Magnetic properties of Cu(L-aspartato)$(H_2O)_2$: A linear chain antiferromagnet

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Specific heat, magnetic susceptibility, and magnetization measurements were performed in polycrystalline samples of the copper complex of the amino acid L-aspartic acid [called Cu(L-asp)]. The specific heat was measured between 3 and 45 K, while dc and ac susceptibilities were measured between 1.8 and 300 K. The magnetization data were obtained as a function of an applied field up to 9 T, at various fixed temperatures between 2 and 10 K. The specific heat and magnetic susceptibility curves show peaks at 3.95 K and 6.9 K, respectively, and approach zero at lower and higher temperatures. This behavior cannot be accounted for by considering only the superexchange paths provided by the σ skeleton of aspartic acid. If this were the case, a uniform J_0 along the asp-Cu-asp-Cu-asp chains would be expected. The data were well fitted, proposing for Cu(L-asp) a behavior characteristic of an alternating linear chain antiferromagnet. Each $S=\frac{1}{2}$ copper ion is coupled with an isotropic exchange interaction $J_0/k=(-5.3\pm0.1)$ K with one copper neighbor in the chain, and $\alpha J_0/k=(-1.5\pm0.1)$ K with the other $[\alpha=(0.29\pm0.02)]$. The average g value is $g=2.165\pm0.002$. Considering the alternating chain model, the susceptibility and magnetization data suggest also the presence of an additional interchain ferromagnetic coupling, which (within a mean-field approximation) leads to $J'/k=(0.7\pm0.1)$ K. Other exchange paths are proposed to explain the data. An important finding is that hydrogen bonds may support relatively large values of J. [S0163-1829(99)11925-8]

I. INTRODUCTION

Considerable efforts have been made in order to achieve a better understanding of quantum Heisenberg spin chains and layers. The classical papers,[1–3] dealing mainly with the eigenstates of linear chains, were rewarded by the discovery of real compounds showing this low-dimensional magnetic behavior.[4,5] Detailed calculations of the thermodynamic properties of spin chains were reported by Bonner and Fisher[6] (BF) who extrapolated to infinite chains results obtained for finite chains of spins $S=\frac{1}{2}$. Since then there has been a continuously growing set of experimental information about inorganic and organic compounds showing one- or two-dimensional magnetic behavior. This and the discovery of the high-T_c superconducting materials showing 2D magnetic ordering have given a renewed impulse to theoretical studies of low-dimensional spin arrays. This line of research has been reviewed by several authors.[3,7–9]

Alternating spin chains, in which each spin has different exchange couplings with its neighbors to the right and to the left, have been investigated theoretically[10,11] and experimentally.[12–17] Most of these studies have dealt with cases in which all interactions are antiferromagnetic, although cases with alternating antiferromagnetic and ferromagnetic interactions have been analyzed recently.[18,19] The study of alternating chains was stimulated by the discovery of $S=\frac{1}{2}$ compounds having uniform spin chains, which at a certain temperature T_{sp} display the so-called spin-Peierls transition, below which a temperature-dependent dimerization of the chain sets in.[20,21]

Recently, some of us reported the crystal structure, magnetic susceptibility, and electron paramagnetic resonance (EPR) measurements for the copper complex of L-aspartic acid,[22] Cu(L-aspartato)$(H_2O)_2$, $[Cu(CO_2NH_2CHCH_2CO_2)(H_2O)_2]$ [hereafter called Cu(L-asp)]. Susceptibility data were obtained in polycrystalline samples above 5 K. EPR measurements were performed in oriented single crystals at room temperature. The magnetic susceptibility $[\chi(T)]$ versus temperature $[T]$ data[22] displayed a broad maximum at 7 K, decreasing toward lower and higher temperatures. This is the qualitative behavior expected for a 1D spin chain, and the temperature of the maximum is an indication of the development of short-range magnetic order of the spins in the chain. These experimental results were compared to the predictions of BF (Ref. 6) for uniform antiferromagnetic chains with nearest-neighbor exchange interactions. That model reproduced the general aspects of the shape of the observed susceptibility $\chi(T)$ curve, but failed to agree with the magnitude and shape of the data around the maximum and at low T. To account for these

discrepancies we proposed[22] an additional interchain interaction J' and, using the mean-field approximation of Hatfield *et al.*,[23] we obtained $J_0/k=-5.3$ K and $J'/k=2.2$ K. This value for the ferromagnetic interchain interaction J' was not much smaller than the intrachain antiferromagnetic interaction J_0 and raises doubts about the applicability of such an approximation. This result indicated that magnetic measurements performed at lower temperatures were needed in order to make progress in the understanding of the magnetic behavior of Cu(L-asp). A very intriguing result[22] was the observation of a relatively large magnitude for the superexchange coupling J_0, in a lattice where the superexchange paths connecting the copper ions were assumed to be associated with the long σ bonds involving five diamagnetic atoms provided by the skeleton of the aspartic acid molecule and by some hydrogen bonds.

