EPR Data on Ni(II) Doped Cu(II) Acetate Monohydrate Single Crystals: Evidence of $Ni^{2+}-Cu^{2+}$ Exchange-Coupled Pairs

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Electron paramagnetic resonance measurements on nickel(II) doped copper(II) acetate monohydrate single crystals have been made. In the liquid helium temperature range, spectra have been observed which may be assigned to $Ni^{2+}-Cu^{2+}$ strongly coupled mixed pairs in the state of total spin $S = 1/2$. This result represents a definite difference of magnetic behaviour from the case of the nickel(II) doped dicopper(II) tetra(μ-benzoato-O,O')bis(quinoline) complex, which has the same sandwich dimeric structure but shows spectra indicative of a $S = 3/2$ state. Apart from this difference, unusual EPR data are found such as pronounced misalignments of g with respect to the relevant pair axes and very large values of the hyperfine coupling constant of the copper nucleus, which characteristically recall that case.

Introduction

It is well known that a pair of exchange-coupled paramagnetic ion shows spin-hamiltonian parameters which may be largely different from the usual ones exhibited by the two ions in monomeric structures. When two different ions are involved ($S_1 \neq S_2$), such parameters are characteristically different for pair states corresponding to different total spin quantum numbers $S = |S_1 - S_2|, \ldots, S_1 + S_2$. Generally it is found that, in the strong isotropic exchange limit, the values agree well with a simple perturbative model in term of single-ion parameters, i.e. of the values characteristic of the two ions when uncoupled. Explicit formulas are given, for example, by Buluggiu [1, 2].

Following this model, the spectra of a $Ni^{2+}-Cu^{2+}$ system ($S_{Ni} = 1$, $S_{Cu} = 1/2$) in a first-order approximation should conform to the equations

$$S = 1/2\,, \quad \mathscr{H}_S = \mu_B \boldsymbol{H} \cdot \boldsymbol{g} \cdot \boldsymbol{S} + \boldsymbol{I}_{Cu} \cdot \boldsymbol{A}'_{Cu} \cdot \boldsymbol{S}\,, \tag{1}$$

$$\boldsymbol{g} = \tfrac{4}{3}\, \boldsymbol{g}_{Ni} - \tfrac{1}{3}\, \boldsymbol{g}_{Cu}\,, \tag{2}$$

$$\boldsymbol{A}'_{Cu} = -\tfrac{1}{3}\, \boldsymbol{A}_{Cu}\,; \tag{3}$$

$$S = 3/2\,, \quad \mathscr{H}_S = \mu_B \boldsymbol{H} \cdot \boldsymbol{g} \cdot \boldsymbol{S} + \boldsymbol{I}_{Cu} \cdot \boldsymbol{A}'_{Cu} \cdot \boldsymbol{S} + \boldsymbol{S} \cdot \boldsymbol{D} \cdot \boldsymbol{S}\,, \tag{4}$$

$$\boldsymbol{g} = \tfrac{2}{3}\, \boldsymbol{g}_{Ni} + \tfrac{1}{3}\, \boldsymbol{g}_{Cu}\,, \tag{5}$$

$$\boldsymbol{A}'_{Cu} = \tfrac{1}{3}\, \boldsymbol{A}_{Cu}\,, \tag{6}$$

$$\boldsymbol{D} = \tfrac{1}{3}\, \boldsymbol{D}_{Ni} + \tfrac{1}{3}\, \boldsymbol{\Delta}\,, \tag{7}$$

where $\boldsymbol{g}_{Ni}$, $\boldsymbol{g}_{Cu}$, $\boldsymbol{A}_{Cu}$, and $\boldsymbol{D}_{Ni}$ are the single-ion tensors $\boldsymbol{g}$, $\boldsymbol{A}$, $\boldsymbol{D}$ for nickel and copper ions and $\boldsymbol{\Delta}$ is the symmetric part of the anisotropic exchange tensor.

