Temperature shift of EPR line in exchange-coupled spin groups

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We investigated the temperature-dependent exchange shift of the EPR line in a complex compound of the coupled ion Cu(2) with two iminoxy radicals. The magnetic system of the complex consists of triads of exchange-coupled spin. At $T > 30$ °K, the position of the EPR line of the single crystal is determined by the average g factor $g = (g_{Cu} + 2g_R)/3$, and at $T = 4.2$ °K it is determined by the g factor of the Cu(2) ions.

Temperature-dependent shifts of the EPR line were observed in the case when the spins were oriented by a strong magnetic field[1] and near the Néel point in antiferromagnets.[2] In the case of sufficiently strong exchange interaction in a system of spins with nonequivalent g-factors, a difference between the Boltzmann populations of the exchange multiplets can lead to a temperature shift of the EPR line. We present here the results of an investigation of a temperature-dependent shift of the EPR line in single crystals of a complex compound of the copper ion Cu(2) with two iminoxy-radicals (Ṙ).[3] The localization of the unpaired electron on the fragment N-O makes the iminoxyl radicals convenient objects of the investigation of the ferromagnetism of organic compounds.[4] The investigation of the magnetic properties of this compound have shown that the magnetic system of the complex consists of triads of exchange-coupled spins Ṙ—Ṙ—Cu(2), which is in turn confirmed by the crystal-structure data.[5] The EPR spectra at 4.2 °K as well as the structure data show that the exchange interactions $J_{\dot{R}} - \dot{R} = J_0$ greatly exceeds the interactions $J_{\dot{R}\text{-}Cu} = J'$, and from data on the temperature dependence of the static magnetic susceptibility of the crystals we get from J_0/k the value ~20 °K. (The susceptibility was measured in the interval 1.3—300 °K with a Faraday balance.) The investigation of the EPR spectra over single crystals of the complex in the temperature region 12.2—300 °K was carried out with a modified RÉ-1301 ($\nu_0 = 3300$ MHz). In the entire temperature interval 4.2—300 °K, the EPR spectrum of the single crystal consists of one symmetrical line (Fig. 1), the position of which depends on the orientation described by an axially-symmetrical g factor. The width of the EPR line is independent of the temperature up to $T \sim 20$ °K ($\delta H \sim 20$ Oe), and increases somewhat in the interval $12.2\ \text{°K} < T < 20$ °K (δH 40 Oe at 4.2 °K). At all the sample orientations one observes a temperature-dependent shift of the EPR line towards weaker magnetic fields (Fig. 2). Since the g-factor of the iminoxyl radical $g_{\dot{R}}$ ($g_{xx} = 2.0009$, $g_{yy} = 2.006$, $g_{zz} = 2.003$) is close to the g-factor of the free electron and differs appreciably from the g-factor $g_{Cu(2)}$ of the copper ion,[6] it follows that the presence of a single EPR line indicates that exchange interaction $J'' \gg \Delta g \beta H$ is present between the triads ($\Delta g = g_{Cu} - g_{\dot{R}}$). The investigated complex is apparently the simplest case of a triad of interacting spins of $S = 1/2$.[7,8] This makes it easy to determine the scheme of the exchange levels of the triad and to calculate the temperature dependence of the magnetic susceptibility and the EPR line shift. The determination of the eigenvalues of the Hamiltonian of a three-spin system with strong exchange G_0 between unpaired electrons of radicals with weak exchange $g\beta H < J' \ll J_0$ between the Cu(2) ion and the radicals leads to a system of energy levels consisting of one quartet with $S = 3/2$ and two doublets with $S = 1/2$ (Fig. 2); the corresponding values of the g-factors for the quartet and for the upper and lower doublets are

$$g_{3/2} = \frac{2g_{\dot{R}} + g_{Cu}}{3}, \quad g_{1/2} = \frac{4g_{\dot{R}} - g_{Cu}}{3}, \quad g'_{1/2} = g_{Cu}$$

and the corresponding contribution to the magnetic susceptibility are

$$\chi_{3/2} = \frac{5N_0\beta^2}{2kT} \frac{g^2_{3/2}}{3 + \exp(J_0/kT)}, \quad \chi_{1/2} = \frac{N_0\beta^2}{4kT} \frac{g^2_{1/2}}{3 + \exp(J_0/kT)},$$

$$\chi_{Cu} = \frac{N_0\beta^2}{4kT} \frac{g^2_{Cu}\exp(J_0/kT)}{3 + \exp(J_0/kT)},$$

where N_0 is the total number of spins. We then have for the total susceptibility of the complex

$$\chi(T) = \frac{N_0\beta^2}{4kT}\left[\frac{g^2_{Cu}\exp(J_0/kT) + (g^2_{1/2} + 10g^2_{3/2})}{3 + \exp(J_0/kT)}\right]. \qquad (1)$$

