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Single-crystal EPR study of the bimetallic ferrimagnetic chain MnCu(EDTA)·$6H_2O$

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Abstract

A single-crystal EPR study of the bimetallic chain compound MnCu(EDTA)·$6H_2O$ is reported. The angular dependence of the linewidth is discussed in relation to the magnetic dipole–dipole interaction, manganese zero-field splitting (ZFS) and copper hyperfine coupling. The calculation of the second moments indicates that ZFS is comparable to the dipolar contribution. The EPR data support the one-dimensional character of the compound.

Introduction

The behavior of one-dimensional ferrimagnets has been widely investigated in the last decade from both theoretical [1–4] and experimental points of view [5–11]. Different experimental techniques such as magnetic susceptibility or heat capacity measurements are currently used for their characterization, and novel theoretical models are now available to discuss these static properties. EPR is also being employed to obtain useful information on the spin dynamics and on the interactions of these low-dimensional materials [12–14].

As a part of our studies on 1D ferrimagnets, we have examined the single-crystal EPR spectra of the bimetallic ferrimagnetic chain MnCu(EDTA)·$6H_2O$ (in short [MnCu]). This compound belongs to an extensive isostructural series of infinite zigzag chains [5–7] built up with alternated 'hydrated' and 'chelated' octahedra bridged by carboxylate groups: –$Mn(H_2O)_4O_2$–Cu(EDTA)–$Mn(H_2O)_4O_2$–Cu(EDTA)– (Fig. 1). Its magnetic properties [7] showed the characteristic features of 1D ferrimagnets, with a minimum of the χT product at $T=0.28$ K, and were discussed from a Heisenberg model to give an antiferromagnetic exchange interaction of *c*. 0.15 cm^{-1} ($H=2JS_iS_j$). Furthermore, the presence of an antiferromagnetic ordering at $T_c=0.20$ K allowed us to estimate an interchain to intrachain ratio of the order of 10^{-3}, emphasizing the good one-dimensional character of the compound.

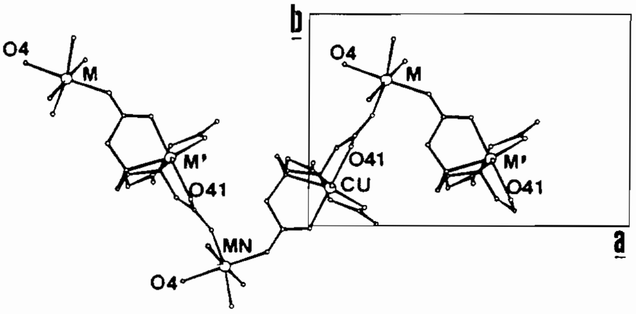

Fig. 1. Pluto view of the bimetallic chain along the *ac* plane. In our case M = Mn(II) and M' = Cu(II).

Experimental

Suitable single crystals of MnCu(EDTA)·$6H_2O$ were obtained from aqueous solutions containing the tetrasodic salt of the EDTA ligand and the corresponding amounts of the metal nitrates, after addition of acetone until incipient turbidity and slow cooling. Well shaped single crystals were oriented by using a Nonius Enraf CAD-4 four circles diffractometer. Single-crystal spectra were recorded at both X and Q band frequencies with a Varian E9 spectrometer. In the X band experiment the crystal was rotated by means of a goniometer and a quartz rod, while at the Q band frequency the magnet was rotated. Low temperature spectra were obtained only at the X band, by use of an Oxford-Instruments ESR continuous flow cryostat.

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Results and discussion

Single-crystal EPR spectra of a crystal showing well developed $\bar{1}00$, $\bar{1}10$, $\bar{1}10$, $\bar{1}\bar{1}0$ and 110 faces were recorded with the static magnetic field in the *bc*, *ac* and *ab* planes of the orthorhombic lattice $Pna2_1$. Only one signal centered at $g=2.0$ was observed for each orientation of the crystal in the static magnetic field, at both X and Q band frequencies. No half field transitions are observed.