In this paper we report more detailed magnetic data for Cu(L-asp). Specific heat $[c(T)]$ measurements have been performed in the temperature range $3<T<45$ K, where the magnetic contribution is the largest. Magnetic susceptibility and magnetization data have also been obtained. The specific heat vs T curve displays a peak value $c_{\max}/R$ much higher than that expected for a uniform chain. The susceptibility data display a peak at about 6.9 K and show that $\chi(T)\rightarrow 0$ at low temperatures. This last result is not expected for uniform Heisenberg spin chains,[6,24] and was not detected in previous measurements[22] performed at higher T. Moreover, the shape of the observed temperature dependence of the magnetic susceptibility does not agree with that predicted for uniform chains.

We show here that the specific heat and magnetic data for Cu(L-asp) may be explained as corresponding to a spin chain with alternating exchange interactions. Magnetization data at high fields proved to be very useful to clarify this behavior. We have also analyzed the data in terms of exchange anisotropy [since according BF (Ref. 6) this may also explain the experimental results], without success. No evidence of structural changes below room temperature or of a spin-Peierls transition was found in this system. Our results are discussed and explained in terms of the structure of Cu(L-asp) (Ref. 22) and the bonds connecting the copper ions which provide paths for superexchange interactions.

II. EXPERIMENTAL RESULTS AND QUALITATIVE DISCUSSION OF THE DATA

Copper (L-aspartato) dihydrate was prepared as reported before.[22] The specific heat data were obtained with an adiabatic calorimeter in the temperature range $3<T<45$ K in polycrystalline samples prepared as explained by Siqueira *et al.*[25] The vibrational contribution, proportional to T^3, was corrected . Thus, the magnetic contribution to the specific heat $c(T)/R$ is plotted as a function of T in Fig. 1. Their behavior resembles that expected for a linear chain of spins, with a maximum value at 3.95 K. However, the maximum value observed for the specific heat is $c_{\max}/R=0.473\pm0.004$, much larger than the value $c_{\max}/R=0.35$ corresponding to a uniform Heisenberg spin chain.[4,6]

A Quantum Design MPMS-2 superconducting quantum interference device (SQUID) magnetometer and PPMS ac susceptometer were used to obtain the susceptibility and

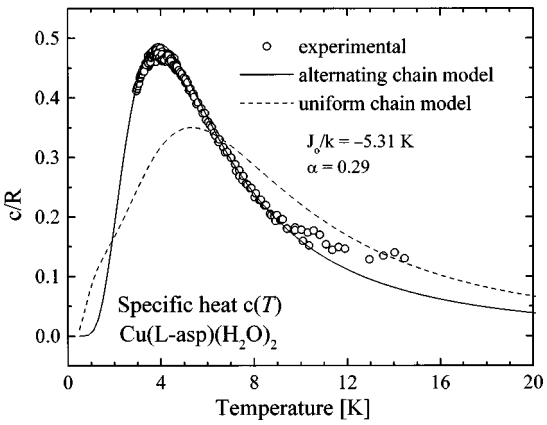

FIG. 1. Magnetic contribution to the molar specific heat as a function of T for Cu(L-asp) [plotted as $c(T)/R$; here $R=Nk=8.3145$ J/(mole K)]. The solid line gives the best global fit to the data obtained with the alternating Heisenberg spin chain model, including interchain coupling. The dotted line correspond to the prediction of the BF model (Ref. 6) for a uniform spin chain, and is included for comparison.

magnetization data. The dc magnetic susceptibility $\chi(T)$ of Cu(L-asp) was measured in an applied field of $B=0.1$ T in the temperature range $1.8<T<300$ K. The results for $1.8<T<20$ K are shown in Fig. 2, after being corrected for the diamagnetic-temperature-independent contribution, which was done using standard tabulated values.[26] We did not consider the (very small) temperature-independent paramagnetism. The ac magnetic susceptibility of the same sample was also measured from 2 to 100 K with results coincident with those given in Fig. 2 within the accuracy of the experimental data. A Curie-Weiss plot of the inverse susceptibility data in the high-temperature range (inset of Fig. 3) displays the be-

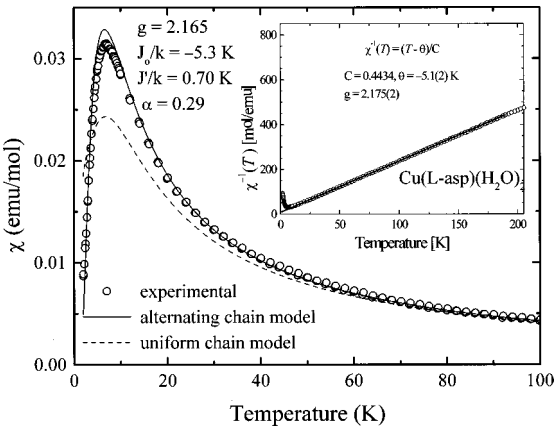

FIG. 2. Molar dc magnetic susceptibility data of Cu(L-asp), measured at 0.1 T in the temperature range between 1.8 and 40 K. Data points are corrected for the diamagnetic contribution. The solid line gives the best global fit to the data obtained with the alternating Heisenberg spin chain model, including interchain coupling. The dashed line is obtained as explained in the text, ignoring the interchain interactions J'. The dotted line corresponds to the prediction of the BF model (Ref. 6) for a uniform spin chain, and it is included for comparison. The inset shows a Curie-Weiss plot of the susceptibility data. The solid line gives the best fit of the data to the Curie-Weiss law, with the values of C and θ included in the figure.

