Exchange Alternation and Single-Ion Anisotropy in the Antiferromagnetic Heisenberg Chain $S = 1$. Magnetic and Thermal Properties of the Compound $Ni_2(EDTA)\cdot 6H_2O$

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A Heisenberg model for a $S = 1$ antiferromagnetic chain, which takes simultaneously into account two alternating exchange parameters, J_1 and J_2, and a single-ion anisotropy parameter, D, is developed by using the Bonner–Fisher procedure. The magnetic susceptibility and specific heat properties of this system as function of $\alpha = J_2/J_1$ and $\beta = D/|J_1|$ are discussed. For the susceptibility data, rational unified expressions which reproduce in a satisfactory manner the theory are proposed and used to analyze the magnetic behavior of the alternating chain system $Ni_2(EDTA)\cdot 6H_2O$. The fit of the data agrees with the presence of a weak dimerization for the Ni(II) chain ($\alpha = 0.9$). On the other hand, comparable values for exchange and single-ion anisotropy parameters are found($J_1/k = -8$ K; $\beta \sim 1$). These results are supported by the specific heat data. In particular, a good agreement between the exchange parameters determined from the two complementary experiments is obtained.

1. Introduction

One-dimensional (1D) magnetism is characterized by a close and rich coupling between models and materials.[1] This area has seen a spectacular development in recent years with the chemical preparation of novel types of low dimensional magnetic materials, which have then motivated the development of new models in order to explain their properties.[2] One of the systems that has been particularly active from both theoretical and experimental points of view is the exchange-alternating linear chain with spins $S = {}^1/_2$.[3,4] The interest for this system is connected with the problem of a spin–Peierls transition,[5] by which a uniform antiferromagnetic chain can undergo a dimerization due to the coupling with the phonon system. An additional stimulus is related with the discovery of chain compounds in which ferromagnetic and antiferromagnetic exchange interactions are alternating along the chain.[6] The theory for this kind of system has been recently developed.[7]

The $S = 1$ alternating antiferromagnetic chain has received much less attention, although examples of nickel (II) chains with alternating structures are known.[8] From the theoretical point of view, only the case with uniform exchange interactions has been treated. Thus, Weng[9] and de Neef[10] calculated the thermodynamical properties of these magnetic systems, including the exchange anisotropy effects. Furthermore, Blöte[11] studied the influence of the single-ion anisotropy on the specific heat properties. From the experimental point of view, nickel (II) chains have recently seen a renewed interest in connection with the Haldane conjecture[12] which, in a J-uniform antiferromagnetic chain with integer spin values, predicts the presence of an energy gap between the singlet ground spin state and the first excited states. Probably, this prediction represents the most significant theoretical contribution of the last decade in low dimensional magnetism. Although a quantum energy gap has been experimentally found in several Ni(II) chains,[13] it is often very difficult to conclude that this is a Haldane gap since other factors, as for example the exchange alternation or a single-ion anisotropy can also lead to an energy gap. This reason, together with the existence of alternating nickel (II) chain compounds,

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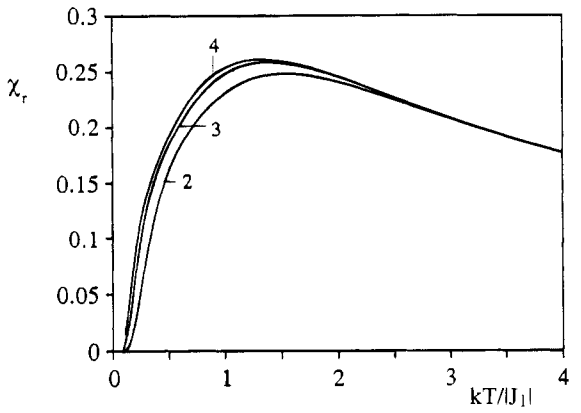

Figure 1. Thermal dependence of the reduced susceptibility for *J*-uniform antiferromagnetic rings ($\alpha = 1$, $\beta = 0$)) of different lengths ($N = 2$, 3, and 4).

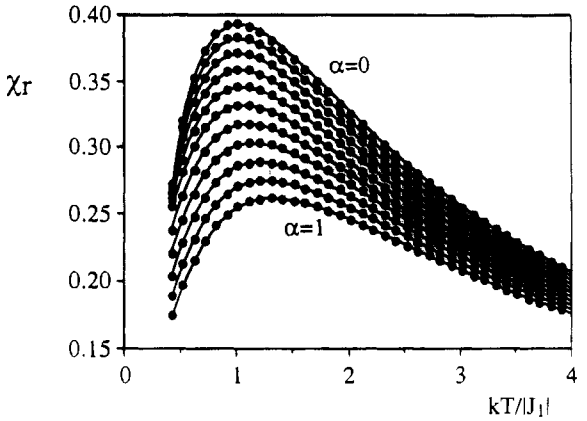

Figure 2. Thermal dependence of the reduced susceptibility of the $N = 4$ ring for various values of the alternating parameter α (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0). The solid lines represent the fitting of the numerical results (●) (Table 1).

justify the development of suitable theoretical models for the characterization of this class of 1D systems.

