Multifrequency ESR in ET$_2$MnCu[N(CN)$_2$]$_4$: A radical cation salt with quasi-two-dimensional magnetic layers in a three-dimensional polymeric structure

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(Received 24 April 2009; revised manuscript received 24 July 2009; published 9 September 2009)

The radical cation salt, ET$_2$MnCu[N(CN)$_2$]$_4$, [ET=bi(ethylenedithio)tetrathiafulvalene] with an unusual three-dimensional anionic polymeric network is studied by x-ray diffraction, static susceptibility measurements, and electron spin resonance (ESR) at frequencies between 9 and 420 GHz. The magnetic properties are determined by the alternating two-dimensional layers of the Mn$^{2+}$ ions of the network and the partially charged ET molecules. At ambient temperature the overlap between Mn$^{2+}$ ions and ET molecules is weak and an exchange integral $J_{\text{Mn-ET}}=4.10^{-2}$ K is estimated from their resolved ESR lines. At lower temperatures, ET$_2$MnCu[N(CN)$_2$]$_4$ is not a simple system of weakly interacting paramagnetic ions in spite of the isotropic, Curie-like static susceptibility. There are first-order phase transitions at 292 K and in the range of 120–180 K. One of the lattice constants shows anomalous temperature dependence below 292 K. Anisotropic ESR shifts appear below 150 K, which we explain by demagnetizing fields of the platelike crystals and an exchange-narrowed fine structure. The latter contributes significantly to the shift when the populations of Zeeman levels are altered in high magnetic fields at low temperatures. We estimated the exchange coupling between Mn$^{2+}$ ions within a layer, $J_{\text{Mn-Mn}}=−48$ K and determined the fine structure parameters below 150 K, showing a distortion in the plane of the Mn$^{2+}$ ions.

DOI: 10.1103/PhysRevB.80.104407

I. INTRODUCTION

The synthesis of magnetic molecular conductors is a flourishing field of material science. 1 Layered molecular materials where physical properties are tuned by modifying the widely different molecular constituents are one of the most promising approaches. A common scheme is to form a charge transfer salt with alternating layers of TTF-derivative cations (TTF=tetrathiafulvalene) and transition metal complex anions. The narrow band of overlapping chalcogen π orbitals that protrude from the planar TTF-derivative molecules is sensitive to fine details of the anion layers. The π-electrons are confined to the two-dimensional (2D) layers formed by the cations. The overlap between the π-electron band and electrons in the neighboring anionic layers is usually weak.

One of the current challenges in the field is to understand how the coupling between the magnetic d electrons of the anions and the delocalized π-electron band of the cations leads to the diverse ground states observed. For example, in the family of the quarter filled β-ET$_2$Cr(C$_2$O$_4$)$_3$ compounds [ET=bi(ethylenedithio)tetrathiafulvalene] the ground state of the unpaired radical cation electrons can be an antiferromagnetic insulator, a superconductor, or a metal2 depending on fine details of the interaction between the anion layers and the molecular arrangement of the ET layers. Some compounds in this class of materials are rather exotic, e.g., coexistence of ferromagnetic order and metallic conductivity was found in β-ET$_2$MnCr(C$_2$O$_4$)$_3$, a system of alternating insulating magnetic two-dimensional polymeric layers of binuclear anion molecules and conducting ET molecular layers. 3 The recently synthesized radical cation salt, ET$_2$MnCu[N(CN)$_2$]$_4$, 4 investigated in this paper differs from the above mentioned materials in that a three-dimensional (3D) polymeric anion network encages the ET molecules (Fig. 1). In spite of the 3D anion network, the magnetic structure is quasi-2D and there are well separated layers of interacting octahedrally coordinated Mn$^{2+}$ ions and semiconducting layers of ET radical cations. In the present high field electron spin resonance (ESR) study we show that this material has an interesting magnetic structure with at least two phase transitions in the temperature range from room temperature to 100 K. The ESR lines of the manganese ions and ET molecules are resolved above 150 K in high magnetic fields. The observation of resolved ESR lines of the cationic molecular layers and magnetic ions in the neighboring anionic layers 5, 6 is an indication of an extremely weak overlap. In a typical experiment, the ESR lines are resolved if the exchange energy between these layers is of the order of or less than 10$^{-6}$ eV. On the other hand, 2D magnetic interactions within the Mn layers are strong and give rise to large anisotropic ESR shifts below 150 K. However, as the interactions between layers are weak, no 3D magnetic order is reached down to 1.8 K and the static susceptibility is almost isotropic at all temperatures.