Figure 3 shows a comparison of $\chi(T)$ calculated from formula (1) with the experimentally observed values for a polycrystalline sample. It was assumed here that $g^2_{Cu} = (g^2_{\parallel Cu} + 2g^2_{\perp Cu})/3$, where $g_{\parallel Cu} = 2.18$ and $g_{\perp Cu} = 2.05$ are the values of the g-factor of Cu(2) obtained at 4.2 °K,

$$g^2_{3/2} = \frac{g^2_{\parallel 3/2} + 2g^2_{\perp 3/2}}{3}, \quad g^2_{1/2} = \frac{g^2_{\parallel 1/2} + 2g^2_{\perp 1/2}}{3}, \quad J_0/k = 19\ \text{°K}.$$

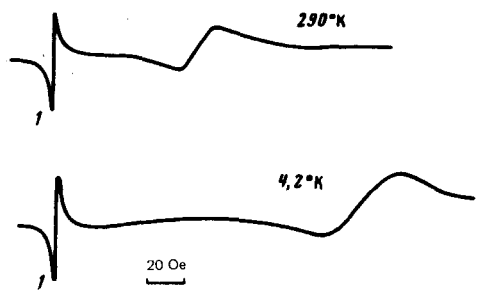

FIG. 1. Position of EPR line at arbitrary orientation of the single crystal, $T = 290$ °K and 4.2 °K; 1—DPPH marker.

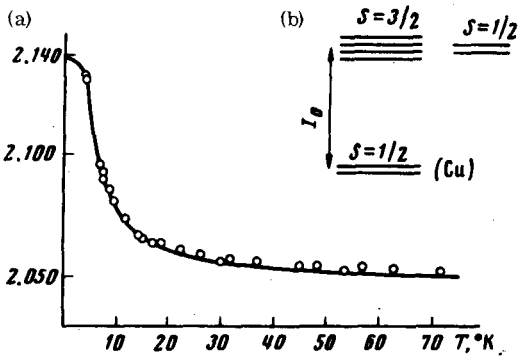

FIG. 2. a) Temperature shift of EPR line. The magnetic field is directed along the c axis (the crystals of the complex belong to the triclinic syngony[5]): circles—experimental results, solid curve—calculation of formula (2). b) Energy level scheme of triad in a strong magnetic field.

The agreement between the $\chi(T)$ calculated by formula (1) with experiment indicates that the level scheme assumed in Fig. 2 is correct.

Whereas at high temperatures ($kT \gg J_0$) the contribution to the susceptibility is made by all three interacting spins, at $kT \ll J_0$, i.e., at helium temperatures, the paramagnetism of the system is due only to the copper ions, i.e., to the lower doublet in accordance with the data on the EPR line position (Fig. 2). In the absence of exchange interaction between the triads, the EPR spectrum of the crystal would consist, in accordance with the level scheme of Fig. 2, of several lines determined by the g-factors $g_{3/2}$, $g_{1/2}$, and g_{Cu}. In the presence of these interactions ($J'' \gg \Delta g\beta H$), however, the EPR spectrum will consist of one line whose position must be determined by the average g-factor

$$g(T) = g_{Cu}\frac{\chi_{Cu}}{\chi} + g_{3/2}\frac{\chi_{3/2}}{\chi} + g_{1/2}\frac{\chi_{1/2}}{\chi}. \qquad (2)$$

A result similar to (2) was obtained rigorously for the case of exchange collisions of nonequivalent paramagnetic particles in a liquid.[9]

Figure 2 shows the function $g(T)$ obtained from formula (2) at $J_0/k = 19$ °K for a given crystal orientation. We see that the agreement with the experimental results is complete.

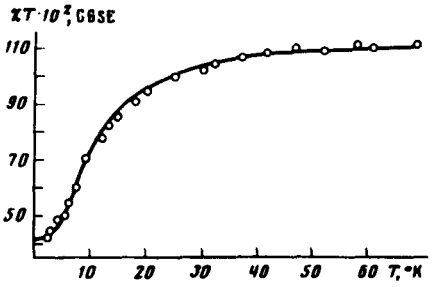

FIG. 3. Temperature dependence of the magnetic susceptibility of the complex: circles—experimental results, solid curve—calculated from formula.

Thus, at high temperatures ($kT \gg J_0$) all three systems of the exchange levels of the triad contribute to the EPR line and the line position is determined by the average g-factor $(g_{Cu} + 2g_{\parallel})/3$. At low temperatures ($kT \ll J_0$) the paramagnetic resonance is determined in practice by the Cu(2) ions and the position of the EPR line is determined by their g-factor. The effect of the temperature shift of the EPR line should be observed in a large number of spin systems in the presence of strong and weak exchange interactions between groups of non-equivalent spins.

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