Recently, EPR data on a nickel-copper pair have been reported which contrast considerably with this expectation [3]. This fact is not surprising owing to the incomplete generality of the model. The interesting point is that the cited pair obtained by doping the dicopper(II) tetra(μ-benzoato-O,O')bis(quinoline) complex $[Cu_2(Bz)_4(Quin)_2]$ is, as far as we know, the only example examined to date of an heteronuclear pair adopting the well known sandwich structure of the copper acetate type, see Figure 1. Having in mind the historical importance of this dimeric arrangement in EPR and magnetic susceptibility studies, it

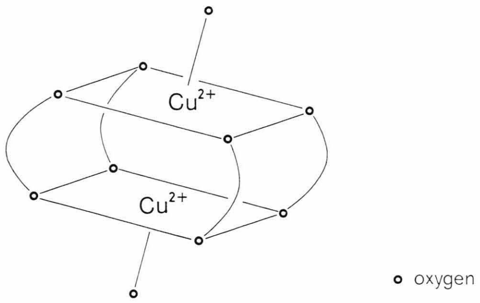

Fig. 1. Dimeric structure of copper acetate monohydrate.

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appears useful to increase the experimental information about similar systems and to clarify if the observed discrepancies are characteristic of the sandwich structure or merely accidental.

In the present paper we report preliminar results of an EPR study on $Ni^{2+}-Cu^{2+}$ pairs obtained by doping the pure copper acetate matrix and discuss these in the light of the available data.

Experimentals

Single crystals of nickel-doped copper acetate monohydrate were grown by slow evaporation from an aqueous solution which contained about 60% copper acetate and 40% nickel acetate. Previous data on the analogously grown zinc-doped complex [4, 5] suggest that nickel enters the crystals as substitutional impurity with a concentration of a few ‰. The composition of the crystals was checked by chemical analysis after the EPR measurement. The resultant Ni to Cu ratio was of about 0.1 atomic percent or less.

Electron paramagnetic resonance spectra were recorded at the X-band frequency by a Varian E-Line EPR spectrometer and at the Q-band frequency by a Varian V4502 EPR spectrometer. In both cases a 100 kHz field modulation was used. The magnetic fields were measured by means of a DPPH marker.

The direction of the magnetic field was regularly changed (by steps of 15°) to sweep three mutually orthogonal planes (crystal orientation was chosen casually). For each direction, EPR spectra were recorded at room temperature, at liquid nitrogen temperature, and (for the X-band only) at liquid helium temperature. The tensors $\boldsymbol{g}$, $\boldsymbol{D}$, $\boldsymbol{A}'_{Cu}$ were then determined with respect to these planes for all temperatures by a procedure similar to that of Geusic and Brown [6] for $\boldsymbol{g}$, extended to cover $\boldsymbol{D}$ and $\boldsymbol{A}'_{Cu}$ according to Lund and Vänngård [7], and corrected for second-order effects on $\boldsymbol{g}$ as proposed by Buluggiu and Vera [8].

Results and Discussion

The room and liquid nitrogen temperature spectra, see Fig. 2, may be described by the spin-hamiltonian

$$\mathscr{H}_S = \mu_B \boldsymbol{H} \cdot \boldsymbol{g} \cdot \boldsymbol{S} + \boldsymbol{S} \cdot \boldsymbol{D} \cdot \boldsymbol{S} + (\boldsymbol{I}_{Cu1} + \boldsymbol{I}_{Cu2}) \cdot \boldsymbol{A}'_{Cu} \cdot \boldsymbol{S}, \tag{8}$$

where $S = 1$ and $\boldsymbol{g}$, $\boldsymbol{D}$, and $\boldsymbol{A}'_{Cu}$ have the values given in Table 1. They coincide, as obvious, with the well known data of the undoped copper acetate complex [9, 10]. A specific discussion of these will, therefore, not be repeated here. We limit ourselves to recall some facts. Two distinct signals are present due to the two differently oriented $Cu^{2+}-Cu^{2+}$ dimeric units of the host matrix. Within the errors, the tensors $\boldsymbol{g}$, $\boldsymbol{D}$, and $\boldsymbol{A}'_{Cu}$ have coincident axes. These, as known [9], are parallel to the salient molecular directions with the maximum values (z axis) along the copper-copper direction and the y axis lying in the crystallographic ac-plane. This information can be utilized to deduce the orientation of the three mutually orthogonal planes with respect to the unit cell without a preliminary orientation of the crystal. So we obtain absolute rather than relative directions although crystal orientation was, as said, casual.