The angular dependence of the linewidth in the three principal planes is given in Fig. 2. The room temperature values obtained at X and Q band frequencies compare well in the *ab* and *bc* planes, the worst agreement being found in the *ac* plane, where a difference as large as 30 G was observed in some orientations. However, the difference never exceeds the 10–12% of the X band linewidth value, allowing us to assume an essentially frequency independent linewidth with experimental error. The more pronounced angular dependence of the linewidth is observed in the *ac* plane, with maxima along the two crystal axes ($\Delta B_{pp}(a^X)=245$ G and $\Delta B_{pp}(c^X)=255$ G at room temperature) and a minimum ($\Delta B_{pp}=130$ G) at about 45°. The low temperature spectra show a general broadening of the lines ($\Delta B_{pp}(a^{LT})=308$ G, $\Delta B_{pp}(b^{LT})=233$ G and $\Delta B_{pp}(c^{LT})=285$ G) without any evidence of g shift. The values observed for the linewidths clearly indicate that the exchange narrowing regime is not reached in the present compound. We will try to analyze the different contributions to the broadening of the EPR lines in order to have more insight into the electronic structure of the [MnCu] ferrimagnetic chain. We will examine the broadening effects of the dipolar coupling, of the manganese(II) single ion zero-field splitting, and of the hyperfine coupling of Cu(II) by computing their contributions to the second moment of the EPR lines.

The dipolar contribution to the second moment can be evaluated using the Kubo-Tomita formalism [16]. For identical spins this is given by

$$M_2^{\text{dip}}=(3/4)S(S+1)\sum_i\sum_j r_{ij}^{-6}\{(3\cos^2\theta_{ij}-1)^2 + \sin^4\theta_{ij}\exp[-(1/2)(2\omega_o/\omega_e)^2] + 10\cos^2\theta_{ij}\sin^2\theta_{ij}\exp[-(1/2)(\omega_o/\omega_e)^2]\} \quad (1)$$

where ω_o and ω_e are the Zeeman and exchange frequencies, respectively, and θ_{ij} and r_{ij} are the angle formed by the static magnetic field with the vector connecting the two paramagnetic interacting centers, and the distance between them, respectively. In our case, due to the presence of two different ions in the chain, when we calculate the Mn–Cu interactions we change the $S(S+1)$ term by $2S_{Mn}(S_{Mn}+1)S_{Cu}(S_{Cu}+1)/[S_{Mn}(S_{Mn}+1)+S_{Cu}(S_{Cu}+1)]$. For [MnCu] an exchange interaction of $2J\approx 0.30$ cm^{-1} was obtained by magnetic and specific heat measurements [7]. In a tridimensional spin system, when the exchange frequency, ω_e, becomes comparable to the Zeeman ones ($\omega_o\approx 0.31$ cm^{-1} and ≈ 1.17 cm^{-1} at X and Q band frequency, respectively), the importance of the non-secular terms in determining the dipolar broadening of the EPR lines strongly depends on the ω_o/ω_e ratio, and a frequency dependence of the linewidth is expected with broader lines at lower frequency. On the other hand, in the one-dimensional systems the modulation provided by the Zeeman interaction is fast enough to destroy the long time divergence of the non-secular term and the secular term of the linewidth is expected to dominate over the other two non-secular terms, due to spin diffusion effects [16, 17]. This hypothesis is in agreement with the results, which show that the calculated variation of the dipolar contribution to M_2 allows us to reproduce the angular behavior only when the secular term is considered (Fig. 3). In particular this term reproduces the large angular dependence of ΔB_{pp} in the *ac* plane, with a minimum of ΔB_{pp} between a and c; although the agreement is worse in the other two planes, the smaller angular dependence in these is also reproduced.

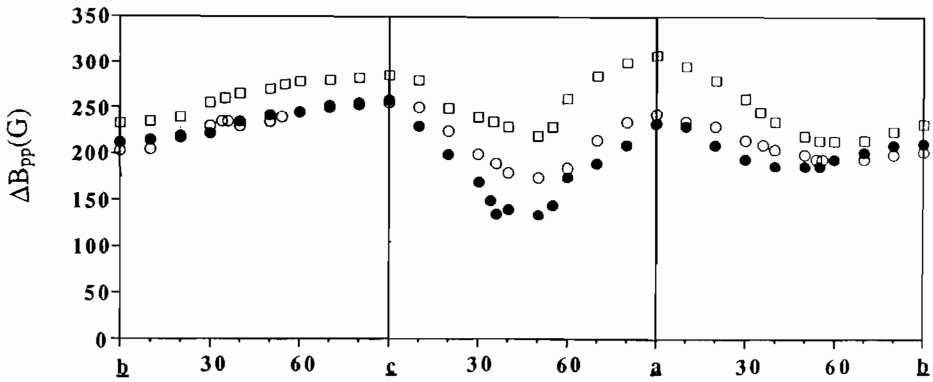

Fig. 2. Angular dependence of the linewidth ΔB_{pp} (G) in the three crystallographic planes at X band (room temperature (○) and low temperature (□)) and Q band (●).