In this paper we develop this theory from a model that takes simultaneously into account Heisenberg exchange alternation and single-ion anisotropy. The corresponding spin Hamiltonian can be written as

$$H = -J_1\left[\sum_{i=1}^{N} S_{2i}S_{2i+1} + \alpha\sum_{i=1}^{N} S_{2i}S_{2i-1}\right] + D\sum_{i=1}^{2N}(S_{iz})^2 \quad (1)$$

where N is the number of spin pairs, J_1 and J_2 ($= \alpha J_1$) are the two nearest neighbor antiferromagnetic exchange interactions, and D is the axial zero field-splitting of the spin $S = 1$. As the hamiltonian is written a positive D value represents the situation in which the $|M_S\rangle = 0$ component of the spin triplet is stabilised by an energy D with respect to the $|M_S\rangle = \pm 1$ components.

By using a closed-chain computational procedure similar to that developed in other 1D systems,[7,14] we have calculated the magnetic susceptibility and specific heat behaviors of the *J*-alternating $S = 1$ Heisenberg chain as a function of both exchange alternation ($\alpha = J_2/J_1$) and single-ion anisotropy ($\beta = D/|J_1|$) parameters. A detailed description of the computational program is reported in ref 7. In the first part of the work we present the magnetic and thermal behaviors of this 1D system, together with the deduction of rational unified expressions that reproduce in a satisfactory manner the theoretical susceptibility data. In the second part, these results are used to analyze the properties of the alternating chain system Ni_2-(EDTA)·$6H_2O$.

2. Magnetic Properties

Numerical Results. All the magnetic curves are plotted in terms of reduced (dimensionless) quantities. The reduced temperature is defined as $T_r = kT/|J_1|$ and the reduced susceptibility as $\chi_r = \chi_M|J_1|/[2N_A g^2\mu_B{}^2/3]$. With this definition the product $\chi_r T_r$ tends to unity in the high temperature limit. In Figure 1 we report the thermal variation of the magnetic susceptibility for *J*-uniform antiferromagnetic rings of various lengths (up to $N = 4$, that is eight spins). The magnetic data show a rather rapid convergence when N increases, in such a way that above $T_r \approx 0.4$ the curves for $N = 3$ and 4 differ by less than 5%. This observation suggests that above this temperature the $N = 4$ ring should describe the infinite chain behavior in a satisfying manner, making unnecessary to extrapolate the finite-ring results. Furthermore, the convergence becomes more and more rapid as we approach the dimer limit, so that for the alternating cases, the $N = 4$ curves closely describe the infinite system even at lower temperatures. In the following we focus on the behavior of the $N = 4$ ring.

The influence of the exchange alternation is reported in Figure 2. The main effect of the alternation is to increase the height of the maximum in χ, which increases from $\chi_r = 0.26$ ($\alpha = 1$) to 0.39 ($\alpha = 0$), while the corresponding temperature only shows a small decrease from $T_r = 1.32$ ($\alpha = 1$) to 1.02 ($\alpha = 0$).

The influence of local anisotropy for different values of the exchange alternation parameter α is shown in Figures 3 and 4. For positive D values the height of the maximum in χ decreases when β is increased, while its position remains nearly unchanged. On the other hand, this effect becomes more pronounced as α decreases, that is, as we approach the dimer limit. A similar evolution of the curves is observed for negative D values, but now the position of the maximum is slightly shifted toward higher temperatures when the anisotropy is increased (Figure 4). Since the values commonly found for the anisotropic parameter ($|\beta| = D/|J_1|$) are lesser than 1, the above results emphasize that in real systems the influence of local anisotropy will remain a weak effect, very difficult to evidence from the magnetic susceptibility data.[15] Furthermore, we notice that α and β parameters have similar effects on the computed magnetic curves and so, they must be strongly correlated. Thus, for real systems having D values of the same order of magnitude than J_1 , a reliable value of the alternation parameter will be extracted from the fitting of the data if D can be evaluated independently.

