The ferrimagnetic compounds $CoM[M'(EDTA)]_2 \cdot 4H_2O$(M,M' = Co,Ni): Magnetic characterization of $CoCo[Ni(EDTA)_2] \cdot 4H_2O$

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We report on the magnetic properties of the ordered bimetallic compound $CoCo(NiEDTA)_2 \cdot 4H_2O$ (abbreviated as [CoCoNi]). The structure consists of ordered bimetallic layers formed by alternating octahedral sites of Co and Ni(II); tetrahedral Co sites connect different Co-Ni layers. We discuss the low-dimensional ferrimagnetic behavior of this compound in terms of a model that assumes three spin sublattices exchange coupled by an Ising interaction.

INTRODUCTION

An attractive approach to construct molecular ferromagnets consists of assembling ordered bimetallic chains so as to obtain two- or three-dimensional (2D or 3D) ordered bimetallic lattices. Based on this strategy, we have obtained a new phase of bimetallic materials of formula $M'M[M'(EDTA)_2]4H_2O$ {in short [M'MM']; M,M' = Co, Ni(II); M' = Co, Zn(II)}.[1-4] The structure of this series[1] consists of ordered bimetallic layers of alternating octahedral sites M and M', with tetrahedral sites M' connecting different layers (Fig. 1). In this paper we discuss the magnetic behavior of [CoCoNi] in terms of a model that assumes three spin sublattices exchange coupled by an Ising interaction.

MODEL

The magnetic behavior of this compound shows, upon cooling, the typical $\chi_m T$ minimum of low-dimensional ferrimagnets around 1 K and a peak at ~ 0.4 K, suggesting a transition to long range ordering (Fig. 2).

In discussing these magnetic properties it is noted that the resulting (3D) ferrimagnetic lattice is too complex to be modeled, and some justified simplifications need to be introduced. First of all, there are two nonequivalent connections between M and M' within the layers (Fig. 1), which may give rise to alternating exchange couplings. Furthermore, there is a third exchange coupling between M' and M'.

By assuming that one of the exchange couplings within the layer is much smaller than the other two, the problem is reduced to a one-dimensional system. In fact, in the related bimetallic chain compounds $CoM'(EDTA) \cdot 6H_2O$ (M' = Co, Ni, and Cu), a significant exchange alternation along the chain ($J'/J < 0.1$) has been observed.[5,6] This strong dimerization can be related with the configuration of the two carboxylate groups bridging Ni with its Co neighbors within the layer: As can be seen in Fig. 3, they form dihedral angles of 0° and 90° with the equatorial plane of Ni (N_1-O_{13}-O_{22}-O_{23}). This orthogonality of the carboxylates would reduce significantly the coupling through the Co···Ni···Co' pathway, and may therefore be at the origin of the J alternation.

According to the above scheme, the resulting magnetic lattice is reduced to a chain formed by three sublattices which are ordered according to the sequence A-B-A--C--A-B-A--C, where A,B, and C refer to the sites Ni, Co, and Co', respectively; dotted and full lines denote the two non-negligible exchange couplings. The sequence of magnetic moments along the chain may be schematized as

$$--S_a(g_a)\text{-}S_b(g_b)\text{-}S_a(g_a)$$

$$--S_c(g_c)\text{--}S_a(g_a)\text{-}S_b(g_b)\text{-}S_a(g_a)\text{--}.$$

Dealing with the [CoCoNi] system, $S_a = 1$ for Ni(II), and $S_b = S_c = 1/2$ for Co(II) ions in octahedral and tetrahedral sites; g_a, g_b, and g_c are the corresponding Landé factors at these sites. We have assumed that the tetrahedral Co(II) can be described below 4 K as a spin doublet, since

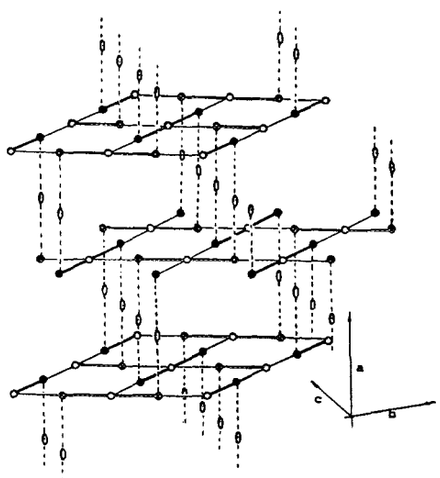

FIG. 1. Schematic diagram of the structure of $CoCo(NiEDTA)_2 \cdot 4H_2O$ showing the layers of alternating octahedral sites (Ni, filled circles, Co, open circles) and tetrahedral Co sites connecting them (ellipses).

