

ON THE SPIN-SPIN INTERACTION IN PARAMAGNETIC SALTS

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The spin-spin interaction through phonon exchange is calculated for copper Tutton salt in a static magnetic field. It is shown that the spin-spin interaction through phonon exchange may have the same order of magnitude as the dipolar interaction in paramagnetic salts. This interaction is temperature-independent and the magnitude of the interaction is about 10^{-3} cm^{-1} at the distance between the nearest neighbouring magnetic ions, 12 Å.

§ 1. Introduction

The mechanism of the exchange interaction in paramagnetic salts is not well known yet. A great number of authors¹⁾ have already investigated this spin-spin interaction experimentally. They got the same order of magnitude which one can expect from the dipolar interaction. In paramagnetic salts it is very long distance between the two magnetic ions and there is diamagnetic ions among them. Then one cannot expect such a large value of the dipole-dipole interaction. Some authors²⁾ tried to explain this mechanism. One may expect that it is a certain indirect interaction of the magnetic spin, for example, like superexchange interaction. Sugihara³⁾ also suggested the mechanism of exchange interaction and showed the order of magnitude 10^{-3} cm^{-1} in nickel Tutton salts. Now in the present article we shall deal with the exchange interaction in copper Tutton salt in a static magnetic field.

§ 2. Orbital State in Crystalline Field

The structure of copper Tutton salts is $M_2^+Cu(SO_4)_2 \cdot 6H_2O$ (M^+ is a monovalent cation, for example, NH_4^+ , K^+ , Rb^+ , Cs^+ etc.), and each divalent cation is surrounded by a slightly distorted octahedron of six water molecules just like a trivalent cation in alums. The orbital state in the ground state of free Cu^{++} ion is in $(3d)^9$, ${}^2D_{5/2}$ ($L=2$, $S=\frac{1}{2}$). In a crystalline field, the level is splitted into Γ_3 and Γ_5 by a cubic field and furthermore they are lifted by an orthorhombic field as shown in Fig. 1.

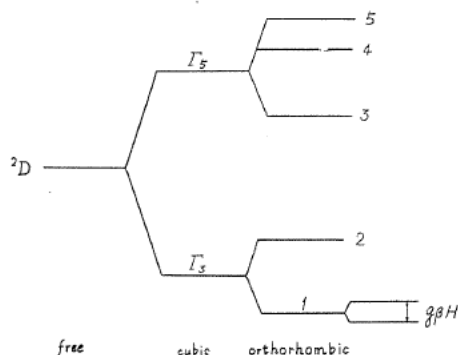


FIG. 1. Splitting of orbital states of Cu^{++} by a crystalline field.

The values of g -factor of Cu-K-Tutton⁴⁾ are at 90° K

$$g_x = 2.14, \quad g_y = 2.04, \quad g_z = 2.36. \quad (1)$$

We can estimate the magnitude of $\Gamma_3 - \Gamma_5$ level splitting, Δ , and the spin-orbit coupling constant⁵⁾, λ ,

$$\left. \begin{aligned} \Delta &= 15,500 \text{ cm}^{-1} \\ \lambda &= -710 \text{ cm}^{-1} \end{aligned} \right\} \quad (2)$$

The separation between level 1 and 2 in the Γ_3 level is not known because it has no effective g -factor.

§ 3. Effective Hamiltonian

An original Hamiltonian required by our eventual purpose is given as follows:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \quad (3)$$

where \mathcal{H}_0 is the unperturbed Hamiltonian, \mathcal{H}' the perturbed Hamiltonian and

$$\mathcal{H}_0 = \mathcal{H}_{\text{orb}} + \mathcal{H}_L + \mathcal{H}_{zS}, \quad (4)$$

$$\mathcal{H}' = \mathcal{H}_{zO} + \mathcal{H}_{sO} + \mathcal{H}_{OL}. \quad (5)$$

Here \mathcal{H}_{orb} is the Hamiltonian for the orbital motion of d -electron of Cu^{++} , \mathcal{H}_L that for the lattice vibrations, $\mathcal{H}_{zS} = 2 \mu_B \mathbf{H} \cdot \mathbf{S}$, $\mathcal{H}_{zO} = \mu_B \mathbf{H} \cdot \mathbf{L}$ (μ_B = the Bohr magneton) respectively the spin and orbital part of the Zeeman energy, $\mathcal{H}_{sO} = \lambda \mathbf{L} \cdot \mathbf{S}$ the spin-orbit interaction and \mathcal{H}_{OL} the orbit-lattice interaction introduced by Van Vleck⁶⁾. The spin-spin interaction is neglected assuming that the sample is magnetically dilute.

Now we shall consider the exchange spin-spin interaction that i -spin emits (or absorbs) one phonon and j -spin absorbs (or emits) it. Then many various processes of the interaction appear by eliminating the orbital motion in the perturbational calculation and the effective term among them is of the following type:

$$\mathcal{H}_{ij} = \sum_{\mathbf{k}, \nu} \sum_{\delta = \pm 1} \langle n_{\mathbf{k}\nu} | \mathcal{H}_{SL}^{(i)} | n_{\mathbf{k}\nu} - \delta \rangle \langle n_{\mathbf{k}\nu} - \delta | \mathcal{H}_{SL}^{(j)} | n_{\mathbf{k}\nu} \rangle / \delta \hbar \omega_{\mathbf{k}\nu}, \quad (6)$$

where $n_{\mathbf{k}\nu}$ is the phonon number with wave vector \mathbf{k} and polarization ν , $\mathcal{H}_{SL}^{(i)}$ the Hamiltonian of i -th ion inducing the spin-lattice relaxation as given by

$$\begin{aligned} \mathcal{H}_{SL}^{(i)} &= \sum_{t=2}^5 \sum_{t'=3}^5 \langle \Gamma_t | \mathcal{H}_{OL} | \Gamma_t \rangle \langle \Gamma_t | \mathcal{H}_{sO} | \Gamma_{t'} \rangle \langle \Gamma_{t'} | \mathcal{H}_{zO} | \Gamma_1 \rangle / \Delta_t \Delta_{t'} \\ &+ (\text{interchanged terms with } \mathcal{H}_{zO}, \mathcal{H}_{sO} \text{ and } \mathcal{H}_{OL}), \end{aligned} \quad (7)$$

where Γ_t and $\Gamma_{t'}$ are the states which belong to Γ_t and $\Gamma_{t'}$ respectively.

