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Field-dependent thermodynamics and quantum critical phenomena in the dimerized spin system $Cu_2(C_5H_{12}N_2)_2Cl_4$

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Experimental data for the uniform susceptibility, magnetization, and specific heat for the material $Cu_2(C_5H_{12}N_2)_2Cl_4$ (CuHpCl) as a function of temperature and external field are compared with those of three different dimerized spin models: alternating spin chains, spin ladders, and the bilayer Heisenberg model. It is shown that because this material consists of weakly coupled spin dimers, much of the data are insensitive to how the dimers are coupled together and what the effective dimensionality of the system is. When such a system is tuned to the quantum critical point by application of a field, dimensionality shows up in the power-law dependences of thermodynamic quantities on the temperature. We discuss the temperature window for such a quantum critical behavior in CuHpCl. [S0163-1829(98)05838-X]

Quantum disorder and spin-gap phenomena in insulating and doped magnetic systems have attracted much interest recently. A number of novel materials have been synthesized, which have a gap in the spin excitation spectrum and consequently exhibit activated thermodynamic behavior at low temperatures. Examples of such systems include CaV_nO_{2n+1},[1] $(VO_2)P_2O_7$,[2] $SrCu_2O_3$,[3] $CuGeO_3$,[4] $Na_2Ti_2Sb_2O$,[5] and a number of organic materials such as $Cu_2(C_5H_{12}N_2)_2Cl_4$ (CuHpCl).[6,7] While the relationship of spin-gap behavior to high-temperature superconductivity remains one of the most intriguing problems in condensed matter physics,[8,9] insulating materials are of interest in their own right, providing a rich interplay of quantum chemistry, strong quantum fluctuations, frustration, and dimensionality crossovers.

The material CuHpCl is particularly interesting for a variety of reasons. First, from the point of view of spin-$\frac{1}{2}$ models, it is truely in the strong-coupling limit, where pairs of spins are strongly coupled to each other, forming a spin dimer, and these pairs are then weakly coupled to the rest of the system. This provides a testing ground for strong-coupling theories of the quantum disordered phase. Second, the exchange energy scale is small enough so that by application of an external magnetic field one can drive the system through a phase transition from the quantum disordered to a magnetically ordered phase. Third, there is, potentially, a hierarchy of energy scales so that there is a temperature window of low-dimensional quantum critical behavior, which at the lowest temperatures will crossover to three-dimensional behavior.

We present here results of finite-temperature strong-coupling expansions around dimerized Hamiltonians. We have developed a method combining a conventional many-body perturbation theory in the interaction representation with cluster expansion techniques to carry out these expansions by fully automated computer programs. Technical details of these calculations will be presented elsewhere.[10] At high temperatures, this approach is related to conventional high-temperature expansions. But unlike those, the strong-coupling expansions show excellent convergence down to very low temperatures for a range of parameters, and thus allow one to reliably compare experimental data with model Hamiltonians over the entire temperature range. We have calculated the uniform susceptibility, magnetization, internal energy, and specific heat of three different classes of model Hamiltonians by this method. These include two quasi-one-dimensional models, the alternating spin chain and the two-leg spin ladder, and one quasi-two-dimensional (quasi-2D) model, the spin bilayer. These models have been the focus of numerous theoretical investigations in recent years.[11–13] However, ours is a comprehensive numerical study of the field- and temperature-dependent thermodynamics of these models.

The material CuHpCl consists of quasi-1D polymeric chains,[14] where two spin-$\frac{1}{2}$ copper atoms are relatively close to each other and are physically quite far from other pairs of atoms. Based on the linear polymeric structure, quasi-1D models of weakly coupled spin dimers have been favored for this system. However, the physical distances for pairs of atoms between different polymers and those within a given polymer are comparable. Furthermore, one can identify exchange pathways that lead to an interaction between spins on different chains as well as those in a given chain. Thus, in the absence of any first-principles calculation, the spin Hamiltonian for this system and the effective dimensionality is not *a priori* obvious. The majority of the experimental data on the material has been interpreted in terms of one-dimensional dimerized spin models,[6,7,15] where the exchange coupling for the dimers is about 13 K, whereas the coupling between spins on neighboring dimers is about 3 K. However, there are two pieces of experimental data which are in conflict with this picture. First, on application of a strong magnetic field when the spin gap vanishes, a finite-temperature transition has been observed at temperatures of order 1 K, whereas no such finite-temperature phase transition can exist in a strictly one-dimensional system. Second, neutron diffraction spectra on powder samples do not show any evidence of Van Hove singularities expected from the quasi-1D models.[7]

