Magnetization of $Cu_2(C_5H_{12}N_2)_2Cl_4$: A Heisenberg spin-ladder system

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We study the magnetization of a Heisenberg spin ladder using exact-diagonalization techniques, finding three distinct magnetic phases. We consider the results in relation to the experimental behavior of the copper compound $Cu_2(C_5H_{12}N_2)_2Cl_4$ and deduce that the compound is well described by such a model with a ratio of bond strengths (J/J') of the order of 0.2, consistent with results from the magnetic susceptibility. The effects of temperature, spin impurities, and additional diagonal bonds are presented and we give evidence that these diagonal bonds are indeed of a ferromagnetic nature. [S0163-1829(96)51542-0]

There has been considerable recent theoretical interest in coupled chain systems for a variety of reasons: First the systems provide an interesting step from the relatively well understood one-dimensional behavior towards two-dimensional systems (i.e., a dimensional crossover). A second reason for interest lies in the unusual and exotic behavior exhibited by spin ladder systems, for example a spin gap[1] and on doping, hole pairing, and a finite superfluid density.[2] A third, and indeed the dominant, motivation for this paper lies in the increasing number of compounds which can be well described by considering the behavior of strongly correlated electrons confined to coupled chains. The compounds $(VO_2)P_2O_7$ (Ref. 3) and $SrCu_2O_3$ (Ref. 4) may be described by ladder spin systems and recently doping has been achieved in $La_{1-x}Sr_xCuO_{2.5}$.[5] In this paper we shall concentrate on the magnetic behavior of the new copper compound $Cu_2(C_5H_{12}N_2)_2Cl_4$ (Ref. 6) which in contrast to the other examples, exhibits a spin gap which is relatively small, thereby allowing a study of the magnetic effects with a relatively modest magnetic field. We will show that the magnetization of the material is well described by the Heisenberg model on a ladder system.

Recent experimental work on $Cu_2(C_5H_{12}N_2)_2Cl_4$, including magnetization, susceptibility, and spin resonance experiments, has been presented by Chaboussant *et al.*[6] The material is thought to consist of effectively isolated coupled chains as shown in Fig. 1. Superexchange gives rise to a coupling along the chains (strength J) and an interchain coupling (strength J'); there is an additional diagonal coupling J_{cb}. We shall first neglect J_{cb} since its relative strength is believed to be small although we shall include it later in the paper. Using the susceptibility data, perturbation theory, and a high-temperature series expansion, Chaboussant *et al.* have deduced a bond ratio $J'/J \sim 5.5$.

The Hamiltonian we shall use to describe the compound is the Heisenberg model on a ladder $(2\times L)$ system, defined by

$$\mathcal{H} = J' \sum_j \mathbf{S}_{j,1}\cdot\mathbf{S}_{j,2} + J\sum_{\lambda,j} \mathbf{S}_{j,\lambda}\cdot\mathbf{S}_{j+1,\lambda} + \sum_{\lambda,j,\alpha,\gamma} g_{\alpha\gamma}\mu_B H^{\alpha} S^{\gamma}_{j,\lambda}, \quad (1)$$

where λ $(=1,2)$ labels the two legs of the ladder (oriented along the x axis), j is a rung index $(j=1,\ldots,L)$, and J and J' are the bond strengths along and between the ladders, respectively. The final term represents an applied field in the direction α; we simplify this term to $g\mu_B \Sigma H_z S_z$ although we should note that anisotropic effects may have minor, but observable effects.

The behavior of this Hamiltonian in zero applied field $(H=0)$ and at zero temperature is now relatively well understood[1] and is perhaps best understood by first considering the limit $J=0$. In this case, the ground state has total spin zero and is formed by creating a singlet bond on each rung; excitations require one of these singlet bonds to be broken to form a triplet at an energy cost J'. This gapped state persists with the introduction of interchain coupling J and the triplets can propogate and form a coherent band with dispersion $J'+J\cos k$. A gap, and the associated dispersion, has been observed experimentally in the compound we are considering[6] and it is believed that in a zero applied field the energy spectrum of the system consists of a total-spin-zero ground state, a gap to the first excited state (triplet), and at higher energies, (bands of) states with even larger values of total spin.

