Dipolar fields in a low-dimensional paramagnet: Cu(L-leucine)$_2$

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Abstract. A strong temperature variation in the gyromagnetic factor of the electron paramagnetic resonance line of bis(L-leucinato) copper (II) has been observed in single-crystal samples between 2 and 300 K. In order to characterize the magnetic properties and to evaluate the importance of short-range order effects we have also measured the magnetic susceptibility on powder samples. The data on the g-shift are interpreted as the combined effect of the dipole–dipole interaction between copper ions, and the spin polarization induced by the applied magnetic field when the temperature is lowered. The layered distribution of the Cu ions in the crystal lattice makes this effect non-negligible and determines the quasi-two-dimensional behaviour of the shift.

1. Introduction

The temperature dependence of EPR spectra due to the change in level population when $kT \leqslant h\nu$ has been studied by Kambe and Usui [1] and in more detail by McMillan and Opecowsky [2] and by Svare and Seidel [3]. The position and shapes of the resonances were discussed using the temperature-dependent line moment theory. Qualitatively, the idea is that the magnetization of a paramagnetic crystal, at low temperatures and in a strong field, may shift the position of the resonance line; similarly, this same effect is expected to lead to a decrease in the linewidth as the local order is increased.

The temperature dependence of the resonance field in low-dimensional systems was discussed by Nagata and Tazuke [4], who studied this effect in short-range-ordered Heisenberg chains in $CsMnCl_3 \cdot 2H_2O$. The one-dimensional behaviour of the spin dynamics in these materials, where the Mn^{2+} ions are arranged in chains, was described by Nagata and Tazuke using analytical results [5] for the spin-correlation functions, and a proper prediction of the observed g-shifts was obtained.

A similar temperature variation in the gyromagnetic factor to that described above was observed in recent years in single crystals of four Cu(II) aminoacid complexes [6]. Because Cu^{2+} ions are arranged in layers in these compounds, and because of the striking similarity with the shifts observed in the Mn^{2+} linear chain compound, this behaviour was related with short-range magnetic correlations within the copper planes. However, while the g-shifts in the Mn compounds were observed in a temperature range where the chains were magnetically short-range ordered, the variations in line position in the Cu layered aminoacid compounds were observed at $T \leqslant 50$ K, i.e.

at temperatures where magnetic order due to exchange coupling ($J/k \simeq 0.2$ K) [7] is not expected. An explanation for this different behaviour was proposed in [8] by considering the dipolar fields originating in the spin system to be polarized by the external field as the temperature is lowered. A more formal approach to this problem was recently given by Calvo and Passeggi [9]. Using the linear response formalism and the Anderson–Kubo theory, they discussed the effects due to the contributions of anisotropic exchange (symmetric and antisymmetric), and of the hyperfine interaction.

In this work we analyse the temperature-dependent g-shift in bis(L-leucinato)Cu(II) single crystals [10] (Cu(L-leu)$_2$) measured at Q band ($\nu \simeq 35$ GHz). All previously reported measurements of this temperature dependence in copper aminoacid salts were done at X band ($\nu \simeq 9$ GHz), and it was of interest to determine the field dependence of the g-shift. In Cu(L-leu)$_2$ the distance between copper layers is larger (more than 30%) than in other studied copper aminoacid complexes, and we expected to observe a relative increase in short-range order effects. In order to determine the importance of spin correlation, we made magnetic susceptibility measurements in the same temperature range. We show that correlation effects are negligible, and we discuss our data with the simple picture of a local field at each Cu^{2+} site due to the dipolar interaction with the other copper moments polarized by the external magnetic field. This effect, usually not taken into account, is important in these copper aminoacid complexes because of the layered distribution of the copper ions in the lattice.

2. Experimental results

The molecular and crystal structure of Cu(L-leu)$_2$, Cu(H$_2$NCH(CO$_2$)CH$_2$CH (CH$_3$)$_2$)$_2$, was reported in [11]. It crystallizes in the monoclinic P2$_1$ space group with two molecules per unit cell, related by a 180° rotation around the $\hat{b}$ axis. Thus, there are two chemically equivalent but magnetically non-equivalent types of copper ion. The copper ions are arranged in layers parallel to the a–b plane, separated by 1.44 nm; within a layer, each copper ion has six nearest neighbours in a hexagonal arrangement at about 0.54 nm, and connected by carboxylate and hydrogen bridges.