In this study, we find that the uniform thermodynamic quantities for these models in zero field are very insensitive to the way in which the dimers are coupled together. In particular, the susceptibility data for this material are well described by either an alternating chain model or a spin-ladder model or even a bilayer model. This may appear surprising as the latter model is not apparently consistent with the structure of the material. The fact that one can nevertheless obtain a good quantitative description of the susceptibility measurements is a strong argument that thermodynamic properties are determined by local effects, thus rendering them almost insensitive to the dimensionality. This is easily understood in leading order of perturbation theory: in a strongly dimerized system the Curie-Weiss constant Θ_w, which is the important parameter controlling the high-temperature susceptibility, and the singlet triplet excitation gap Δ, which is the relevant energy scale controlling the low-temperature susceptibility, are altered from their noninteracting dimer values in the same combination, independent of how the dimers are coupled together. Still, the extent to which one is able to fit the experimental data by adjusting the parameters in the three models is surprising. The theoretical calculations of the specific heat in the three cases are also close to each other, although they deviate from what is found experimentally.

It should be noted that the asymptotic low-temperature behavior of thermodynamic quantities do indeed depend on the spin dispersion along different directions. The dimensionality enters directly into the power-law prefactors multiplying the activated behavior.[16] This study shows that such prefactors are essentially impossible to see in strongly gapped systems.

We argue that a robust way to determine the dimensionality of the spin system is by tuning it to the quantum critical point by application of a magnetic field. The spin gap in zero field, together with the g factors, determines the critical field. As the spin gap disappears, the thermodynamic quantities develop power-law dependences on the temperature.[17] Given that these materials are ultimately three dimensional, an important question is, is there a temperature window where the low-dimensional quantum critical behavior can be observed? We find that at temperatures above 1 K, where our expansions still show good convergence, the asymptotic low-temperature power laws are difficult to determine in an unbiased manner. However, in a crude sense, quantum critical behavior begins to set in at a temperature of order 5 K. By studying the consistency with expected behavior in one and two dimensions, one can determine the dimensionality of the systems below this temperature. This crossover temperature scale for the onset of power laws is consistent with recent NMR measurements.[15]

The quasi-1D models that we wish to study are given by the Hamiltonian

$$\mathcal{H}=J_{\perp}\sum_i \mathbf{S}_{A,i}\cdot\mathbf{S}_{B,i}+J_l\sum_i [\mathbf{S}_{A,i}\cdot\mathbf{S}_{A,i+1}+\mathbf{S}_{B,i}\cdot\mathbf{S}_{B,i+1}] + J_a\sum_i \mathbf{S}_{B,i}\cdot\mathbf{S}_{A,i+1}. \tag{1}$$

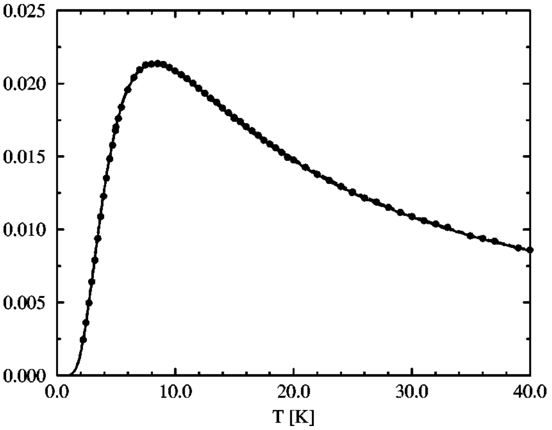

FIG. 1. Uniform susceptibility χ in zero field per spin vs temperature T. The lines are partial sums of series for the three models discussed in the text. The curves are almost indistinguishable and provide an excellent fit to the experimental data of Hammar *et al.* (Ref. 7).

Here, $\mathbf{S}_{A,i}$ and $\mathbf{S}_{B,i}$ represent the two spins in the unit cell i of the chain. The antiferromagnetic intradimer coupling $J_{\perp}>0$ is much stronger than the exchange constants J_l and J_a between different dimers. We will focus on the two limiting cases of this general model: the alternating spin chain with $(J_l=0,\ J_a\neq 0)$ and the spin ladder defined by $(J_l\neq 0,\ J_a=0)$.

