# Magnetism and EPR spectra of the two-sublattice manganese chain Mn$_2$(EDTA)·9H$_2$O

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We report on the magnetic behavior and single-crystal EPR spectra of the chain complex Mn$_2$(EDTA)·9H$_2$O characterized by two different alternating sites for the manganese ions. Magnetic susceptibility data are indicative of weak antiferromagnetic exchange interactions between the manganese ions, showing a maximum of about 3 K. This behavior can be accurately described on the basis of a Heisenberg chain model that assumes classical spins, giving $J/k = -0.72$ K and $g = 2.0$. The EPR spectra are typically low dimensional, with an angular dependence of the linewidth of the type $(3\cos^2\theta - 1)^n$ ($n = 4/3$ or 2). Nevertheless, such a behavior cannot be reproduced from a one-dimensional model with dipolar broadening. An alternative broadening mechanism arising from single-ion zero-field splitting is then suggested.

## I. INTRODUCTION

Large interest in the study of the static thermodynamic properties of one-dimensional (1D) systems has recently been stimulated by the discovery of new materials, for instance the ferrimagnetic chains.[1] Nevertheless, very few investigations have been devoted to the spin dynamics of this type of systems.[2] As a part of our studies on low-dimensional magnets, we have examined the magnetism and single-crystal EPR spectra of the two-sublattice manganese chain Mn$_2$(EDTA)·9H$_2$O in order to obtain information on magnetic interactions and spin dynamics.

## II. RESULTS AND DISCUSSION

### A. Structure

The structure of [Mn(H$_2$O)$_4$Mn(EDTA)(H$_2$O)] ·4$n$(H$_2$O) consists of infinite zig-zag chains parallel to the $a$ axis of the orthorhombic cell with alternating Mn(II) coordination sites. One manganese ion, indicated as [Mn1], is hexacoordinated to four water molecules and to two oxygen atoms of the EDTA ligands, while the other, [Mn2], is heptacoordinated to four oxygen atoms and to two nitrogen atoms belonging to the EDTA ligand and to a water molecule. On the other hand, slight alternating Mn1-Mn2 distances occur along the chain which are related to different bridging carboxylate topologies.

### B. Magnetic properties

Magnetic susceptibility data down to 2 K are indicative of weak antiferromagnetic exchange interactions between the manganese ions, with $\chi T$ decreasing at low temperatures, and $\chi$ showing a maximum about 3 K (Fig. 1). Owing to the large spin of Mn(II), these data have been fitted with a classical-spin Heisenberg chain model.[3] A very satisfying description of the experiment, in all the range of temperatures, is obtained with the following set of parameters: $J/k = -0.72$ K and $g = 2.0$ (in the Hamiltonian the exchange constant is written as $-J$). This result suggests that the effect of other factors, as a $J$ alternation due to the alter-

nating metallic distances, or the single-ion zero-field splittings, are negligible in the present case. On the other hand, as regards the interchain interactions, the occurrence at $T_c \approx 1.5$ K of a transition to long-range magnetic ordering,[4] suggests that these are quite important. Thus, using the Richards expression,[5] that relates the $j/J$ ratio ($j$ being the interchain interactions) with the critical temperature $T_c$, we obtain $j/J \approx 0.03$.

### C. Single-crystal EPR spectra

Suitable EPR single crystals of Mn$_2$(EDTA)·9H$_2$O show well-developed 101 and 1̄01̄ faces, so that the spectra were recorded rotating around three orthogonal directions $X$, $Y$, and $Z$ with $Y$ parallel to $b$ and $X$, perpendicular to the 101 face, making an angle of 41.5° with $a$.

Only one signal centered at $g = 2$ is observed for each orientation of the static magnetic field at both $X$- and $Q$-band frequency, showing a practically frequency-independent
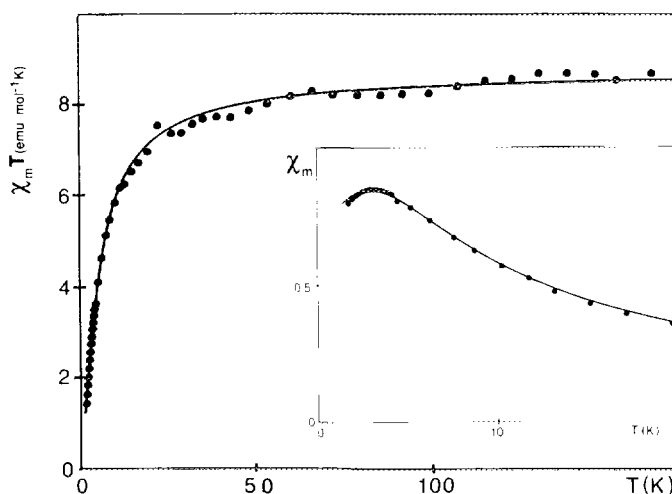
FIG. 1. Magnetic behavior of Mn$_2$(EDTA)·9H$_2$O. The full line corresponds to the best fit with the Heisenberg classical spin chain model ($J/k = -0.72$ K, $g = 2.0$).