Fitting of the Numerical Data to Closed Form Expressions. In order to handle the above numerical results for the analysis of experimental data, it is convenient to fit these theoretical susceptibility curves to a unified expression of χ_r versus T_r, with α and β as parameters. Following a similar procedure to that reported by Hatfield et al.[4] for the alternating antiferromagnetic chain of spins $S = {}^1/_2$, we have found that the simplest rational expression that better reproduces the numerical results of an alternating chain of spins $S = 1$ has the form

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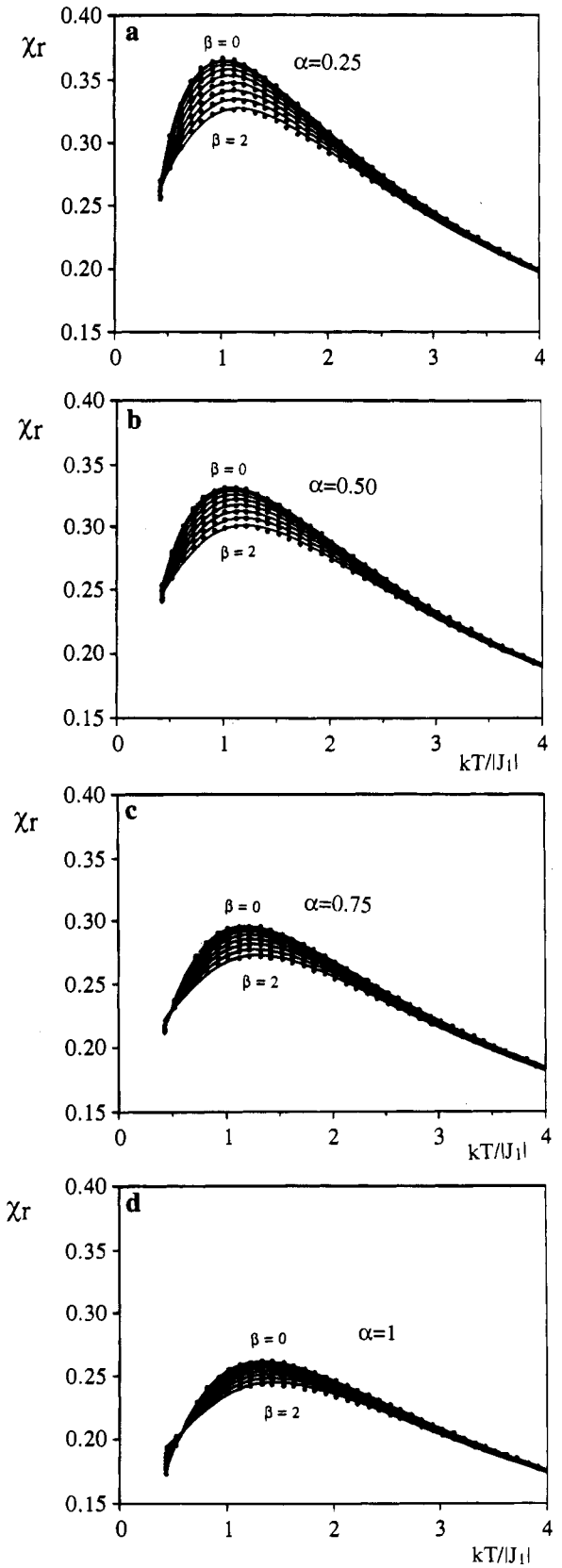

Figure 3. Influence of the local anisotropy ($D > 0$) on the magnetic properties of alternating chains with different α values. β is 0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75, and 2.0. Solid lines represent the fit to rational functions (Table 2).

$$\chi_r = [AT_r^2 + BT_r + C]/[T_r^3 + DT_r^2 + ET_r + F] \quad (2)$$

where A, B, ..., and F are the best fitting parameters. In view of the definition of χ_r, the parameter A is fixed to 1. For the remaining parameters, a careful study of their evolution with α allows to note in a first step that for $\beta = 0$, B is nearly independent of α (B = 0.50), while C shows a linear evolution in the range $0 < \alpha < 0.5$ ($C = -0.07096 + 0.34191\alpha$), being almost constant in the range $0.5 < \alpha < 1$ ($C = 0.1$). By fixing these three parameters in the fitting of the curves reported in Figure 2, a regular evolution of the remaining parameters can be obtained, which allows one to express the $D-F$ parameters as second degree polynomials in α at most:

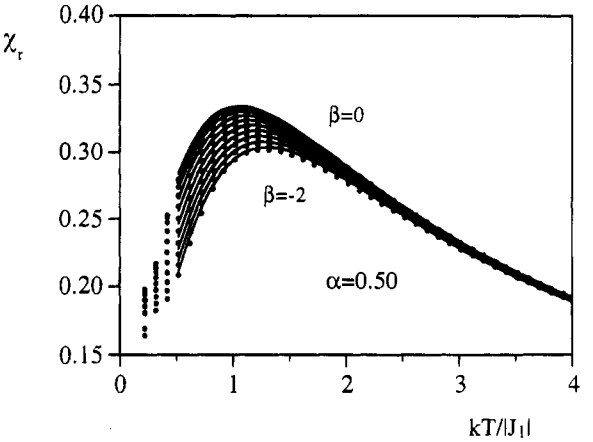

Figure 4. Influence of the local anisotropy ($D < 0$) on the magnetic properties of alternating chains with an intermediate α value (α = 0.5). β is 0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75, and 2.0. Solid lines represent the fit to rational functions (Table 3).

$$X = x_0 + x_1\alpha + x_2\alpha^2 \quad (3)$$

The resulting x_i coefficients are summarized in Table 1. The proposed unified expression for χ_r conveniently reproduces the theoretical curves, in the overall temperature range (Figure 2). The agreement criterion R, defined as the square of the relative deviations, is less than 10^{-5} for all the cases.