The paper is organized as follows. Section II describes sample growth and the instruments used in this study. The
II. EXPERIMENTAL

Single crystals of ET$_2$MnCu[N(CN)$_2$]$_4$ were grown by the electrochemical method described elsewhere. The crystals are diamond shaped shiny black platelets with typical dimensions of 0.7 $\times$ 0.7 $\times$ 0.07 mm$^3$. According to x-ray measurements, the longer and shorter diagonals of the diamond coincide with the $b$ and $c$ axes of the crystal, respectively. We denote the direction perpendicular to the $(b,c)$ plane by $a^\prime$. We used the morphology to orient the crystals for the ESR and superconducting quantum interference device (SQUID) magnetization measurements. The deviation between the $a$ and $a^\prime$ directions is small ($6^\circ$) and we refer to $g$ factor and susceptibility measurements along $a^\prime$ as along a “main axis”.

X-ray crystallographic data were collected using the same crystal as in a previous work on a Bruker Smart diffractometer with graphite-monochromated MoK $\alpha$ radiation ($\lambda = 0.71073$ Å) in an $\omega$-scan mode. The structure was solved by direct methods and successive Fourier difference synthesis using SHELXS-97 (Ref. 7) and SHELXL-97 (Ref. 8) programs. The refinement was done by the full matrix least-squares method in an anisotropic approximation for all non-hydrogen atoms using the SHELXL-97 (Ref. 8) program. All hydrogen atoms were placed in geometrically calculated positions. Corrections for x-ray absorption were performed.

Static magnetization was measured on a single crystal with a Quantum Design MPMS-5S SQUID magnetometer between 1.8 and 300 K and magnetic fields up to 5 T.

Three electron spin resonance spectrometers were used: home built spectrometers at 75, 150, 222.4, and 225 GHz in Budapest, and at 210, 315, and 420 GHz in Lausanne, and a commercial Bruker ELEXSYS 500 at 9.4 GHz. We used polycrystalline KC$_{60}$ (Ref. 9) as a $g$-factor reference ($g_{K_{60}} = 2.0006$) for the high-frequency measurements. We determined $g_{K_{60}}$ by comparing it to Mn:MgO at 222.4 GHz ($g_{MgO} = 2.0009$). We tested the most important results (splitting of ET and Mn$^{2+}$ ESR lines, temperature, orientation, and frequency dependence of ESR resonance) on 2 or more crystals. Results of measurements on different crystals are similar.

III. STRUCTURE

ET$_2$MnCu[N(CN)$_2$]$_4$ has an unusual structure in which the ET radical cations are embedded in a 3D polymeric network of bimetallic dicyanamide [dca=N(CN)$_2$] anions. In simple salts, dca ligands bridging transition metal ions in the anion polymer are known to mediate magnetic interactions.

There are several short intermolecular contacts between the magnetic anion network and the organic radical cations. The structure is monoclinic with $\beta = 96^\circ$. Octahedrally coordinated manganese ions connected by dicyanamide (dca) ligands in the $(b,c)$ plane. Magnetic properties arise mostly from the manganese ions.

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 Resistivity measurements revealed a transition between two semiconducting phases (semiconductor I and II) at 292 K. X-ray measurements indicate a small structural change at this transition with a redistribution of the charge among ET molecules. The weak conductivity has been attributed to the ET layers.
MULTIFREQUENCY ESR IN ET₂MnCu[N(CN)₂]₄

X-ray diffraction data were obtained at 330 and 280 K, above and below the phase transition and at 123 K. Crystallographic data are summarized in Tables I and II. These data confirm that the phase transition at 292 K is driven by a charge redistribution on the ET radical cations.