Owing to the antiferromagnetic character of the exchange interaction in the copper-copper pair ($J \sim 300\ \mathrm{cm}^{-1}$), the intensity of the copper acetate spectra decreases as temperature decreases and, below ~ 30 K, the signal of the host matrix dis-

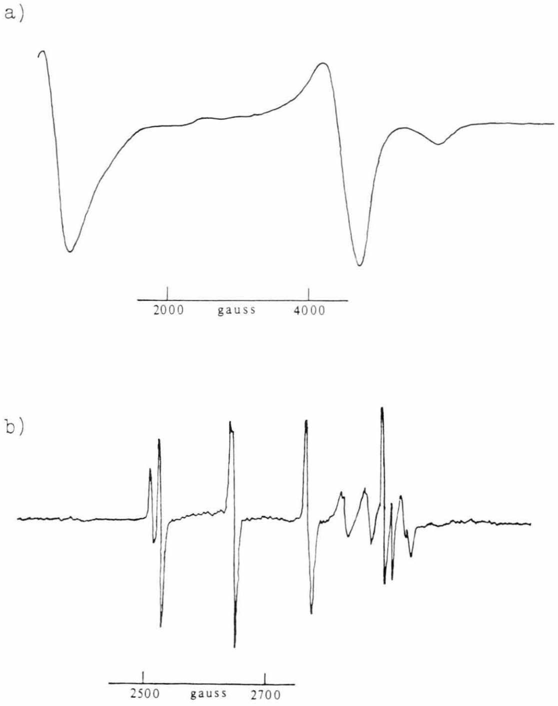

Fig. 2. Typical X-band EPR spectra of nickel-doped copper acetate monohydrate. a) Powder at $T = 296$ K. b) Single crystal at $T = 4.2$ K.

Table 1. EPR data on Ni(II)-doped Cu(II)acetate monohydrate. The values for the fine and hyperfine splitting constants are given, as usual, in cm^{-1}.

$Cu^{2+}-Cu^{2+}$ pair [a]			
$S = 1$, $\mathcal{H}_S = \mu_B \boldsymbol{H} \cdot \boldsymbol{g} \cdot \boldsymbol{S} + \boldsymbol{S} \cdot \boldsymbol{D} \cdot \boldsymbol{S} + (\boldsymbol{I}_{Cu1} + \boldsymbol{I}_{Cu2}) \cdot \boldsymbol{A}'_{Cu} \cdot \boldsymbol{S}$			
$g_z = 2.353 \pm 0.001$	$D_z = 0.219 \pm 0.001$	$A'_{Cuz} = 0.008$	
$g_x = 2.055 \pm 0.002$	$D_x = -0.097 \pm 0.001$	$A'_{Cux} < 0.001$	
$g_y = 2.076 \pm 0.001$	$D_y = -0.122 \pm 0.001$	$A'_{Cuy} < 0.001$	
$Ni^{2+}-Cu^{2+}$ pair [b]			
$S = 1/2$, $\mathcal{H}_S = \mu_B \boldsymbol{H} \cdot \boldsymbol{g} \cdot \boldsymbol{S} + \boldsymbol{I}_{Cu} \cdot \boldsymbol{A}'_{Cu} \cdot \boldsymbol{S}$			
$g_{z'} = 2.615 \pm 0.001$		$A'_{Cuz} = 0.0150 \pm 0.0001$ [c]	
$g_{x'} = 2.157 \pm 0.001$		$A'_{Cux''} \sim 0$	
$g_y = 2.346 \pm 0.001$		$A'_{Cuy''} = 0.0026 \pm 0.0005$	
mutual angles (deg)			
	$A'_{Cux''}$	$A'_{Cuy''}$	A'_{Cuz}
$g_{x'}$	54 ± 5	115 ± 5	47 ± 1
g_y	54 ± 8	37 ± 8	91 ± 2
$g_{z'}$	122 ± 3	66 ± 3	43 ± 1

