Paramagnetic Resonance of Copper Complex Salts

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A paramagnetic resonance experiment was performed on $Cu(NH_3)_4SO_4 \cdot H_2O$ and $Cu(NH_3)_4(NO_3)_2$. The character of the $Cu(NH_3)_4^{++}$ group was analyzed and it was found that the g values of this group are small compared with that of the $Cu(H_2O)_4^{++}$ group. This can be explained by two methods, one of which is the covalent bonding hypothesis, the other being the usual ionic hypothesis. The exchange interaction of these salts is very large, which is considered to be the result of covalent bonding structure.

FROM the results of many experiments already performed by many investigators, it has been made clear that the ground state of the paramagnetic Cu^{++} ion in crystals is ^2D, and because of perturbations such as the crystalline electric field and spin-orbit coupling, the effective g value obtained in the paramagnetic resonance experiment varies from about 2.05 to 2.40 when the angle between the crystal axis and the external magnetic field is varied. These experiments were performed satisfactorily on some hydrated crystals such as $CuSO_4 \cdot 5H_2O$, copper Tutton salts, etc.[1] Recently, Bleaney and Ingram studied the paramagnetic resonance of ferric complex salts,[2] which have been considered as typical examples of materials having anomalously low magnetic moments. As already pointed out by Abragam and Pryce,[3] the hypothesis of a covalent bond which might exit between the Cu^{++} ion and the surrounding H_2O molecules is unsuitable for these crystals. Thus, the Cu^{++} ion and the surrounding H_2O are only in a coordinated configuration and do not form a covalent bond structure.

On the other hand, it has been pointed out by Pauling[4] that the $Cu(NH_3)_4^{++}$ group forms a covalent bond of $(3d)(4s)(4p)^2$ structure. We measured the g values of this complex group, using single crystals of the two salts $Cu(NH_3)_4SO_4 \cdot H_2O$ and $Cu(NH_3)_4(NO_3)_2$ at room temperature, by means of paramagnetic resonance absorption at 21 000 Mc/sec. Figure 1 shows the absorption curves of powdered ammonium complex salts, and also that of powdered copper sulfate for comparison with the former. From this, it is obvious that the g values of the complex salts are quite close to 2. Figure 2 shows the values of g as a function of the angles between the crystal axes and the external magnetic field in a $Cu(NH_3)_4SO_4 \cdot H_2O$ single crystal. From these data, we can get the principal values of the g tensor as shown in Table I.

Unfortunately, we cannot deduce the values of $g_{||}$ and $g_\perp$ because of the lack of x-ray data, but comparing with the values of $g_\alpha = 2.25$, $g_\beta = 2.20$, and $g_\gamma = 2.05$ obtained in the case of $CuSO_4 \cdot 5H_2O$, the values of $g_{||}$ and $g_\perp$ in our case may be expected to be comparatively small and near to 2. To explain this result, we performed the following calculation. As has been already mentioned, the electronic structure of $Cu(NH_3)_4^{++}$ is $(3d)(4s)(4p)^2$. It is easily deduced that one $4p$ electron is almost free, and perhaps its state may be $4p_z$ because of the covalent bond structure.[3] However to calculate the deviation of the g values from 2, we started with
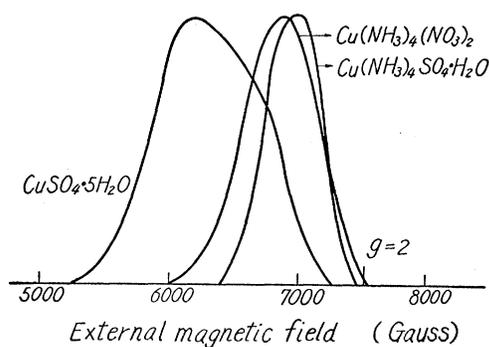
Fig. 1. Resonance curves of copper ammonium complex salt (powder).

[1] For example, R. D. Arnold and A. F. Kip, Phys. Rev. **75**, 1199 (1949).
[2] B. Bleaney and D. J. E. Ingram, Proc. Phys. Soc. (London) **A65**, 953 (1952).
[3] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **206**, 164 (1951); A. Abragam, Physica **17**, 209 (1951).
[4] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940).
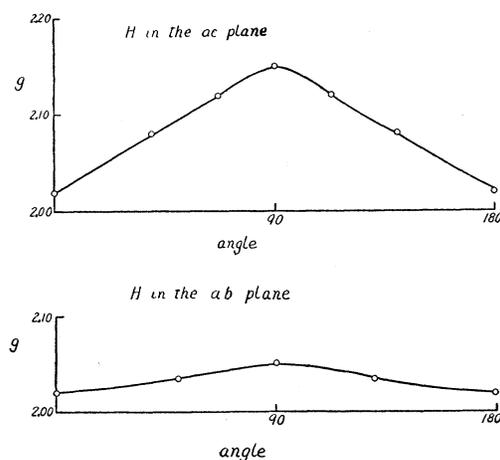
Fig. 2. Variation of g values with the angle between the static field H and the crystal axis in $Cu(NH_3)_4SO_4 \cdot H_2O$.

