

MOLECULAR
MAGNETISM

Magnetic Resonance in Copper(II) *bis*-[4-(2'-Oxo-3'-3'-3'-trifluoropropylidene)- 2,2,5,5-tetramethyl-3-imidazoline-1-oxyl] $\text{Cu}(\text{C}_{10}\text{H}_{13}\text{F}_3\text{N}_2\text{O}_2)_2^1$

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Abstract—Magnetic resonance measurements were carried out on powder samples of CuL_2 ($L = \text{C}_{10}\text{H}_{13}\text{F}_3\text{N}_2\text{O}_2$) with an orthorhombic structure (space group $P21$, lattice parameters $a = 10.556$, $b = 20.598$, $c = 5.787$ Å, $Z = 2$). The CuL_2 compound belongs to molecular-type compounds. Every molecule contains one copper atom and two free radicals situated at the nearest oxygen atoms with ferromagnetic exchange interaction about 20 K. The absorption line obtained is typical of powder samples with an axial g value. On the base of existing models, it was possible to derive from the experimental spectra the main values of the g tensor ($g_{\perp} = 2.109$, $g_{\parallel} = 2.041$) of the exchange-coupled CuL_2 molecule and its individual linewidth ($\Delta H = 165$ Oe). The second moment of the resonance line determined from the dipole–dipole interaction between nearest molecules $M_2 = 0.14 \times 10^{19} H_z^2$ was calculated in the point-dipole approximation. It was shown that the linewidth value obtained may be explained taking into account the small exchange interaction $J = 0.14$ K between the nearest molecules.

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1. INTRODUCTION

Molecule-based magnets are a broad rapidly developing class of magnetic materials that expand the materials properties typically associated with magnets to include low density, transparency, electrical insulation, and low-temperature fabrication, as well as to combine magnetic ordering with other properties such as photoresponsiveness. Essentially, all of the common magnetic phenomena associated with conventional transition-metal- and rare-earth-based magnets can be found in molecule-based magnets. Although discovered less than two decades ago, magnets with ordering temperatures exceeding room temperature, very high (27.0 kOe or 2.16 MA/m) and very low (several Oe or less) coercivities, and substantial remanent and saturation magnetizations have been achieved. In addition, exotic phenomena including photoresponsiveness have been reported. The advent of molecule-based magnets offers new processing opportunities. For example, thin-film magnets can be prepared by means of low-temperature chemical vapor deposition and electrodeposition methods.

The resonance properties of the CuL_2 ($L = \text{C}_{10}\text{H}_{13}\text{F}_3\text{N}_2\text{O}_2$) compound are treated on the powdered samples. It turns out to be possible to determine the effective g value anisotropy and to get some evaluations

on single-ion anisotropy constant and intermolecular exchange coupling value.

2. THE CRYSTAL STRUCTURE
AND EXPERIMENTAL TECHNIQUE

The powdered samples were prepared by using a method described in [1]. The CuL_2 compound has an orthorhombic structure with lattice parameters $a = 10.556$, $b = 20.598$, $c = 5.787$ Å, $Z = 2$, space group $P21$. The structure projection onto (001) plane is shown in Fig. 1. The CuL_2 compound belongs to molecular-type compound. The CuL_2 molecules are situated at 1/4 and 3/4 positions along the c axis. Every molecule has 12 neighbors with Cu–Cu distances of 5.787 Å (two molecules), 10.556 Å (two molecules), and 11.87 Å (eight molecules at the corners of the elementary parallelepiped).

This crystal structure allows one to consider every molecule as a quasi-isolated cluster; the shortest distance from Cu^{2+} ion to the oxygen atom of the paramagnetic radical of the molecule under consideration is 5.36 Å, and to the oxygen atom of the paramagnetic radical of the nearest (along c -axis) molecule, 5.79 Å. Thus, the magnetic properties of this compound are governed by three-centered linear exchange-coupled clusters with exchange integrals J between Cu^{2+} ion and

¹ The text was submitted by the authors in English.