[a] Values deduced from Q-band spectra ($\nu = 34.55$ GHz) at $T = 82$ K. The signs of D are relative rather than absolute. The A'_{Cu} values are from Ref. [9]. The directions in the crystal of the x, z, x' and z' axes are shown in Figure 3. Obviously, the y axis is perpendicular to the shown plane (K_2 direction).

[b] Values deduced from X-band spectra ($\nu = 9.11$ GHz) at $T = 4.2$ K.

[c] For the isotope Cu^{65} the value $A'_{Cuz} = 0.0160$ cm^{-1} was measured, in the exact ratio of the nuclear magnetic moments $\mu^{65}/\mu^{63} = 1.07$.

appears completely [9]. The spectrum due to the mixed $Ni^{2+}-Cu^{2+}$ pairs appears just in this range of low temperatures ($T < 15$ K). It consists of two distinct signals corresponding to the two copper-copper species of the matrix (Figure 2b). Each signal is splitted in four resonance lines of comparable intensity due to the hyperfine interaction with the copper nucleus ($I_{Cu} = 3/2$), the only nucleus in the pair having not zero magnetic moment.

The values and angular variation of the absorption fields are characteristic of an $S = 1/2$ system and may be closely reproduced by the spin-hamiltonian

$$\mathcal{H}_S = \mu_B \boldsymbol{H} \cdot \boldsymbol{g} \cdot \boldsymbol{S} + \boldsymbol{I}_{Cu} \cdot \boldsymbol{A}'_{Cu} \cdot \boldsymbol{S}, \quad (9)$$

where the values and mutual angles for the constants are given in Table 1. Figure 3 visualizes the directions in the crystal. Both the S and $\boldsymbol{g}$ data confirm that the signals are due to nickel-copper coupled pairs (Ni^{2+} paramagnetic). As a matter of fact, one notes that the $\boldsymbol{g}$ principal values, unusual for monomeric species of both ions, are very similar to the values previously reported for $Ni^{2+}-Cu^{2+}$ exchange-coupled systems in the $S = 1/2$ state [11, 12]. With respect to those cases, however, noticeable differences are found. In particular, two axes of $\boldsymbol{g}$ (x', z') deviate sensibly (ca. 45°) from the relevant molecular directions, and the values of the hyperfine constant appear too large when compared with (3). However, the $\boldsymbol{A}'_{Cu}$ principal values are found approximately in the expected directions with the maximum value ($\boldsymbol{A}'_{Cuz}$) along the copper-copper axis of the host pair. This circumstance allows us to identify unambiguously the copper-copper species related to the single nickel-copper signal.

It is interesting to compare the present results with those of Bencini et al. [3] relative to the $Cu_2(Bz)_4(Quin)_2$ host matrix. The high temperature data are almost coincident. This confirms from a magnetic point of view the substantial equivalence of the copper-copper sites. In spite of this, the liquid helium temperature spectra (i.e. the nickel-copper spectra) appear completely different. In [3] the signals are indicative of a state $S = 3/2$ in presence of strong crystal field splitting. However, some facts are noted which recur in the two cases. For example, the mixed pair spectra are observable in the same temperature region. Another point is that a small angle (14°) between the nickel-copper g_z axis and the copper-copper direction was observed also in $Cu_2(Bz)_4(Quin)_2$. We are not able, at present, to give the proper explanation of this misalignment. We note only that, as an effect, a sensible alignment between the $\boldsymbol{g}$ tensors of the two different units is produced. Thus, apart from the axes y_1 and y_2 which within the errors coincide in the crystallographic ac-plane both for nickel-copper and copper-copper pairs, one measures an angle of ca. 20° between z'_1 and z'_2 (x'_1 and x'_2) for nickel-copper pairs to be compared with an angle of ca. 66° between the copper-copper directions z_1 and z_2 (x_1 and x_2), see Figure 3. This fact may well be due to skew-symmetric intra-pair exchange or to some local stretching effect induced by the accomodation of nickel in the copper site. However, in principle it may be also due to relevant inter-pair exchange coupling [13]. To decide this, it would be advantageous to compare EPR spectra recorded at different microwave frequencies. Unfortunately we are

