] calculated an approximate relationship for J'/J (the ratio of inter- to intrachain exchange constants) in terms of kT_N/J, where T_N is the temperature at which three-dimensional ordering would take place (i.e., the Néel temperature). Extrapolating his results, our present measurements indicate that, for CTSel·H_2O, $J'/J < 0.1$.

B. $Cu[NH_2(CH_2)_3NH_2]_2SO_4 \cdot H_2O$

The net measured specific heat of CPDS·H_2O contains an anomaly rising approximately as $1/T^2$ below 4 K, as is shown in Fig. 6. Because of the structural similarity of this material to CTS·H_2O, the specific heat was analyzed in terms of the Bonner-Fisher linear-chain results, assuming antiferromagnetic ordering. With this assumption, the value of the interchain exchange-interaction constant J was obtained graphically by plotting the measured data as CT^2 versus T^5 for $kT/|J| \geq 3$, corresponding to the region where the Bonner-Fisher function falls off as $1/T^2$. The $T^5 = 0$ intercept is then proportional to J. From this plot, $|J|/k$ was determined to be 1.09 ± 0.08 K, and the Debye temperature was found to be $\theta = 96 \pm 5$ K. For $kT/|J| < 3$,

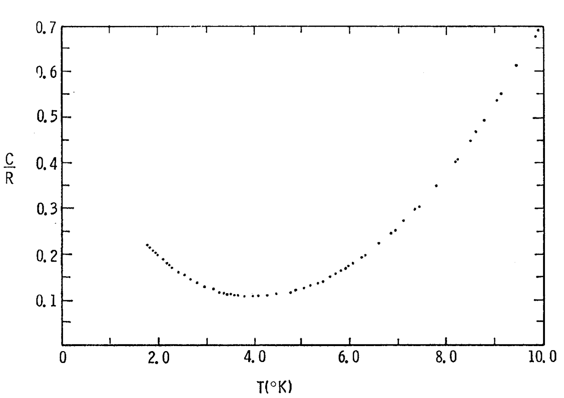

FIG. 6. Net specific heat of $Cu[NH_2(CH_2)_3NH_2]_2SO_4 \cdot H_2O$ from 1 to 10 K.

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

the measured data rises more rapidly than $1/T^2$, in accordance with the Bonner-Fisher results.

We also attempted to use the same computer fitting program employed for CTSel·H_2O to determine the exchange constant from Eq. (3), but were unable to do so successfully, apparently because of the lack of data near the anomaly peak.

C. Dependence of J on Interionic Separation

It has been noted that the linear-chain structure in the compounds CTS·H_2O, CTSel·H_2O, and CPDS·H_2O are similar, so that these materials are virtually isomorphous from the point of view of the magnetic interactions. It seems reasonable, therefore, to combine the results for the exchange-interaction constants in these materials in order to obtain the dependence of J upon ion separation. The results to date for all the copper tetrammine compounds are shown in Table I, while the dependence of J upon linear-chain dimension is shown in Fig. 7. If a relation of the form $J=ar^{-n}$ is assumed (as indicated in the figure), a fit gives $n=10.9\pm0.3$, where r is proportional to the separation of Cu^{++} ions as given by the lattice constant in the chain direction and where the quoted error represents that arising from the mathematical fit and does not include experimental uncertainty. However, if the variation of J is compared with either volume or interchain spacing, no apparent trend is shown. These results further support the belief that the structural linkage and magnetic chain coincide.

The variation of J with separation found here is of particular interest: It is obtained in a case where the variation of superexchange with a particular lattice dimension can be clearly established. Such information is relatively scarce. In one study that has been reported, Bloch has examined the pressure dependence of magnetic transition temperatures in three-dimensional systems. After correcting for the effect of thermal expansion on the paramagnetic Curie constant and for zero-temperature volume anomalies due to magnetoelastic effects, he concludes that in a number of simple cubic insulators the exchange interaction depends upon the 10/3 power of volume or the 10th power of interionic separation.[37] It is interesting that we obtain a nearly equivalent value of the exponent. However, that this result is not a universal one is shown by the results of the variation of exchange interaction between nearest and next-nearest neighbors Gd^3 ions in $LaCl_3$, where the exponent varies as the inverse 13th and 22nd powers, respectively.[38] It should be noted, however, that over the range of r considered, one really cannot distinguish between a power-law dependence and an exponential dependence, $J\propto e^{-ar}$. This would also seem to be the case for the other reports of the separation dependence of J.

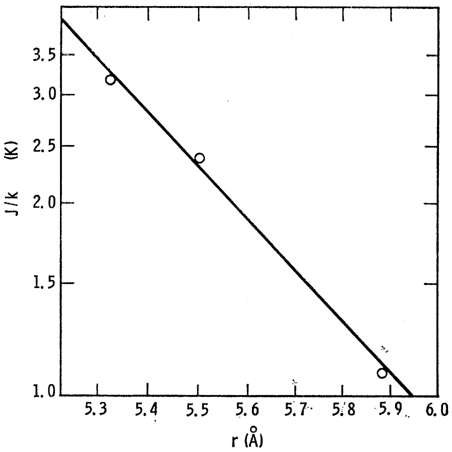

FIG. 7. Variation of J versus r to give n where $J=ar^{-n}$.

We expect to extend these considerations by studying both the pressure and temperature dependence of J in these materials.

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[37] D. Bloch, J. Phys. Chem. Solids **27**, 881 (1966).

[38] M. T. Hutchings, R. J. Birgeneau, and W. P. Wolf, Phys. Rev. **168**, 1026 (1968).