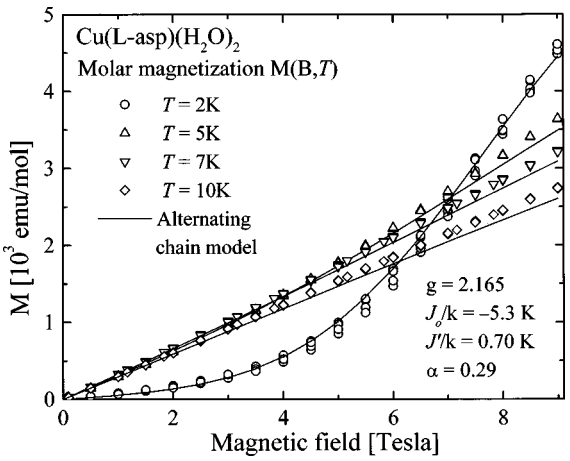

FIG. 3. Molar magnetization data for Cu(L-asp) as a function of applied magnetic field for different temperatures. The solid line gives the best global fit to the data obtained with the alternating Heisenberg spin chain model, including interchain coupling.

havior $\chi^{-1}(T)=(T-\theta)/C$ with $C=0.4434(4)$ (emu K)/mol and a Weiss constant $\theta=-5.12$ K. This value of C leads to an average g factor, of $g=2.175$ for the copper ions, in good agreement with the average value $g=2.169$ obtained from single-crystal EPR data.[22] Like the specific heat, the experimental susceptibility curve of Fig. 2 displays features resembling those corresponding to uniform chains. However, to explain the observed magnitude of the maximum $\chi(T)$ with a uniform spin chain model requires either an unphysical value of the g factor for Cu(II) or, as shown previously,[22] large interchain couplings. Moreover, the susceptibility data approach zero as $T\rightarrow 0$, a result not expected for linear uniform chains with isotropic exchange.[6] This was not observed in Ref. 22 as the data were obtained above 5 K. In order to obtain additional insight into this system we performed magnetization measurements as a function of field in the range between 0 and 9 T, at fixed temperatures 2, 5, 7, and 10 K. These results are displayed in Fig. 3.

III. CRYSTAL STRUCTURE OF Cu(L-asp) AND POSSIBLE SUPEREXCHANGE PATHWAYS

The crystal structure of Cu(L-asp) at room temperature is monoclinic, space group $C2$, $a=9.504$ Å, $b=10.038$ Å, $c=7.555$ Å, and $\beta=94.01$, with four molecules per unit cell $(Z=4)$.[22] In this group, the three symmetry-related atoms are obtained from the first at (x,y,z) by the symmetry operations $(-x,y,-z)$, $(\frac{1}{2}+x,\frac{1}{2}+y,z)$, and $(\frac{1}{2}-x,\frac{1}{2}+y,-z)$. The molecular structure around the copper ion is square pyramidal, having an amino nitrogen and a carboxylate oxygen from the glycine ring of the amino acid, an oxygen from the other carboxylate group, and a water molecule (W1), as equatorial ligands. Another water molecule (W2) is at the apex of the pyramid [see Fig. 4(a)]. Aspartic acid, $HO_2C(CH_2)CHNH_2CO_2H$ (together with glutamic acid), is peculiar among amino acids. It has two carboxylate groups, one in the amino acid group at one end and the other at the end of the side chain. In Cu(L-asp) the aspartic acid molecule binds one Cu(II) ion through the carboxylate oxygen and the amino nitrogen of the glycine ring, and to another copper