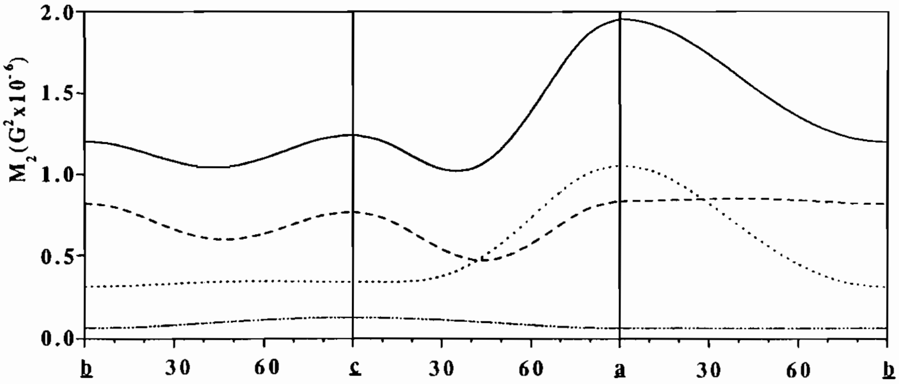

Fig. 3. Calculated total second moment (——) showing the three contributions: the secular part of the dipolar second moment (– – –), the ZFS of Mn(II) (·····) and the hyperfine of Cu(II) (–·····–··).

The single-ion contributions (ZFS of Mn(II) and hyperfine coupling of Cu(II)) depend on the directions and values of the corresponding axial tensors. This information can be obtained from an EPR study of the isostructural ZnZn(EDTA)·6H_2O compound.

An axial single ion ZFS gives a contribution to the second moment of the type [16]

$$\begin{aligned} M_2{}^{\mathrm{zfs}} = {} & (1/20)(2S-1)(2S+3)D^2\{(3\cos^2(\phi)-1)^2 \\ & + \sin^4(\phi)\exp[-(\omega_o/\omega_e)] \\ & + 10\cos^2(\phi)\sin^2)\phi)\exp[-(1/2)(\omega_o/\omega_e)^2]\} \end{aligned} \quad (2)$$

where ω_o and ω_e have been defined above, and ϕ is the angle of the magnetic field with the unique axis of the zero-field splitting tensor, D. From the powder spectrum of a sample containing a ratio Mn/Zn of ~1% (Fig. 4(a)) we obtain $|D| \approx 5.4 \times 10^{-3}$ cm^{-1}. This value leads to a contribution to M_2 which has the same order of magnitude as the dipolar one. Information on the directions of D can be obtained from a single crystal EPR study of a Mn(II)-doped [ZNZn] sample. The spectra along the three crystal axes are shown in Fig. 4. The very small anisotropy of Mn(II), together with the presence in an orthorhombic crystal of four magnetically non-equivalent sites, prevented a fit of the D-tensor from being obtained. However, the fact that along a, the signals are observed over a more extended field range than along b and c, suggests that the axial direction of D is not too far from a. With this consideration in mind, we have found that the agreement with the experimental angular dependence of the linewidth can be improved by assuming that the ZFS is directed along the Mn–O4 direction, which is at ~25° from a, 70° from b, and 75° from c. In particular, the variation of ΔB_{pp} in the ab plane is now better reproduced.

As regards the Cu(II) ion, we observe that its coordination polyhedron can be described as an elongated octahedron with the axial direction along the atom O41 (see Fig. 1). This ion exhibits an axial EPR spectrum [6] with $g_{\parallel} = 2.27$ and $g_{\perp} = 2.02$, and a hyperfine coupling $A_{\parallel} = 159$ G. From these data we can evaluate the hyperfine contribution to M_2 using the expression derived for axially symmetric g and A tensors with common principal axes [15, 18].