Figure 3 shows the central C=C bond lengths in the ET radical cations above and below the phase transition. The central C=C bond length in the ET molecule depends on the charge of the molecules.11–13 The bond lengths change most near the phase transition. At 330 K the central C=C bond lengths correspond to the same 0.5 oxidation state within experimental error in all the four different radical cations, designated by A, B, C, and D. Below the transition, radical cations A and C change little and their oxidation state remains 0.5. In radical cation B the bond length decreases to a value that is characteristic to the neutral ET molecule. In molecule D the central C=C bond length elongates and the oxidation state is approximately +1.11,13 Probably, the charge redistribution on the ET radical cations is stimulated by their rearrangement (Table II). The anomalous, i.e., negative thermal expansion of the a lattice parameter shown by x-ray diffraction below the phase transition at 292 K hints at a structural modulation.14

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>123 K</th>
<th>280 K</th>
<th>330 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(000)</td>
<td>2312</td>
<td>2312</td>
<td>2312</td>
</tr>
<tr>
<td>μ(Mo-Kα), mm⁻¹</td>
<td>1.673</td>
<td>1.643</td>
<td>1.629</td>
</tr>
<tr>
<td>a/Å</td>
<td>32.0699(16)</td>
<td>32.0575(19)</td>
<td>32.059(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>10.5282(6)</td>
<td>10.6643(6)</td>
<td>10.7160(7)</td>
</tr>
<tr>
<td>c/Å</td>
<td>12.3039(6)</td>
<td>12.3731(8)</td>
<td>12.4218(8)</td>
</tr>
<tr>
<td>β/°</td>
<td>95.953(4)</td>
<td>96.000(5)</td>
<td>96.255(5)</td>
</tr>
<tr>
<td>V/Å³</td>
<td>4131.9(3)</td>
<td>4206.8(4)</td>
<td>4242.0(5)</td>
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<td>2θ max./°</td>
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<td>50.70</td>
</tr>
<tr>
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<tr>
<td>R</td>
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<td>0.0523</td>
<td>0.0555</td>
</tr>
<tr>
<td>GOF</td>
<td>1.044</td>
<td>1.017</td>
<td></td>
</tr>
</tbody>
</table>

TABLE II. Values of dihedral angles between the ET radical cations in the structure of the (ET)₂CuMn[N(CN)₂]₄ salt at different temperatures. Relative reorientation of molecule C is remarkable.

<table>
<thead>
<tr>
<th>Value of the dihedral angle between the neighboring radical cations, °</th>
<th>123 K</th>
<th>280 K</th>
<th>330 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-B</td>
<td>67.7</td>
<td>68.6</td>
<td>68.4</td>
</tr>
<tr>
<td>B-D</td>
<td>46.6</td>
<td>46.2</td>
<td>46.0</td>
</tr>
<tr>
<td>D-C</td>
<td>83.0</td>
<td>84.2</td>
<td>81.1</td>
</tr>
<tr>
<td>C-A</td>
<td>62.0</td>
<td>61.8</td>
<td>59.0</td>
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IV. MAGNETIC MEASUREMENTS

A. Magnetic susceptibility

Previous static susceptibility measurements in powder samples showed a simple paramagnetic behavior with weak antiferromagnetic correlations at low temperatures. The present SQUID magnetization measurements on single crystals along a', b, and c show that the susceptibility χ is almost isotropic. There is a slight anisotropy below 5 K where χ is 5% larger in the b direction than in the a' and c directions.

The comparison of the magnetization versus magnetic-field curves with Brillouin functions agrees with an assumption that above 5 K magnetism arises from nearly free Mn²⁺ ions with S=5/2 spin and the S=1/2 spins formally carried by every second ET (Fig. 4). Since the mass of the sample

![Figure 3](104407-3)
proves that the smaller line comes from the ET molecules. The intensity ratio of the lines measured from Lorentzian fits is small and their lines are resolved in high magnetic fields. Their line is resolved at high frequencies.