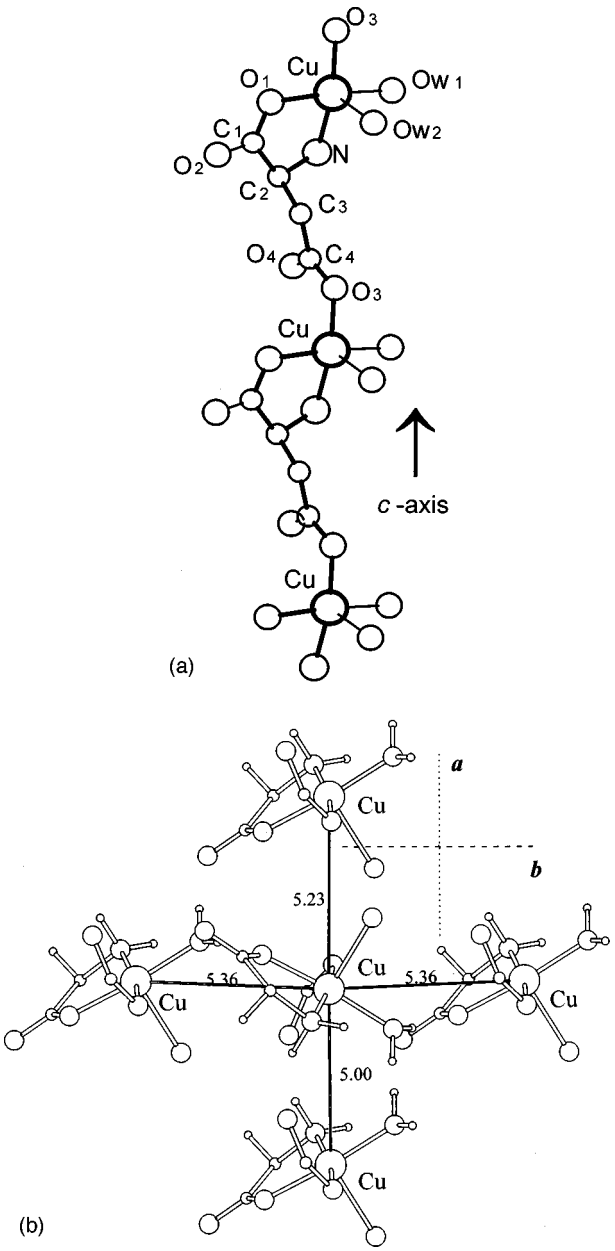

FIG. 4. (a) Chain of copper ions along the c axis in Cu(L-asp), as obtained from the crystallographic data (Ref. 22). It shows how copper ions are connected by the σ skeleton of the L-aspartic acid molecules. (b) Projection of the chains along the c axis showing the interactions of one chain with the four neighbor chains.

through one of the oxygens of the other carboxylate group. Thus, it displays polymeric chains asp-Cu-asp-Cu-asp-Cu-asp along the c axis. Figure 4(a) displays one of these chains and illustrates how the amino acid molecules connect the copper ions. Within each chain, every copper atom and L-aspartic molecule are obtained by simple lattice translations along c. The superexchange pathways within the chains are provided by the σ skeleton of the amino acid which involves five diamagnetic atoms. The Cu-Cu distance in this chain is 7.55 Å , and the superexchange path has a total length of 9.75 Å . The magnitude of the exchange interaction arising from this path will be called J_σ. Figure 4(b) displays a projection of the structure along the direction of the chain, parallel to the c axis. As shown in this figure, one central

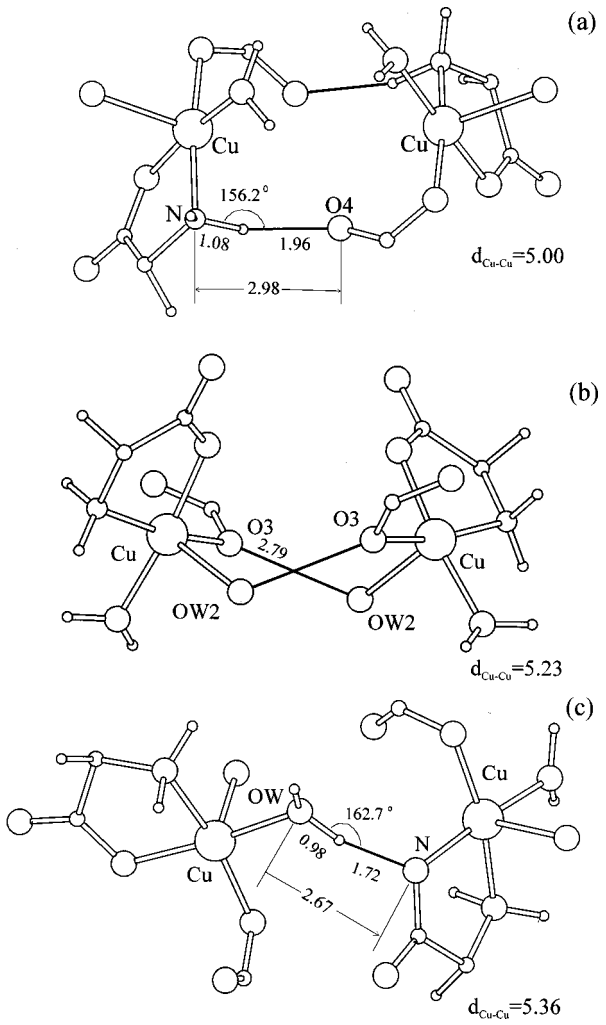

FIG. 5. Interchain connections: (a) copper atoms at 4.999 Å, (b) copper atoms at 5.23 Å, and (c) copper atoms at 5.36 Å.

