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The exchange interactions and magnetic behaviour of Cu(L-alanine)_2 : specific heat measurements

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Abstract. We report specific heat measurements in the temperature range $0.05 \text{ K} \leq T \leq 1.95 \text{ K}$ for the copper–amino acid complex Cu(L-alanine)_2 . The data display a peak at 0.068 K, and a broad maximum at 0.55 K. Above 0.2 K they reflect a one-dimensional antiferromagnetic spin-chain behaviour. The temperature dependence of the specific heat is compared to that calculated for Heisenberg finite spin chains in order to evaluate the magnitude and characteristics of the exchange interaction. We obtain an antiferromagnetic exchange coupling parameter $J_0/k = (-0.57 \pm 0.01) \text{ K}$ between nearest-neighbour copper ions. The peak observed at 0.068 K indicates a transition to a phase with three-dimensional magnetic order. The effect of this phase transition on the specific heat measured at higher temperatures is analysed. The experimental results, together with existing magnetic susceptibility and EPR data, are discussed considering the crystal structure and the superexchange paths connecting the copper ions in Cu(L-alanine)_2 . The nature of the spin chains and the possibility of competing exchange interactions between first and second copper neighbours along the chains are analysed in order to model the magnetic behaviour of Cu(L-alanine)_2 .

1. Introduction

Several studies of the magnetic properties of metal-amino acid complexes have been reported [1–11]. There are two types of motivation for these investigations. These materials are convenient for modelling exchange interactions transmitted along molecular segments and bonds which occur in metalloproteins. The magnitudes of the observed exchange interactions can be related to the nature and properties of the bonds connecting the unpaired spins (superexchange paths) [12–15], and compared to magnetic data in metalloproteins [16]. Then, for some purposes, x-ray determination of complex structures in single crystals of macromolecules may be replaced by the simpler measurement of a magnetic interaction [17, 18]. This allows the possibility of studying the differences in structures of related metalloproteins (e.g., chemically or genetically replaced) [17, 18]. The magnetic properties of metal–amino acid complexes are also interesting in their own right, as shown by experimental data reported for complexes of amino acids with copper [1–9] and nickel [10–11]. In these systems the metal ions form chains and layers. Low-dimensional

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magnetic behaviour is observed as a consequence of this structure and of the chemical bonds connecting the metal ions. The possibility of synthesizing and growing single crystals of many closely related compounds makes these materials an interesting family to study. As an example, specific heat measurements at very low temperatures in the isomer and isostructural copper–amino acid complexes Cu(L-but)_2 and Cu(D,L-but)_2 , having coppers in layers, indicate a one-dimensional magnetic behaviour due to differences in the exchange paths between coppers along different directions within the layers [9]. Also, the small structural differences of the pairs of isomer complexes Cu(L-but)_2 and Cu(D,L-but)_2 , and Cu(L-met)_2 and Cu(D,L-met)_2 , produce measurable changes of the dimensionality of the room temperature spin dynamics, as observed by EPR [7]. Transitions to magnetically ordered phases have been previously observed in two metal–amino acid compounds in magnetic susceptibility [1], specific heat [4,10] and neutron diffraction experiments [11].

One of the best studied copper–amino acid complexes is Cu(L-alanine)_2 . Magnetic susceptibility data obtained between 0.013 and 240 K indicated a behaviour similar to that expected for antiferromagnetic Heisenberg chains [6]. This behaviour can be understood using the theory proposed by Bonner and Fisher [19] for spin chains with the nearest-neighbour isotropic exchange coupling parameter $2J_0$, using $J_0/k = -0.52$ K. These susceptibility data do not show any peak which could indicate the existence of a magnetic phase transition within the temperature range investigated. EPR data in single crystals of Cu(L-alanine)_2 were reported by Yokoi and Ohsawa [20]. More recently, room temperature measurements of the frequency and angular dependence of the EPR g -factor and linewidth of single crystal samples were also reported [6]. The linewidth data were analysed with a model which considers the collapse due to the exchange interaction of the resonances of the two rotated crystallographic sites for copper ions in Cu(L-alanine)_2 [6,21]. The magnetic susceptibility and EPR results were interpreted as being due to zigzag chains of copper spins, exchange coupled through carboxylate bridges [6]. In addition, the temperature dependence of the g -tensor, measured between 1.5 K and room temperature, reflects the dipolar coupling of a layered arrangement of copper ions [8]. The crystal structure of Cu(L-alanine)_2 has been investigated in detail [22,23]. In this paper we report measurements of the magnetic contribution to the specific heat [$C_{mag}(T)$], in powdered samples of Cu(L-alanine)_2 as a function of temperature T , in the range $0.05 \leq T \leq 1.95$ K. Above 0.2 K the data reflect an antiferromagnetic linear chain behaviour [6]. The intrachain exchange interaction parameter calculated from the specific heat results is in agreement with that obtained previously from the susceptibility data. The presence of a heat capacity peak at 0.068 K indicates a magnetic phase transition. These experimental results are discussed together in terms of the magnetic behaviour and the exchange interactions between copper ions in Cu(L-alanine)_2 .