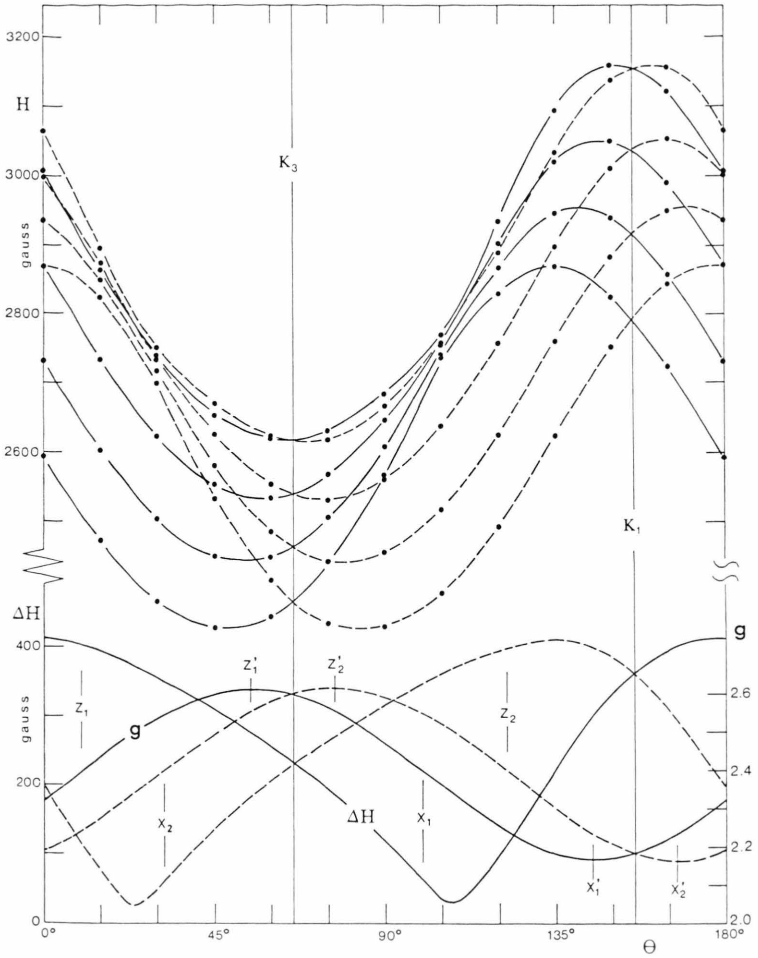

Fig. 3. Resonance fields and principal directions (± few degrees) in the plane of largest magnetic anisotropy at $\nu = 9.106$ GHz and $T = 4.2$ K. The plane contains the copper-copper direction (z axis) of both the dimeric species and coincides with the K_1K_3-plane of [9]. Within the errors it contains also the x, x' and z' axes. The different nickel-copper pairs are distinguished by solid or dashed lines. The points are the experimental fields. The lines (π-periodic) are the theoretical fields deduced from the data of Table 1. The total hyperfine spread of the fields (ΔH) and the g factor are also visualized.

not able to do this because our Q-band apparatus is not equipped for liquid helium temperatures.

