1D antiferromagnetism in spin-alternating bimetallic chains

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The magnetic and thermal properties of the ordered bimetallic chain $CoNi(EDTA)\cdot 6H_2O$ in the very low-temperature range are reported. The magnetic behavior does not exhibit the characteristic features of 1D ferrimagnets, but a continuous decrease of $\chi_m T$ towards zero at absolute zero. This 1D antiferromagnetic behavior results from an accidental compensation between the moments located at the two sublattices. This behavior, as well as the specific-heat results, are modeled on the basis of an Ising-exchange model that considers both alternating spins and Landé factors, and a zero-field splitting on the Ni site.

I. INTRODUCTION

One of the most remarkable advances in magnetochemistry in the last few years is the discovery of a new type of low-dimensional magnetic system, namely ferrimagnetic chains or 1D ferrimagnets.[1] Their distinctive magnetic behavior arises from the failure of the antiferromagnetic exchange to compensate for the two magnetic sublattices involved. Ordered bimetallic chains provide typical examples of this kind of system. On the other hand, a spin-alternating bimetallic chain can also be antiferromagnetic, provided that an accidental compensation of the two magnetic moments occurs.[2–4] This possibility appears to be realized in the compound $CoNi(EDTA)\cdot 6H_2O$, which behaves in the investigated temperature range (down to 1 K) as a compensated antiferromagnetic chain. This behavior, as well as the specific-heat results, are modeled on the basis of an Ising-exchange model that considers alternating spins and Landé factors, and a zero-field splitting on the Ni site.

II. RESULTS

$CoNi(EDTA)\cdot 6H_2O$ belongs to an isostructural series of bimetallic compounds formulated as $MM'(EDTA)\cdot 6H_2O$ [M, M' = Mn, Co, Ni, Cu, Zn(II)]. Their structure consists of infinite zigzag chains, built up from two alternating octahedral sites, which are selectively occupied by the two metal ions.[5] In the present case the chain may be schematized as

$$\text{--Co}(H_2O)_4O_2\text{—Ni(EDTA)--}$$
$$\text{Co}(H_2O)_4O_2\text{—Ni(EDTA)--,}$$

where dashed and full lines refer to alternating metallic distances.

The magnetic properties of [CoNi] show a continuous decrease of the product $\chi_m T$ upon cooling, instead of the minimum in the $\chi_m T$ vs T curve characteristic of 1D ferrimagnets. This can be understood from the nature of the two magnetic sublattices involved. Thus, Co(II) can be described, at low enough temperature ($T < 20$–30 K), by a spin $\frac{1}{2}$ with anisotropic Landé values ($g_{\parallel Co} = 5.90$ and $g_{\perp Co} = 3.88$), while the Ni(II) has $S = 1$ and an isotropic g value around 2.25–2.30. As a consequence, the two local magnetic moments, defined as $g_i S_i$ (i = Co,Ni), are nearly equal ($g_{Co}/g_{Ni} \approx 2$), so that we expect almost complete compensation of the ground state and hence, a regular antiferromagnetic chain behavior. Notice that this argument deals with classical moments. In the quantum case, the compensation value depends on the exchange anisotropy, but, in any case, it remains close to the classical result. For example, in a $[\frac{1}{2}\text{-}1]$ spin-alternating chain this varies between $g_a/g_b = 2$ in the Ising case, and to 2.67 in the Heisenberg one.[2–4]

III. ANALYSIS OF THE MAGNETIC PROPERTIES

Owing to the anisotropy of the Co(II) ion, an anisotropic exchange model is expected to be appropriate for the analysis of the magnetic properties. We will focus on the Ising model, for which exact solutions can be derived. Assuming two alternating exchange couplings, J and J', we have derived[6] closed-form expressions of the thermodynamic quantities of interest (parallel magnetic susceptibility and specific heat) for the two-sublattice chain with spins $[\frac{1}{2}\text{-}S]$, including a local crystal-field anisotropy D on the second sublattice. The total spin Hamiltonian including the Zeeman term can be written as

$$\mathrm{H} = -J\sum S^z_{2i-1}S^z_{2i} - J'\sum S^z_{2i}S^z_{2i+1} - \left(g_a\sum S^z_{2i-1} + g_b\sum S^z_{2i}\right)\mu_B H - D\sum\left[(S^z_{2i})^2 - (S_{2i})^2\right],$$

where $S_a = \frac{1}{2}$ and $S_b = S$ for odd and even sites, respectively. g_a and g_b are the corresponding Landé factors, and D is the zero-field splitting on site b.

