Ferrimagnetic Heisenberg chain; influence of a random exchange interaction

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We report on the magnetic behavior of "rigid" ferrimagnetic chains isolated in bimetallic complexes of the EDTA and "flexible" ones obtained in the amorphous variety. As shown by LAXS, the only noteworthy difference in the amorphous state is the random distribution of bond angles between nearest neighbors within chains. The "rigid" bimetallic chains in CoNi(EDTA)6H_2O are described in terms of Heisenberg model with an exchange coupling $J = -7.5$ K. The behavior of the amorphous variety somewhat differs, following the law $X = AT^{-0.8}$ typical of REHAC. A classical spin chain model involving a J distribution and alternating g factors allows to explain successfully the temperature dependence of the susceptibility.

Large interest in the thermodynamics of one dimensional (1D) systems has recently been stimulated by the engineering of new materials as for instance the so-called ferrimagnetic chains made up of two unequal spin sublattices spreading in a 1D network. Very few examples of such bimetallic systems were reported so far, although real efforts are being made by several groups for their synthesis. Note the series MM′ (EDTA) 6H_2O characterized by Beltran *et al.*[1] where M and M′ are divalent transition metals and the complex CuMn $(S_2C_2O_2)_2 n H_2O$ recently studied.[2]

In such systems, the underlying effect of the noncompensation between moments of the two sublattices results in drastic differences with the behavior of a simple antiferromagnetic chain.[3]

On the other hand, several interesting phenomena are strongly enhanced in 1D materials showing some degree of randomness in the exchange couplings.[4] Among the peculiar results to be emphasized, we must note their quasiuniversal thermodynamic behavior (power law variation of the temperature dependence of susceptibility and specific heat). Such a feature is recognized as being the signature of a random exchange Heisenberg antiferromagnetic chain (REHAC).[5]

This paper deals with the magnetic behaviors of crystalline and amorphous bimetallic chain complexes formulated as MM′ (EDTA)6H_2O. The accent will be put on the correlations between local structure and magnetic properties in both systems.

I. EXPERIMENT

The complexes formulated MM′ (EDTA)6H_2O (with M, M′ = Mn, Co, Ni, Cu) form the first series of one-dimensional ferrimagnetic systems in which both the 1D character and the cationic ordering are well established.

In the crystallized complexes, the structural arrangement consists of infinite zig-zag chains with alternating metallic centers. One site (M) is surrounded by two oxygen atoms belonging to bridging acid functions of the EDTA and four water molecules, while the other (M′) exhibits a hexacoordination through the EDTA ligand.[1] The local structure of the amorphous samples was investigated by large angle x–rays scattering (LAXS).[6] Both coordination scheme of the transition metals and chain spreading are shown to be preserved. The only significant feature is the existence of a bond angle distribution between the connected ions so that the amorphous complexes can be viewed as made of flexible chains like ribbons.

Let us now examine the magnetic behavior of the two varieties of Ni_2 (EDTA)6H_2O through a plot of χ_m^{-1} vs T (Fig. 1). We first note a rounded minimum of χ_m^{-1} around 10 K while the amorphous one shows a vanishing χ_m^{-1} when cooling down to absolute zero. The behavior of the former agrees with a Heisenberg exchange coupled chain with an exchange constant $J = -8.05$ K.[1] The high temperature variations clearly indicate that the mean exchange interaction is weaker in the amorphous variety than in the fully

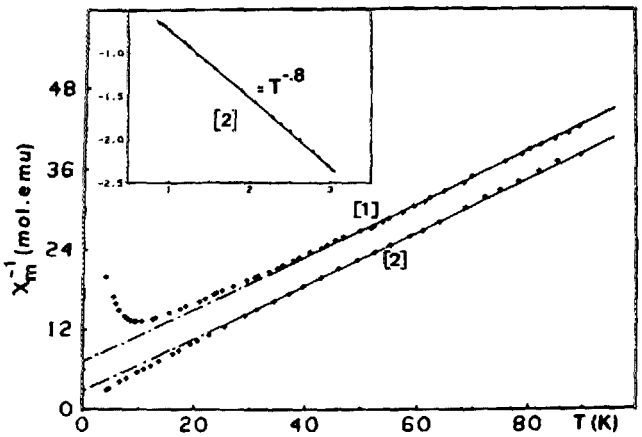

FIG. 1. Magnetic behaviors of the crystallized [1] and amorphous [2] varieties of Ni_2(EDTA)6H_2O. The power law variation in [2] is shown in the inset as $\ln \chi = f(\ln T)$.

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ordered one. Further, the low temperature behavior of the amorphous complex agrees with the power law $\chi_m = AT^{-\alpha}$ ($\alpha = 0.8$), which characterizes REHAC. This indicates that randomness effects cannot be neglected in the theoretical analysis of such materials.