TABLE I. The g values of copper ammonium complex salts.

Substance	g_a	g_b	g_c
$Cu(NH_3)_4SO_4 \cdot H_2O$	2.02±0.02	2.05±0.02	2.15±0.02
$Cu(NH_3)_4(NO_3)_2$	2.07±0.02	2.14±0.02	2.02±0.02

^2P as the ground state of the ion, and considered that the contribution of other higher states is negligible. We then introduced the crystalline electric field, the spin-orbit interaction, and the external magnetic field as perturbations.[5]

As the Cu^{++} ion is placed at the center of four NH_3 molecules which are in a plane, we may assume the symmetry of the electric field to be tetragonal, so that the Hamiltonian is given by the following equation:

$$H = H_0 + D(x^4 + y^4 + z^4) + A(x^2 + y^2) - 2AZ^2 + \lambda(\mathbf{L \cdot S}) + \beta \mathbf{H} \cdot (\mathbf{L} + 2\mathbf{S}).$$

From the above equation, we get the following results:

(1) The ^2P state is not split by the spherically symmetric field.

(2) The degenerate level is split by the tetragonal field into a singlet and a doublet and this splitting is $(6/5)A\langle\gamma^2\rangle_{Av}$.

(3) In addition, because of the $(\mathbf{L \cdot S})$ coupling, the doublet state is separated by an amount of the order of λ. These results are shown in Fig. 3, and the energies are expressed as follows:

$$E_0 \longrightarrow W_0 = \tfrac{1}{2}\{E_0 + E_1 - \tfrac{1}{2}\lambda + [(E_0 - E_1 - \tfrac{1}{2}\lambda)^2 - 2\lambda^2]^{\frac{1}{2}}\},$$

$$\nearrow W_1 = E_1 + \tfrac{1}{2}\lambda,$$

$$E_1 \searrow W_2 = \tfrac{1}{2}\{E_0 + E_1 - \tfrac{1}{2}\lambda - [(E_0 - E_1 - \tfrac{1}{2}\lambda)^2 - 2\lambda^2]^{\frac{1}{2}}\}.$$

(4) The effective g values for each level when the external magnetic field is applied are calculated and are shown in Table II.

From the above results, we can conclude that the lowest state is W_0 (using the notation of Table II). The value $g_{||} = 2$ in the case of the $Cu(NH_3)_4^{++}$ group

TABLE II. The g values of each level.

level	$g_{||}$	$g_\perp$
W_0	2.00	$2\left(1 - \dfrac{\lambda}{E_0 - E_1}\right)$
W_1	4.00	0
W_2	0	$\left\lvert \dfrac{2\lambda}{E_0 - E_1} \right\rvert$

[5] D. Polder, Physica 9, 709 (1942).

may be evidence of covalent bond structure, in agreement with Abragam's work[3] and the present experimental result. Moreover, it is noticed that the sign of the tetragonal field constant A is positive while it is negative in the case of the usual Cu^{++} ion, and the values of the splitting due to the tetragonal field can be calculated to be about 6000 cm^{-1} from our experimental data if we assume that the value of λ is equal to that for the Cu^{++} ion. But this value may be incorrect. Because of the covalent bond structure, the ^2P state is already affected before we consider the crystalline electric field. So in our calculation this effect must be considered, and this is accomplished by varying the $\mathbf{L \cdot S}$ coupling constant λ.

In addition to the above considerations, we must consider the fact that these experimental results can also be explained by the usual method calculated by Polder if we assume the crystalline cubic electric field to be two or three times larger than that of ordinary paramagnetic copper salts. Because of the lack of x-ray data, we cannot say whether the presence of this large electric field is probable. So, as the result of these
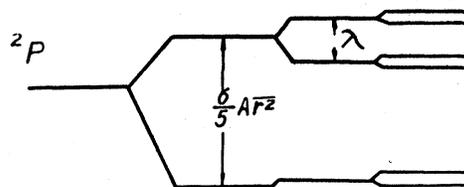
FIG. 3. Energy-level splitting of ^2P state.

considerations, we must consider at least two possibilities for the ground state of the $Cu(NH_3)_4^{++}$ group as distinct from the $Cu(H_2O)_4^{++}$ group.

Another interesting result is the half-width of the absorption lines. Because of the lack of x-ray data, a rigorous application of Van Vleck's theory of dipolar broadening[6] is impossible; however, using the density of the single crystal, we can calculate from the dipolar interaction an approximate value of the half-width of about $\Delta H \sim 400$ gauss. But the experimental data show about $30 \sim 50$ gauss in various directions in the case of $Cu(NH_3)_4SO_4 \cdot H_2O$, and also a slightly larger value for the nitrate. Thus, our experimental results give about $\frac{1}{10}$ of theoretical values. Hence, very strong exchange interactions may be expected. This may be caused by the effect of a larger mean distance for the $4p$ orbit than for the $3d$ orbit in the case of Cu^{++} exchange interactions in the coordinated configuration.

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[6] J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).