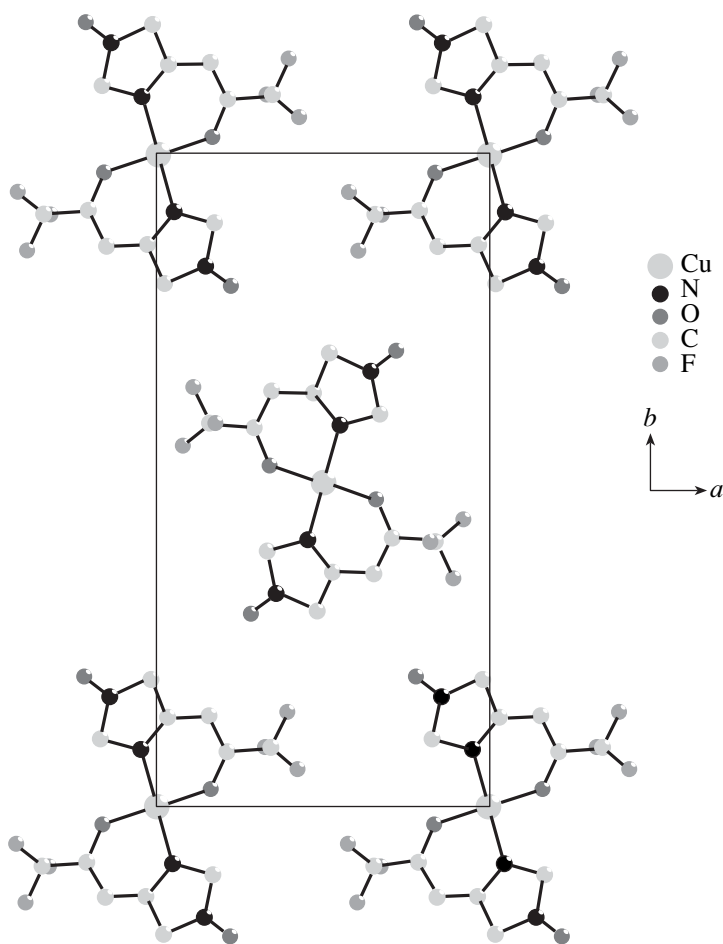


Fig. 1. Projection of the crystal structure onto the (001) plane.

two radicals of the molecule itself and much more weak interaction J' between nearest-neighbor molecules [1].

EPR measurements were carried out at room temperature with X- and Q-band EPR spectrometers.

3. EXPERIMENTAL RESULTS

The EPR spectrum of the powder CuL_2 sample for the Q band ($\nu = 38$ GHz) is shown in Fig. 2. The spectrum represents an absorption line (first derivative) typical of powder samples with an axially symmetric g value. The absorption line obtained is the envelope of a large number of single symmetrical lines, whose position is determined by the microcrystal orientation relative to the applied magnetic field. The existing procedures [2–4] allow deriving the extreme values of the g tensor and the individual single linewidth from such experimental spectra.

The model and experimental (absorption) spectra are shown in Fig. 3.

Under the assumption of the Lorentzian shape of the individual line, the best fitting gives $g_{\perp} = 2.041$, $g_{\parallel} =$

2.109, and $\Delta H = 165$ Oe, where ΔH is the individual linewidth.

4. DISCUSSION

It was shown in [5] that the CuL_2 compound consists of quasi-isolated molecular complexes with parameters $g = 2.04$, $g' = 2.0$, $J = 20$ K, $zJ' = 0.086$ K, where g and g' are the g values of the Cu^{2+} and radicals, respectively; z is the number of the neighboring molecules; and J and J' are the intra- and intermolecular exchange integrals. The positive values of the exchange integrals indicate that the ferromagnetic interaction is dominating in CuL_2 .

So, we assume that the CuL_2 ESR spectrum is governed by molecular clusters with a total spin value $S = 3/2$. In this case, the main mechanisms determining the true value of the individual linewidth are the intercluster dipole-dipole interaction, weak intercluster exchange interaction J' , and the hyperfine splitting (HFS) due to spin interaction with the total nuclear spin of the cluster. The whole EPR spectrum linewidth is determined by the anisotropic exchange-interaction value and the extreme g tensor values.

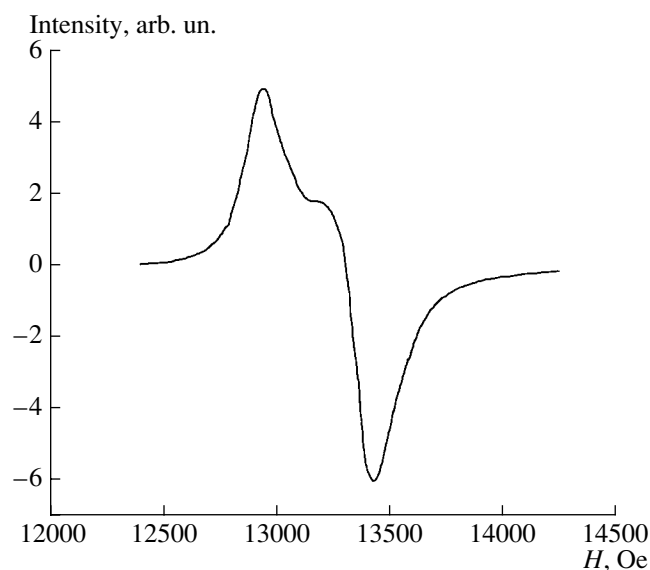


Fig. 2. First derivative of the EPR absorption at room temperature (*Q*-band spectrum).

The HFS contribution to the linewidth was estimated in [6] and, in our case, is about 10 Oe, so we can neglect this contribution.