Measurements were made on thin-plate-like single crystals of dimensions 0.5 mm × 1 mm × 0.1 mm.

2.1. Magnetic resonance

We performed magnetic resonance measurements on an EPR spectrometer operating at Q band (35 GHz) on oriented single crystals of Cu(L-leu)$_2$.

The gyromagnetic factor g of the single spectral line observed was measured

(i) as a function of angle in three crystal planes, for fixed temperatures of 2.7, 4.1, 140 and 293 K and

(ii) as a function of temperature between 2 and 300 K for fixed orientations of the applied field, one parallel and the other perpendicular to the copper planes.

In figure 1 we show the values of $g^2(\theta, \phi)$ measured in the three crystal planes and at different temperatures. The angles θ and ϕ are defined in a coordinate system where $\hat{x} = \hat{a}$, $\hat{y} = \hat{b}$ and $\hat{z} = \hat{c}' = \hat{a} \times \hat{b}$, and where

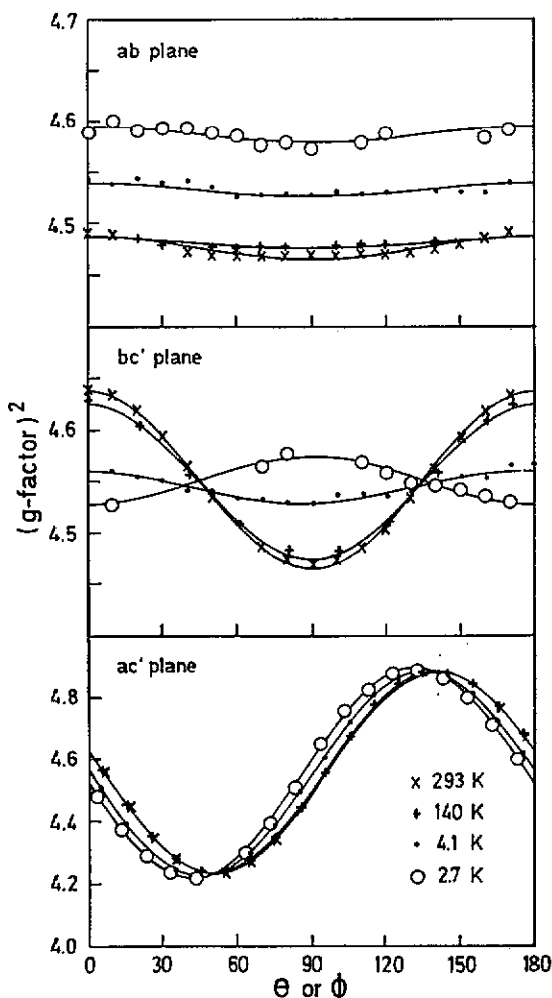$$\hat{h} = H/|H| = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta). \tag{1}$$

Figure 1. Angular variation in the squared gyromagnetic factor measured at different temperatures in the three crystal planes of Cu(L-leu)₂ single crystals. The full curves were obtained at each temperature by fitting the data to a g^2-tensor. The polar and azimuthal angles θ and ϕ are defined in the coordinate system with $\hat{x} = \hat{a}$, $\hat{y} = \hat{b}$, $\hat{z} = \hat{c}' = \hat{a} \times \hat{b}$.

Figure 2 displays the temperature variation in the gyromagnetic factor for H applied along two crystal axes $\hat{b}$ and $\hat{c}'$.

The data in figures 1 and 2 show an unusually large variation in $g^2(\theta, \phi)$ with temperature. The gyromagnetic factor increases with decreasing temperature when H is in the a–b plane of the copper layers, and it decreases with decreasing temperature when $H \parallel \hat{c}'$, the normal to these layers.

The data for each temperature were fitted to an effective spin Hamiltonian

$$\mathcal{H} = \mu_B S \cdot \mathbf{g}_T \cdot H \tag{2}$$

where μ_B is the Bohr magneton, $\mathbf{g}_T$ the gyromagnetic tensor and S the effective spin operator ($S = \frac{1}{2}$). The values for $g^2(\theta, \phi) = \hat{h} \cdot \mathbf{g} \cdot \mathbf{g} \cdot \hat{h}$ were used to evaluate the tensor $\mathbf{g}_T^2$. In table 1 the components of the $\mathbf{g}_T^2$ tensor are given, as obtained by a least-squares fitting of the data. The full curves in figure 1 show very good agreement between measured and calculated values.