In this paper then, we will consider the effects of an applied field on the system, i.e., considering the magnetization curve. With the application of a magnetic field, the states with nonzero total spin are split ($\propto -HS_z$) and, with increasing magnetic field, a magnetized ground state would be expected. In the first section, we calculate $\mathcal{M}(H)$ at zero temperature, and by comparison with experiment we deduce the ratio J/J' relevant to the compound. We then consider the effects of a finite temperature, deduce the relevance of ran-

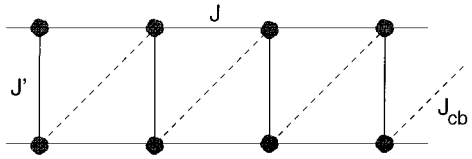

FIG. 1. The Cu-Cu superexchange paths in the compound $Cu_2(C_5H_{12}N_2)_2Cl_4$ (taken from Chaboussant *et al.*).

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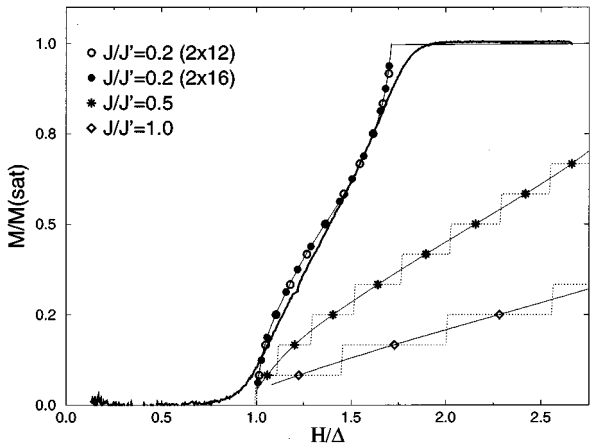

FIG. 2. Magnetization as a function of applied field. $\mathcal{M}(\mathrm{sat})$ is the saturated value of the magnetization and Δ is the singlet-triplet gap with zero applied field. Results are shown for J/J' equal to 0.2, 0.5, and 1.0 along with the experimental data (bold line).

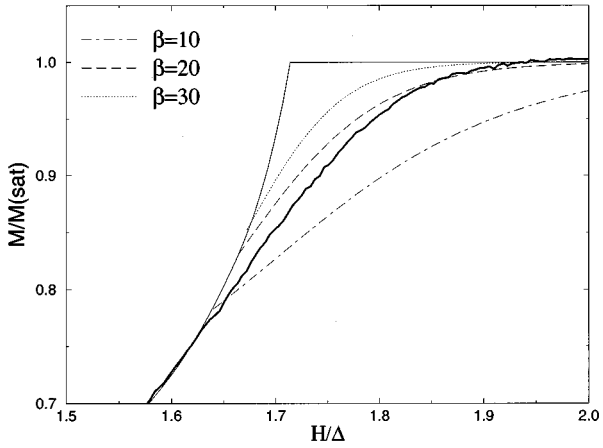

FIG. 3. Magnetization as a function of applied field for various values of temperature $(1/\beta)$. The experimental data (0.42 K $\mapsto\beta\sim 30$) is shown as a bold line.

dom spin impurities, and calculate the effect of introducing the small diagonal interaction. Finally, we discuss other possible relevant factors.

The technique we have used in this study is Lanczos exact diagonalization on 2×12 and 2×16 ladder geometries with periodic boundary conditions. We have considered the momentum of the states [$k_x=(2\pi/L)m$ where m is an integer] and also the parity of the states under a reflection in the symmetry axis along the ladder [even $(R_x=1)$ or odd $(R_x=-1)$]. Since the Hamiltonian commutes with the component of total spin in the z direction (S_z), we may consider the subsets of S_z individually. For a specific value of applied field, we consider the lowest energy state for each subset and can then easily apply the field dependent term of the Hamiltonian $\propto -HS_z$. With increasing applied field, states with larger S_z become more favorable and we obtain a ''staircase'' of states in the magnetization curve until saturation.