chain along *c* is surrounded by two symmetry-related parallel chains at a distance *b*/2 in the *b* direction. The distance from a given Cu ion in the central chain to the nearest copper neighbors in each of these parallel chains is 5.36 Å. Figure 4(b) also shows that a central chain has other two neighbor chains separated by about *a*/2 in the *a* direction. In this case, the distances from a given Cu ion in the central chain to the two closest copper neighbors in the other two chains are equal to 5.00 and 5.23 Å, respectively. Copper ions in the central chain and its four nearest-neighbor chains are interconnected by hydrogen bonds and carboxylate bridges shown in Figs. 5(a), 5(b) and 5(c). Copper neighbors at 5.00 Å are connected by two symmetry-related paths with lengths of 9.50 Å. These paths, made of a sequence of a hydrogen bond and a carboxylate bridge, are shown in Fig. 5(a). Copper neighbors at 5.23 Å are connected by two symmetry-related hydrogen bonds between the apical water oxygen ligand of one copper and an equatorial oxygen ligand to the other copper, as shown in Fig. 5(b). The total length of this path is 7.04 Å. Copper ions separated by 5.36 Å in the *b* direction are connected by a single hydrogen bond involving an equatorial water oxygen ligand to one Cu and an equatorial N ligand to the other, as shown in Fig. 5(c). This is the shortest exchange path, with a total length of 6.59 Å . The

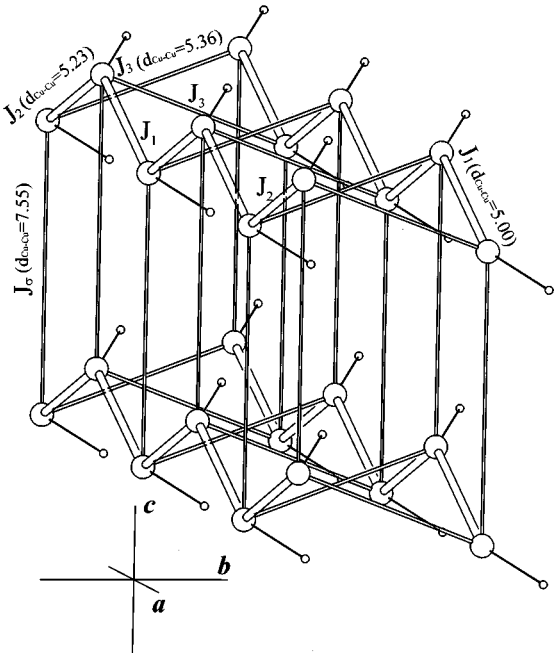

FIG. 6. Exchange network between copper ions in Cu(L-asp). The four types of superexchange paths are shown. As discussed in the text different relative magnitudes of these parameters would produce different magnetic behavior.

magnitudes of the exchange interactions between coppers at 5.00, 5.23, and 5.36 Å will be called J_1, J_2, and J_3, respectively. Figure 6 includes only the copper ions in Cu(L-asp) and shows the geometric arrangement of the four types of superexchange paths (J_σ, J_1, J_2, and J_3). Figures 4, 5, and 6 will be used to discuss the experimental results in terms of the structure. If the contribution of the connections J_1, J_2, and J_3 were negligible (see Fig. 6), one would expect a 1D magnetic behavior with chains along the *c* axis, and intrachain couplings J_σ. As explained before, this situation is not supported by the new experimental evidence. Otherwise, if the different interchain couplings, labeled as J_1, J_2, and J_3 in Figs. 5 and 6, have magnitudes comparable or larger than J_σ, different types of magnetic behavior may be expected. The couplings J_1 and J_2 involve double-exchange pathways. In the case where they are the leading interactions we would expect for Cu(L-asp) the behavior of an infinite alternating spin chain (see Fig. 6). When either J_σ and J_2 or J_σ and J_1, as well as J_2 and J_3, are the leading interactions, we would expect a behavior corresponding to a ladderlike chain. In this work we adopt the first possibility. The distances between the copper atoms coupled by the interactions J_1 and J_2 are the shortest, and the fact that they involve two symmetry-related exchange pathways reinforces this assumption.

IV. LINEAR ALTERNATING SPIN CHAINS

The behavior of an infinite alternating Heisenberg spin chain with *n* spins (*n* even) can be described by the Hamiltonian

$$\mathcal{H}=|J_0|\tilde{\mathcal{H}}, \tag{1}$$

with

$$\tilde{\mathcal{H}} = \tilde{\mathcal{H}}_{ex} + \tilde{\mathcal{H}}_z = -2\frac{J_0}{|J_0|}\sum_{i=1}^{n/2}\left[\mathbf{S}_{2i}\cdot\mathbf{S}_{2i-1} + \alpha\mathbf{S}_{2i}\cdot\mathbf{S}_{2i+1}\right] + \sum_i y S_{iz}, \tag{2}$$

where $\tilde{\mathcal{H}}_{ex}$ and $\tilde{\mathcal{H}}_z$ are the scaled exchange and Zeeman interactions, respectively. In Eq. (2), $y = g\mu_B B/|J_0|$, where B is the magnetic field applied along z. The eigenvalues of the chains and the thermodynamic properties of the system described by Eqs. (1) and (2) were calculated by Duffy and Barr[10] for $0<\alpha<1$, $n\leqslant 10$, and extrapolated to chains with $n\to\infty$. Solutions for alternating chains with $n=12$ and 14 spins have also been reported.[12,18] Hatfield[16] gave algebraic expressions which reproduce well the results calculated[10] for the magnetic susceptibility and provide a way to fit the models to the experimental data in order to estimate the parameters J_0 and α.