The data were analysed following the method in [12]. The octahedral coordination around the copper ions leads us to assume axial symmetry for the molecular
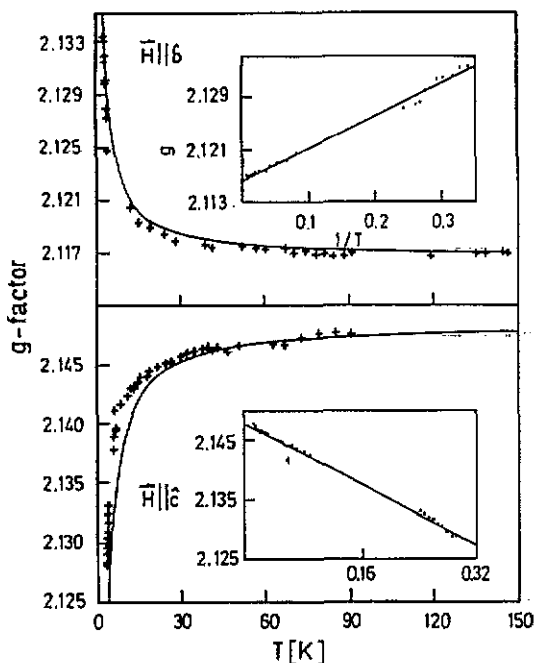
Figure 2 Temperature variation in the g-factor measured between 2 and 300 K for H along the crystal axes $\hat{b}$ and $\hat{c}' = \hat{a} \times \hat{b}$. The inset shows the value of g as a function of inverse temperature, with a linear square fitting. The full lines correspond to the model discussed in the text.

Table 1. Values of the components of the g_T^2 tensors, the molecular factors $g_{\parallel}$ and $g_{\perp}$, the polar angle Θ_M and azimuthal angle Φ_M, giving the orientation of the molecular axis at one site in the $x, y, z \equiv a, b, c'$ reference system, and the angle 2α between the molecular axis of the two copper sites, calculated from the data at the different temperatures of the experiment. The components xy and yz are zero owing to the crystal symmetry. The values of Θ_M, Φ_M and 2α in parentheses are calculated from crystallographic data [11].

	Value at the following temperatures			
	293 K	140 K	4.1 K	2.7 K
$(g^2)_{xx}$	4.483(1)	4.490(1)	4.542(1)	4.593(2)
$(g^2)_{yy}$	4.467(1)	4.474(1)	4.527(1)	4.577(2)
$(g^2)_{zz}$	4.634(1)	4.628(1)	4.563(1)	4.526(2)
$(g^2)_{xz}$	0.316(1)	$-0.319(1)$	$-0.330(1)$	$-0.338(2)$
$g_{\parallel}$	2.262	2.264	2.278	2.293
$g_{\perp}$	2.058	2.057	2.055	2.054
Θ_M (deg)	132 (133.5)	132	127	123
Φ_M (deg)	44 (44.7)	44	44	44
2α (deg)	118 (118.6)	117	112	108

gyromagnetic tensors, with $g_{\perp}$ in the equatorial plane of ligands, and $g_{\parallel}$ perpendicular to it. Thus, we can calculate $g_{\parallel}$, $g_{\perp}$, the orientation (Θ_M, Φ_M) of the molecular axis of one site and the angle 2α between the axes of the two copper sites for each temperature. These values are given in table 1, together with those calculated from crystallographic data [11]; the agreement between these values and our results at 293

and 140 K is excellent, indicating that axial symmetry is a good assumption for our problem. The room temperature data are in good agreement with those obtained by Steren *et al* [7].

When the temperature is lowered, there is a significant variation in these angles, indicating that some interaction was not included in the Hamiltonian in equation (2).

The insets in figure 2 show that the *g*-shift along the crystal axes can be well described by a $1/T$-dependence:

$$g_d(T) = g_d(0) + C_d/T \tag{3}$$

for $d = \hat{b}$ or $\hat{c}'$. We obtained from a least-squares fit (full lines in the inset of figure 2) the values

$$g_b(0) = 2.1162(3) \qquad C_b = 50(1) \times 10^{-3} \text{ K}$$
$$g_c(0) = 2.1478(1) \qquad C_c = -64(1) \times 10^{-3} \text{ K.}$$

The above experimental results can be interpreted with a simple phenomenological model. Since no structural or magnetic phase transitions are observed as the temperature is lowered, we attribute the observed temperature dependence as due to magnetic interactions between Cu^{2+} ions that induce a shift in the gyromagnetic factor. We introduce a gyromagnetic tensor g_0 for isolated Cu ions; when those ions are in the magnetic lattice, the effective field acting on them is given by the applied external field H plus an internal field H_i due to Cu neighbours. Then equation (2) is replaced by

$$\mathcal{H} = \mu_B S \cdot \mathbf{g}_0 \cdot (H + H_i). \tag{4}$$

At high temperatures the spins are randomly oriented and $H_i = 0$, but $H_i \neq 0$ at low temperatures, if there is a preferred spin orientation.

