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Evidence for Exchange-Coupled Linear Chains in $Cu(NH_3)_4SO_4 \cdot H_2O$†

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Published values of specific heat and magnetic susceptibility for $Cu(NH_3)_4 SO_4 \cdot H_2O$ show broad maxima at a temperature roughly ten times the Néel temperature. It is shown that the behavior of these quantities above the Néel temperature may be explained qualitatively, and also quantitatively at temperatures near the maxima, in terms of an isotropic, antiferromagnetic exchange interaction between neighboring spins in linear chains of copper ions. The exchange energy, $|J|/k$, is equal to 3.15±0.2°K.

THE specific heat[1–3] of $Cu(NH_3)_4SO_4 \cdot H_2O$ shows a broad maximum at about 3°K and a fairly sharp peak at 0.37°K, presumably due to antiferromagnetic ordering of the spins on the copper ions. Similarly, the magnetic susceptibility[3,4] reaches a broad maximum at about 3.5°K and indicates a Néel temperature of 0.37°K. The "anomalous" magnetic and thermal properties of this material have been explained[1,3–5] by the suggestion that the magnetic exchange interaction is strong within linear chains of copper ions lying parallel to the c axis of the crystal,[6] and much weaker between copper ions lying in different chains.[7] The specific heat maximum at 3°K is presumably due to the "strong" exchange interaction within each chain. The interaction between chains eventually brings about antiferromagnetic ordering, but only at a much lower temperature. Below we present evidence which supports, quantitatively as well as qualitatively, the hypothesis of exchange-coupled linear chains.

Recently, Bonner and Fisher[8] have computed the specific heat and susceptibility of short chains (actually closed "rings") of spin-$\frac{1}{2}$ atoms coupled by an isotropic exchange interaction

$$\mathcal{H} = -2J \sum_{i=1}^{N} \mathbf{S}_i \cdot \mathbf{S}_{i+1}, \qquad \mathbf{S}_{N+1} \equiv \mathbf{S}_1, \tag{1}$$

for values of N from 2 to 11. Curves of specific heat or susceptibility as a function of temperature show a very systematic progression as N increases. This permits a fairly good estimate of these quantities in the limit of an infinite chain (the case of interest) for temperatures above $|J|/k$, and a reasonable guess as to the behavior at lower temperatures.

Figure 1 shows the experimental data for the magnetic susceptibility multiplied by the temperature, together with theoretical curves[8] for the same quantity calculated for antiferromagnetic coupling ($J<0$) in chains containing $N=10$ and 11 atoms. Our normalized susceptibility $\bar{\chi}$ is related to the molar susceptibility χ by

$$\bar{\chi} = k\chi / N_0 g^2 \mu^2, \tag{2}$$

where k is the Boltzmann constant, N_0 Avagadro's number, μ the Bohr magneton, and g the electron g factor. We used g values obtained by paramagnetic resonance[9]: $g_a=2.05$, $g_b=2.11$, $g_c=2.18$ (the subscript refers to the crystal axis). The normalized susceptibilities for the different crystal axes agree to within 3 or 4 %; the difference is too small to be shown conveniently in Fig. 1.

The curves for $N=10$, 11 in Fig. 1 were drawn for a value of J/k equal to -3.15°K; this is the only adjustable parameter and is equivalent to applying a scale factor to the temperature. We expect the susceptibility curve for an infinite chain to lie between the curves for

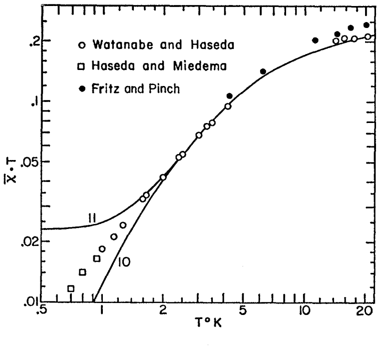

FIG. 1. Normalized magnetic susceptibility of $Cu(NH_3)_4 SO_4 \cdot H_2O$, multiplied by the temperature, as a function of temperature. The solid curves are calculated values for chains containing 10 and 11 spins.

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[6] The crystal structure has been determined by F. Mazzi, Acta Cryst. **8**, 137 (1955), and M. Simerská, Czech. J. Phys. **4**, 277 (1954). We use Mazzi's designations for the crystal axes.

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[9] H. Abe and K. Ono, J. Phys. Soc. Japan **11**, 947 (1956). Substantially the same values were obtained by E. H. Carlson and R. D. Spence, J. Chem. Phys. **24**, 471 (1956), and somewhat lower values by T. Okamura and M. Date, Phys. Rev. **94**, 314 (1954).