In Fig. 2 we show results from the 2×12 system for various values of the ratio J/J' (and also the case $J/J'=0.2$ as an example of the 2×16 system). In addition, we plot the experimental results for the lowest available temperature (0.42 K). The magnetization is normalized in such a way that the saturated system has magnetization unity and the applied field is normalized such that the value at which magnetization becomes nonzero is unity. For the cases with J/J' equal to 0.5 and 1.0, we have plotted the staircase structure resulting from the finite system; using the midpoints of the ''steps'' we have drawn a smooth magnetization curve. For the case $J/J'=0.2$, the results from the two system sizes are almost identical indicating that the finite size effects are very small (this is also true for other J/J').

Immediately we notice that two critical fields may be defined: For an applied field $H<H_{c1}$ the magnetization remains zero (in a singlet ground state); the field H_{c1} corresponds to the singlet-triplet gap at zero applied field. Then, with increasing magnetic field $H_{c1}<H<H_{c2}$, the magnetization increases until it reaches its saturation value at H_{c2}. At this point it is worthwhile mentioning the work of Affleck[7] concerning gapped, integer spin antiferromagnetic chains: In an axially symmetric situation the ground state above H_{c1} may be considered as a condensate of low-energy bosons; varying the field varies the chemical potential of the bosons and the boson number corresponds to the magnetization. In the limit of zero boson density ($H\mapsto H_{c1}$ from above) the magnetization is shown to behave as $\mathcal{M}(H)\propto\sqrt{H-H_{c1}}$ and there is a power law decay in the staggered magnetization orthogonal to the applied field:[8] For $H_{c1}<H<H_{c2}$ the spins exhibit a canted spin structure with a uniform magnetic moment in the direction of the applied field. The square root singularity appears consistent with the theoretical behavior in Fig. 2.

We emphasize that the theoretical results with $J/J'=0.2$ are extremely close to the experimental data, and this ratio is consistent with that deduced by Chaboussant *et al.* by analyzing susceptibility data. Notice however the rounding of the experimental data in the region of the critical fields H_{c1} and H_{c2} and the stronger singular behavior in the theoretical results. The aim of the remainder of this paper is to discuss the origin of these effects and we first extend our results to take into account the finite temperature, specifically looking at the rounding behavior close to H_{c2}.

It is easy to calculate the complete spectrum of energy levels (by considering each subset of S_z separately) and consequently the thermodynamic quantities can be calculated. For a specific value of the applied field the magnetization is defined by

$$\mathcal{M}=\frac{\Sigma_{n,S_z}\exp(-\beta E_n^{S_z})S_z}{\Sigma_{n,S_z}\exp(-\beta E_n^{S_z})}, \tag{2}$$

where $E_n^{S_z}$ is the energy of the nth eigenvalue of the Hamiltonian [Eq. (1)] with a z component of spin S_z. Since we are only interested in the region of the magnetization curve close to H_{c2}, we restrict the summation over S_z to $S_z\geqslant 8$ (for the 2×12 ladder); states with smaller S_z contribute only minimally in this region (this has been checked) and also subsets with $S_z<8$ include many more states and computational limitations become important.