2. Experimental details and analysis of the data

Cu(L-alanine)_2 [$\text{Cu}(\text{CO}_2\text{CHCH}_3\text{NH}_2)_2$] is the copper complex of the amino acid L-alanine. Our sample was obtained from the reaction of a solution of the amino acid with basic copper carbonate. It was purified by repeated crystallization. Single-crystal plates of up to 5 mg were grown by slow evaporation at room temperature. In order to maximize the thermal conductivity of the sample, as needed for specific heat measurements, about 100 mg of powdered crystals of Cu(L-alanine)_2 were packed with copper powder, as described in [9]. The sample was mounted in a calorimeter within an evacuated thermal shield attached to a dilution refrigerator [24]. The semi-adiabatic method was used, with external time constants of between 30 and 120 min. Changes of the thermal link between the thermal shield and the sample carried out in these experiments in order to lower the minimum temperature of the

measurements without deteriorating the quality of the data. Power was applied for intervals of about 100 s so as to produce changes in temperature of about 4%. The addendum specific heat was measured independently, and was less than 1% of the sample specific heat in the whole temperature range studied here. The dispersion of the data was less than 2%.

The measured specific heat is the sum of a magnetic contribution $C_{\text{mag}}(T)$ and a vibrational contribution. As shown in [9] the vibrational contribution, usually proportional to T^3 , amounts to less than 1% of the maximum value in the range of temperatures of our experiments. Hence, the values measured for the specific heat may be safely considered as the magnetic contribution C_{mag} . The experimental results are displayed in figure 1 as C_{mag}/R ($R = N_{\text{Av}}k = 8.3145 \text{ J K}^{-1}$) versus T , after subtracting the contributions of the sample holder and calorimeter.

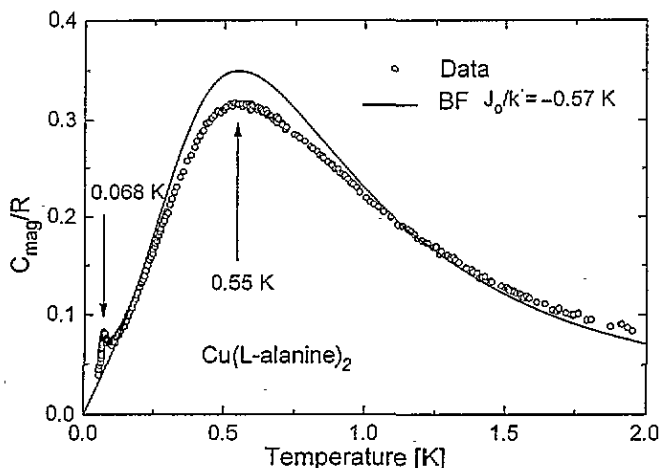


Figure 1. Specific heat data for $\text{Cu}(\text{L-alanine})_2$ in the temperature range $0.050 \leq T \leq 1.95 \text{ K}$. The contributions of the sample holder and calorimeter have been subtracted. The solid line gives the prediction for an infinite chain obtained by a least-squares fit of equation (A1) to the data above 0.2 K.

The specific heat data are analysed in two temperature ranges as detailed below.

(a) $T > 0.2 \text{ K}$. *Range of spin-chain contribution.* Within this range of temperature, the data in figure 1 display behaviour similar to that predicted by Bonner and Fisher (BF) [19] for a chain in which each member is a spin 1/2 described by

$$\mathcal{H} = -2J_0 \sum_{i=j+1} S_i \cdot S_j \quad (1)$$

with antiferromagnetic Heisenberg exchange interaction of magnitude $2J_0$ between neighbour spins in a chain. We review in the appendix the main findings of the BF model for the specific heat, and introduce a method to analyse the experimental data in these terms. The peak experimental value $C_{\text{max}}/R = 0.318$, observed at $T_{\text{max}} = 0.55 \text{ K}$, is smaller than the peak value $C_{\text{max}}/R = 0.3497$ predicted by BF at $kT_{\text{max}}/J_0 = 0.961$. A least-squares fit of the algebraical function which reproduces the BF results (see equation (A1) in the appendix), to the specific heat data above 0.18 K in figure 1 gives $J_0/k = (-0.57 \pm 0.01) \text{ K}$. The solid curve in figure 1 was calculated using equation (A1) for this value of J_0 . It depends on a single parameter (J_0) and is in reasonable agreement with the experimental data. The main disagreement occurs in the range of the broad maximum at $T = 0.55 \text{ K}$, where the experimental values are about 10% smaller than the predictions. There is a

smaller disagreement in the highest temperature range where these values are slightly larger than the predictions. Only a very small part of this discrepancy could be attributed to the vibrational contribution to the specific heat.

(b) *The specific heat peak at low temperatures.* The specific heat data of figure 1 display a relatively narrow specific heat peak at 0.068 K, superimposed to the linear temperature dependence predicted at low temperature by the BF model. We show in figure 2 the result of subtracting from the experimental values the linear term calculated from the data for neighbouring values of temperature, outside the peak. The resulting peak, centred at $T_c = 0.068$ K, has a width of 0.023 K at half intensity and a peak value $C_{mag}/R = 0.0386$.