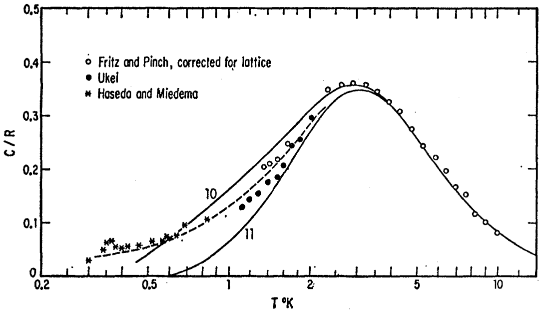

FIG. 2. Specific heat of $Cu(NH_3)_4SO_4 \cdot H_2O$, divided by the gas constant, as a function of temperature. The solid curves are calculated values for chains containing 10 and 11 spins. The dotted curve is an extrapolation to low temperatures of results obtained for finite chains.

$N = 10$, 11. The experimental susceptibility appears to be reasonably consistent with a linear chain hypothesis.

For an infinite antiferromagnetic chain, the susceptibility[10] at $T = 0°$ is not zero, but falls to 0.69 times its maximum value, the latter determined by calculations on finite chains.[8] It may be significant that just above the Néel temperature (naturally, a comparison with linear chain calculations cannot be made at lower temperatures) the susceptibility of $Cu(NH_3)_4SO_4 \cdot H_2O$, for all three axes, is about 0.65 of its maximum value.

Specific heat data from various sources are plotted in Fig. 2. Values given by Fritz and Pinch have been "corrected" for a lattice contribution[11] by the somewhat arbitrary procedure of subtracting a quantity $0.32(T/10)^3$ from the published values of C/R, where R is the gas constant. Hence, the points above 5°K in Fig. 2 are of little significance. However, the estimated lattice contribution is almost negligible (≈ 0.01) at 3°K where the specific heat maximum occurs. The maximum occurs. The maximum value of C/R, 0.360, is very close to the value, 0.35 (independent of J), estimated from theory[8] for an infinite linear chain with isotropic, antiferromagnetic exchange interaction. On the other hand, the infinite Ising chain yields a maximum value of 0.439 for C/R, considerably larger than the experimental value.

The curves for $N = 10$, 11 in Fig. 2 have been drawn for the same value of $J/k(-3.15°K)$ employed for the susceptibility curves in Fig. 1. The dotted curve represents an extrapolation of the results for finite chains to low temperatures,[8] where it is expected that the specific heat will be proportional to T.

The paramagnetic resonance lines of $Cu(NH_3)_4SO_4 \cdot H_2O$ are exchange narrowed. The linewidth has been computed using the theory of Kubo and Tomita,[12] assuming an exchange interaction along the c axis with the value of J given above. The result for the dc magnetic field along the a axis is a half-width at half-maximum of about[13] 3–5 G, as against the observed value of 9 G.[14] The discrepancy is perhaps due to the effects of hyperfine interaction[15] or anisotropic exchange. The linewidth data would seem to indicate that anisotropic exchange, if present, is of the same order of magnitude as the dipolar interaction, and hence much weaker than the isotropic exchange.

In conclusion, both the magnetic susceptibility and the magnetic contribution to the specific heat of $Cu(NH_3)_4SO_4 \cdot H_2O$ at temperatures above 0.5°K appear to be satisfactorily explained to within experimental accuracy and theoretical precision on the basis of linear chains of copper ions with an isotropic, antiferromagnetic exchange interaction between nearest neighbors.[16] The exchange energy $|J|/k$ is equal to $3.15 \pm 0.2°K$. The data discussed above do not, of course, establish that the strongest exchange interaction is along the crystalline c axis, though this seems plausible from the crystal structure.

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[10] R. B. Griffiths, Phys. Rev. **133**, A768 (1964).

[11] See Ref. 1 on the difficulty of separating "lattice" and "magnetic" contributions to the specific heat.

[12] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

[13] In the Kubo and Tomita theory it is necessary to guess at a functional form for certain correlation functions [See Eq. (8.6) in Ref. 12]. If, in place of a Gaussian function, one employs (for instance) a Lorentzian function, the calculated linewidths increase by a factor of $\pi^{1/2}$.

[14] H. Abe and K. Ono, Ref. 9; R. N. Rogers (private communication).

[15] A hyperfine interaction in the solid of the same order as that observed by R. N. Rogers (private communication) in solutions could contribute 1 or 2 G to the linewidth.

[16] *Note added in proof.* Recent measurements by T. Haseda and H. Kobayashi (to be published) of the magnetization as a function of magnetic field in this material at low temperatures are consistent with the hypothesis of exchange-coupled linear chains.