The second-moment M_2 value (proportional to the true linewidth value) governed by the intermolecular dipole–dipole interaction for the powdered sample is [7]

$$M_2 = \frac{3}{5} \gamma_e^4 \hbar^2 S(S+1) \sum_{i,j} r_{i,j}^{-6}, \quad (1)$$

where γ_e is the gyromagnetic electron ratio, S is the total cluster spin, and $r_{i,j}$ is the distance between clusters. In the point-dipole approximation, $M_2 = 0.14 \times 10^{19} \text{ Hz}^2$. The individual linewidth in this case under the assumption of weak intercluster exchange interaction is given [8] as

$$\Delta H = M_2/J' = 250 \text{ Oe}, \quad (2)$$

for the J' value taken from [5].

In accordance with our data for ΔH , the J' value is equal to $J' = 0.14 \text{ K}$, which is a few times larger than that obtained in [5]. Such a discrepancy may be accounted for if we suppose that not all neighboring molecules are in the ground state with a total spin $S = 3/2$ at room temperature. We suppose that a sufficient number of molecules are in an excited state with $S = 1/2$, which may lead to the reduction of the dipole–dipole interactions and of the M_2 value.

The value of the single ion constant D of the cluster may be estimated using the full spectrum linewidth measured at different frequencies. Since the separation between the extreme lines of the fine-structure spectrum is equal to $4D$ for $S = 3/2$ and is independent of the measuring frequency for $D \ll g\mu_B H_0$, for the full linewidth ratio one can write

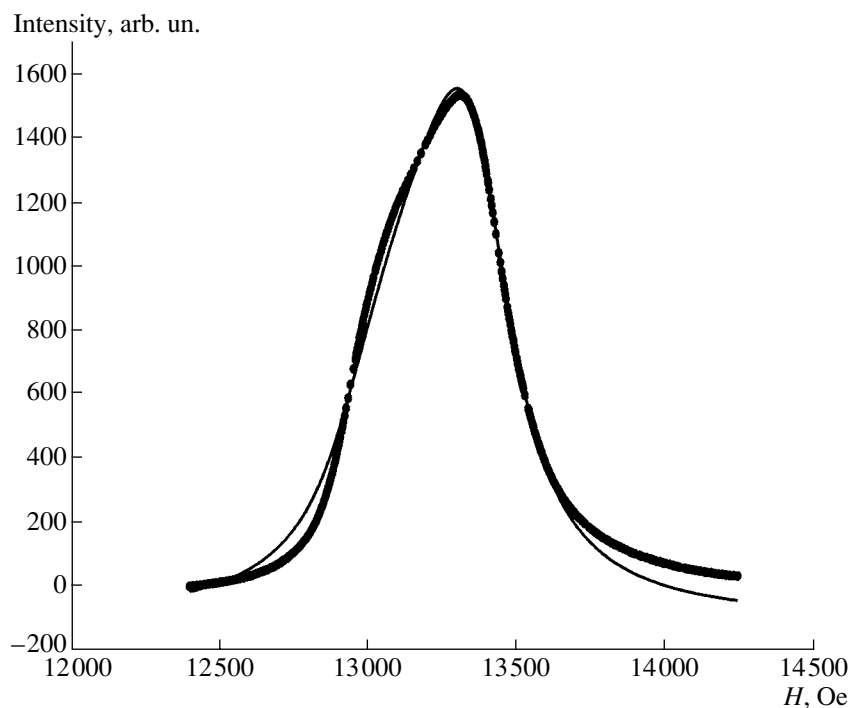


Fig. 3. Experimental (points) and model (solid line) EPR absorption spectra.

$$\frac{h\nu_1/g_{\parallel}\mu_B - h\nu_1/g_{\perp}\mu_B + 4D}{h\nu_2/g_{\parallel}\mu_B - h\nu_2/g_{\perp}\mu_B + 4D} = A. \quad (3)$$

At $D = 0$, this ratio is exactly equal to the ν_1/ν_2 ratio, where ν_1 and ν_2 are the measuring frequencies. In our case, $\nu_1/\nu_2 = 4.222$ and $A = 3.41$. So, the D value derived from Eq. (3) is equal to $D = 8.2$ Oe.

5. CONCLUSIONS

The results obtained allow us to suppose that the $\text{Cu}(\text{C}_{10}\text{H}_{13}\text{F}_3\text{N}_2\text{O}_2)_2$ compound may be considered as a molecular cluster with a total spin $S = 3/2$ and a weak intercluster exchange interaction. The local anisotropy of the crystal field has an axial symmetry and is determined by the g tensor with extreme values $g_{\perp} = 2.041$ and $g_{\parallel} = 2.109$. The frequency dependence of the full spectrum linewidth allows us to derive the single-ion constant D of the individual molecular cluster $D = 8.2$ Oe.

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