The molar specific heat $c(T)$, magnetic susceptibility $\chi(T)$, and magnetization $M(B,T)$ of a system described by Eqs. (1) and (2) can be calculated as

$$c(T) = \frac{Nk}{x^2}\left[\langle\tilde{\mathcal{H}}^2\rangle_{y=0} - \langle\tilde{\mathcal{H}}\rangle^2_{y=0}\right], \tag{3}$$

$$\frac{\chi(T)|J_0|}{Ng^2\mu_B^2} = \frac{1}{x}\langle S_z^2\rangle_{y=0}, \tag{4}$$

$$M(B,T) = -Ng\mu_B\langle S_z\rangle, \tag{5}$$

where $x = kT/|J_0|$ and N is Avogadro's number. In Eqs. (3), (4), and (5) the averages $\langle A\rangle$ of an operator A are calculated per ion in the n-spin chain from the solution of the Hamiltonian $\tilde{\mathcal{H}}$ as

$$\langle A\rangle = \frac{1}{n}\frac{\mathrm{tr}\{A\exp(-\tilde{\mathcal{H}}/x)\}}{\mathrm{tr}\{\exp(-\tilde{\mathcal{H}}/x)\}}, \tag{6}$$

and the thermodynamic properties of an infinite uniform chain can be obtained using Eqs. (3), (4), and (5) from the limiting behavior of Eq. (6) for large n.[6] To compare our experimental results with the predictions of the model we solved the Hamiltonian of Eqs. (1) and (2) for $n=10$, 12, and 14 spins following standard methods.[6,10,27] As suggested by the Curie plot (inset of Fig. 3), we proposed a predominantly antiferromagnetic exchange ($J_0<0$) and varied $-1\leqslant\alpha\leqslant 1$, solving the Hamiltonian of Eqs. (1) and (2) with cyclic boundary conditions. The condition $0<\alpha<1$ pertains to those cases where the coupling of each spin in the chain with both neighboring spins is antiferromagnetic. The condition $-1<\alpha<0$ applies to those cases in which the coupling of each spin is antiferromagnetic with one neighbor but ferromagnetic with the other, the antiferromagnetic coupling being dominant.[18,19] The eigenvalues of the chain with $n=10$, 12, and 14 were calculated in the whole range of α in steps of 0.01, and used to evaluate $c(T)$, $\chi(T)$, and $M(B,T)$ using Eqs. (3), (4), and (5). By comparing the values of $c(T)$, $\chi(T)$, and $M(B,T)$ obtained from the eigenvalues of spin chains of different lengths, we observed that the results for 14 spins can be safely taken as the limit for $n\to\infty$ in the range of the alternation parameter α appropriate for Cu(L-asp). This is not the case for uniform chains ($\alpha=1$), particularly at low T.[6]