In order to compare with a quasi-2D system, we consider the bilayer Heisenberg model, with Hamiltonian

$$\mathcal{H}=J_{\perp}\sum_i \mathbf{S}_{A,i}\cdot\mathbf{S}_{B,i}+J_2\sum_{\langle i,j\rangle}[\mathbf{S}_{A,i}\cdot\mathbf{S}_{A,j}+\mathbf{S}_{B,i}\cdot\mathbf{S}_{B,j}], \tag{2}$$

where $\langle i,j\rangle$ are nearest neighbors on a square lattice, and A and B represent spins in the two layers. The coupling of the system to an external field is described by

$$\mathcal{H}_{ext}=-g\mu_B H\sum_i (S^z_{A,i}+S^z_{B,i}). \tag{3}$$

We perform numerical investigations of these models by applying finite-temperature strong-coupling expansions.[10] The expansion parameter λ is given by ratio of the interdimer to the intradimer coupling, i.e., $\lambda=J_a/J_{\perp}$, $J_l/J_{\perp}$, and $J_2/J_{\perp}$ for the alternating chain, ladder, and bilayer model, respectively. The coefficients of the expansion are polynomials in the variables $J_{\perp}/k_{\mathrm{B}}T$, $1/f=1/(1+\exp[-g\mu_B H/k_{\mathrm{B}}T]+\exp[g\mu_B H/k_{\mathrm{B}}T])$, and $1/Z_0=1/(1+f\ \exp[-J_{\perp}/k_{\mathrm{B}}T])$, where Z_0 is the partition function of an isolated dimer.

Series for the uniform susceptibility χ, the magnetization M, the internal energy E, and the specific heat C are calculated complete to order λ^8, for arbitrary temperature and magnetic field. The series coefficients will be presented elsewhere and made available on the world wide web.

To begin our comparison with the experimental data, we consider first the uniform susceptibility in zero field. We note that there are some deviations between the susceptibility measurements of different groups. We will consider here the measurements of Hammar *et al.*[7] and use them to fix exchange parameters within the three models. In Fig. 1 we compare the experimental data with the models with param-

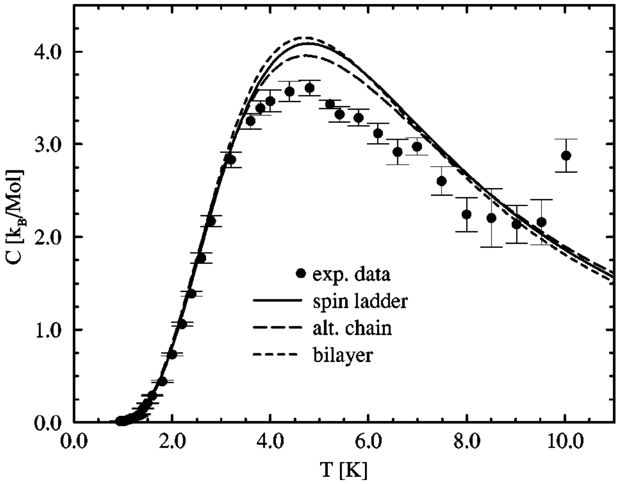

FIG. 2. Specific heat C in zero field per spin vs temperature T. The lines are partial sums of series for the three models discussed in the text compared with experimental data of Hammar *et al.* (Ref. 7).

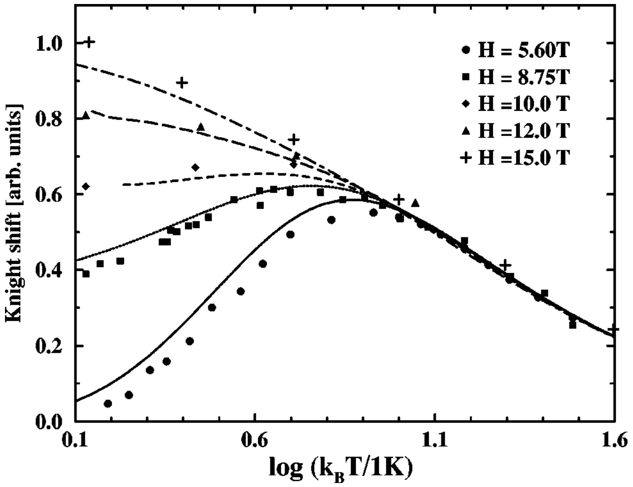

FIG. 3. Knight shift vs ln(T). Partial sums of series for the ladder model at various magnetic fields compared with experimental data of Chaboussant *et al.* (Ref. 6).

eters $J_\perp=13$ K, $J_l=3.5$ K for the ladder, $J_\perp=13.5$ K, $J_a=5.1$ K for the alternating chain, and $J_\perp=13$ K, $J_2=1.9$ K for the bilayer. The fit was obtained with $g=2.04$ as given by Hammar *et al.*[7] We note that the agreement is excellent for all three models. Different models essentially reproduce the experimental data much better than the difference in different experimental results.

We note that a similar ambiguity has also been encountered in studying the system $(VO_2)P_2O_7$,[2] where many initial measurements were interpreted in terms of a spin-ladder model, but more recent neutron scattering measurements suggest that the alternating chain model is more appropriate.

In Fig. 2 the zero-field specific heat measurements[7] are compared with the theoretical models. We note that while the shape of the experimental spectra is very similar and its activated low-temperature behavior and peak position are well reproduced by the series, the overall quantitative agreement with theory is missing. This maybe due to incomplete background subtractions or the presence of nonmagnetic phases in the experimental samples.