The resulting magnetization curve for various values of β is shown in Fig. 3; we concentrate on $J/J'=0.2$ since this

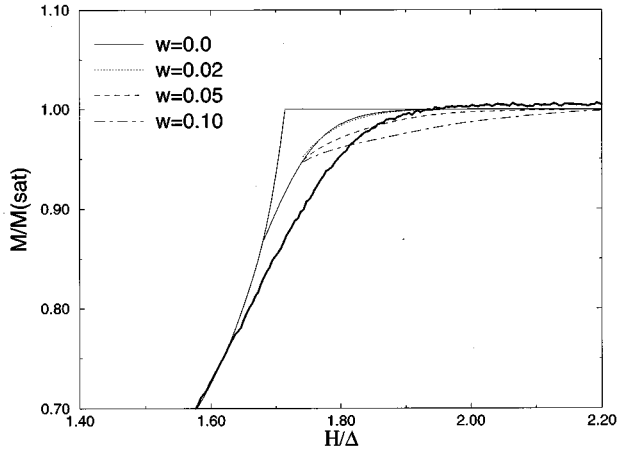

FIG. 4. Magnetization as a function of applied field including random spin impurities. Various impurity weights are shown for a temperature corresponding to $\beta=30$. The experimental data is shown as a bold line.

corresponds closely to the effective ratio in the compound. It is immediately obvious that the effect of temperature is to cause a rounding of the magnetization curve, much as observed experimentally. From experimental considerations, we would expect a temperature corresponding to $\beta\sim J'/T\sim 13.2/0.42\sim 31$ (where the 13.2 originates from the fact that we have normalized such that J' is unity, see Ref. 6). Therefore, while temperature does indeed effect the magnetization curve in the vicinity of the critical fields, there must be some other factor to explain the small discrepancy between the theory and experiment.

The next step is to understand the effects that result due to the presence of random spin impurities. We include a term in the Hamiltonian to describe the interaction of the local spins with random magnetic fields:

$$\mathcal{H}_{\rm imp}=\sum_{j,\lambda} w_{j,\lambda}S^z_{j,\lambda}\,, \tag{3}$$

where $w_{j,\lambda}$ is the impurity strength at the site j,λ (as defined in the initial Hamiltonian), chosen randomly between $-w/2$ and $w/2$ and $S^z_{j,\lambda}$ is the z component of spin on that site. In order to conserve the reflection symmetry, we choose the impurity weight of the two sites on a particular rung to be equal ($w_{j,1}=w_{j,2}$). The inclusion of random spin impurities breaks the translational symmetry of the system (k_x is no longer a good quantum number) and we also note that it is necessary to average over several realizations of the disorder due to statistical fluctuations.

In Fig. 4 we show the effects of including random spin impurities with various weights w. The dominant effect of the impurities appears to be an increase in the critical field H_{c2}: a higher field must be applied to achieve saturated magnetization. The effect on the rounding of the magnetization curve does not however appear to be the origin of the small discrepancy in shape of $\mathcal{M}(H)$ between the experimental and theoretical results.

As a final investigation, we examine the possible importance of a diagonal cross bond ($J_{\rm cb}$) as shown in Fig. 1. To include this affect we add the following term to the Hamiltonian