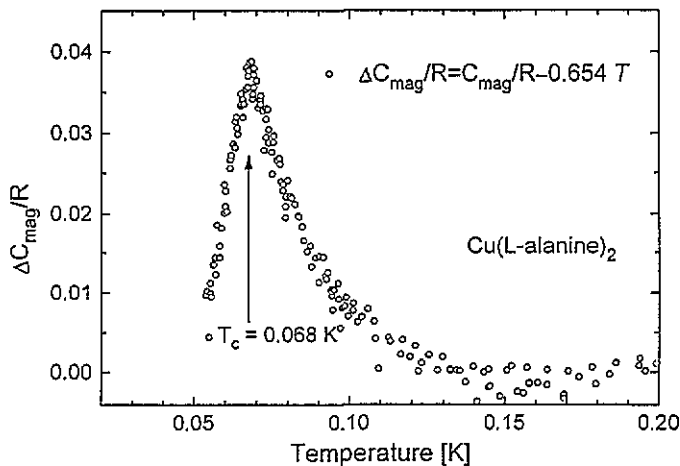


Figure 2. The specific heat peak at 0.068 K is displayed after the linear contribution observed for $C_{mag}(T)/R$ around the peak is subtracted.

3. Crystal and molecular structure of $\text{Cu}(\text{L-alanine})_2$

In order to understand the magnetic susceptibility and the EPR data we introduced in [6] a model explaining why $\text{Cu}(\text{L-alanine})_2$, a compound made essentially of copper layers, displays a behaviour characteristic of a 1D spin chain.

The structural data for $\text{Cu}(\text{L-alanine})_2$ reported by Hitchman *et al* [23] are similar to those reported earlier by Dijkstra [22]. However, they show a different chirality and, more important for our purpose, give the positions of all the atoms in the unit cell with the accuracy provided by modern crystallographic techniques. Copper ions have an octahedral coordination, and are bonded to the amino nitrogen and one carboxylate oxygen of two amino acid molecules in the equatorial positions. The two apical ligands are carboxylate oxygens belonging to other amino acid molecules. Figure 3(a) depicts the $\text{Cu}(\text{L-alanine})_2$ molecule, as reported in [23]. For simplicity, the H atoms are not included. There are two of these molecules (A and B) in rotated positions in the unit cell, and figure 3(b) shows how they are arranged in layers parallel to the bc crystal plane. It also shows the main chemical connections between type A copper, with its six copper neighbours within the layer, two molecules of type A, and four molecules of type B. They provide the paths for superexchange interactions in $\text{Cu}(\text{L-alanine})_2$, which are described with greater detail in figures 4(a), (b).

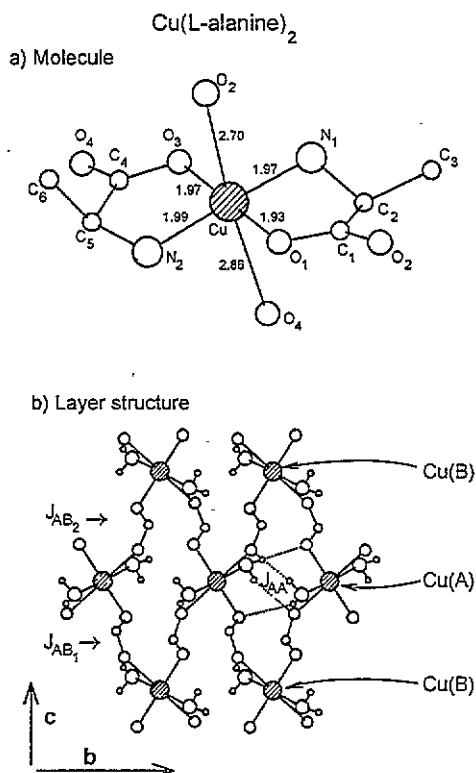


Figure 3. (a) The $\text{Cu}(\text{L-alanine})_2$ molecule as determined by x-ray crystallography [23]. Distances are given in Å. (b) A copper ion and its six copper neighbours are shown together with their ligands, in order to display the layered structure of the copper ions in $\text{Cu}(\text{L-alanine})_2$ and the chemical paths connecting copper neighbours.

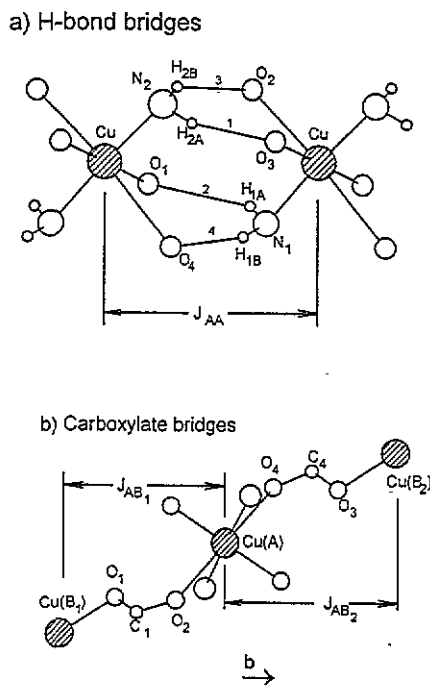


Figure 4. Details of the chemical paths for superexchange. (a) H bonds; (b) carboxylate bridges. The distances and angles involved are given in table 1.