Mn fine structure transitions, which are motionally narrowed into a single line. ET molecules contribute also to the ESR as Mn 2+ and ET spins are resolved at higher frequencies. In all measurements there is a single Mn line for the two ions within a molecular layer have a relatively large ex-

tended magnetic susceptibility. We measured the absolute intensity of the ESR spectrum using a spin $S = 1/2$ reference, CuSO$_4 \cdot 5$H$_2$O. The mass of the sample was determined from the Mn 2+ and ET spins are resolved at higher frequencies and temperatures above 120 K. The Mn ESR alone, the frequency dependence of the shift is nonlinear. However, the intensity-weighted average shift of the two lines is linear with frequency; this suggests that the Mn$^{2+}$ and ET have exchange coupled resonances with slightly different $g$ values. The condition for resolving narrow lines of closely spaced magnetic species with $g$ factors, $g_1$ and $g_2$ is that the line separation is larger than the exchange energy

$$\Delta \epsilon = (g_1 - g_2) \mu_B B > J. \quad (1)$$

We use this expression to estimate the exchange interaction between the spin species. We assume that at 420 GHz the splitting of the lines is little affected by the exchange and represents the $g$-factor splitting of the two magnetic species. The measured splitting of 66 mT is thus equivalent to $\Delta g = 0.009$. The splitting decreases at lower frequencies and cannot be resolved below 200 GHz, thus it approximately equals to the exchange interaction at this frequency. Based on these numbers the estimated exchange coupling is $|J_{\text{Mn-ET}}| = 0.04$ K. The sign, i.e., whether the coupling is fer-

B. Electron spin resonance at high temperatures

1. ESR active sites

The ESR spectrum consists of a single line at room temperature and 9.4 GHz. We measured the absolute intensity of the ESR spectrum using a spin $S = 1/2$ reference, CuSO$_4 \cdot 5$H$_2$O. The mass of the sample was determined from its linear dimensions measured under a microscope. The measured molar susceptibility ratio of reference and sample, $\chi_{\text{sample}}/\chi_{\text{CuSO}_4} = 1.4 \pm 0.3$ is close to 38/3, the value expected for free $S = 5/2$ Mn$^{2+}$ ions and $S = 1/2$ spins on every second ET molecule. This proves that the ESR arises from all Mn fine structure transitions, which are motionally narrowed into a single line. ET molecules contribute also to the ESR as their line is resolved at high frequencies.

2. Resolved ESR of Mn and ET at high temperatures

For magnetic field $B$ in the $a'$ direction, the resonances of the Mn$^{2+}$ and ET spins are resolved at higher frequencies (315 and 420 GHz) and temperatures above 120 K (Fig. 5). In all measurements there is a single Mn line for the two Mn$^{2+}$ ions in differently oriented (CN)$_6$ octahedra, thus Mn$^{2+}$ ions within a molecular layer have a relatively large exchange. The same is true for the ET molecules. However, at high temperatures the overlap between Mn$^{2+}$ and ET spins is small and their lines are resolved in high magnetic fields. The intensity ratio of the lines measured from Lorentzian fits proves that the smaller line comes from the ET molecules (Fig. 5).

The shifts of the two lines versus frequency at 300 K are plotted in Fig. 6. Below 210 GHz there is a common resonance at all temperatures. Taken the Mn ESR alone, the fr
Magnetic or antiferromagnetic could not be determined from the ESR spectra.

Although it is uncommon to detect separate resonances of spin species with $g/H_{11015}$ in dense magnetic systems, it is not unheard of among the layered ET compounds. Resolved resonances of conduction electrons and paramagnetic ions were detected in the organic metals $ET_4NH_4Cr(C_2O_4)_3\cdotDMF$ (Ref. 6) and $ET_3CuCl_4\cdotH_2O$ (Ref. 5).