In a subsequent step, a unified expression of χ_r for the alternating chain with local anisotropy is determined. To do that, each family of curves characterized by an α value and different β's (see Figure 3), has been fitted to expression 2, blocking in the fit the parameters A, B, and C to their previous values, and allowing to vary the remaining parameters. The resulting $D-F$ parameters can be then conveniently expressed as second degree polynomials in β:

$$X = y_0 + y_1\beta + y_2\beta^2 \quad (4)$$

Finally, we have found that the variation of the y_i's coefficients can be fitted, in turn, to second and third degree polynomials in α. The final expressions for the X_i parameters are summarized in Tables 2 and 3 for positive and negative D values, respectively. Thus, substituting these expressions in eq 2, a general expression for the thermal variation of the magnetic susceptibility as a function of the parameters α and β is obtained, which allows to reproduce in the overall temperature range all the theoretical curves with an agreement criterion, defined as the square of the relative deviations, much better than 1% ($R = 10^{-4}$). Expression 2 is valid for the antiferromagnetic $S = 1$ Heisenberg chain in the following range of α, β and T_r parameters. Positive D values: $0.25 < \alpha < 1$, $0 < \beta < 2$, $T_r > 0.4$. Negative D values: $0 < \alpha < 1$, $0 < \beta < 2$, $T_r > 0.5$.

3. Magnetic Specific Heat

Convergence. In Figure 5 we report the evolution of the specific heat, C_p, with N for the case $\alpha = 0.9$ and $\beta = 0.5$.

Table 1. Alternating Chain without Local Anisotropy, with $A-F$ Parameters for the Rational Expression 2 Given as a Function of the Polynomials in α: $X(\alpha) = x_0 + x_1\alpha + x_2\alpha^2$

	A	B	C	D	E	F
$\alpha \le 0.5$	$a_0 = 1$	$b_0 = 0.5$	$c_0 = -0.07096$	$d_0 = 1.136963$	$e_0 = 1.04853272$	$f_0 = 0.4447955$
	$a_1 = 0$	$b_1 = 0$	$c_1 = 0.34191$	$d_1 = 0.748419$	$e_1 = -0.8077223$	$f_1 = 1.162769$
	$a_2 = 0$	$b_2 = 0$	$c_2 = 0$	$d_2 = 0$	$e_2 = 1.375320$	$f_2 = 0$
$\alpha > 0.5$	$a_0 = 1$	$b_0 = 0.5$	$c_0 = 0.1$	$d_0 = 1.136963$	$e_0 = 1.605652$	$f_0 = 0.4447955$
	$a_1 = 0$	$b_1 = 0$	$c_1 = 0$	$d_1 = 0.748419$	$e_1 = -1.462219$	$f_1 = 1.162769$
	$a_2 = 0$	$b_2 = 0$	$c_2 = 0$	$d_2 = 0$	$e_2 = 1.668971$	$f_2 = 0$

Table 2. Alternating Chains with Positive Local Anisotropy with Coefficients for the Polynomial Expressions of the Parameters D, E, and F

$D(\alpha,\beta) =$	$a = 1.138586098 + 0.77641703\alpha - 0.0155286\alpha^2$
$a + b\beta +$	$b = 0.016602534 + 0.1103444\alpha - 0.29334334\alpha^2$
$c\beta^2$	$c = 0.0811058 + 0.03832416\alpha + 0.02998674\alpha^2$
$E(\alpha,\beta) =$	$a' = 1.032522389 + 0.1410407\alpha + 0.5365886015\alpha^2$
$a' + b'\beta +$	$b' = -0.11857766 - 0.4049098\alpha + 1.03496136\alpha^2$
$c'\beta^2$	$c' = 0.3813648 - 0.12743406\alpha - 0.0653920\alpha^2$
$F(\alpha,\beta) =$	$a'' = 0.45021124 + 1.052788\alpha + 0.1696811\alpha^2$
$a'' + b''\beta +$	$b'' = 0.1561556 + 0.277095\alpha - 0.69774181\alpha^2$
$c''\beta^2$	$c'' = -0.207825 + 0.1519149\alpha - 0.0470349\alpha^2$

Table 3. Alternating Chains with Negative Local Anisotropy with Coefficients for the Polynomial Expressions of the Parameters D, E, and F