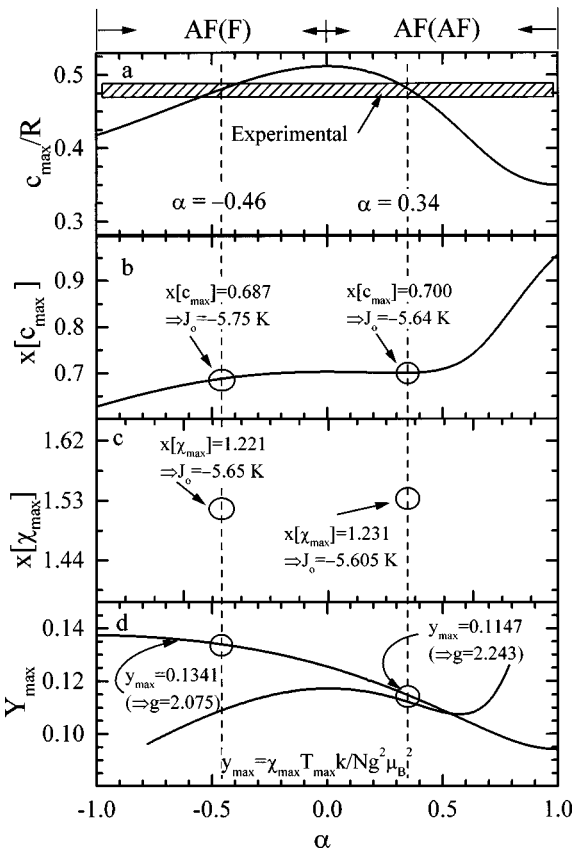

FIG. 7. Values calculated as a function of α using Eqs. (3) and (4) and the Hamiltonian of Eq. (2) for chains of 14 spins. (a) Maximum value for the specific heat ($c_{\max}/R$). The experimental value of $c_{\max}/R$ for Cu(L-asp) is indicated by the horizontal dashed area. The two possible values of α which explain the observed peak value of $c(T)$ in Fig. 2 are indicated as vertical dashed lines. (b) Position $x_{\max}=kT_{\max}/|J_0|$ at this peak, as a function of the alternation parameter α. (c) Position $x_{\max}=kT_{\max}/|J_0|$ where the maximun value of $\chi_{\max}(T)$ occurs. (d) Values of $\chi_{\max}T_{\max}k/Ng^2\mu_B^2$. In panels (b), (c), and (d) the possible values of J_0 and g obtained from the experimental data using the calculated curves are $\alpha=0.34$ and $\alpha=-0.46$.

V. MODEL CALCULATION AND FITTING PROCEDURES

In order to compare the data with the predictions of the alternating chain model and evaluate the parameters J_0, α,J', and g we proceeded in two steps. First we estimated a set of values of the parameters of the model which reproduce the main features of the experimental results, i.e., the susceptibility and specific heat peaks, without considering interchain interactions. The specific heat depends only on α and J_0, while the magnetic susceptibility also depends on the average g factor. We calculated the peak value $c_{\max}/R$ of the specific heat and the value of $x=kT/|J_0|$ at this maximum, as a function of the alternation parameter α in the whole range mentioned above using Eq. (3) and the eigenvalues of the 14-spin chain. The results of these calculations are given as solid lines in Figs. 7(a) and 7(b), respectively. The experi-

mental value $c_{max}/R=0.473\pm0.004$ from Fig. 1, indicated in Fig. 7(a) by the horizontal dashed area, can be reproduced by two possible values $\alpha\approx0.34$ and $\alpha\approx-0.46$, indicated by dashed vertical lines in Fig. 7. As shown in Fig. 7(b), the former corresponds to $x(c_{max})=0.700$ and the latter to $x(c_{max})=0.687$. Since the observed value for $T(c_{max})$ is 3.95 K, the two possibilities for the set of parameters (α,J_0) which fit the specific heat maximum are ($\alpha=0.34$, $J_0=-5.64$ K) and ($\alpha=-0.46$, $J_0=-5.75$ K). The susceptibility data in the temperature range of its maximun are analyzed using Figs. 7(c) and 7(d). There we plot the value $x[\chi_{max}]$ of $x=kT/|J_0|$ at which the maximum of the susceptibility χ_{max} occurs [Fig. 7(c)] and $\langle S_z^2\rangle_{max}=\chi_{max}T_{max}k/Ng^2\mu_B^2$ at this maximum, as a function of α from [Fig. 7(d)] using Eq. (4). Considering the experimental value $\chi_{max}=0.0314$ emu/mol at 6.9 K, we obtain from Figs. 7(c) and 7(d) the values ($\alpha=0.34$, $J_0=-5.60$ K, $g=2.243$) and ($\alpha=-0.46$, $J_0=-5.65$ K, $g=2.075$). Both set of values of J_0 obtained from Fig. 7(c) compare well with those obtained from the specific heat data [Fig. 7(b)] and do not allow us to define a single value of α. The g values obtained for each α are in reasonable agreement with the EPR results,[22] and they do not help to select a unique value. An additional piece of information can be obtained from the ratio $T(c_{max})/T(\chi_{max})$. However, the experimental value of $T(c_{max})/T(\chi_{max})=x(c_{max})/x(\chi_{max})=0.572$ is compatible with both possibilities for α [$x(c_{max})/x(\chi_{max})=0.56$ at $\alpha=-0.46$ and $x(c_{max})/x(\chi_{max})=0.57$ at $\alpha=0.34$], and consequently does not allow us to select a clearly unique result. Thus, we should search for a detailed fit of the experimental results in both ranges of α, around 0.34 and around -0.46.

In a second stage of the fitting we considered all experimental points in Figs. 1, 2, and 3, and calculated $c(T)$, $\chi(T)$, and $M(B,T)$ using Eqs. (3), (4), and (5) [including also the interchain interaction J' effects on $M(B,T)/B$ or $\chi(T)$, within a mean-field approximation]. For each set of the four parameters we calculated the mean-square deviation $\sigma_Z(J_0,\alpha,g,J')$,

$$\sigma_Z(J_0,\alpha,g,J')=\left\{\frac{\sum_j[(Z_j)_{expt}-(Z_j)_{calc}]^2}{\sum_j(Z_j)_{expt}^2}\right\}^{1/2} \quad (7)$$