The *g*-shifts that we measured at 35 GHz are of the same magnitude as those observed in similar compounds and at lower frequencies (9 GHz) [6]. Hence, we conclude that it is a real '*g*-shift', i.e. that the internal field H_i is proportional to the external field H. We then assume the following relationship:

$$H_i = 4\pi \chi_T H \tag{5}$$

with χ_T a dimensionless tensor quantity, and then, from equations (4) and (5), we obtain for the gyromagnetic tensor

$$\mathbf{g}_T = (1 + 4\pi \chi_T)\mathbf{g}_0. \tag{6}$$

Equation (6) shows that the *g*-shift does not depend on the applied magnetic field (i.e. on the frequency), and that the temperature dependence is that due to χ_T.

It should be kept clearly in mind that, although we have been referring to a temperature-dependent *g*-shift, it could be more appropriate to talk about a temperature dependence of the magnetic field for resonance due to a temperature-dependent internal field, as revealed by equations (4) and (6). The concept of '*g*-shift' is used in order to differentiate it from an internal magnetic field not proportional to the external field, as observed, for example, in the EPR of magnetic impurities in magnetically ordered compounds [13]. In the latter case, the temperature-dependent shift of the field for resonance does not depend essentially on the frequency of the EPR experiment, while in our case it is the apparent *g*-value that is independent of frequency.

2.2. Magnetic susceptibility

Insight into the origin of the internal field described above can be obtained through magnetic susceptibility measurements.

Magnetic susceptibility of a powder sample as a function of temperature was measured in the range from 2 to 300 K using a Faraday magnetometer. Figure 3 shows the temperature dependence of the inverse of the magnetic susceptibility, where we have subtracted the diamagnetic contribution originated in the L-leu molecules and the Cu^{2+} ions, and a small positive constant contribution $\chi_{VV} = 1.3 \times 10^{-3}$ emu g^{-1} due to the Van Vleck paramagnetism of the Cu^{2+} ions in octahedral coordination.
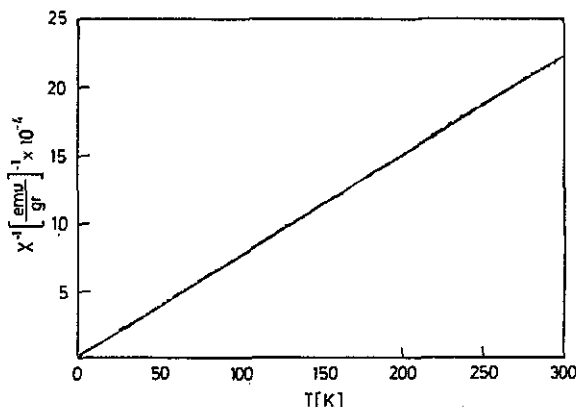

Figure 3. Magnetic susceptibility data obtained for a powder sample of $Cu(L\text{-leu})_2$ in a Curie-type χ^{-1} versus T plot. The full line represents a square fitting with a Curie law, after subtracting diamagnetic and Van Vleck paramagnetic contributions from the ions.

A perfect paramagnetic behaviour is observed in all the measured temperature range, down to 2 K. It was fitted with a Curie–Weiss law $\chi(T) = C_{CW}/(T + T_{CW})$ (full line in figure 3), yielding the values $C_{CW} = 1.31(1) \times 10^{-3}$ emu K g^{-1} and $T_{CW} = 0.54(1)$ K. From C_{CW} we obtained the effective magnetic moment $\mu_{eff} = 1.848(7)\mu_B$, which agrees, within experimental error, with that calculated from our high-temperature EPR g-factor ($\mu_{eff} = 1.843(1)\mu_B$). Using mean-field relations, an antiferromagnetic exchange constant $J/k \simeq 0.18$ K can be derived from T_{CW}, in accordance with the value obtained from an analysis of the room-temperature EPR linewidth in [7].