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the zero-field splitting is expected to be larger than 10 K. In view of the anisotropy of octahedral Co(II) in similar sites (with $g_{\parallel} \gg g_{\perp}$), an anisotropic exchange model (Ising type) is expected to describe conveniently the magnetic properties of this compound.

The full Hamiltonian is written as

$$H = \sum \{ -JS^z_{4i}S^z_{4i+1} - JS^z_{4i+1}S^z_{4i+2} - J'S^z_{4i}S^z_{4i-1} - g_{4i}\mu_B HS^z_{4i} - g_{4i+1}\mu_B HS^z_{4i+1} - g_{4i+2}\mu_B HS^z_{4i+2} - g_{4i+3}\mu_B HS^z_{4i+3} - D\{[(S^z_{4i})^2 - (S_{4i})^2] + [(S^z_{4i+2})^2 - (S_{4i+2})^2]\}\},$$

where S^z_j stands for the z component of the spin located on site j; J and J' are the exchange couplings of the pairs Ni-Co and Ni-Co', respectively. D is the zero-field splitting of Ni(II), and $g_{4i} = g_{4i+2} = g_a$; $g_{4i+1} = g_b$; $g_{4i+3} = g_c$. This can be solved exactly by the transfer matrix method if the external magnetic field is assumed to be along the z axis.[7]

Following a similar procedure to that reported for other ferrimagnetic chains,[3,4] the transfer matrix for the system under consideration is

$$T = \begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix},$$

$$T_{11} = A*E + B*G,$$

$$T_{12} = A*F + B*H,$$

$$T_{21} = C*E + D*G,$$

$$T_{22} = C*F + D*H,$$

$$A = r^{1/2}\{K^{-1} + 2\cosh[(J_+ + g_b\mu_B H)\beta]\},$$

$$B = r^{1/2}\{K^{-1} + 2\cosh[(J_- + g_b\mu_B H)\beta]\},$$

$$C = r^{-1/2}\{K^{-1} + 2\cosh[(J_- - g_b\mu_B H)\beta]\},$$

$$D = r^{-1/2}\{K^{-1} + 2\cosh[(J_+ - g_b\mu_B H)\beta]\},$$

$$E = t^{1/2}\{K^{-1} + 2\cosh[(J_+ + g_b\mu_B H)\beta]\},$$

$$F = t^{1/2}\{K^{-1} + 2\cosh[(J_- - g_b\mu_B H)\beta]\},$$

$$G = t^{-1/2}\{K^{-1} + 2\cosh[(J_- + g_b\mu_B H)\beta]\},$$

$$H = t^{-1/2}\{K^{-1} + 2\cosh[(J_+ - g_b\mu_B H)\beta]\},$$

$$K = \exp(D\beta), \quad r = \exp(g_a\mu_B H\beta),$$

$$t = \exp(g_c\mu_B H\beta),$$

$$\beta = 1/k_B T,$$

$$J_+ = (J + J')/2, \quad J_- = (J - J')/2.$$

The largest eigenvalue of the matrix (T) can be considered as the effective partition function per pair of sites Z, in the limit of very long chains. So, we obtain the following expression for the zero-field parallel susceptibility:

$$\chi_{\parallel} = \left(\frac{N}{\beta}\right)\frac{S_0'' + (S_0S_0'' - 2P_0'')/(S_0^2 - 4P_0)^{1/2}}{S_0 + (S_0^2 - 4P_0)^{1/2}},$$

where S_0 and P_0 are the values at zero field of the trace S and the determinant P of (T), respectively, and S_0'' and P_0'' are the second derivatives of S and P with respect to H, at zero field. For the specific heat, we obtain

$$\frac{C_m}{R} = \beta^2\left[\frac{Z_0''}{Z_0} - \left(\frac{Z_0'}{Z_0}\right)^2\right],$$