II. HEISENBERG FERRIMAGNETIC CHAIN

We consider a Heisenberg quantum chain made up of two spin sublattices namely S_a and S_b. Let S_i ($i = 1, 2, \ldots, 2N$) be the current spin vector whose value (S_a or S_b) depends on the site parity.

Assuming a $2N$ spin closed chain, the Hamiltonian to be solved is given by

$$\mathcal{H} = -J\sum_{i=s}^{N} \mathbf{S}_{2i}(\mathbf{S}_{2i-1} + \mathbf{S}_{2i+1}), \tag{1}$$

where a negative J value refers to an antiferromagnetic coupling and cyclic boundary conditions impose $\mathbf{S}_{2N+1} = \mathbf{S}_1$.

For finite rings of N pairs ($S_a - S_b$), the eigenvalue problem consists in solving a $(2S_a + 1)^N \cdot (2S_b + 1)^N$ energy matrix. As previously shown in similar studies, a very significant reduction of the computational work is obtained by taking fully into account the geometrical and spin space symmetries of the $2N$-site closed chain.[3]

This reduces the size of the largest block matrix to be diagonalized by a factor depending on the spin multiplicities. For the $(1/2 - 1)_N$ closed chain, for instance, the reduction factor is about $4N^2$, making the problem tractable up to $N = 5$[3].

The determination of the magnetic susceptibility χ necessitates to compute the contributions χ_1 and χ_2 related to the first and second-order Zeeman effects, respectively. χ_1 corresponds to the diagonal matrix elements of

$$M^z = g_a \sum_{i=1}^{N} S^z_{2i-1} + g_b \sum_{i=1}^{N} S^z_{2i} \tag{2}$$

within the states which diagonalize $\mathcal{H}$, while χ_2 is the sum of contributions arising from nondiagonal terms of M^z. The computations were performed on finite rings of increasing size $(\frac{1}{2} - S)_N$ for $S = 1$ to $\frac{5}{2}$, then entrapolated to the thermodynamic limit ($N \to \infty$) by means of the relation

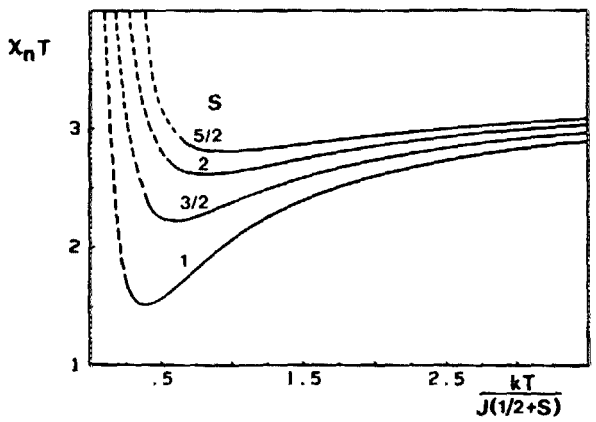

FIG. 2. Temperature dependence of the normalized $\chi_n T$ product for the $(1/2 - S)_{N\to\infty}$ ferrimagnetic chains. The part of the curves in dashed line is given with an error about 5%.

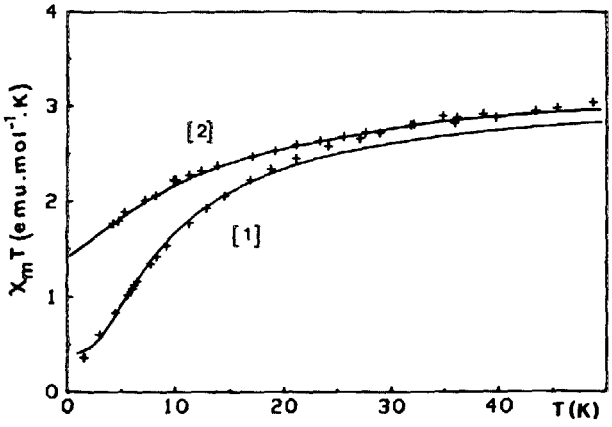

FIG. 3. Experimental and theoretical (full line) magnetic behaviors of the crystallized [1] and amorphous [2] CoNi(EDTA)6H_2O complexes. Results of the fits are given in the text.

$\chi_\infty = \chi_N + a/N^\alpha$. They are reported in Fig. 2 as plots of $\chi_n T$ vs $kT/J(1/2 + S)$ for $g_a/g_b = 1$ (second-order Zeeman contributions vanish). The normalized function

