

Variation of Exchange Integral J with Lattice Spacing from Specific-Heat Measurements on Linear-Chain Antiferromagnets^{*†}

R. N. Rogers[‡] and Leonard Finegold[§]

Department of Physics and Astrophysics, University of Colorado, Boulder, Colorado 80302

and

Bruno Morosin

Sandia Laboratories, Albuquerque, New Mexico 87115

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The specific heat of the copper tetrammine salt $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{NH}_3$ has been fitted to the Bonner-Fisher theory for linear magnetic chains of spin $\frac{1}{2}$ and with isotropic nearest-neighbor interaction, in the range 1–20 K. The exchange constant is $J = 2.96 \pm 0.02$ K. The results are compared with other similar linear-magnetic-chain copper salts to further confirm the simple power-law dependence of exchange interaction versus interionic spacing.

I. INTRODUCTION

Theoretical calculations in one dimension are generally easier and intuitively more understandable than those in higher dimensions.¹ Ordering in such one-dimensional systems is of interest to studies of phase transitions and other critical-point phenomena. Lowndes, Finegold, Rogers, and Morosin² have summarized briefly the specific-heat-vs- T results of several experimental systems containing Cu^{++} ions which correspond closely to infinite chains of antiferromagnetically coupled $S = \frac{1}{2}$ spins.

The most complete calculations on the magnetic behavior of one-dimensional chains (or rings) of (ferro- or) antiferromagnetically coupled $S = \frac{1}{2}$ spins, N spins long, are those of Bonner and Fisher,³ who used the Hamiltonian

$$\mathcal{H} = -2J \sum_{i=1}^N [\gamma \vec{S}_i \cdot \vec{S}_{i+1} + (1-\gamma) S_i^z S_{i+1}^z] - g \mu_B \sum_{i=1}^N \vec{H}_i \cdot \vec{S}_i \quad (1)$$

It is seen that Eq. (1) reduces to the completely anisotropic Ising Hamiltonian for $\gamma = 0$ and to the isotropic "pure-Heisenberg" Hamiltonian for $\gamma = 1$, where J is the exchange constant, \vec{S}_i the spin on the i th site, and \vec{H}_i the magnetic field. In their work Bonner and Fisher were able to justify the extrapolation of their results to the case where the number of spins is infinite; it is with their extrapolated results that the specific heats have been compared. In their treatment the actual exchange (or super-exchange) interaction is described 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 . Lowndes *et al.*² showed that low-temperature specific-heat measurements on the copper tetrammine compounds $\text{Cu}[\text{NH}_2(\text{CH}_2)_3\text{NH}_2]_2\text{SO}_4 \cdot \text{H}_2\text{O}$ [bis(1,3-propanediamine) copper sulfate monohydrate, here-

after CPDS· H_2O] and $\text{Cu}(\text{NH}_3)_4\text{SeO}_4 \cdot \text{H}_2\text{O}$ (copper tetrammine selenate monohydrate, hereafter CTSel· H_2O) were indeed a good fit to the Bonner-Fisher calculations for $\gamma = 1$. These results together with published results on $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ ^{4,5} (copper tetrammine sulfate monohydrate, hereafter CTS· H_2O) were used to estimate the power dependence n of J upon the x-ray-determined intercopper spacing r according to $J = Ar^{-n}$.

In this paper we show that similar specific-heat and x-ray measurements on the closely related $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{NH}_3$ (copper tetrammine sulfate monoammoniate, hereafter CTS· NH_3) support the above interpretation. The compound CTS· NH_3 is isomorphous to CTS· H_2O .^{6,7} Together, these measurements serve to emphasize that the linear-chain antiferromagnetic system is one of the very few instances which permit a good experimental measurement of the variation of exchange constant with lattice spacing.

II. EXPERIMENTAL

A. Sample Preparation and Structure Determination

Samples of CTS· NH_3 were prepared by reacting powdered anhydrous CuSO_4 with liquid NH_3 . The reaction rate was controlled by adding only small quantities of liquid NH_3 as well as cooling the round bottom flask in liquid nitrogen. After the addition of a large excess of liquid NH_3 , the cold slurry was allowed to slowly warm to room temperature resulting in the slow evaporation of NH_3 gas yielding dry crystals of CTS· NH_3 . Care was taken to ensure that no exchange of NH_3 with atmospheric water vapor would occur. Infrared spectra confirmed the absence of crystallized water in such prepared material.