Decreasing the temperature from 300 to 120 K, the Mn and ET lines shift toward each other and gradually merge into a single line (Fig. 7). On cooling, the two lines merge gradually below 180 K and cannot be resolved below 130 K (Fig. 7). The ESR spectra show a hysteresis with temperature cycling, but we have not studied this hysteresis systematically. We identify the merging of the lines as a phase transition between 180 and 120 K. The transition is probably related to the localization of spins in the ET layers and the anomalous temperature dependence of the lattice constants. Further measurements are required to better understand the nature of the transition.

The Mn and ET lines are not resolved in the $b, c$ plane, presumably because the $g$ factors of the spin species differ less in this plane than in the $a'$ direction. The width of the single line in the $(b, c)$ plane has a quadratic frequency dependence above 75 GHz (Fig. 8). This quadratic frequency dependence may arise from the complete exchange narrowing of the $g$-factor split ET and Mn ESR lines. In the strong exchange limit, the width of the line is proportional to the square of the $g$-factor splitting.$^{16}$

$$g\mu_B\Delta B \sim \left(\hbar\Delta\omega/J\hbar\right)^2.$$  \hspace{1cm} (2)

thus at frequencies where the splitting is much larger than the exchange frequency ($\Delta\omega >> J/\hbar$), a linearly frequency dependent splitting appears, while at lower frequencies a single line with a quadratically frequency dependent width is observed.

Below 75 GHz a new line broadening mechanism appears. The line broadens by about 2.2 mT between 75 and 9.4 GHz in both in-plane directions at all temperatures from room temperature down to 100 K. At present we do not have a consistent explanation.

C. Determination of the low-temperature crystal fields

In contrast with the almost isotropic magnetization, there are large anisotropic ESR shifts at low temperatures (Fig. 9). The shifts are temperature dependent and saturate in a field

$$\Delta B_{max}.$$
of 15 T and at 3 K at 80 mT, −120 mT and 40 mT in the a, b, and c directions, respectively. We attribute these shifts to dipolar fields and fine structure splitting. It is unusual that these interactions shift the line and not only broaden it. However in high magnetic fields at low temperatures, only the lower lying Zeeman levels are populated, following the Boltzmann distribution. The ESR is a motionally narrowed average of all transitions and it shifts toward the frequencies of the transitions between more populated levels.

At temperatures below about \( k_BT < 5\mu_B B_\text{res} \) (where \( B_\text{res} \) is the resonance field) the line splits into several components in an uncontrolled way. Mechanical strains rendering the fine structure inhomogeneous are the likely reason for this splitting. We use the first moment of the spectrum to quantify the resonance field of these split lines.

1. Dipolar shifts

Dipolar interactions give rise at high fields and low temperatures to large anisotropic ESR shifts, which we calculate classically. In the first step, we calculate the local magnetic field at a Mn site as a function of Mn\( ^{2+} \) magnetization and then we solve the equation of motion for the magnetization to find the resonance frequency. To determine the local field, the average demagnetizing field due to Mn\( ^{2+} \) and ET spins was calculated approximating the shape of the sample with an infinite flat plate with demagnetizing factors \( n_{xx} = n_{yy} = 0 \) and \( n_{zz} = 1 \). (x, y, and z are orthogonal coordinates along c, b, and a\( ^* \), respectively). To take into account the anisotropic local environment, the average demagnetizing field was replaced in a spherical volume centered on an Mn site by the numerically calculated sum of the dipole fields of Mn\( ^{2+} \) and ET spins.

We first calculated the local field at \( T = 0 \) temperature with all moments aligned along the external field, \( B_0 \),

\[
B_{0z} = B_0 + \mu_0 g M.
\]

At \( T = 0 \) the magnetization is \( \mu_0 M = 66.9 \) mT and \( \alpha_{xx} = 0.5978, \alpha_{yy} = 0.5516, \alpha_{zz} = -1.1493 \). Although the crystal is monoclinic, the tilt is small and the off-diagonal elements of the matrix \( \alpha_i \) are negligibly small (\( \sim 10^{-2} \)).