There are four possible H bonds involving the amino protons which connect pairs of copper neighbours of the same type (AA or BB) along the b axis. They are labelled as 1 to 4 in figure 4(a). As shown in that figure, two of them (1 and 2) connect the equatorial nitrogen ligands to copper (N_1 and N_2 in figure 3) to the equatorial oxygen ligands O_1 and O_3 of the copper neighbour. The other two H bonds (3 and 4) connect these nitrogens to the apical oxygen ligands O_2 and O_4 to copper. The interatomic distances and angles involved in the H bonds shown in figure 4(a) are given in table 1(a). The electron density of the copper ground orbital state along the directions of the apical bonds $\text{Cu}-\text{O}_2$ and $\text{Cu}-\text{O}_4$ is low. It is clear therefore that H bonds 3 and 4 (figure 4(a)) are less efficient at transfer of exchange couplings than H bonds 1 and 2, which involve the shorter and more electron-rich equatorial bonds $\text{Cu}-\text{O}_1$ and $\text{Cu}-\text{O}_2$. Thus, they may be ignored in our analysis. The H-bond labelled 1 is shorter, and has an angle α ($\text{N}-\text{H}\cdots\text{O}$) closer to 180° than that of H bond 2. We can assume then that it plays a more important role as a superexchange link. Nevertheless, H bonds 1 and 2 together provide the link which supports the coupling $J_{AA}(=J_{BB})$ between neighbouring copper pairs of equal type along the b -axis (figure 4(a)).

Table 1. Distances (Å) and angles (deg) involved in the H bonds (figure 4(a)) and in the carboxylate bridges (figure 4(b)) in the structure of Cu(L-alanine)₂ [23]. The angles $\alpha(\text{Cu}-\text{O}_{ap})$ are measured between the directions from the copper ions to the apical ligands and the normal to the best plane for the equatorial ligands to copper.

(a) H bridges	Type	$d(\text{N}-\text{H})$	$d(\text{H}-\text{O})$	$d(\text{N}-\text{O})$	$\alpha(\text{NHO})$
1) N ₂ -H _{2A} -O ₃	Equatorial	0.86	2.13	2.97	163
2) N ₁ -H _{1A} -O ₁	Equatorial	0.68	2.53	3.09	141
3) N ₂ -H _{2B} -O ₂	Apical	0.86	2.32	3.06	143
4) N ₁ -H _{1B} -O ₄	Apical	0.87	2.19	3.03	161
(b) CO ₂ bridges	$d(\text{Cu}-\text{O}_{eq})$	$d(\text{O}_{eq}-\text{C})$	$d(\text{C}-\text{O}_{ap})$	$d(\text{O}_{ap}-\text{Cu})$	$\alpha(\text{Cu}-\text{O}_{ap})$
Cu-O ₁ -C-O ₂ -Cu	1.93	1.28	1.23	2.70	12
Cu-O ₃ -C-O ₄ -Cu	1.97	1.28	1.24	2.86	7

As shown in figure 3(b), there are two different carboxylate bridges connecting coppers of A and B types in Cu(L-alanine)₂. Since the positions occupied by the copper ions have no inversion symmetry in the $P2_1$ space group [23, 25], the carboxylate bridges connecting a type A copper with the two type B coppers in the lower part of figure 3(b) are different from those connecting this A-type copper to the two coppers in the upper side. We call J_{AB_1} and J_{AB_2} the magnitudes of the exchange associated with each of these paths, and describe them with more detail in figure 4(b). J_{AB_1} is related to the path involving the Cu-O₂ bond (2.70 Å), while J_{AB_2} is related to the path involving the Cu-O₄ bond (2.86 Å). Since the former bond is considerably shorter than the latter, and taking into account the results in [26], it is expected that $|J_{AB_1}| \gg |J_{AB_2}|$. However, since the structure of Cu(L-alanine)₂ differs in many aspects from those of the compounds studied in [26], it is difficult to estimate the magnitudes of J_{AB_1} and J_{AB_2} from the structural data in figure 4(b).

4. Discussion and conclusions

4.1. Layered structure versus spin-chain behaviour

The experimental values of the heat capacity and magnetic susceptibility [6] for Cu(L-alanine)₂ indicate that above 0.2 K the magnetic behaviour is similar to that expected for spin chains. Depending on the magnitudes of the couplings J_{AB_1} , J_{AB_2} and $J_{AA} = J_{BB}$ which produce this one-dimensional behaviour of a system of spins arranged in layers, one encounters different situations described below and in figures 5(a)–(c).

4.1.1. Case (a): $|J_{AA}| \gg |J_{AB_1}|$ and $|J_{AA}| \gg |J_{AB_2}|$. In this situation (figure 5(a)), the predominant coupling is along the b axis. The magnetic excitations travel along this direction through the couplings $J_{AA} = J_{BB}$. The chains are made of type A spin or of type B spin. The relevant superexchange pathways are the H bridges (figure 4(a)), while the carboxylate bridges (figure 4(b)) do not contribute. The effective coupling is $J_0 = J_{AA} = J_{BB}$.

4.1.2. Case (b): $|J_{AB_1}| \gg |J_{AB_2}|$ and $|J_{AB_1}| \gg |J_{AA}|$. In this situation (figure 5(b)) the predominant coupling is also in the direction of b , but the excitations travel in zigzag chains through couplings J_{AB_1} . These chains are made of alternating spins of types A and B, and are uncoupled from other similar chains because J_{AB_2} is small. In this case the effective