$$\chi_n T = \frac{10\chi T}{Ng^2\beta^2\{\frac{3}{4} + S(S+1)\}} \tag{3}$$

takes uniformly the value 10/3 in the high temperature limit. Then, the curves show a minimum all the less pronounced as S differs from $\frac{1}{2}$, and further diverge at decreasing temperatures according to the power law $\simeq T^{-\alpha}$ ($\alpha = 0.8$–1) in the same way as regular ferromagnetic chains. Obviously, such a divergence disappears when g_a/g_b approaches the compensation value given by $g_a/g_b = \frac{4}{3}(S + 1)$. In this limit, the systems behave like antiferromagnetic chains. The complex CoNi(EDTA)6H_2O deserves some attention owing to the spins of the ions under consideration [high spin Co(II) is well described, at low temperature, by $S = \frac{1}{2}$ while Ni(II) corresponds to $S = 1$] and the ratio between Landé factors. These, estimated by EPR measurements, correspond to $g_{Co} = 4.50$ and $g_{Ni} = 2.30$. The ratio between g values being close to the compensation value, we expect a weak magnetic moment in the ground state as displayed in Fig. 3. Finally, the above model provides a very satisfying description of the experimental data for $J = -7.5$ K (curve [1]). The discrepancy observed for $T > 20$ K indicates that $S = \frac{1}{2}$ is no longer a good quantum number for Co(II). The first excited states, thermally populated, must be taken into account.

III. RANDOM EXCHANGE COUPLED BIMETALLIC CHAIN

According to structural investigations by LAXS, we assume, in the amorphous [CoNi] complex, open chains with random exchange interactions between nearest neighbors. The classical spin approximation allows for the easy accounting of the J distribution. Using the procedure described by Thorpe,[7] the partition function is expressed in closed form:

$$Z = \prod_{i=1,N} \frac{\sinh(J_i/kT)}{J_i/kT}. \tag{4}$$

The magnetic susceptibility is evaluated from the pair corre-

lation functions $\langle \mathbf{M}_n \mathbf{M}_{n+p} \rangle = \langle g_n \mathbf{S}_n g_{n+p} \mathbf{S}_{n+p} \rangle$ with g_n depending on the n parity.

Setting $g_+ = \frac{1}{2}(g_1 + g_2)$, $g_- = \frac{1}{2}(g_1 - g_2)$, and $F_0 = \langle F(J_i/kT) \rangle$ [with $F(J_i/kT) = \coth(J_i/kT) - kT/J_i$], the susceptibility can be written[6]

$$\chi = \frac{N\beta^2}{3kT}\left(g_+^2 \frac{1+F_0}{1-F_0} + g_-^2 \frac{1-F_0}{1+F_0}\right). \tag{5}$$

Obviously, F_0 depends on the J distribution. Assuming a square distribution centered at J and of width 2λ, we can express F_0 under the condensed form:

$$F_0 \frac{kT}{2\lambda} \ln \frac{(J-\lambda)\sinh[(J+\lambda)/kT]}{(J+\lambda)\sinh[(J-\lambda)/kT]}. \tag{6}$$

For discussing the influence of the relative width of the J_i distribution, we put $g_1 = g_2$. Let L be the correlation length of the chain. At low temperature, the system behaves like a set of independent rigid strings, each one of length L. Thus, the susceptibility per site is given by

$$\chi \simeq \frac{1}{kT} \frac{m_L^2}{L}, \tag{7}$$

where m_L is the magnetic moment carried by a rigid string. For a ferromagnetic coupling, $m_L = L\beta$, while for an antiferromagnetic one, $m_L = \beta/2$.

Owing to the magnetic compensation which is complete for even L values only, the correlation length may be defined through

$$L^2 = \frac{\Sigma p^2 |\langle \mathbf{S}_0 \mathbf{S}_p \rangle|}{\sum_p |\langle \mathbf{S}_0 \mathbf{S}_p \rangle|}. \tag{8}$$

In the present study, $\langle \mathbf{S}_0 \mathbf{S}_p \rangle$ appears as a product of p factors and we may write

$$|\langle \mathbf{S}_0 \mathbf{S}_p \rangle| = a^p S^2$$

$$\text{with } a = \exp\{\overline{\ln[F(J_i/kT)]}\}. \tag{9}$$

According to the $F(J_i/kT)$ expression, we get

$$L \simeq \frac{|J|}{kT \ln(4|J|/kT)}. \tag{10}$$

Inserting these results and the expressions for m_L into χ, we confirm the low-temperature divergence of Eq. (5). Obviously, the above remarks fail as soon as $g_1 \neq g_2$.

In order to compare theoretical prediction with experiment, we needed the usual scaling factors.[6]

The best agreement with the data of the [CoNi] complex obtained by least squares refinement is given in Fig. 3 (curve [2]). It corresponds to $J = -5.95$ K, $\lambda = 13.40$, $\bar{g}_{Co} = 4.76$, $\bar{g}_{Ni} = 2.10$.

The extrapolated nonzero value of $\chi_m T$ when $T \to 0$ K appears to be well predicted from a distribution of the interactions including both ferromagnetic and antiferromagnetic couplings ($\lambda > |J|$). Clearly, an infinite linear system with a distribution favoring only one kind of coupling would be irrelevant in the present case.

Lastly, it is to be emphasized that the use of a classical spin formalism, instead of a quantum one is convenient but gives an exchange constant overestimated by some 20–30%. In spite of these remarks, the structural models are shown to be largely supported by magnetic investigations for both materials.

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