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linewidth. The low-temperature spectra do not show any remarkable evidence of $g$ shift effects, with only a general broadening of the lines. The angular dependence of the linewidth in the $XZ$ ($ac$) plane at room temperature is reported in Fig. 2. This behavior can be reproduced with functions of the type

$$\Delta B_{pp} = a + b(3 \cos^2 \theta - 1)^n, \qquad (1)$$

with $n = 2, 4/3$; $\theta$ is the angle of the static magnetic field with $a$. The linewidth along $b$ is comparable to that along $c$. The experimental angular dependence of the linewidth is an evidence for low-dimensional magnetism.[6] An angular dependence of the linewidth described by Eq. (1) with $n = 4/3$, where $\theta$ is the angle of the static magnetic field with the chain axis, is typical of a well-behaved linear chain Heisenberg antiferromagnet. A $n = 2$ in Eq. (1) can reflect the importance of broadening mechanisms different from interchain dipolar interaction or a bidimensional behavior, with the $\theta$ angle of the external magnetic field perpendicular to the magnetic plane of the compound. The line shapes are almost Lorentzian at all angular settings. In order to discuss the angular dependence of the linewidth we focus on the structural features of the compound.

Considering the spins localized on the Mn(II) ions we attempted to estimate the angular dependence of the dipolar broadening effect on the EPR lines by evaluating the secular part of the second moment relative to the [Mn]-[Mn] interactions[7]

$$M_2 = \tfrac{3}{4}S(S + 1)\mu_B^2 g^2 \sum_i \sum_j r_{ij}^{-6}(3 \cos^2 \theta_{ij} - 1)^2, \qquad (2)$$

where $\theta_{ij}$ and $r_{ij}$ are, respectively, the angle formed by the static magnetic field with the vector connecting the two paramagnetic interacting centers, and the distance between them. In the calculations, the summation over $i$ accounts for nonequivalent sites in the unit cell. Each [Mn1] is surrounded by four nearest-neighbors [Mn2] atoms: two [Mn2] belonging to the same chain of the central [Mn1] at 617.7 and 619.3 pm, and the other two belonging to different chains at 612.4 pm (Fig. 3). The calculated angular dependence of the linewidth does not reproduce the experimental data. In fact, as expected on the basis of the structural data, the strongest
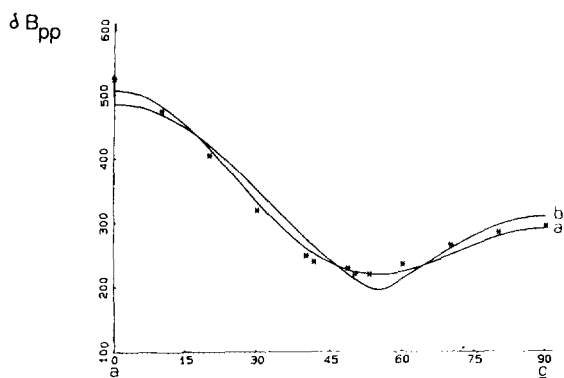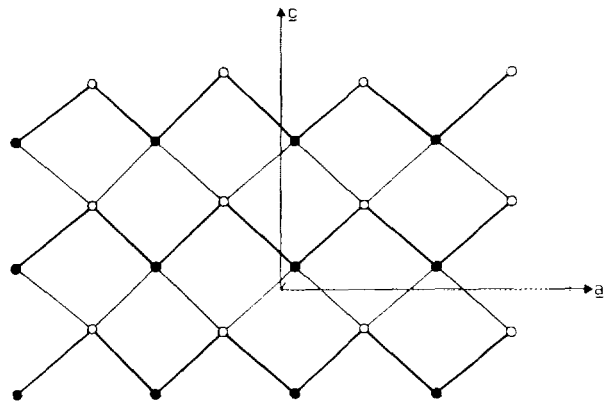


FIG. 3. Schematic view of the manganese "lattice" in Mn$_2$(EDTA) ·9H$_2$O showing the connections between the chains. Filled and open points correspond to hexacoordinated [Mn1] and heptacoordinated [Mn2] manganese ions, respectively.

calculated dipolar interaction is in the $ac$ plane, with maxima along $X$ and $Z$ axes, and not, as experimentally observed, along the orthorhombic axes, thus indicating that the one-dimensional model with dipolar broadening is not adequate.

An angular dependence of the linewidth of the type $(3 \cos^2 \theta - 1)^2$ is also expected for bidimensional systems, where $\theta$ is now the angle between the direction of the static magnetic field and perpendicular to the magnetic plane. In the present compound, however, no reliable exchange pathways yielding to magnetic bidimensionality can be found in the $bc$ plane, perpendicular to the direction exhibiting maximum linewidth.

Between other possible broadening mechanisms, the single-ion zero-field splitting must be taken into consideration.[2] [Mn1] and [Mn2] can have different $\mathbf{D}$ tensors but, unfortunately, it is not possible to obtain independent information on their principal values and directions. Literature data for Mn(II) compounds indicate that $\mathbf{D}$ generally does not exceed 0.1 for Mn(II) in distorted octahedral environments, even if several systems appear to have larger zero-field splitting,[8] but similar information is not available for heptacoordinated manganese ions. However, it can be expected to be fairly large and comparable to the exchange interaction. Thus, a large zero-field splitting with principal axes parallel to $a$ might explain the angular dependence of the linewidth, but until independent experimental information is obtained, we can not speculate further on this point.

## ACKNOWLEDGMENTS

FIG. 2. Angular dependence of the $\Delta B_{pp}$ linewidth in the $ac$ plane at room temperature and $Q$-band frequency. Full lines correspond to the best fits to the expression (1), for (a) $n = 2$ and (b) $n = 4/3$.

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