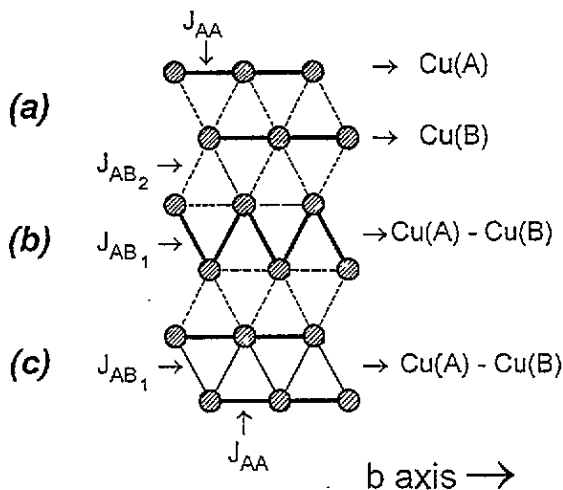


Figure 5. Schematic diagrams of the exchange interaction network in $\text{Cu}(\text{L-alanine})_2$. The circles represent the copper ions (types A and B). The lines connecting these circles represent the exchange interactions coupling the spins. The cases (a), (b), and (c) analysed in the text for possible spin-chain behaviour of the layered structure are sketched.

coupling is $J_0 = J_{AB_1}$ along the chain; this situation corresponds to the model introduced in [6].

4.1.3. Case (c): the general case where $|J_{AB_1}| \gg |J_{AB_2}|$, with arbitrary values of $|J_{AA}|$. In this case (figure 5(c)) there are exchange couplings between nearest copper neighbours (through J_{AB_1}), and between next-nearest neighbours (through J_{AA} or J_{BB}) along the chains. The presence of two types of couplings can produce competition or frustration of these interactions. The temperature dependence of the thermodynamic properties departs from that expected for a chain with only nearest-neighbour interactions, as shown by Ananthakrishna *et al* [27]. These authors propose (adapting the notation to that used here) that $J_{AA} = \alpha J_{AB_1}$ and calculate $\chi_m(T)$ and $C_m(T)$ for different values of α . Obviously (see figure 5(c)), if J_{AA} is positive (ferromagnetic coupling with next-nearest copper neighbours) the effects of J_{AA} and J_{AB_1} add up, whereas if J_{AA} is negative the two interactions compete destructively. The condition $|\alpha| \gg 1$ corresponds to case (a) considered in section 4.1.3 above. If $|\alpha| \ll 1$, the zigzag chain model with negligible next-nearest-neighbour coupling is applicable (the case (b) in section 4.1.2 above). If $|\alpha| \sim 1$ one can think of double chains, where each chain is coupled through the H bonds, while J_{AB_1} acts as a coupling between chains [28]. These intermediate situations offer a wide variety of possible magnetic behaviours [27, 28].

4.2. Intralayer exchange interactions

In order to estimate the contribution of the superexchange pathways displayed in figures 4(a) and 4(b), we consider our experimental results and the structure of $\text{Cu}(\text{L-alanine})_2$ [23]. We analyse first J_{AB_1} and J_{AB_2} through the carboxylate bridges. Levstein and Calvo [26] studied the set of isomorphous copper-amino acid complexes $\text{Cu}(\text{L-methionine})_2$, $\text{Cu}(\text{L-phenylalanine})_2$, and $\text{Cu}(\text{L-leucine})_2$. They found that it is possible to relate the magnitude of the exchange interaction through equatorial-apical carboxylate bridges like those of figure 4(b), to the distance from copper to the apical oxygen ligand. These results, and

the different distances between copper and the apical oxygen ligands O_2 and O_4 (2.70 and 2.86 Å) justify the fact that $|J_{AB_2}| \ll |J_{AB_1}|$, a reason for which Cu(L-alanine)_2 , a compound with coppers in layers, shows a spin-chain behaviour. J_{AA} and J_{AB_1} act as couplings within the chains, while J_{AB_2} , separates the chains, as in figure 5(c).

From the EPR results at room temperature we infer that $0.17 \text{ K} < |J_{AB_1}|/k < 0.24 \text{ K}$ [6, 21]. The lower limit corresponds to the assumption $|J_{AB_1}| \approx |J_{AB_2}|$, while the higher limit corresponds to the more realistic assumption $|J_{AB_1}| \gg |J_{AB_2}|$. If the results of Levstein and Calvo [26] are used to estimate $|J_{AB_1}|/k$, a value smaller than that calculated from the EPR data is obtained. This can arise from the structural differences between Cu(L-alanine)_2 and the compounds studied in [26]. In particular, the angle $\alpha(\text{Cu}-O_{ap})$ between the direction of the apical ligand and the normal to the plane of equatorial ligands (table 1(b)) is larger in Cu(L-alanine)_2 . This produces a larger contribution of the d_{z^2} orbital state to the $d_{x^2-y^2}$ ground state of copper [23]. The resulting increased electron density in the direction of the apical ligand would then be reflected in a larger value of $|J_{AB_1}|/k$. This difference in magnitude does not invalidate the condition $|J_{AB_2}| \ll |J_{AB_1}|$. The specific heat data reported here yield $J_0/k = -0.57 \text{ K}$, in good agreement with the susceptibility data [6] which give $J_0/k = -0.52 \text{ K}$. We conclude then that the coupling through the carboxylate bridge (J_{AB_1}) evaluated by EPR is insufficient to explain the magnetic data. The hydrogen bonds have to play a role as superexchange paths, and the situation of the magnetic interactions along the spin chain is as sketched in figure 5(c). This conclusion is also supported by the observed reduction in the specific heat peak with respect to that expected for a spin chain with nearest-neighbour interactions (see the solid line in figure 1). This indicates that J_{AA} is not negligible and that both J_{AB_1} and J_{AA} correspond to antiferromagnetic interactions. As discussed before, in such cases the competing nature of the interactions tends to lower the specific heat of the chain [27].

