The 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 behaviour of the new 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 ‘chain’ to ‘rung’ 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.

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There has been considerable recent theoretical interest in coupled chain systems for a variety of reasons: Firstly the systems provide an interesting step from the relatively well understood one-dimensional behaviour towards two-dimensional systems (i.e. a dimensional crossover); A second reason for interest lies in the unusual and exotic behaviour exhibited by spin ladder systems, for example a spin gap and on doping, hole pairing and a finite superfluid density. A third, and indeed the dominant, motivation for this article lies in the increasing number of compounds which can be well described in coupled chain systems for a variety of reasons: A second reason for interest lies in the understanding of high $T_c$ superconductors, for example a spin gap and on doping, hole pairing and a finite superfluid density. A third, and indeed the dominant, motivation for this article lies in the increasing number of compounds which can be well described in coupled chain systems for a variety of reasons: A second reason for interest lies in the understanding of high $T_c$ superconductors.

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. The material is thought to consist of effectively isolated coupled chains as shown in figure. 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 firstly 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 $J'/J \approx 5.5$.

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

$$\mathcal{H} = J' \sum_j S_{j,1} \cdot S_{j,2} + J \sum_{\beta,j} S_{j,\beta} \cdot S_{j+1,\beta} + \sum_{\beta,j,\alpha,\gamma} g_{\alpha\gamma} \mu_B H^\alpha S_{j,\beta}^\gamma$$

(1)

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

The behaviour of this Hamiltonian in zero applied field ($H = 0$) and at zero temperature is now relatively well understood 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 propagate 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, and it is believed that in 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. 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 random 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 $2 \times 12$ and $2 \times 16$ ladder geometries with periodic boundary conditions. We have considered the momentum of the states ($k_z = \frac{2\pi}{L} m$ where $m$ is an integer) and also the parity of the states under a reflection in the symmetry axis along the ladder (even ($R_z = 1$) or odd ($R_z = -1$)). 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 $\propto -H S_z$. With increasing applied field, states with larger $S_z$ become more favourable and we obtain a ‘staircase’ of states in the magnetization curve until saturation.

In figure 2 we show results from the $2 \times 12$ system for various values of the ratio $J/J'$ (and also the case $J/J' = 0.2$ as an example of the $2 \times 16$ system). In addition, we plot the experimental results for the lowest available temperature (0.42K). 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 non-zero 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 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 ($H \rightarrow H_{c1}$ 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. 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 behaviour in figure 2.

We emphasise 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 analysing 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 behaviour in the theoretical results. The aim of the remainder of this article is to discuss the origin of these effects and we firstly extend our results to take into account the finite temperature, specifically looking at the rounding behaviour 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

$$\mathcal{M} = \frac{\sum_n S_z \exp (-\beta E_{nS_z}^S) S_z}{\sum_n S_z \exp (-\beta E_{n}^S)}$$

where $E_{nS_z}^S$ is the energy of the nth eigenvalue of the hamiltonian (equation 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 $S_z \geq 8$ (for the $2 \times 12$ ladder); states with smaller $S_z$ contribute only minimally in this region (this has been checked) and also subsets with $S_z < 8$ include

![FIG. 2. Magnetization as a function of applied field. $\mathcal{M}(sat)$ is the saturated value of the magnetization and $\Delta$ 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).](image-url)
many more states and computational limitations become important.

The resulting magnetization curve for various values of \( \beta \) is shown in figure 3; we concentrate on \( J/J' = 0.2 \) since this 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 \( \beta = \frac{J}{J'} \sim \frac{13.2}{18} \sim 31 \) (where the 13.2 originates from the fact that we have normalised such that \( J' \) is unity, see reference [6]). Therefore, whilst 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 the inclusion of random spin impurities, i.e. including a term in the Hamiltonian to describe the interaction of the local spins with random magnetic fields. The additional term included in the Hamiltonian has the form

\[
\mathcal{H}_{\text{imp}} = \sum_{j, \beta} w_{j, \beta} S^z_{j, \beta}
\]

where \( w_{j, \beta} \) is the impurity strength at the site \( j, \beta \) (as defined in the initial Hamiltonian), chosen randomly between \(-w/2\) and \(w/2\) and \( S^z_{j, \beta} \) 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 \((k_x \text{ is no longer a good quantum number})\) and we also note that it is necessary to average over several realizations of the disorder due to statistical fluctuations.

In Figure 3 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 \( H_{c2} \); the effect on the rounding of the magnetization curve does not however appear to be the origin of the small discrepancy in shape of \( M(H) \) between the experimental and theoretical results.

As a final investigation, we examine the possible importance of a diagonal cross bond \( (J_{cb}) \) as shown in figure 4. To include this affect we add the following term to the Hamiltonian

\[
\mathcal{H}_{cb} = J_{cb} \sum_j S^z_{j,1} \cdot S^z_{j+1,2}
\]

As suggested experimentally [6], we take \( J_{cb} \) to be smaller than both \( J \) and \( J' \). In figures 4a and 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 \( J_{cb} \) 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 \( 2 \times 10 \) system (it has been verified that finite size effects are negligible). As previously, the results are normalised such that \( J' \) is unity, saturated magnetization has value unity, and \( H_{c1} \) is unity. In figure 4a, we show the experimental data and the theoretical results corresponding to \( J = 0.2 \) \( (J_{cb} = 0) \) as shown previously, and \( J = 0.225 \) with the cross bond strength ranging from 0 to 0.2. A similar plot (figure 4b) shows data corresponding to \( J = 0.18 \) and negative \( J_{cb} \) with the cross bond strength ranging from 0 to -0.15.

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

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![Graph of magnetization as a function of applied field including diagonal cross bonds $J_{cb}$ of various strengths.](image)

Summarising the results above, we find that the Heisenberg model on a ladder geometry describes well the magnetization of $Cu_2(C_5H_12N_2)_2Cl_4$ 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 $H_{a}$ is not applied perpendicular to the plane of the chains and hence the magnetization $M$ 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 neighbour interactions also gives similar results). We can however make reasonable deductions about the effective interactions present in the compound.

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