$D(\alpha,\beta) = a +$	$a = 1.11847352 + 0.8070096\alpha - 0.0573343\alpha^2$
$b\lvert\beta\rvert +$	$b = -0.0067190 + 0.0.40660648\alpha - 0.21702374\alpha^2$
$c\lvert\beta\rvert^2 +$	$c = -0.0400383 + 0.40660648\alpha - 0.21702374\alpha^2$
$d\lvert\beta\rvert^3$	$d = -0.0071947 + 0.10504280\alpha - 0.052961680\alpha^2$
$E(\alpha,\beta) = a' +$	$a' = 1.0556458 + 0.14334620\alpha + 0.61724458\alpha^2$
$+ b'\lvert\beta\rvert +$	$b' = 0.0185237 - 0.15150865\alpha + 0.06033760\alpha^2$
$c'\lvert\beta\rvert^2 +$	$c' = 0.1468270 - 1.39128271\alpha + 0.60620434\alpha^2$
$d'\lvert\beta\rvert^3$	$d' = 0.0121360 - 0.3449764\alpha + 0.13669768\alpha^2$
$F(\alpha,\beta) = a'' +$	$a'' = 0.4488044 + 1.04049579\alpha + 0.124473026\alpha^2$
$+ b''\lvert\beta\rvert +$	$b'' = -0.0042444 + 0.11645276\alpha - 0.01546729\alpha^2$
$c''\lvert\beta\rvert^2 +$	$c'' = 0.0733828 + 1.02045458\alpha - 0.25579105\alpha^2$
$d''\lvert\beta\rvert^3$	$d'' = 0.0184448 + 0.23915749\alpha - 0.05672648\alpha^2$

This evolution is much more complicated than that found for the magnetic susceptibility curves, with successive curves crossing at low temperatures. On the other hand, the convergence is more rapid as the exchange alternation is increased. Thus, while in the uniform case ($\alpha = 1$) the position of the maximum varies from $T_r = 1.04$ for $N = 2$, to 0.85 for $N = 4$, in the alternating case ($\alpha = 0.5$) this varies from $T_r = 0.77$ for $N = 2$, to 0.66 for $N = 4$. We also notice that the reduced temperature above which the curves for $N = 3$ and 4 are almost coincident, decreases with the exchange alternation (from ca. 0.4 in the $\alpha = 1$ case to ca. 0.25 in the $\alpha = 0.5$ case). As conclusion, we can say that the behavior of the $N = 4$ ring approaches more and more that of the infinite chain as the exchange alternation increases (i.e. as the α parameter decreases). However, compared with the magnetic susceptibility curves, the converge is significantly slower and therefore, the $N = 4$ ring should describe the infinite chain behavior in a satisfying manner above the maximum in C_p, at best. Hence, no numerical fit to polynomial expressions has been tried for the specific heat curves.

Influence of Exchange Alternation and Local Anisotropy. The curves for $N = 4$ giving the thermal variation of the magnetic specific heat for various α and β values are plotted in Figure 6. A general inspection of this figure allows us to notice that the local anisotropy has a more pronounced effect on the specific heat curves than the exchange alternation. Thus, independently of the degree of J-alternation, the main effect of the local anisotropy is to broaden the specific heat curves as β is increased. This broadening becomes more pronounced as α approaches the dimer limit. A second effect of the anisotropy is to increase both the height and position of the C_p maximum. Again, this effect becomes more pronounced as α approaches the dimer limit. The coordinates of the maximum in C_p for various α and β values are summarized in Table 4.

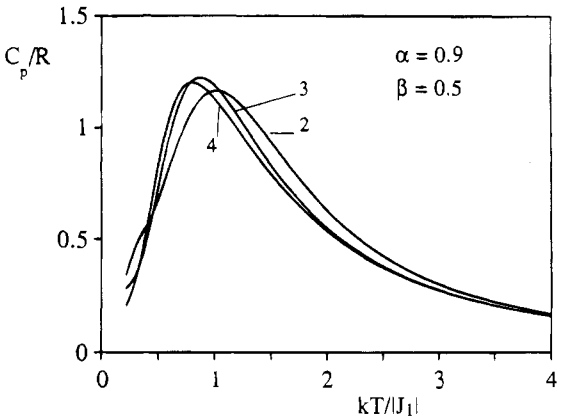

Figure 5. Specific heat of alternating rings of different lengths (N = 2, 3, and 4) for $\alpha = 0.9$ and $\beta = 0.5$.

From the above discussion it appears that for these 1D systems, specific heat measurements should be a good complement to the magnetic measurements. Thus, magnetic susceptibility data are expected to provide useful information on the degree of exchange alternation, while they are relatively insensitive to the local anisotropy of these systems. In turn, specific heat data appear to be mostly sensitive to the local anisotropy effects.