We obtain the ESR shifts from the magnetic free-energy density \( F \)

\[
F = -MB - \frac{1}{2} \mu_0 g M^2 + \frac{1}{2} \mu_0 M^2 M
\]

and

\[
M \times (-\text{grad}_M F) = \frac{1}{\gamma} \frac{dM}{dt}
\]

where \( \gamma \) is the gyromagnetic ratio and the g-factor anisotropy is neglected.

We solve the equation of motion for small perturbations around the equilibrium to obtain the resonance frequency \( \omega/2\pi \), assuming \( \mu_0 M \ll B_0 \). The zero temperature dipolar shift with the external field along the z axis is

\[
\Delta B_M = -\frac{\omega}{\gamma} + B_0 = \frac{\mu_0 M}{2} (\alpha_{xx} - \alpha_{zz} - 2\alpha_{zz}).
\]

There are similar expressions for the b and c directions. We find \( \Delta B_M = 1.918\mu_0 M, \Delta B_{M_b} = -0.910\mu_0 M, \) and \( \Delta B_{M_c} = -1.007\mu_0 M. \)

We extended the calculation to finite temperatures by assuming that the temperature dependence of the magnetization \( M(T) \), follows that of the sum of noninteracting Mn\( ^{2+} \) and ET spins. This is a good approximation from room temperature to 25 K, where the measured susceptibility is paramagnetic and the ratio of the two Brillouin functions is quasi-constant. The ESR dipolar shifts \( \Delta B_M(T), \Delta B_{M_b}(T), \) and \( \Delta B_{M_c}(T) \), calculated by replacing \( M \) with \( M(T) \) in Eq. (6), are plotted in Fig. 9. Although dipolar shifts are large, they clearly do not explain the observed anisotropy at low temperatures.

In the following we discuss the origin of the large anisotropic shifts remaining after the measured ESR shifts \( \Delta B_{\text{mean}}(T) \) (with respect to the KC\( 60 \) reference) are corrected for the calculated dipolar shifts, \( \Delta B_i(T) = \Delta B_{\text{mean}}(T) - \Delta B_{M_i}(T), \) \( i = a^*, b, \) and \( c \). These remaining shifts are negative and of similar magnitude along the \( a^* \) and \( b \) directions and positive and approximately twice as large along the c direction. At 210 GHz the saturated \( \Delta B_i(T=0) \) values are \( -58 \) mT, \( -56 \) mT and 99 mT for \( i = a^*, b, \) and \( c \), respectively.

2. Two-dimensional correlations

Anisotropic ESR shifts in low-dimensional antiferromagnetic spin systems were studied by Nagata et al.\textsuperscript{17,18} who explained their experimental observations by the combined effect of antiferromagnetic correlations and the dipole-dipole interaction. They derived an expression that relates the anisotropy of the ESR to the magnetic susceptibility. (Sample shape dependent demagnetizing effects were subtracted separately.) Uniaxial single ion anisotropy was taken into account up to second order, but only with a special orientation perpendicular to the 2D structure.

In our case the measured shifts, corrected for sample shape dependent demagnetizing effects, but not for local dipole fields are 3.4, –83, and 65 mT along the \( a^*, b, \) and \( c \) directions, respectively. The predictions of Nagata’s model, due to its assumption of uniaxial symmetry of all interactions would be of the form \( \Delta_{a^*/2} = -\Delta_b = -\Delta_\gamma \) in contradiction with our observation of an anisotropy in the \( (b, c) \) plane. Thus, the Nagata model cannot describe the dominant source of the observed low-temperature shifts.