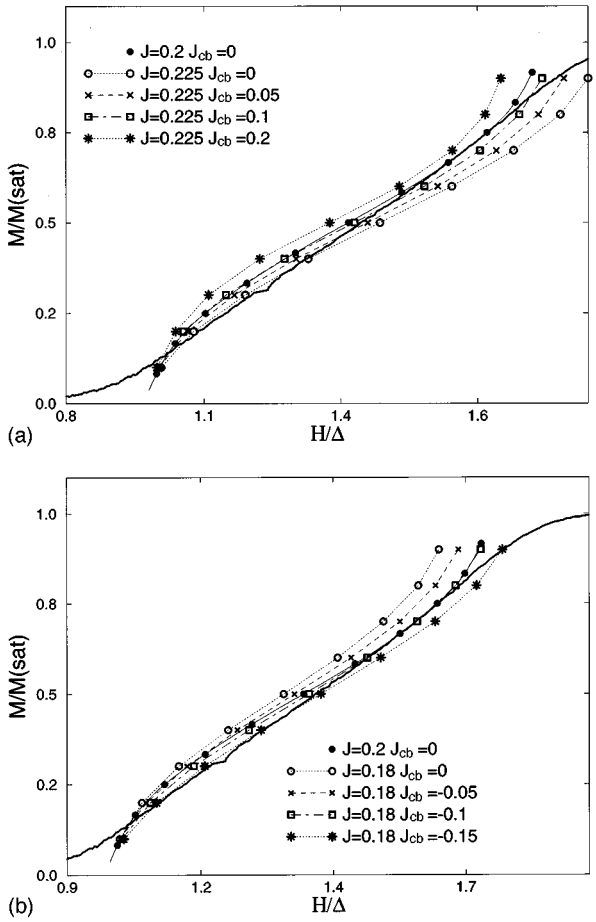

FIG. 5. Magnetization as a function of applied field including diagonal cross bonds $J_{\rm cb}$ of various strengths. (a) corresponds to $J=0.225$ and positive $J_{\rm cb}$ while (b) corresponds to $J=0.18$ and negative $J_{\rm cb}$. The experimental data is shown as a bold line and the result corresponding to $J=0.2$ $J_{\rm cb}=0$ is also included for comparison.

$$\mathcal{H}_{\rm cb}=J_{\rm cb}\sum_j \mathbf{S}_{j,1}\cdot\mathbf{S}_{j+1,2}\,. \tag{4}$$

As suggested experimentally,[6] we take $J_{\rm cb}$ to be smaller than both J and J'. In Figs. 5(a) and 5(b) we show the magnetization curve for various sets of parameters, the choice of which has been led by the desire to keep H_{c2}/H_{c1} close to the experimentally deduced value (increasing $J_{\rm cb}$ increases the effective interchain coupling and to keep this ratio constant, J must simultaneously be increased). The results were calculated for zero temperature on a 2×10 system (it has been verified that finite size effects are negligible). As previously, the results are normalized such that J' is unity, saturated magnetization has value unity, and H_{c1} is unity. In Fig. 5(a) we show the experimental data and the theoretical results corresponding to $J=0.2$ ($J_{\rm cb}=0$) as shown previously, and $J=0.225$ with the cross bond strength ranging from 0 to

0.2. A similar plot [Fig. 5(b)] shows data corresponding to $J=0.18$ and *negative* cross bond strength ranging from 0 to -0.15.

Several interesting features are apparent in the results. First, introducing the cross bond interactions does not affect the overall behavior of the magnetization curve. The major effects are to first change H_{c1} (this effect is not apparent due to the normalization), and second to change the shape of the magnetization curve slightly. Positive $J_{\rm cb}$ in fact changes the shape away from the experimental behavior, seeming to increase the singularity behavior. Surprisingly, a negative $J_{\rm cb}$ appears to shift the theoretical curve closer to the experimental behavior, with say $J=0.18$ $J_{\rm cb}=-0.1$ being a reasonable parameter choice. The results seem therefore to suggest a ferromagnetic diagonal interaction, and further investigations of the orbital behavior in the compound are required to deduce if this is reasonable.

Summarizing the results above, we find that the Heisenberg model on a ladder geometry describes well the magnetization of $Cu_2(C_5H_{12}N_2)_2Cl_4$ with a ratio $J/J'\sim 0.2$. Temperature causes a rounding of the magnetization curves in the vicinity of the critical fields and random spin impurities tend to increase H_{c2}. Diagonal bonds improve the theoretical/experimental agreement further and we suggest that the diagonal interactions appear to be ferromagnetic. The discrepancy that still exists however is perhaps not surprising since we are using only a simple Heisenberg model. Some complications may arise due to the fact that in the experimental data provided, the field H_α is not applied perpendicular to the plane of the chains and hence the magnetization $\mathcal{M}$ is not parallel to the applied field: there is a g-factor anisotropy.

Another point we should make is that we find various choices of parameters which give reasonably good agreement with the experimental results. Fitting the magnetization curve alone is not sufficient to allow the relative strengths of the parameters to be fixed extremely accurately (the Heisenberg chain with both nearest and next-nearest neighbor interactions[9] also gives similar results). We can however make reasonable deductions about the effective interactions present in the compound.

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