4.3. The specific heat peak at 0.068 K

In the case of ideal 1D magnetic systems with short-range interactions, ordering can only occur only at $T = 0 \text{ K}$ [29]. Weak interchain interactions are needed to produce a non-zero transition temperature to a three-dimensional ordered phase. In these situations the ordering temperature is related to the ratio of the magnitudes of interchain to intrachain exchange interactions, and may be relatively low [30, 31]. This ratio gives a measure of the degree of 1D magnetic character of the material. Another type of magnetic phenomenon may occur if the lattice is not rigid: a magnetoelastic distortion may occur, producing a magnetoelastic (spin-Peierls) transition as observed in some insulating 1D antiferromagnetic materials [32]. Below this transition temperature a dimerization of the spin chain proceeds continuously and progressively. This dimerization precludes additional magnetic ordering at lower temperature and the system remains paramagnetic down to 0 K. A complete dimerization of the chain would produce a slightly different shape of $C_{mag}(T)$, and a peak value $C_{max}/R = 0.512$ (per spin) at $x = kT_{max}/|J_0| = 0.705$, corresponding to independent spin dimers coupled antiferromagnetically with a magnitude $|J_0|$. More importantly, even a partial dimerization, like that observed in alternating chains, would produce that $\chi(T) \rightarrow 0$ for $T \rightarrow 0$ [33]. Since it was observed [6] that $\chi(T)$ converges to a non-zero value at very low T , the possibility of a spin-Peierls transition can be discarded for Cu(L-alanine)_2 . We therefore conclude that the specific heat peak at 0.068 K shown by the data in figure 2 corresponds to a transition to a three-dimensional ordered magnetic phase. In order to interpret this transition we display, in figure 6, the experimental values of $C_{mag}(T)/RT$ as a function of temperature. We include as a solid line the values of C_{mag}/RT calculated with

the Bonner and Fisher model using the polynomial function of equation (A1) of the appendix. The magnetic entropy per spin S_{mag}/R in $\text{Cu}(\text{L-alanine})_2$ and the BF prediction can be obtained by integrating the curves given in figure 6. Within the experimental uncertainty the total areas under the curves for $0 \leq T \leq \infty$ have the same value $S_{\text{mag}}/R = \ln 2 = 0.693$, corresponding to the magnetic entropy per spin $S = 1/2$ accumulated when going from an ordered spin array at 0 K to a completely disordered array at $T \rightarrow \infty$. The entropy change associated with the short-range magnetic ordering of $\text{Cu}(\text{L-alanine})_2$ (at temperatures where the spin-chain behaviour dominates) is lower than that calculated for the model chain. This is compensated by the area of the peak around $T = 0.068$ K. Then, an important part of the difference between the experimental values of C_{mag}/R , and the BF predictions for an antiferromagnetic chain is a consequence of the magnetic phase transition observed at lower temperatures. This difference is needed to compensate for the effect of the specific heat peak at the transition on the entropy. Due to the low transition temperature involved, the relatively small specific heat peak at 0.068 K has an important effect at higher temperatures. Similar reductions of the peak value of C_{max}/R were observed for the copper-amino acid isomer complexes $\text{Cu}(\text{L-but})_2$ and $\text{Cu}(\text{D,L-but})_2$ [9]. The present results suggest that transitions to ordered magnetic phases may also occur in these compounds, below the lowest temperature reached in those specific heat measurements (0.070 K) [9].

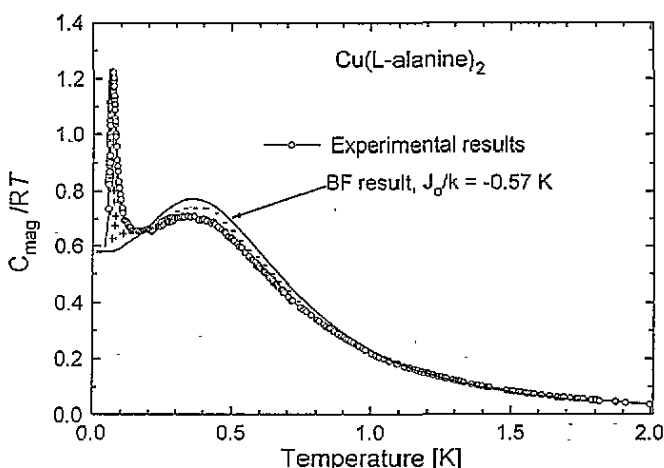


Figure 6. Experimental results for C_{mag}/RT versus temperature; the data points are connected by a line a guide to the eye. The solid line is the prediction of Bonner and Fisher obtained from equation (A1). The areas between these curves are indicated by plus and minus signs and indicate the differences in the magnetic contributions to the entropy for $\text{Cu}(\text{L-alanine})_2$ and for an ideal spin chain.

An order of magnitude estimate of the interlayer exchange interactions J' can be obtained from the value 0.068 K observed for the transition temperature. Using the results of Hennessy *et al* [34] who estimated the transition temperature in terms of J' using the random phase approximation, we obtain $J'/k \approx 0.006$ K between copper ions in neighbouring layers separated by about 9.2 Å. This small value is still larger than that calculated for the dipole-dipole interaction.