4. The Alternating Chain NiNi(EDTA)·6H$_2$O

This compound belongs to the isostructural family MM′(EDTA)·6H$_2$O (abbreviated as [MM′], where M = Mn, Co, Ni, Zn, and Mg and M′ = Co, Ni, Cu, and Zn^{+2}) in which two different octahedral sites, denoted as "hydrated" and "chelated", are linked through carboxylate bridges from the EDTA to give infinite zigzag chains[16] (Figure 7). Due to the two types of topologies adopted by the carboxylate bridges (anti−anti and

Table 4. Position of the Maximum in C_p for Different α and β Values

		$\beta = 0.0$	$\beta = 0.25$	$\beta = 0.50$	$\beta = 0.75$	$\beta = 1.0$	$\beta = 1.25$	$\beta = 1.50$	$\beta = 1.75$	$\beta = 2.0$
$\alpha = 0.25$	$kT/\lvert J_1\rvert$	0.52250	0.54050	0.58650	0.64250	0.69950	0.75850	0.81950	0.88350	0.95250
	C_p/R	1.0340	1.0369	1.0469	1.0642	1.0885	1.1187	1.1531	1.1890	1.2244
$\alpha = 0.50$	$kT/\lvert J_1\rvert$	0.65550	0.65250	0.66350	0.69550	0.74550	0.80350	0.86550	0.93050	0.99850
	C_p/R	1.0728	1.0879	1.1159	1.1378	1.1513	1.1623	1.1768	1.1931	1.2197
$\alpha = 0.75$	$kT/\lvert J_1\rvert$	0.74150	0.74050	0.74750	0.77150	0.81150	0.86050	0.92150	0.98650	1.0545
	C_p/R	1.1385	1.1560	1.1890	1.2135	1.2223	1.2206	1.2169	1.2176	1.2247
$\alpha = 1.00$	$kT/\lvert J_1\rvert$	0.84350	0.84050	0.84650	0.86550	0.89750	0.94150	0.99450	1.0565	1.1215
	C_p/R	1.1595	1.1746	1.2053	1.2314	1.2439	1.2441	1.2378	1.2314	1.2291

anti−syn type), alternating exchange coupling along the chain is to be expected. Thus, the system may be schematized as

$$\text{--M}(H_2O)_4O_2\text{−M(EDTA)--M}(H_2O)_4O_2\text{−M(EDTA)--}$$

where dashed and full lines refer to the two kinds of exchange parameters.

From the magnetic point of view these compounds constitute a versatile series of 1D ferrimagnets, in which many choices of alternating spins and exchange anisotropies can be easily specified. In the [NiNi] case, the magnetic susceptibility data were previously discussed under the assumption of uniform Heisenberg and Ising chains, ignoring exchange alternation and the single-ion anisotropy.[8a] Surprisingly, the Ising model gave a better overall fit to the data. In the present work we reinterpret these data from the alternating Heisenberg model. The magnetic characterization is completed with the analysis of the specific heat data.

Magnetic and Thermal Results. The magnetic behavior, studied in the range 4−300 K, shows a rounded maximum in χ at ca. $T = 10$ K, in agreement with the presence of antiferromagnetic exchange interactions (Figure 8). The specific heat properties for [NiNi] and for the isostructural compound [$Ni_{0.66}Zn_{1.34}$] have been studied in the range 0.1-30 K and are plotted in Figures 9 and 10. The thermal study of the Zn-containing compound was realized in order to determine the zero-field splitting of nickel(II) in the chelated site, since in this compound Ni(II) is selectively occupying this site.[17] Both systems exhibit a rounded bump around 6 K and 3 K for [NiNi] and [$Ni_{0.66}Zn_{1.34}$], respectively, followed by a sharp increase at higher temperatures, which corresponds to the lattice contribution. In order to obtain the magnetic specific heat contribution, we have subtracted from the raw data the specific heat of the isomorphous non magnetic compound [ZnZn] (dotted lines in the figures).[18] The specific heat data of [ZnZn] was fitted to the high-temperature data of the magnetic compounds by scaling the temperature axes. The resulting magnetic contribution is displayed in the figures as full circles. Finally, it is to be noticed that in the [NiNi] chain no λ-peak, characteristic of a magnetic ordering, is detected down to 0.1 K, which emphasizes the good 1D character for this system.

Analysis and Discussion. Before discussing the magnetic and thermal properties of the [NiNi] chain, it is convenient to determine the ZFS axial parameter of Ni(II). The fitting of the specific heat data of [$Ni_{0.66}Zn_{1.34}$] to expression 5[19] allows one to obtain a D/k value of 8.7 (±0.05) K.

$$C_p/R = [2(D/kT)^2 \exp(-D/kT)/(1 + 2\exp(-D/kT))^2] \quad (5)$$

The fit reproduces in a very satisfactory way both the position and height of the experimental Schottky anomaly (solid line of Figure 9). The resulting parameter accounts for the local anisotropy of Ni(II) in the chelated site, only. A similar study for evaluating the single-ion anisotropy in the hydrated site is not possible in the present system. In any case, according to the structural features of the two sites, which indicate that the hydrated site is the less distorted, a smaller D value is expected for this site. As a consequence, a D-alternation is also to be expected, which is not considered in the present model. Despite this simplification, this model should remain a convenient approach for the analysis of the magnetic data since, as we have pointed out before, anisotropy effects are less relevant than exchange alternation effects.