3. Motionally narrowed fine structure

We propose that the large low temperature anisotropy in \( \Delta B_i(T) \), the ESR resonance shift corrected for dipolar shifts, arises from the single ion anisotropy of Mn\( ^{2+} \) ions. A magnetic ion in a crystal interacts with the electrical charges of its environment, the so called crystal field. As a result, for spins greater than \( \frac{1}{2} \), the fine structure lines split, which can be described by the so called zero-field splitting (ZFS) parameters in the corresponding spin Hamiltonian. In dilute
magnetic systems the ZFS parameters are usually derived from the magnetic-field orientation dependence of the fine structure lines. In magnetically dense systems, the fine structure is not resolved and only few studies go beyond a qualitative description.\textsuperscript{19}

Here we determine the ZFS parameters of Mn\textsuperscript{2+} ions to second order in the spin operators from the temperature dependence of the single exchange-narrowed line. In our simplified model, we assume that the fine structure merges into a single resonance line as a consequence of exchange narrowing. A similar model was used previously for dilute alloys.\textsuperscript{19}

The spin Hamiltonian of the Mn\textsuperscript{2+} ion is:

\[ H = H_Z + H_{ZFS} + H_{EX} \]

\[ = \sum_j \left( g \mu_B B S_j + \frac{1}{3} J_{20} O_2^2(j) + \frac{1}{3} J_{b2} O_2^2(j) \right) + \frac{1}{2} \sum_{j<k} J_{Mn-Mn} S_j S_k. \]

(7)

Here \( B \) is the local magnetic field at the Mn site, \( S_j \) is the Mn\textsuperscript{2+} spin vector operator at site \( j \), and we neglected the anisotropy of the \( g \) factor. The average ZFS of the Mn\textsuperscript{2+} ions in the two different distorted (CN)\textsubscript{6} octahedra is parameterized by \( b_{20} \) and \( b_{22} \). \( O_2^2(j) = 3 S_j^2 - S(S+1) \) and \( O_2^2(j) = S_j^2 - S_j^2 \) are second order Stevens operators at site \( j \) and the fourth order terms are omitted. \( J_{Mn-Mn} \) is the average isotropic exchange energy. The \( x \), \( y \), and \( z \) axes are along \( a \), \( b \), and \( a^* \), respectively. The shifts arise from the temperature-dependent populations of the energy levels.

Figure 10 illustrates the way the model leads to anisotropic shifts that are in good agreement with the observations. The Zeeman term, \( H_Z \), shifts the magnetic levels of the free Mn\textsuperscript{2+} ion into six equally spaced energy levels. The ZFS term, \( H_{ZFS} \), shifts the Zeeman levels unevenly and without \( H_{EX} \) it would rise to the ESR fine structure of an isolated Mn\textsuperscript{2+} ion embedded in the (CN)\textsubscript{6} octahedron [Fig. 10(b)]. The relative intensities of these lines change at low temperatures and high magnetic fields \((g \mu_B B > k_B T)\) as the higher lying levels depopulate following the Boltzmann distribution. At very low temperatures and high magnetic fields, only the lowest lying \(-S/2\) level is populated and all intensity shifts to the \(-5/2 \rightarrow -3/2\) transition. The exchange term \( H_{EX} \), is a true many-body term, which we treat qualitatively by assuming that the observed single line appears at the intensity-weighted average resonance field of the fine structure lines. Incomplete exchange narrowing of the fine structure is well known to contribute to the ESR line width.\textsuperscript{16} At the low temperatures and high fields of the experiments changes in the thermal population of the energy levels shift the resonance significantly.

We suppose crystal fields are temperature independent below 120 K and calculate the ZFS parameters from the measured anisotropic shifts at 210, 315, and 420 GHz and at temperatures 2 and 110 K. We find the ZFS parameters \( b_{20} \approx -340\) MHz and \( b_{22} \approx 1057\) MHz. The temperature dependence of the calculated shift is shown in Fig. 10(a) for \( B//b \) and results are similar in the other two directions. The above second-order parameters indicate that the local environment is strongly distorted from cubic symmetry along the \( c \) axis. This is different from the structure expected from x-ray measurements at ambient temperatures, which suggests that the distortion is largest along \( a^* \) and the anisotropy within the \((b,c)\) plane is smaller. X-ray measurements below 100 K, well below the broad phase transition about 150 K could directly verify our model.