Direct combination of excess concentrated (~28%) NH_4OH with anhydrous CuSO_4 was shown to consistently produce material which contained some

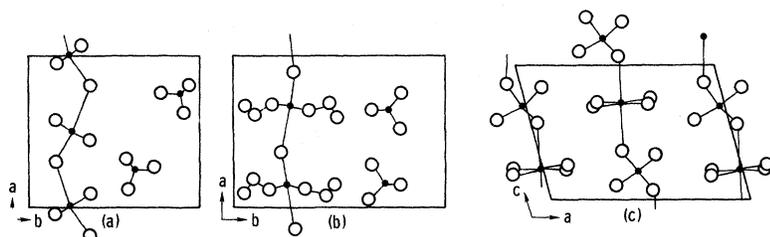


FIG. 1. Line-drawing representation of the crystal structures of (a) $\text{CTS} \cdot \text{H}_2\text{O}$, (b) $\text{CPDS} \cdot \text{H}_2\text{O}$, and (c) CTSeI . Only the atoms in the upper $\frac{1}{2}$ of the unit cell are included in each case for clarity. In each case the Cu-ligand chains run vertically on the drawings. The other related copper tetrammine compounds $\text{CTS} \cdot \text{NH}_3$ and $\text{CTSeI} \cdot \text{H}_2\text{O}$ are isomorphous to $\text{CTS} \cdot \text{H}_2\text{O}$ and hence are represented by (a).

H_2O rather than NH_3 in the crystalline lattice. Some rapidly precipitated material (using especially dried alcohol) proved to be $\sim 95\%$ NH_3 substituted; a portion of this material later was employed in this study.

$\text{CuK}\alpha$ photographs taken with a 114.5-mm Debye-Scherrer camera proved $\text{CTS} \cdot \text{NH}_3$ to be isomorphous with $\text{CTS} \cdot \text{H}_2\text{O}$ with essentially identical lattice constants. Unsuccessful attempts were made to grow larger crystals (~ 0.2 mm) suitable for a single-crystal study (i) by evaporation of large amounts of NH_3 solution prepared in the above manner and (ii) by use of concentrated NH_4OH (such slow growth invariably was found to allow water to crystallize as confirmed by infrared spectroscopy).

A comparison of the lattice constants of the copper tetrammine structures examined to date is given in Table I; the crystal structures are illustrated in Fig. 1.

B. Apparatus

The calorimeter and cryostat are closely similar to those described previously.^{2,9,10} The apparatus uses the heat-pulse method and a germanium resistance thermometer.¹¹ It has been used for measurements on pure copper¹² and provides results in good agreement with those of other workers.¹³ Tests have also been made on the smoothness of the temperature scale of the thermometer.¹⁴ Tem-

perature increments were kept sufficiently small so as not to be a source of error.

To improve the effective thermal diffusivity of the powdered crystallites, about 10 g of the sample was mixed with an approximately equal mass of fine copper powder and compressed into a cylinder, as described previously.^{2,10}

III. RESULTS AND DISCUSSION

A. Specific-Heat Results

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 $C_{\text{max}}/R \approx 0.35$ at a temperature $kT_{\text{max}}/J = 0.962$. The net measured specific heat of the sample⁶ in the temperature region 1–20 K was fitted to the equation

$$C/R = aC_{\text{BF}}(kT/J) + cT^3 + dT^5 + eT^7, \quad (2)$$

using the computer program developed for the work of Ref. 8, where $C_{\text{BF}}(kT/J)$ 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 best fit to Eq. (2) is then

$$|J|/k = 2.96 \pm 0.02 \text{ K},$$

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

Sample	a (Å)	b (Å)	c (Å)	β (Å)	J/k (K)
$\text{CTS} \cdot \text{NH}_3$	10.65	11.99	7.07		2.90 ^a
$\text{CtSeI} \cdot \text{H}_2\text{O}$	11.0	11.3	7.2		2.36 ^b
$\text{CPDS} \cdot \text{H}_2\text{O}$	11.764	15.874	7.172		1.09 ^b
$\text{CTS} \cdot \text{H}_2\text{O}$	10.651	11.986	7.069		3.15 ^c
CTSeI^d	10.313	10.759	7.405	104.43	0.24 ^b
CTN^e	10.840	23.6931	6.902		3.70 ^f

^aThis work.

