Exchange Interactions in Cu$(NH_3)_4SO_4 \cdot H_2O$†

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Considering the specific heat, the magnetic susceptibility, and the crystal structure of Cu$(NH_3)_4SO_4 \cdot H_2O$, we conclude that this substance has the magnetic linear chain property. The ratio of the exchange integrals $|J_1|$ within the chain and $|J_2|$ between the chains cannot be determined by the former theories. In this paper we have determined it as about 0.01 by the Green function method.

THE specific heat of Cu$(NH_3)_4SO_4 \cdot H_2O$ has been measured by Fritz and Pinch[1] from 4.2 to 1.3°K and by Haseda and Miedema[2] extended down to 0.03°K. Both groups have observed a broad Schottky-type maximum near 3°K, and Haseda and Miedema have also observed a small sharp maximum at 0.37°K.

The magnetic susceptibilities measured by Watanabe and Haseda[3] are anisotropic along the three principal crystalline axes. Each of them has a broad maximum near 3°K. Below 0.37°K the susceptibility along the c axis becomes independent of the temperature.

The crystal structure of Cu$(NH_3)_4SO_4 \cdot H_2O$ has been determined by Mazzi.[4] The Cu ions are located in linear chains parallel to the c axis and are linked as —Cu^{++}—H$_2$O—Cu^{++}—H$_2$O—. The linkage between two Cu ions in neighboring chains is —Cu^{++}—NH$_3$—SO$_4$—NH$_3$—Cu^{++}—. Therefore, we can expect that the exchange interaction between two Cu ions within a chain is much larger than that between the chains.

We denote the exchange integrals in the chain and between the chains by J_1 and J_2, respectively. From the magnetic susceptibility behavior mentioned above, it may be concluded that J_1 is negative (antiferromagnetic). If we neglect J_2 completely, the crystal can be regarded as a bundle of isolated antiferromagnetic linear chains. Many theories predict that a linear chain with antiferromagnetic exchange interactions cannot become antiferromagnetic, and that the specific heat and the magnetic susceptibility will have a broad maximum at a certain temperature. This temperature is given approximately by $|J_1|/k$, where k is the Boltzmann constant. In Cu$(NH_3)_4SO_4 \cdot H_2O$ both maxima are located at about 3°K. Consequently, we may estimate that $|J_1|/k$ is about 3 deg.

If we introduce a nonvanishing J_2, it is possible to get theoretically a Néel point T_N of finite temperature. As pointed out by Haseda and Miedema, the small sharp peak of the specific heat at 0.37°K and the temperature-independent susceptibility below 0.37°K indicate that Cu$(NH_3)_4SO_4 \cdot H_2O$ becomes antiferromagnetic below

0.37°K, that is, $T_N = 0.37$°K. This suggests that J_2 in this crystal is not zero, although it may be quite small.

Several years ago the author[5] and Marshall[6] independently explained a large residual specific heat above the Néel point in CuCl$_2 \cdot 2H_2O$ observed by Friedberg.[7] Both theories are based on the model that a Cu ion in CuCl$_2 \cdot 2H_2O$ is strongly coupled by the exchange integral $|J_1|$ with neighboring Cu ions along the c axis, and is weakly coupled by the exchange integral J_2 with neighboring Cu ions in the ab plane. The author used the refined molecular field theory for the Heisenberg model, while Marshall used the Bethe-Peierls theory for the Ising model. The expression for T_N derived by the author is

$$\exp[2|J_1|/kT_N] = (4 + z\eta)/(z\eta), \qquad (1)$$

where

$$\eta \equiv |J_2|/|J_1|, \qquad (2)$$

and z is the number of neighbors in the ab plane (in this case $z = 4$). This formula gave $\eta = 0.3$ for CuCl$_2 \cdot 2H_2O$, while Marshall obtained $\eta = 0.2$.

If we apply this formula to Cu$(NH_3)_4SO_4 \cdot H_2O$ by putting $|J_1|/k = 3$, $T_N = 0.37$, and $z = 4$, we get $\eta \approx e^{-16}$, which is exceedingly small. Marshall's theory gives a similar result. This means that these theories are not applicable to the case of small η.