4.4. Conclusions

The specific heat data for Cu(L-alanine)_2 indicate an antiferromagnetic spin-chain behaviour, with a transition to a 3D magnetically ordered phase at 0.068 K. The data in figure 1 allow the evaluation of $J_0/k = -0.57$ K as the magnitude of the antiferromagnetic exchange interaction along the chain. These results, together with previous magnetic susceptibility and EPR data [6], and the crystallographic information about Cu(L-alanine)_2 , indicate that the chemical paths for superexchange interactions between copper ions are H bonds and carboxylate bridges. Nearest copper neighbours along the zigzag chains are connected by carboxylate bridges, as concluded in [6]. These exchange interactions, with magnitude J_{AB_1} , are those obtained from the EPR data [6, 21]. In addition, hydrogen bonds, connecting next-nearest neighbours in the zigzag chains, contribute to the exchange with a magnitude J_{AA} . Both contributions are antiferromagnetic and compete destructively to produce the effective value J_0 evaluated from the specific heat and the magnetic susceptibility data. We conclude that $|J_{AA}| > |J_0| > |J_{AB_1}|$, all values being negative (antiferromagnetic). The presence of three-dimensional ordering, marked by a specific heat peak at 0.068 K produces a decrease in the specific heat broad maximum observed at 0.55 K. A similar effect is expected from the simultaneous occurrence of J_{AA} and J_{AB_1} . This makes it difficult to extract two separate values for these two magnitudes from the specific heat data. However, according to the results of Ananthakrishna *et al* [27], the small discrepancy between the values of J_0 obtained here from the specific heat data (-0.57 ± 0.01 K), and in [6] from the magnetic susceptibility data (-0.52 ± 0.01 K) support the assertion that both J_{AA} and J_{AB_1} are negative and contribute to the magnetic properties of Cu(L-alanine)_2 .

The value of J_{AA} obtained for the exchange coupling through the H bonds, should be compared with the values reported previously for Cu(L-but)_2 and Cu(D,L-but)_2 [9]. In these two copper-amino acid compounds two H bridges connect the copper ions through their equatorial N and O ligands. They are identical (related by an inversion centre) in the case of Cu(D,L-but)_2 , and different (as for Cu(alanine)_2) in the case of Cu(L-but)_2 . The values $J_0/k = (-0.64 \pm 0.01)$ K and $J_0/k = (-0.84 \pm 0.01)$ K were obtained for Cu(L-but)_2 and Cu(D,L-but)_2 , respectively [9]. The similarity of the results for Cu(L-but)_2 and Cu(L-alanine)_2 gives us confidence that these figures are representative of exchange couplings through typical pairs of H bonds connecting metal ions in metal-amino acid complexes. We are not aware of calculations of the exchange coupling parameter for copper ions connected through H bonds which could apply to our problem.

From this work we conclude that the specific heat peak observed at 0.068 K marks a transition to a 3D magnetically ordered phase at low temperatures. Isothermal magnetization measurements at high fields in single-crystal samples are needed in order to gain a better understanding of the nature of the transition.

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Appendix

In a classical paper, Bonner and Fisher [19] (BF) solved the Hamiltonian of our equation (1), corresponding to finite chains in which each component is a spin 1/2 with nearest-neighbour exchange interactions. They calculated the thermodynamic properties for ferromagnetic and antiferromagnetic chains of N spins for N up to 11, and extrapolated their results for the magnetic susceptibility χ and the specific heat to infinite chains. As a result BF reported graphs and numerical tables for $\chi(T)$ and $C_{\text{mag}}(T)$ as a function of a reduced temperature ($kT/|J|$). These tables have been widely used to fit experimental data for spin chains [35]. Calculations for finite chains up to 16 spins and new methods of extrapolating these values to infinite chains have been recently reported by Fabricius *et al* [36, 37], whose results have been used here.

In order to simplify the comparison of the predictions of the BF theory to experimental results, Hall [38] (see also [39]) introduced a polynomial function which reproduces well the values calculated for the magnetic susceptibility for $kT/|J_0| > 0.5$. This function was used to fit the susceptibility data of Cu(L-alanine)_2 [6] in order to calculate $J_0/k = -0.52$ K. In view of the simplicity of this method of fitting susceptibility data, we have used a similar procedure in the analysis of the specific heat data. We propose

$$\frac{C_{\text{mag}}(x)}{R} = \frac{x + Ax^2 + Bx^3}{3 + Cx + Dx^2 + Ex^3 + Fx^4 + Gx^5} \quad (\text{A1})$$

with $x = kT/|J_0|$. For $x \rightarrow 0$ this expression gives the value $C_{\text{mag}}/R = x/3$, as predicted by the Bethe ansatz in the thermodynamical limit [40]. To fit the seven parameters A, \dots, G involved in equation (A1) we obtained values for the specific heat of finite Heisenberg chains of up to 16 spins, obtained using the eigenvalues for these chains reported by Fabricius *et al* [36]. These results were extrapolated to infinite chains as in [36]. The least-squares fit of the results for $x \geq 0.30$ gives $A = -1.675\,924$, $B = 2.019\,551$, $C = -6.095\,436$, $D = 6.274\,510$, $E = 0.469\,065$, $F = -2.161\,535$, and $G = 2.363\,938$. Equation (A1) reproduces the results of BF [19] and Blöte [41] within the reported accuracy for all values of x , and provides a useful way to analyse experimental data.