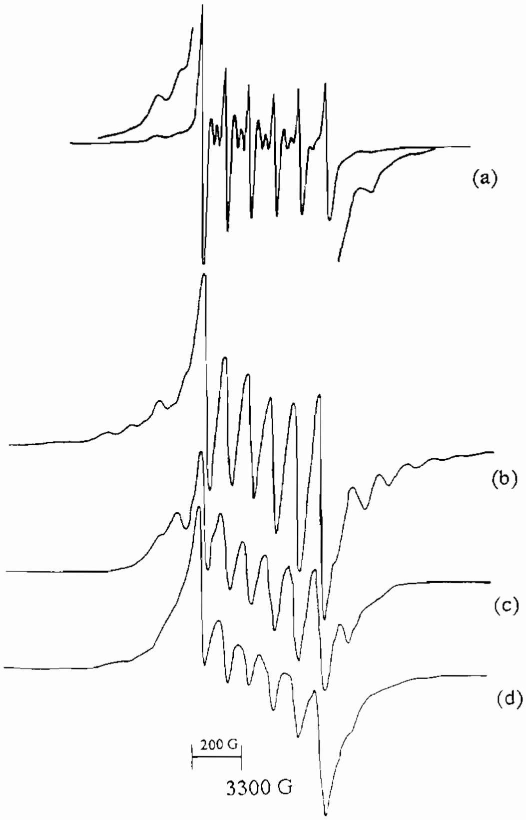

Fig. 4. X band spectra of the Mn-doped ZnZn(EDTA)·6H_2O: (a) powder spectrum; (b), (c) and (d) are the crystal spectra along the a, b and c directions, respectively.

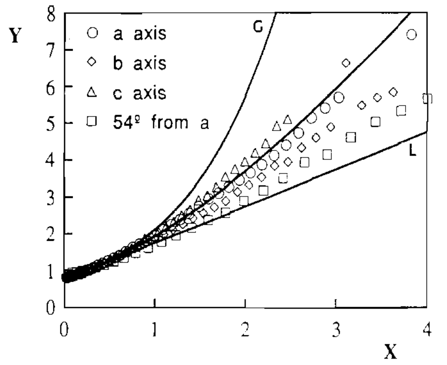

Fig. 5. Line shape analysis. Plot of $Y=[(I'_m/I')/(B-B_0)-(1/2\Delta B_{pp})]^{1/2}$ vs. $X=[(B-B_0)/(\Delta B_{pp})]^{1/2}$ for Lorentzian (L), Gaussian (G), and the Fourier transform of $\exp(t^{-3/2})$ functions and for the observed line shapes at the indicated directions. I' is the derivative EPR absorption and I'_m is the maximum. B_0 is the central field of the signal.

$$M_2^{\mathrm{hyp}}=\left(\frac{1}{3}\right)I(I+1)\left(\frac{K^2(\phi)}{g^2(\phi)}\right)+\left(\frac{1}{6}\right)\times I(I+1)\left(\frac{A_{\parallel}^2A_{\perp}^2g^2(\phi)}{K^2(\phi)}+A_{\perp}^2+E^2(\phi)\right) \qquad (3)$$

where

$$K^2(\phi)=A_{\parallel}^2g_{\parallel}^2\cos^2(\phi)+A_{\perp}^2g_{\perp}^2\sin^2(\phi)$$

$$g^2(\phi)=g_{\parallel}^2\cos^2(\phi)+g_{\perp}^2\sin^2(\phi)$$

$$E(\phi)=\frac{(A_{\perp}^2-A_{\parallel}^2)}{K(\phi)g(\phi)}g_{\parallel}g_{\perp}\sin(\phi)\cos(\phi)$$

I is the nuclear spin quantum number and ϕ is the angle of the external magnetic field with the axial direction. As we can see in Fig. 3 this term is smaller than dipolar and ZFS terms, and furthermore is almost isotropic.

Finally, with regard to the line shape, an analysis of the spectra with the field along the three crystal axes, and at 54° from *a* (in the *ac* plane) shows that to a large extent, the line shape resembles that of one-dimensional magnetic materials (Fig. 5). Thus, along *a*, the chain direction, it is very close to the Fourier transform of $\exp(-t^{3/2})$, while at 55° from *a* it is nearly Lorentzian. This result provides some evidence of the good magnetic isolation of the chains, in agreement with the magnetic data [7].

Conclusions

We have presented in this paper the EPR properties of the ferrimagnetic chain $\mathrm{MnCu(CDTA)\cdot 6H_2O}$. The angular dependence of the single crystal EPR linewidths has been discussed taking into account dipolar interactions between the paramagnetic centers, zero-field splitting of Mn(II) and hyperfine coupling of Cu(II). In the bimetallic chains reported so far, the angular dependence of the linewidth was only discussed in relation to dipolar interactions [12, 13]. In our case, due to the large intermetallic separations, both dipolar and ZFS contributions are found to be comparable, although the stronger angular dependence of the dipolar contribution makes it the leading term. The little angular dependence of the ZFS contribution is a direct consequence of the structure of the compound. In fact, we notice that, due to the zigzag features of the chains, the axial directions of the four non-equivalent manganese sites are completely missaligned (the angles between these directions are in the range 30–50°). Finally, the enhancement of the secular dipolar contributions, as well as the line shapes support the good one-dimensional character of the bimetallic [MnCu] chain, in full agreement with thc structural isolation of the chains (the shortest interchain Mn–Mn distance is 7.34 Å).

Acknowledgements

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