As regards the hyperfine interaction, A'_{Cu} results (as said) substantially different from the value $A_{\mathrm{Cu}}/3$ expected on the basis of (3). Paradoxally, apart from the sign not revealed by EPR, it appears closer to the single-ion value A_{Cu} as measured in zinc-doped copper acetate [4, 5]. In $Cu_2(Bz)_4(Quin)_2$ a comparably large difference of values was observed for $S = 3/2$. That was considered related to the small reduction from $A_{\mathrm{Cu}}/3$ measured by Kokoszka et al. [12, 14] for nickel-copper pairs in the $S = 1/2$ state and was ascribed to super-transferred hyperfine interaction due to the closeness of the nickel unpaired electrons to the copper nucleus.

If we take into account the super-transferred hyperfine interaction by the relevant spin-hamiltonian

$$\mathscr{H}_{\mathrm{hyp}} = \boldsymbol{S}_{\mathrm{Cu}} \cdot \boldsymbol{A}_{\mathrm{Cu}} \cdot \boldsymbol{I}_{\mathrm{Cu}} + \boldsymbol{S}_{\mathrm{Ni}} \cdot \boldsymbol{A}_{\mathrm{STHI}} \cdot \boldsymbol{I}_{\mathrm{Cu}}, \quad (10)$$

where $\boldsymbol{A}_{\mathrm{STHI}}$ is an effective tensor, in place of (3) and (6) we obtain

$$A'_{\mathrm{Cu}} = -\frac{A_{\mathrm{Cu}}}{3} + \frac{4}{3} A_{\mathrm{STHI}}, \quad (11)$$

$$A'_{\mathrm{Cu}} = \frac{A_{\mathrm{Cu}}}{3} + \frac{2}{3} A_{\mathrm{STHI}}, \quad (12)$$

respectively. Thus, changes from $A_{\mathrm{Cu}}/3$ of opposite sign for $S = 1/2$ and $S = 3/2$ have to be expected. The point is that the pairs examined in [12, 14] are not of a sandwich type and so do not seem very suitable for a comparison. In the more proper case of the copper acetate matrix for $S = 1/2$ we observe a notable increase rather than a weak reduction of A'_{Cu} with respect to $A_{\mathrm{Cu}}/3$. Our $A'_{\mathrm{Cu}z}$ value

($\pm 150 \times 10^{-4}$ cm^{-1}) and that of Bencini et al. [3] ($\pm 94 \times 10^{-4}$ cm^{-1}), depending on the unknown mutual sign, may be contemporaneously accounted for by (11) and (12) in one of the two cases: $A_{\mathrm{Cu}z} = -38 \times 10^{-4}\,\mathrm{cm}^{-1}$ and $A_{\mathrm{STHI}z} = -122 \times 10^{-4}\,\mathrm{cm}^{-1}$ or $A_{\mathrm{Cu}z} = -338 \times 10^{-4}\,\mathrm{cm}^{-1}$ and $A_{\mathrm{STHI}z} = 28 \times 10^{-4}\,\mathrm{cm}^{-1}$, where the sign of $A_{\mathrm{Cu}z}$ is arbitrarily assumed negative. Therefore, when compared with usual single-ion values, the copper role appears underestimated in the first possibility and overestimated in the second one. Thus we conclude that anomalously large values of the hyperfine coupling constant appear characteristic of the $Ni^{2+}-Cu^{2+}$ sandwich structure in both possible total spin states. However, a simple STHI mechanism does not appear to be sufficient to explain such anomalies.

As regards the value of the intra-pair exchange, the fact that at low temperatures $S = 1/2$ spectra are observed seems to support antiferromagnetic nickel-copper coupling. On the basis of a similar argument in $Cu_2(Bz)_4(Quin)_2$, ferromagnetic coupling no smaller than 20 cm^{-1} has been hypothized. This drastic difference of magnetic behaviour between closely similar structures appears to us not completely convincing. It seems to suggest that the EPR assignment of a ferromagnetic or antiferromagnetic character for a nickel-copper bond is another not trivial matter, possibly due to S-dependent spin-lattice effects.

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