References

- [1] Newman P R, Imes J L and Cowan J A 1976 *Phys. Rev. B* **13** 4093
- [2] Levstein P R, Steren C A, Gennaro A M and Calvo R 1988 *Chem. Phys.* **120** 449
- [3] Hoffmann S K, Gozlar J and Szczepaniak L S 1988 *Phys. Rev. B* **37** 7331
- [4] Wakamatsu T, Hashiguchi T, Nakano M, Sorai M, Suga H and Zhi-Chen T 1989 *Chinese Sci. Bull.* **34** 1795
- [5] Levstein P R, Calvo R, Castellano E E, Piro O E and Rivero B E 1990 *Inorg. Chem.* **29** 3918
- [6] Calvo R, Passeggi M C G, Novak M A, Symko O G, Nascimento O R and Terrile M C 1991 *Phys. Rev. B* **43** 1074
- [7] Levstein P R, Pastawski H M and Calvo R 1991 *J. Phys.: Condens. Matter* **3** 1877
- [8] Calvo R and Passeggi M C G 1991 *Phys. Rev. B* **44** 5111
- [9] Siqueira M L, Rapp R E and Calvo R 1993 *Phys. Rev. B* **48** 3257
- [10] Calvo R, Nascimento O R, Torikachvili M S and Maple M B 1982 *J. Appl. Phys.* **53** 2671
- [11] Pringle O A, Calvo R and Parra R E 1985 *Phys. Rev. B* **31** 358
- [12] Anderson P W 1959 *Phys. Rev.* **115** 2; 1963 *Magnetism* vol 1, ed G T Rado and H Suhl (New York: Academic)
- [13] Hay J P, Thibeault J C and Hoffmann R J 1975 *J. Am. Chem. Soc.* **97** 4884
- [14] Kahn O 1985 *Angew. Chem. Int. Edn. Engl.* **24** 834
- [15] Willet R D, Gatteschi D and Kahn O (ed) 1984 *Magneto Structural Correlations in Exchange Coupled Systems (NATO Advanced Studies Institute Series C)* vol 140 (Dordrecht: Reidel)

- [16] Solomon E I and Wilcox D E 1984 *Magneto Structural Correlations in Exchange Coupled Systems (NATO Advanced Studies Institute Series C)* vol 140, ed R D Willet, D Gatteschi and O Kahn, (Dordrecht: Reidel) pp 463-96
- [17] Butler W F, Calvo R, Fredkin D R, Isaacson R A, Okamura M Y and Feher G 1984 *Biophys. J.* **45** 947
- [18] Calvo R, Passeggi M C G, Isaacson R A, Okamura M Y and Feher G 1990 *Biophys. J.* **58** 149
- [19] Bonner J C and Fisher M E 1964 *Phys. Rev.* **135** A640
- [20] Yokoi H and Ohsawa H 1973 *Bull. Chem. Soc. Japan.* **46** 2766
- [21] The value for J_{AB} obtained from the EPR data in [6] has to be divided by 2 in order to be compared with values obtained from the susceptibility data. This problem arises because the definition of the exchange Hamiltonian (equation (13) of that paper) is different from that used to interpret the susceptibility data.
- [22] Dijkstra A 1966 *Acta Crystallogr.* **20** 588
- [23] Hitchman M A, Kwan L, Engelhardt L M and White A H 1987 *J. Chem. Soc. Dalton Trans.* **1987** 457
- [24] Rapp R E, Siqueira M L, Viana R J and Norte L C 1992 *Rev. Sci. Instrum.* **63** 5390
- [25] *International Tables for X-Ray Crystallography* 1974 (Birmingham: Kynoch)
- [26] Levstein P R and Calvo R 1990 *Inorg. Chem.* **29** 1581
- [27] Ananthakrishna G, Weiss L F, Foyt D C and Klein D J 1976 *Physica B* **81** 275
- [28] Curéty J, Georges R, Drillon M, Bellaiche M and Benkhoja K 1992 *Phys. Rev. B* **46** 3527
- [29] De Jongh L J and Miedema A R 1974 *Adv. Phys.* **23** 1
- [30] Oguchi T 1964 *Phys. Rev. A* **133** 1098
- [31] Duffy Jr W, Venneman J E, Strandburg D L and Richards P M 1974 *Phys. Rev. B* **9** 2220
- [32] Bray J W, Itterante L V, Jacobs I S and Bonner J C 1983 *Extended Linear Chain Compounds* vol 3, ed J S Miller (New York: Plenum)
- [33] Duffy W and Barr K P 1968 *Phys. Rev.* **165** 647
- [34] Hennessy M, McElwee C D and Richards P M 1973 *Phys. Rev. B* **7** 930
- [35] Carlin R L 1986 *Magnetochemistry* (Berlin: Springer)
- [36] Fabricius K, Löw U, Mutter K-H and Ueberholz P 1991 *Phys. Rev. B* **44** 7476
- [37] Fabricius K, Löw U and Mutter K-H 1993 *Z. Phys. B* **91** 51
- [38] Hall J W 1977 *PhD Thesis* University of North Carolina
- [39] Hatfield W E, Weller R R and Hall J W 1980 *Inorg. Chem.* **19** 3825
Hatfield W E 1981 *J. Appl. Phys.* **52** 1985
- [40] Babujian H M 1982 *Nucl. Phys. B* **215** 317
- [41] Blöte H W J 1974 *Physica* **78** 302; 1975 *Physica B* **79** 427