It should be pointed out that no deviations from a Curie–Weiss law due to short-range effects are observed down to the lowest measured temperature (2 K)†.

3. Discussion

The measured experimental data presented, together with the structural information given in [11], show that, in the temperature range from 2 to 300 K, $Cu(L\text{-leu})_2$ can be considered as a low-dimensional paramagnet.

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† Specific-heat measurements in a similar copper complex, $Cu(\alpha\text{-AIB})_2$ [8], support the idea that magnetic correlations in these compounds are negligible above 5 K. In fact, at 0.45 K, the magnetic entropy is only 14% lower than the maximum value $S = R \ln 2$.

All the characteristics of the internal field described in equation (5), i.e. the $1/T$-dependence, the proportionality with the applied magnetic field H and the anisotropy reflecting the layered distribution of the Cu^{2+} ions, can be accounted for by considering the local field produced at a Cu^{2+} site due to the dipolar interaction with the other copper magnetic moments. It is well known that, for a laminar distribution of magnetic moments, the induced dipolar field evaluated at a certain site is parallel to the external field when applied parallel to the plane but is antiparallel if it is applied perpendicular to the plane (figure 4). This is consistent with the observed anisotropy of the g-shift as implied by equation (6); the g-factor will increase with decreasing temperature when the external field is applied parallel to the copper layers and will decrease when applied normal to the layers.
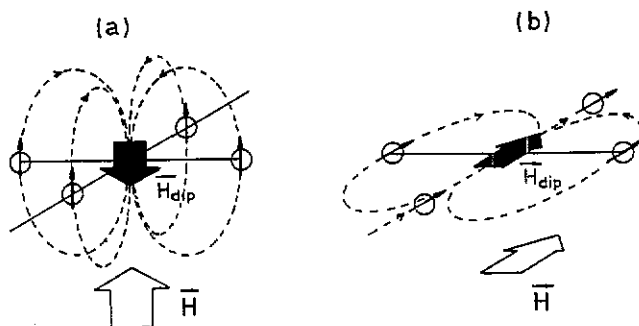

Figure 4. Schematic diagram of the induced dipolar fields in a planar arrangement of magnetic moments, for (a) H normal to the plane and (b) H parallel to the plane.

In order to obtain a quantitative estimation of this effect, we have to evaluate the local field

$$H_{\text{local}} = H + H_{\text{dip}} \tag{7}$$

with

$$H_{\text{dip}} = \sum_{\mu} \frac{3(\hat{n} \cdot \mu)\hat{n} - \mu}{r^3} \tag{8}$$

where μ is the magnetic dipolar moment, $\hat{n}$ the position versor and r the distance from the dipole to the considered position.

Dipoles at distances greater than perhaps ten lattice constants from the reference site make a smoothly varying contribution to this sum, a contribution which may be replaced by a surface integral [14]. Hence, the sum over all dipoles can be grouped in two terms: one due to the particular discrete distribution of dipoles in the lattice, and the other a form factor described by a demagnetization factor [15]. The discrete summation near the reference site is zero in the case of a cubic or disordered array, but non-zero in the general case. Evaluation of equation (8), using the structural data in [11] and the g-factor obtained from the high-temperature EPR, gives the following internal fields when the external field H is applied in the $\hat{b}$ or $\hat{c}'$ direction:

$$H_b = 2.55 \times 10^{-2} H/T \qquad H_{c'} = -4.61 \times 10^{-2} H/T.$$

Here T is the numerical value of the absolute temperature. It is important to note that, although the discrete part in equation (8) is the most important, because of the platelet structure of the sample the demagnetization factor contributes with a similar anisotropy and temperature behaviour to about 25% of the total magnitude of the internal field. This internal field corresponds to a g-shift given by

$$\Delta g_b = 54 \times 10^{-3}/T \qquad \Delta g_{c'} = -99 \times 10^{-3}/T.$$

These values should be compared with the experimental data in equation (3). We show in figure 2 by full curves the theoretical curve obtained in this way for both orientations. The agreement between the experimental values and the predictions of our model are acceptable, indicating that it contains the most relevant physical ingredients for our problem.

As a concluding remark, we could say that the apparent anomaly of the g-factor can be simply understood as originating from internal dipolar magnetostatic fields in a low-dimensional paramagnet. In fact, only structural information is required to provide acceptable predictions of the magnitude, the anisotropy and the temperature and external field dependences of the observed g-shift.

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