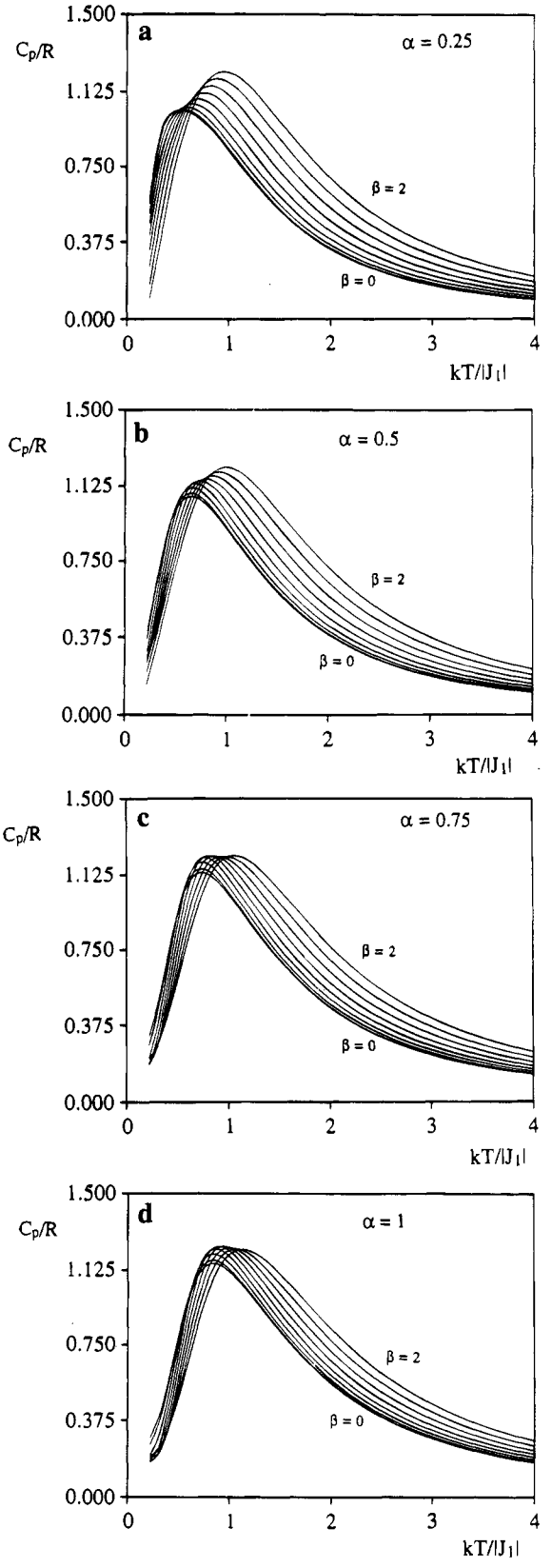

Figure 6. Specific heat for $N = 4$ rings with different α and β values (β = 0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75, and 2.0).

For the analysis of the magnetic susceptibility of the title compound, the polynomial expressions developed in the first part of the work has been used. The D value has been fixed to

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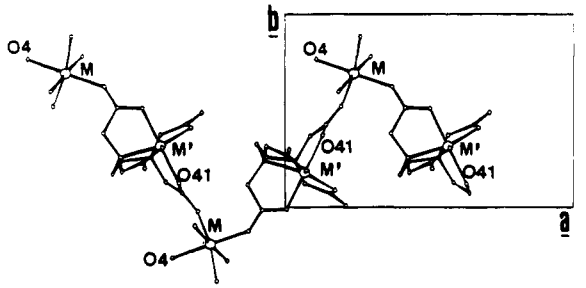

Figure 7. Pluto view of the MM'(EDTA)·6H_2(O) chain along the *ab* plane

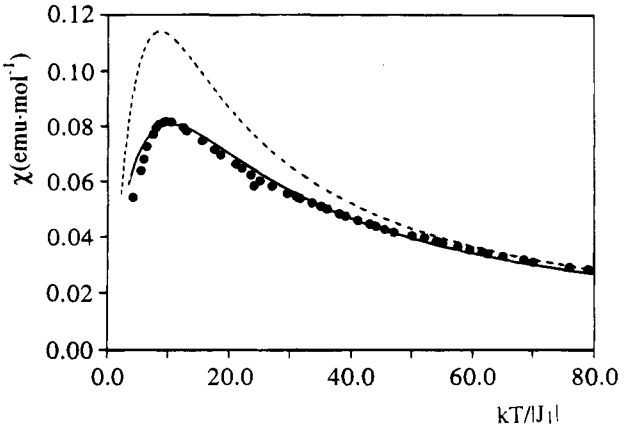

Figure 8. Magnetic susceptibility of the compound NiNi(EDTA)6H_2O. The full line corresponds to the fit form the alternating chain model (J_1/k = −8 K, α = 0.9, D/k = 8.7 K, and g = 2.2). The dashed line corresponds to the fit from the dimer model (J_1/k = −8 K, D/k = 8.7 K, and g = 2.15).