Before we move on to field-dependent measurements, we turn to the calculation of the critical field. The triplet dispersion has been calculated to high orders by zero-temperature dimer expansions.[13,18] For the parameters chosen, the gap is determined to be 10.0 K for the ladder model, 10.24 K for the alternating spin chain, and 9.1 K for the bilayer model, which taking $g=2.04$, translates into critical fields of 7.30, 7.45, and 6.65 T, respectively. Given the experimental observation of critical fields of 7.2(1) T by Hammar *et al.*[7] and approximately 7.7 T by Chaboussant *et al.*,[6] this argues in favor of the one-dimensional models.

In Fig. 3 we compare the Knight shift measurements of Chaboussant *et al.*[15] with the M/H ratio calculated for the ladder model. Again the two models were found to be hardly distinguishable down to quite low temperatures. We keep the exchange constants from the previous comparisons, but the vertical scale is arbitrary. Given that the zero-field data of the two groups disagree somewhat, the agreement, found here, is quite good. The convergence of these expansions breaks down once the gap closes but only at fairly low temperatures, when the correlation length becomes large.

In Fig. 4 we show the temperature dependence of the magnetization for the two models, when the system is tuned to the quantum critical point. The difference is quite apparent. The low-temperature power-law behavior is known[19] to be $M\propto T^{1/2}$ in $d=1$ and $M\propto T$ in $d=2$. Although asymptotic low-temperature behavior may set in only at extremely low temperatures, the difference between the two curves is quite apparent. In 1D the magnetization approaches zero with an infinite slope, whereas in 2D it appears to do so with a finite or zero slope. By checking the consistency with linear or square-root behavior one can distinguish the two cases quite clearly at temperatures as high as 4 K. The material CuHpCl undergoes a three-dimensional phase transition around 1 K: hence, the window for observing quantum critical behavior maybe very limited. We note that in recent measurements of the nuclear relaxation rates for this material Chaboussant *et al.* observe a fairly sharp upturn around 5 K,[15] which they interpret as evidence for quantum critical behavior. This crossover temperature scale is consistent with what we find here.

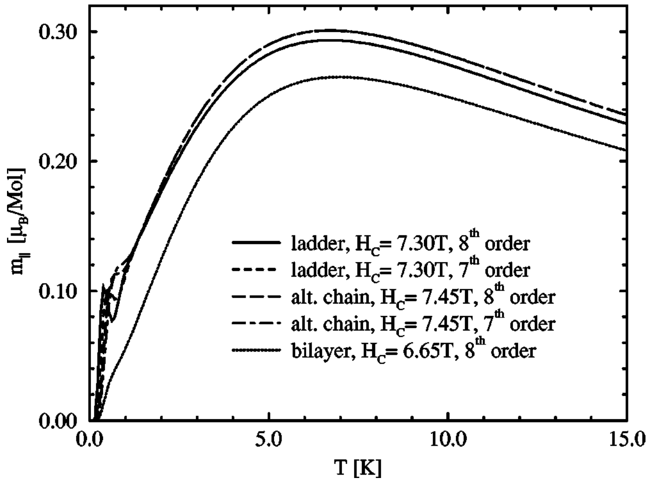

FIG. 4. Magnetization $m_\parallel$ per spin vs temperature T for the critical field H_c as discussed in the text.

Assuming the spin-ladder model, a mean-field treatment[20] of the transition temperature would lead to interchain coupling of the same order of magnitude as the coupling along the polymeric chains (of order 1 K). This large interchain coupling would explain the absence of Van Hove singularities in the powder neutron diffraction. On the other hand, if the stronger couplings make it a quasi-2D system, with let us say weaker coupling along the polymeric chains, there could be a finite-temperature Kosterlitz-Thouless phase transition, which could turn into a 3D phase transition even with very weak 3D couplings.

In conclusion, in this paper we have presented finite-temperature strong-coupling expansions for the uniform susceptibility, magnetization, internal energy, and specific heat of a number of dimerized spin models at arbitrary temperatures and fields. These calculations should be quite useful in the experimental determination of exchange parameters for a class of magnetic materials. We also showed that uniform thermodynamic measurements in zero field are not sufficient for determining the nature of the spin Hamiltonian and the dimensionality of the system. We found that the susceptibility data for the material CuHpCl can be equally well fit by a number of different models.

We have also shown that field tuning the system to the critical point may provide a clear way to determine the effective dimensionality of the spin system and to study the associated quantum critical phenomena. Direct measurements of the spin dispersion by neutron diffraction on single crystals should shed more light on the nature of the coupling constants in this material.

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