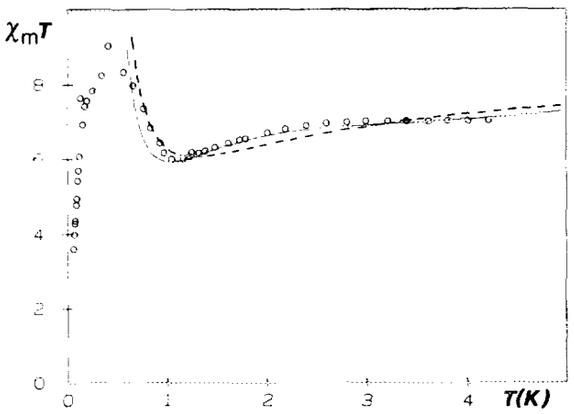

FIG. 2. Plot of $\chi_m T$ vs T for the title compound. Circles indicate experimental points, the full line corresponds to the fit with $g_a = 3.18$, $g_b = 9.8$, $g_c = 5$, $J/k = J'/k = -10$ K, and $D/k = -8$ K. The dashed line to the fit with $g_a = 1.6$, $g_b = 9$, $g_c = 1.6$, $J/k = -2$ K, $J'/k = -9$ K, and $D/k = -3.9$ K

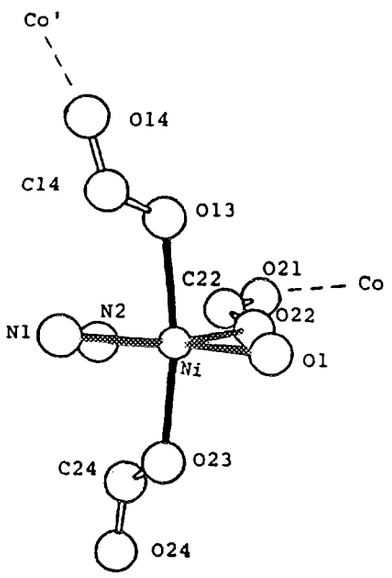

FIG. 3. Coordination of the Ni(II) site showing the orthogonality of the carboxylates bridging it with the octahedral Co(II) neighbors.

where Z_0 is the effective partition function per pair of sites at zero field, and Z_0' and Z_0'' are the first and second derivatives of Z_0 with respect to β.

ANALYSIS OF THE MAGNETIC PROPERTIES OF [CoCoNi]

In order to fit the experimental data, it is reasonable to assume that these may be accounted for by the parallel component of the susceptibility, since the perpendicular contribution remains weak and decreases toward zero upon cooling down. Notice that such an approximation may lead to somewhat unrealistic Landé factors. Only the ratio between them can be considered relevant.

The low-temperature data are illustrated in Fig. 2 through a plot $\chi_m T$ vs T, along with the best-fitted curves. The large number of adjustable parameters makes the fitting procedure a difficult task. Two different cases arise from considering the relative magnitude of the zero-field splitting of Ni(II) with respect to the exchange parameters. For D smaller than J and J', the best fit corresponds to $g_a = 3.18$, $g_b = 9.8, g_c = 5, J/k = J'/k = -10$ K, and $D/k = -8$ K. For D larger than J, the best fit gives $g_a = 1.6$, $g_b = 9$, $g_c = 1.6, J/k = -2$ K, $J'/k = -9$ K, and $D/k = -3.9$ K. For testing the validity of these fits, it is interesting to compare the exchange values with those found in the bimetallic chain CoNi(EDTA)·$6H_2O$. In this compound the exchange interaction between octahedral Co and Ni ions is around -15–20 K. In view of that, we consider that the former set of parameters seems to be more reasonable. In any case, further experimental work, in particular specific heat measurements, are now required in order to confirm the present results.

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