^bReference 2.

^cReference 4.

^dMonoclinic; all others are orthorhombic.

^e $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$.

^fReference 8.

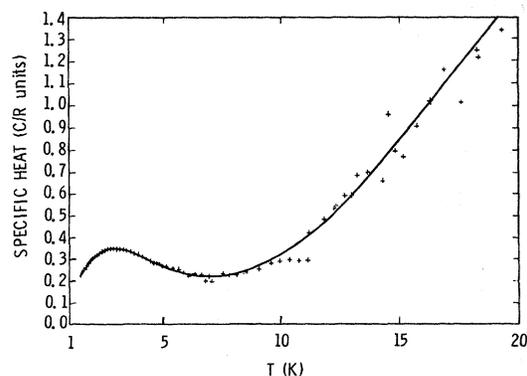


FIG. 2. Least-squares fit to the net measured specific heat of $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{NH}_3$, 1–20 K. The solid line is the computer-fit curve given by Eq. (2).

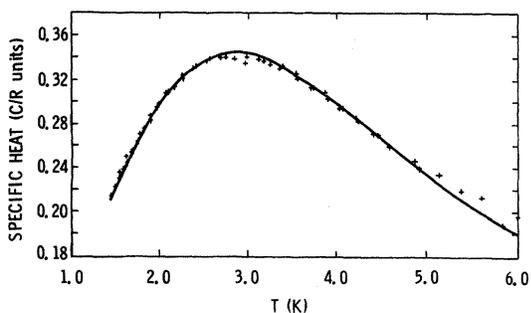


FIG. 3. Least-squares fit to the Bonner-Fisher function alone in the region of the magnetic anomaly. The lattice contribution to the specific heat has been subtracted from the data.

$$a = 0.985 \pm 0.005,$$

$$c = (2.11 \pm 0.02) \times 10^{-4} \text{ K}^{-3},$$

$$d = 4.824 \times 10^{-7} \text{ K}^{-5},$$

$$e = -1.51 \times 10^{-9} \text{ K}^{-7},$$

where the molecular weight of $\text{CTS} \cdot \text{NH}_3$ is 244.76. The fit of Eq. (2) to the data is shown in Figs. 2 and 3. (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.)

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 for these salts is given corroboratively strong support by the goodness of fit for each of the salts.

If the molecular weight is chosen correctly, then the constant a in Eq. (2) should be unity. To make up a sufficiently large sample for our measurements, one sample of high purity had to be mixed with one containing less than 5% of the hydrate $\text{CTS} \cdot \text{H}_2\text{O}$, as indicated by infrared spectroscopy; the observed decrease of the coefficient a from unity is consistent with this.

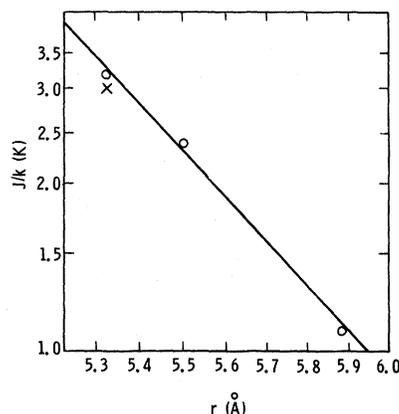


FIG. 4. Variation of J vs r to give n , where $J = Ar^n$. This is Fig. 7 of Ref. 2 with the addition of the (+) to indicate $\text{CTS} \cdot \text{NH}_3$.