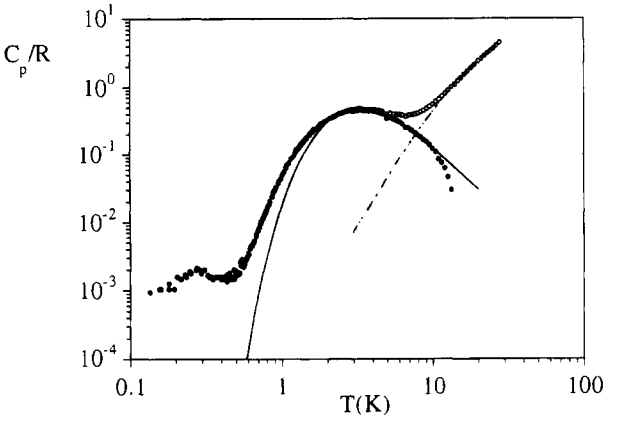

Figure 9. Specific heat of the compound $Ni_{0.66}Zn_{1.34}$(EDTA)6H_2O. The dotted line represents the lattice specific heat and the black points the magnetic contribution. The full line is the fit to a spin triplet with an axial ZFS parameter of D/k = 8.7 K.

that deduced from the specific heat results. The best fitting parameters are as follows: J_1/k = −8.0 (±0.1) K, α = 0.9 (±0.05), D/k = 8.7 K, and g = 2.2(±0.1) (solid line of Figure 8). In the figure we have also reported (dotted line) the magnetic behavior of the corresponding dimer (α = 0). The position of the maximum is mainly dependent on the exchange parameter J_1, while its height is very sensitive to the degree of exchange alternation. Therefore, this fit provides reliable values for J_1 and α, indicating a weak dimerization in the chain.

Although less sensitive to exchange alternation effects, the magnetic specific heat gives a further support to the weak

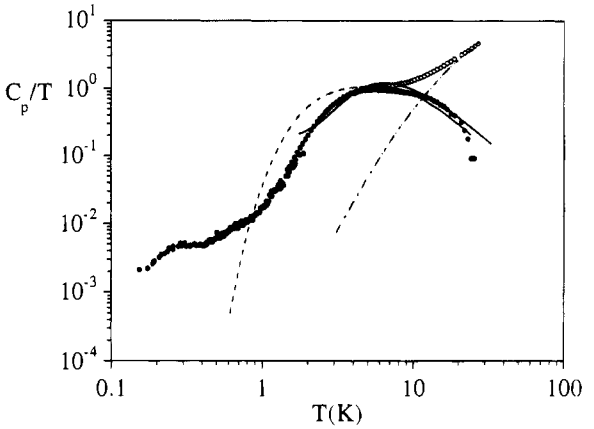

Figure 10. Specific heat of the compound NiNi(EDTA)6H_2O. The line (— • —) represents the lattice specific heat and the black points the magnetic contribution. The (- - -) line is the fit to a dimer model (J_1/k = −8 K, D/k = 8.7 K). The full line is the fitting to an alternating chain model (J_1/k = −8 K, α = 0.9, β = 0.5).

dimerization of the chain. Thus, the dimer model allows to reproduce the position of the Schottky-like anomaly, but not its width, leading to important discrepancies between theory and experiment in the low temperature region (below 4 K, see Figure 10). In turn, the alternating chain model with J_1/k = −8.0 K, α = 0.9, and D/k = 4 K, reproduces, in its application range (T > 3 K, in our case), both the position and the width of the anomaly. There is a good agreement between the exchange parameters obtained from both experiments. However, we observe that, in contrast to the magnetic susceptibility, the D-value estimated for the chelated site, D/k = 8.7 K, does not give a good fit of the C_p data, being necessary to introduce a smaller D value (D/k = 4 K). This difference underlines the larger sensitivity of the specific heat to the anisotropy effects, compared to the magnetic susceptibility. In fact, since the alternation in the Ni(II) anisotropy has been ignored by the model, the D value derived from the specific heat analysis may be viewed as an averaged anisotropy parameter. The reduced D value thus obtained accounts for the smaller anisotropy expected for the hydrated site.

In conclusion, the magnetic characterization of the Ni(II) compound from the alternating chain model developed in this work indicates a weak exchange-alternation in the chain (α = 0.9) and comparable values for both exchange and single-ion anisotropy parameters (J_1/k = −8 K; $\beta \sim 1$). However, the single-ion anisotropy effects have a limited influence on the magnetic behavior of this kind of chains, even in the case of weak exchange interactions (as exemplified by the title compound). In the general situation of intermediate and strong antiferromagnetic exchange interactions ($\beta \ll 1$), the anisotropy effect could be completely neglected, and therefore eq 2 should be sufficient for fitting the experimental data.

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