between the experimental values $(Z_j)_{expt}$ and those calculated with the model, $(Z_j)_{calc}$, for each experimental point of the measured properties [$Z=c(T)$, $\chi(T)$, and $M(B,T)$]. The sum of these deviations gives an appropriate ''weight function'' Σ which should be minimized varying J_0, α,g, and J' in order to obtain the best set of parameters. To achieve this global fitting we used the simulated annealing method.[28–30] This method, introduced by Kirkpatrick *et al.*,[28] is based on a strong analogy between the physics of the annealing process in solids and complicate optimization problems. In particular, it is useful to perform a global fitting to different sources of data. In general these problems do not have a single minimum for Σ, and one needs to look for an absolute, global minimum. The annealing method uses the Monte Carlo algorithm,[31] to simulate the approach to thermal equilibrium of a solid in contact with a thermal bath, and its implementation for fitting data purposes was given by Press *et al.*[30] Using this method we obtained the set of values $J_0/k=(-5.3\pm0.1)$ K, $\alpha=0.29\pm0.01$, $J'/k=(0.7\pm0.1)$ K, and $g=2.165\pm0.002$, which give the best fit of the data (minimun Σ). Figures 1, 2, and 3 include as solid lines the values of $c(T)$, $\chi(T)$, and $M(B,T)$ calculated with this set of parameters. The global agreement is very good, particularly considering the different sources of experimental information fitted. We tried the region around $\alpha=-0.46$, also indicated by Fig. 7, with much poorer results.

The analysis of the experimental data described above indicates a magnetic behavior characteristic of an antiferromagnetic alternating spin chain for Cu(L-asp) with $\alpha=0.29$. This behavior was not detected in our previous study of this compound where the susceptibility data were taken above 5 K and no specific heat data were available. Bonner and Fisher[6] showed that anisotropies in the exchange interaction coupling nearest-neighbor spins increase the magnitudes of the peak values of the specific heat and the magnetic susceptibility of the chain and, more importantly, cause $\chi(T)\rightarrow0$ for $T\rightarrow0$. We have also explored this possibility by following steps similar to those leading to Fig. 7. Our results for this alternative indicated that Cu(L-asp) should behave as a quasipure Ising-like chain [a very unlikely situation for Cu(II) ions]. On the other hand, the fit of the data obtained with this model is very poor. Consequently, the possibility of anisotropic exchange was disregarded from our analysis.

VI. DISCUSSION

We have shown above that our experimental results [$c(T)$, $\chi(T)$, and $M(B,T)$] can be explained assuming for Cu(L-asp) the behavior of an antiferromagnetic alternating spin chain. The chemical paths relevant to transmit exchange interactions between copper ions in Cu(L-asp) are displayed in Figs. 4, 5, and 6. Figure 6 schematizes the network of different exchange paths, and it is intended to clarify the possible magnetic behaviors. Some of them can be described as follows.

(i) When J_1, J_2, and J_3 are much smaller than J_σ, the system would display a uniform chain behavior, with chains along c. This situation was our previous assumption[22] of an antiferromagnetic uniform spin chain, where the superexchange path is provided by the σ skeleton of the amino acid. Our experimental data do not give support to this assumption. This may be explained considering the limit function for the magnitude of the exchange interaction vs distance described by Coffman and Buettner[32] for long-range antiferromagnetic superexchange. The σ skeleton of the amino acid [see Fig. 4(a)] has a total Cu(II)-Cu(II) distance of 9.75 Å, and the predicted J value would be ~0.7 K, which is much smaller than that obtained from the experimental data.

(ii) If J_σ and J_3 were small as compared with J_1 and J_2, an alternating spin chain behavior should be expected, with chains along a. Here J_1 and J_2 are transmitted by paths with lengths of 5.00 and 5.23 Å, via two symmetry-related pathways involving hydrogen bonds and carboxylate bridges [see Figs. 4(a) and 4(b)]. This situation is supported by the experimental data. Exchange interactions transmitted through hydrogen bonds have been studied recently in copper amino acid complexes,[25] showing values of J somewhat smaller

than 1 K. So the present experiments show larger values of J, even when the path are longer.

(iii) If J_σ and either J_1 or J_2 are larger than the other two, then spin ladders along c are formed. It has been pointed out[33] that for some systems it is rather difficult to distinguish between the alternating or the ladder chain behavior to allow for an unequivocal assignment of the paths involved in forming the magnetic structure of these systems.

(iv) If J_σ and J_3 were the dominant interactions, a 2D magnetic behavior would be expected. It does not seem that this is supported by the specific heat and susceptibility data in Figs. 1 and 2. With this assumption one should disregard the contribution of J_3 to the magnetic behavior of Cu(L-asp).

Our experimental data are compatible with more than one of these situations, the most important being the alternating chain and the ladderlike chain. It is worth noting that in both cases the exchange interaction pathways involve hydrogen bonds. Thus, an important finding is that relatively complex and long exchange pathways involving H bonds may give rise to exchange interactions as big as 5 K. As pointed out above, the alternating chain that better explains our data is in the a direction, and is not parallel to the Cu-asp-Cu skeleton. Exchange interactions transmitted through hydrogen bonds have been studied in copper amino acid complexes,[25] showing values of J somewhat smaller than 1 K. The present experiments show larger values of J, even when the paths are longer.

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