We estimate the exchange interaction \( J_{Mn-Mn} \) from the measured \( \Delta \omega \) line width and the \( \omega_p \), “breadth” of the fine structure, i.e., the distance between the outermost fine structure lines that would appear in the absence of Mn–Mn exchange. An approximation\textsuperscript{20} valid for a 2D system is

\[ \Delta \omega = \frac{\omega_p^2}{J_{Mn-Mn}/h} \ln \left( \frac{J_{Mn-Mn}/h}{\omega_p} \right). \]

(8)

The logarithmic term is specific to the 2D nature of the Mn layers; the exchange interaction is less effective in narrowing the lines in a 2D than in a 3D system.\textsuperscript{21} The width of the fine structure in the \( c \) direction is \( \omega_p \approx \gamma \cdot 0.2\) T. Using \( \Delta \omega \approx -5.7\) mT, a value extrapolated from high field data to zero field at 100 K, where the line is the narrowest and is weakly affected by strains or other inhomogeneous terms, we find \( J_{Mn-Mn} \approx -48\) K. The coupling is antiferromagnetic \((J < 0)\) which we deduce from static susceptibility measurements at low temperature. The interaction between the manganese planes is much smaller, as antiferromagnetic correlations...
emerge only below 20 K and there is no sign of a static magnetic order down to 1.2 K.

In principle, ESR also gives information on the fine structure at high temperatures. The resonance is shifted at low frequencies when the ZFS is comparable to or larger than the Zeeman splitting. Shifts at temperatures above 100 K which are not proportional to the frequency between 9.4 and 75 GHz, (Fig. 9), may have this origin.

V. CONCLUSIONS

We investigated the structural and magnetic properties of ET$_2$MnCu[N(CN)$_2$]$_4$, an organic paramagnetic compound with an unusual three-dimensional anionic network. Although the static susceptibility is apparently well described by noninteracting spins above 5 K with only weak antiferromagnetic correlations below, the detailed analysis of the ESR spectra reveal a more complex picture.

The system is composed of weakly interacting magnetic planes, but there is considerable exchange interaction within the 2D subsystems. We estimate an exchange coupling among the manganese ions in the $(b,c)$ plane, $J_{\text{Mn-Mn}} \approx -48$ K, using the line width and the ZFS parameters obtained from the low-temperature shifts. On the other hand, the coupling between the different spin species is so small that their resonances are resolved above 120 K in spite of the similar $g$ values. We estimate an exchange coupling at 300 K of $|J_{\text{Mn-ET}}| \approx 4 \cdot 10^{-2}$ K.

We detected a first-order phase transition between 180 and 120 K, which shows a hysteresis with thermal cycling. The anomalous temperature dependence of the $a$ lattice parameter suggests that a structural modulation develops along the $a$ direction below 292 K. It is plausible that the structural anomaly relates to the phase transition observed in the ESR. More measurements are needed to understand the transition. Preliminary ESR results indicate that x-ray measurements below 120 K could be conclusive.

Static magnetization is almost isotropic at all temperatures while significant ESR shifts were detected below 140 K. We described the spectra quantitatively, assuming a considerable zero-field splitting of the manganese ESR corresponding to a strong distortion of the Mn(CN)$_6$ octahedra in the $(b,c)$ plane. The exchange interaction merges the Mn$^{2+}$ fine structure into a single line, however, it gives rise to anisotropic shifts and the most important ZFS parameters are measurable at low temperature and high magnetic fields.

ACKNOWLEDGMENT

This work was supported by Hungarian State Grants (OTKA) No. PF63954, K68807, NK60984, and NN76727 by the Swiss NSF and its NCCR “MaNEP” and by RFBR-DFG project No. 07-02-91562 (RUS 113/926/0-1). T.F. acknowledges support from the János Bolyai program of the Hungarian Academy of Sciences. B.N. acknowledges support from the Prospective Researcher program No. PBELP2-125427 of the Swiss NSF.