B. Dependence of J on Lattice Spacing

The linear-chain structures in $\text{CTS} \cdot \text{H}_2\text{O}$, $\text{CTSel} \cdot \text{H}_2\text{O}$, and $\text{CPDS} \cdot \text{H}_2\text{O}$ are similar, and so these compounds are virtually isomorphous as far as linear-chain antiferromagnetism is concerned.² Hence, in these compounds the dependence of J upon the Cu^{++} -ion separation r may be examined by taking r as proportional to the lattice constant in the chain direction (a in Table I). A fit to $J = Ar^n$ for these three compounds gave $n = 10.9 \pm 0.3$, and this is shown in Fig. 4, together with the point representing J for the compound $\text{CTS} \cdot \text{NH}_3$ ¹⁵ reported here. Since the compound $\text{CTS} \cdot \text{NH}_3$ has the same structure as $\text{CTS} \cdot \text{H}_2\text{O}$ with the exception of the replacement of the water molecule along the chain by the ammonia molecule, it may be assumed that the difference in J between the two compounds fairly accurately represents the difference in the superexchange paths provided by the two molecules.

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‡Also at University of Colorado, Denver Center, Denver, Colorado 80203.

§1971-2 American Cancer Society Research Scholar,

Department of Biology, University of California, La Jolla, California 92037.

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¹⁵As previously noted in Ref. 2, over this small variation of r a power-law dependence of J cannot be distinguished from an exponential dependence.

Effect of Coherence in the Spin-Lattice Relaxation of a Pair of $s = \frac{1}{2}$ Ions*

Napoléon Gauthier and M. B. Walker

Department of Physics, University of Toronto, Toronto 181, Ontario, Canada

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At temperatures $kT \gg \hbar\omega_0$, ω_0 being the spin-resonance frequency, the relaxation rates of a single spin and a pair are shown to be experimentally indistinguishable. At temperatures $kT \ll \hbar\omega_0$, the pair will relax approximately twice as fast as the single spin, and the decay of the pair will not be precisely exponential. These results are quite different from those obtained previously by Huber.

Some years ago, Huber¹ considered the problem of determining the spin-lattice relaxation time of a pair of identical ions, each having an effective spin $s = \frac{1}{2}$. Huber's result was that, at 0K, the transfer of energy from the pair of spins to the lattice takes place in a time given by

$$T_1(\text{Huber}) = T_{10} [1 - \sin(k_0 r_{12}) / k_0 r_{12}]^{-1},$$

where T_{10} is the spin-lattice relaxation time of a single spin, k_0 is the wave vector of a resonant phonon, and r_{12} is the distance between the two spins. Note that $T_1(\text{Huber}) \gg T_{10}$, when $k_0 r_{12} \ll 1$.

A somewhat similar problem discussed by Dicke² concerns a neutron placed in a uniform magnetic field in the higher of its two spin states. The neutron will radiate a photon via a magnetic-dipole transition and will drop to the lower-energy state. If now, however, a second neutron in its ground state is placed near the first neutron, the radiation process is quite different. The initial state can be considered to be a superposition of singlet and triplet states. The triplet state can decay to the ground state (triplet), but the singlet is not coupled to the triplet via magnetic-dipole-radiation processes. The rate of decay of the singlet state is thus extremely slow, and in the mag-

netic-dipole approximation the singlet state does not decay at all.

In the problem of a pair of $s = \frac{1}{2}$ paramagnetic ions in a crystal, it is also useful to think in terms of the singlet and triplet states of the pair. Huber's calculation is undoubtedly correct if it is interpreted as determining the rate of decay of the singlet state. The point we wish to make, however, is that this is not the decay constant one measures in a spin-lattice-relaxation experiment. The singlet state in fact plays no part in such an experiment, for besides not being able to interact with the phonon field, it cannot interact with an applied microwave field. Hence, if in a saturation-recovery-type experiment,³ for example, a strong uniform microwave field is applied with the intention of saturating the spin system, the population of the singlet state will be unaffected, and the populations of the three triplet levels will be equalized. The power P absorbed from a very weak microwave field is then detected as a means of measuring the return to equilibrium; it is easily seen that

$$P = (n_1 - n_{-1}) W \hbar \omega_0,$$

where n_1 , n_0 , n_{-1} are the populations of the three