In our case, the magnetic susceptibility, as well as the specific-heat data, can be fit setting $S = 1$. In order to reduce the number of adjustable parameters, D has been kept constant and equal to -9 K (the negative sign indicates that

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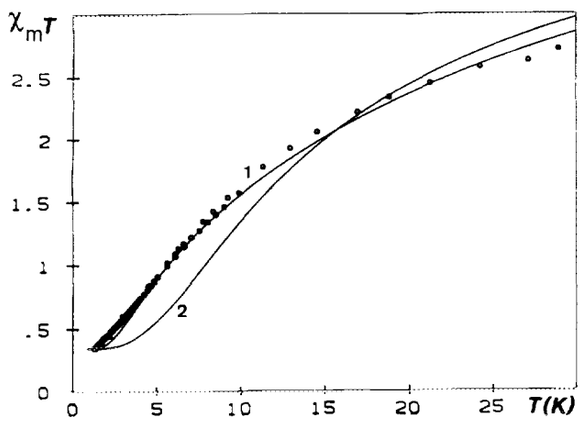

FIG. 1. Magnetic behavior of [CoNi]. Line 1 corresponds to the best fit from the J-regular [$\frac{1}{2}$-1] Ising-chain model. Comparison to the dimer limit using the parameters resulting from the specific-heat fit is given as line 2.

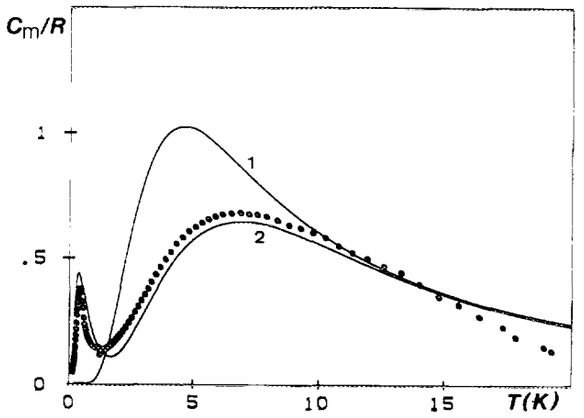

FIG. 2. Magnetic specific heat of [CoNi]. Line 1 corresponds to the theoretical behavior of a J-regular chain using the parameters resulting from the fit of the magnetic data. Line 2 corresponds to the best fit of the data in the dimer limit ($J/k = -26$ K, $J'/k = -1$ K, $D/k = 0$ K).

the state $m_s = 0$ is below the state $m_s \pm 1$). This value has been determined independently from specific-heat measurements on a diamagnetic sample containing the Ni(EDTA) moiety. Further, the perpendicular susceptibility has been taken as temperature independent, since its contribution (related to $g_\perp$) is weak compared to $\chi_\parallel$, and only slightly dependent on temperature.

Despite these simplifications, several different sets of parameters each giving close agreement with experiment can be found, which are either around the regular chain limit ($J = J'$) or around the dimer limit ($J' = 0$).

Thus, we notice that in the chain limit a very good description of the magnetic data is obtained for $J/k = J'k = -20$ K, $D/k = -9$ K, $g_{Co} = 5.2$, and $g_{Ni} = 2.6$ (line 1 in Fig. 1). With respect to the specific heat, this set of parameters reproduces the position of the high-temperature Schottky anomaly, but not its intensity (line 1 in Fig. 2); further, it does not account for the low-temperature peak (at $T = 0.5$ K). This last could be assigned to a Lambda peak corresponding to the occurrence of a long-range magnetic ordering (at T_c). Notice that, under such an assumption, a significant part of the magnetic entropy occurs below T_c, and then the height of the 1D Schottky anomaly is expected to be significantly lower than calculated, as is observed in Fig. 2.

Another possible fit comes from the dimer limit. In the case both peaks in the specific heat are fairly well reproduced by theory (line 2 in Fig. 2), assuming a D parameter equal to zero, $J/k = -26$ K, and $J'/k = -1$ K. However, using these parameters a poor agreement with the magnetic susceptibility data is observed (line 2 in Fig. 1). Notice that the account of a little paramagnetic contribution, arising from the presence of some cationic disorder along the chain, could improve this fit. Further, it is to be noticed that the analysis is based on the Ising model, whereas, in fact, the interactions are possibly in between the Ising and Heisenberg limits as has been suggested[7] in [CoCu] for which the exchange anisotropy becomes $J_\perp/J_\parallel = 0.35$.

Taking into account these remarks, it seems clear that the above analysis does not allow us to come to a conclusion about the two possibilities. At any rate, a comparison with the results obtained with other members of the EDTA family, suggests that the dimeric possibility is more plausible. Thus, significant dimerizations of the chains have been found[6,7] in those systems containing Co(II). Further experimental information, like single-crystal EPR studies, is now required in order to confirm this point.

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