§ 4. Calculation of Spin-Spin Interaction through Phonon Exchange

We now proceed to the calculation of the spin-spin interaction through phonon exchange. Then we can express the orbit-lattice interaction \mathcal{H}_{OL} given by Van

Vleck⁶⁾⁷⁾ and other authors⁸⁾, namely,

$$\mathcal{H}_{OL}^{(i)} = \sum_{k=2}^6 V_k^{(i)} Q_k^{(i)}. \quad (8)$$

Now we may suppose atoms 1, 2, 3 located respectively on the x , y , z coordinate axes, and atoms 4, 5, 6 on the opposite sides of the central atom. Thus

$$\left. \begin{aligned} Q_2 &= \frac{1}{2} [X_1 - X_4 - Y_2 + Y_5], \\ Q_3 &= \left[\frac{1}{2} (X_1 - X_4 + Y_2 - Y_5) - Z_3 + Z_6 \right] / \sqrt{3}, \\ Q_4 &= \frac{1}{2} [Y_1 - Y_4 + Y_2 - X_5], \\ Q_5 &= \frac{1}{2} [Z_1 - Z_4 + X_3 - X_6], \\ Q_6 &= \frac{1}{2} [Z_2 - Z_3 + Y_3 - Y_6], \end{aligned} \right\} \quad (9)$$

where X , Y , Z are displacements of an atom from the ideal octahedral arrangement. If we assume that the radius r of the d -shell is small compared with the interatomic separation R ,

$$\left. \begin{aligned} V_2 &= \sum_i [A(x_i^2 - y_i^2) + B(x_i^4 - y_i^4)] + \dots, \\ V_3 &= \sum_i [A(x_i^2 + y_i^2 - 2z_i^2) + B(x_i^4 + y_i^4 - 2z_i^4)] / \sqrt{3} + \dots, \end{aligned} \right\} \quad (10)$$

$$\left. \begin{aligned} V_4 &= \sum_i [C_{x_i y_i} + E(x_i^3 y_i + x_i y_i^3)] + \dots, \\ V_5 &= \sum_i [C_{x_i z_i} + E(x_i^3 z_i + x_i z_i^3)] + \dots, \\ V_6 &= \sum_i [C_{y_i z_i} + E(y_i^3 z_i + y_i z_i^3)] + \dots, \end{aligned} \right\} \quad (11)$$

where x_i , y_i , z_i are coordinates of the $3d$ -electron.

In the orbital state in an orthorhombic crystalline field, their wave functions are given as follows:

$$\left. \begin{aligned} \phi_1 &= \frac{1}{\sqrt{2}} (\varphi_2 + \varphi_{-2}) + c\varphi_0, \\ \phi_2 &= \varphi_0 - \frac{c}{\sqrt{2}} (\varphi_2 + \varphi_{-2}), \\ \phi_3 &= \frac{1}{\sqrt{2}i} (\varphi_2 - \varphi_{-2}), \\ \phi_4 &= \frac{1}{\sqrt{2}i} (\varphi_1 + \varphi_{-1}), \\ \phi_5 &= \frac{1}{\sqrt{2}} (\varphi_1 - \varphi_{-1}), \end{aligned} \right\} \quad (12)$$

where φ_M 's are eigenfunctions of the component of the orbital angular momentum along the approximate tetragonal axis, and c is a constant determined by the ratio of orthorhombic component to tetragonal one of the crystalline field (assumed $|c| \ll 1$)⁴⁾, and

$$c = 0.15 \quad (13)$$

If we take the complex wave functions of $3d$ -electron as φ_M 's, the matrix elements of \mathbf{L} are

$$\left. \begin{aligned} \langle 1|L_x|5\rangle &= -(1 + \sqrt{3}c), & \langle 2|L_x|5\rangle &= -(\sqrt{3} - c), \\ \langle 3|L_x|4\rangle &= -1, \end{aligned} \right\} \quad (14)$$

$$\left. \begin{aligned} \langle 1|L_y|4\rangle &= 1 - \sqrt{3}c, & \langle 2|L_y|4\rangle &= -(\sqrt{3} + c), \\ \langle 3|L_y|5\rangle &= -1, \end{aligned} \right\} \quad (15)$$

$$\left. \begin{aligned} \langle 1|L_z|3\rangle &= -2i, & \langle 2|L_z|3\rangle &= 2ci, \\ \langle 4|L_z|5\rangle &= i, \end{aligned} \right\} \quad (16)$$

and other matrix elements of \mathbf{L} are zero.

Now we got formulae concerning the effective Hamiltonian of this exchange spin-spin interaction, and we had the same order of magnitude with that of the dipolar interaction, namely about 10^{-3} cm^{-1} , by our order-estimation. In the next paper the author shall deal with the spin-spin interaction processes through phonon exchange and the calculation in detail.

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