Recently the two-time and temperature-dependent Green function method has been used in the antiferromagnetic problem by the author and Honma.[8] We apply this theory to Cu$(NH_3)_4SO_4 \cdot H_2O$. We follow their derivation to get the expression for the Néel point by assuming that the Cu ions are placed on the tetragonal lattice sites and that the exchange integrals between neighbors is $|J_1|$ along the z axis and $|J_2|$ along both the x and y axes. We then obtain an expression for the Néel point as follows:

$$\frac{kT_N}{|J_1|} = \frac{4S(S+1)/3}{I(\eta)}, \qquad (3)$$

where

$$I(\eta) = \frac{1}{\pi^3} \int \int \int_0^\pi \frac{dq_x dq_y dq_z}{\eta(1 - \cos q_x) + \eta(1 - \cos q_y) + (1 - \cos q_z)}.$$

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Here η has been defined in (2) and q_x, q_y, and q_z are the components of a wave number vector $\mathbf{q}$. The triple integral in (3) can be easily reduced to a single integral. This single integral was evaluated by an electronic computer. The results[9] for various η are shown in Table I. Inserting the numerical values, $T_N = 0.37$, $|J_1|/k = 3$, $S = \frac{1}{2}$ into (3) and using Table I, we obtain $\eta \approx 0.01$.

The expression for T_N obtained by the modified molecular field theory or the Bethe-Peierls theory contains only the number of neighbors z. Consequently, these theories do not take account of dependence on structure. On the other hand, the expression of T_N by the Green function method contains $\sum \mathbf{q}$, where $\mathbf{q}$ is the wave number vector. This indicates the Green function method takes account of structure much more precisely

TABLE I. Numerical values for the integral $I(\eta)$.

η	$I(\eta)$
1	0.505
0.1	1.963
0.01	6.405
0.001	20.323

than the other theories. In the present problem the structure dependence is essentially important. In other words, the magnetic property of Cu(NH₃)₄SO₄·H₂O is well described by the linear chain model, but it is slightly modified by the exchange interactions between the chains. This is the reason why the Green function method can give a reasonable value for $|J_2|/|J_1|$, although the other theories fail.

[9] Dr. E. W. Montroll informed me that he has calculated the triple integral analytically. [*Proceedings of the Third Berkeley Symposium on Mathematical Statistics and Probability, December 1954 and June and July 1955* (University of California Press, 1955), p. 209.] The numerical values in Table I are in quite good agreement with his results.

"Forbidden" Hyperfine Transitions in the Electron Paramagnetic Resonance of Mn++ in Cubic MgO

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The so-called "forbidden" hyperfine transitions of the S-state ion Mn++ with selection rules $|\Delta M| = 1$, $\Delta m = \pm 1$ have been observed in the cubic field of MgO. These transitions are shown to be observable in cubic fields because of the mixture of the zero-field splitting parameter a with the off-diagonal hyperfine terms in the spin Hamiltonian which mixes neighboring hyperfine levels. Until now the intensities of these transitions had been calculated only in crystals of axial symmetry and were due to the mixing of levels with axial-field splitting D. The intensity for the cubic-field case is calculated and shows an interesting $(\sin 4\theta)^2$ dependence, as compared with $(\sin 2\theta)^2$ in the axial field case. The splittings of the "forbidden" doublets are calculated to third-order perturbation theory and both the intensities and the splittings agree well with the experimental data.

INTRODUCTION

THE electron paramagnetic spectra of divalent manganese in several single crystals of axial symmetry have shown weak lines occurring between the usual intense main hyperfine lines.[1-7] These were

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first observed by Bleaney and Ingram[8] and are due to the mixing of hyperfine levels by the interaction of the axial-field splitting D with the hyperfine interaction A. Bleaney and Rubins, however, point out that this mixing should occur whenever the magnetic field is not directed along an axis of twofold or higher symmetry.[3] In the present paper, we have observed the forbidden lines in the cubic field of MgO and have shown that they are due to hyperfine mixing with the zero-field cubic splitting a.

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