Quantum Magnetism of $CuGeO_3$

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The magnetic properties of $CuGeO_3$ are shown to be well described by the one-dimensional Heisenberg $S = \frac{1}{2}$ model with competing antiferromagnetic interactions. Provided that the competing exchange is moderately large but smaller than the critical value required to produce a gap in the excitation spectrum without lattice dimerization, the model agrees with a variety of experimental properties. It is argued that competing exchange interactions are a general feature of organic charge transfer compounds, and that they increase the temperature at which a spin-Peierls transition takes place.

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Recently, the magnetic properties of a quasi-one-dimensional inorganic chain compound, $CuGeO_3$, have received a great deal of attention. In spite of the presence of non-negligible interchain interaction, a series of experiments [1–6] have shown that the properties of this material can be well described by a model of spin-$\frac{1}{2}$ Heisenberg chains that undergo a spin-Peierls transition at a temperature $T_{SP} \approx 14$ K. The use of such a model with nearest-neighbor exchange [7] has proved to be quite successful in explaining the magnetic transition of the quasi-one-dimensional organic material TTFCuBDT [8]. In the case of $CuGeO_3$, the assumption of nearest-neighbor exchange appears to work quite well for the scaling of the spin-Peierls gap with the lattice dimerization [6], but we shall show that it does not succeed in giving a consistent description of the uniform susceptibility and the spin excitation spectrum. Indeed, the temperature dependence of the uniform susceptibility [1] is in striking disagreement with that of the spin-$\frac{1}{2}$ nearest-neighbor Heisenberg model [9]. Moreover, the best fit to that susceptibility gave an exchange constant $J = 7.58$ meV, whereas a fit of the low-lying spin excitation spectrum [2,3] to the des Cloizeaux–Pearson [10] spectrum gave $J = 10.4$ meV. These discrepancies require us to reexamine the basic model of the individual chains before going on to incorporate the coupling to the lattice and the interaction between the chains. Here we shall use exact diagonalization studies and a renormalization group analysis of one-dimensional spin-$\frac{1}{2}$ systems to argue that the experiments may be explained by incorporating longer-range competing interactions, which is in fact to be expected from the crystal structure and the electronic structure of $CuGeO_3$.

The existence of a substantial competing interaction can be inferred from the lattice structure. $CuGeO_3$ consists of a set of CuO_2 chains formed by the edges of CuO_6 octahedra and separated by Ge ions. As pointed out by Mattheiss [11], the geometry of the lattice makes it impossible for the O($2p$) orbitals to be directed towards both of the adjacent Cu ions. Then, a hopping between the oxygen ions along the chain results in a superexchange interaction that is extended in space and is much weaker than in many other materials. In particular, the nearest-neighbor exchange constant J is much smaller than the value of 1000 K found in materials such as Sr_2CuO_3, which consists of CuO chains, and has a susceptibility that is well described by a spin-$\frac{1}{2}$ Heisenberg chain with nearest-neighbor exchange [12]. Thus we expect $CuGeO_3$ to be a physical realization of an interesting one-dimensional spin model with competing interactions, and our primary aim is to show that this picture is consistent with experiment.

The effect of the interchain interaction should be important only in the vicinity of the transition. For $T \gg T_{SP}$, the magnetic correlation length along the chains is small, so the interchain interaction should have a negligible effect. At low temperatures the dimerization of the lattice causes the spins along the chains to form singlets; the spin-phonon interaction dominates, and again the interchain interaction has little effect. That this is indeed the case can be seen in the absence of magnetic ordering even at very low temperatures.

In order to study the effects of the competing interactions, we shall consider a simplified model consisting of a spin-$\frac{1}{2}$ chain with first- and second-neighbor antiferromagnetic exchange, given by the Hamiltonian

$$H = J \sum_i (\mathbf{S}_i \cdot \mathbf{S}_{i+1} + \alpha \mathbf{S}_i \cdot \mathbf{S}_{i+2}) . \qquad (1)$$

Although an exact solution for arbitrary values of the competing interaction is not known, the phase diagram and the asymptotic form of the correlation functions are well understood [13–15]. The common approach to the study of these properties is to relate the lattice problem to a continuum field theory; for the Hamiltonian of Eq. (1), and in general for any one-dimensional spin-$\frac{1}{2}$ Hamiltonian, this mapping is carried out by introducing fermion variables via the Jordan-Wigner transformation and taking the continuum limit. The result is an effective field theory in which umklapp scattering is the only

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interaction that can lead to a gap. For $\alpha = 0$, the familiar case of the Heisenberg model, the renormalization group analysis [13] shows that the umklapp interaction is marginal, and that the renormalization group flow slowly reaches the isotropic fixed point; the correlation functions decay as power laws and the spectrum is gapless. In the neighborhood of this point, an interaction of the form $J\delta\sum(-1)^i\mathbf{S}_i \cdot \mathbf{S}_{i+1}$, introduced by a spin-Peierls dimerization of the lattice, is a relevant operator and leads to a gap Δ in the energy spectrum. The gap scales [7] as $\Delta \approx \delta^{2/3}$ although, according to the renormalization group equations, there are logarithmic corrections due to the presence of umklapp scattering [13].

For $0 < \alpha < \alpha_c$, where α_c is a critical value of α, the Hamiltonian still flows to the isotropic fixed point, and the only effect of the competing interaction is to shift the bare value of the coupling constant of the marginal interaction [13,15,16]. It should be emphasized that, once the physical behavior is controlled by this fixed point, the low-energy, long-distance physics does not depend on the restriction to first- and second-neighbor antiferromagnetic exchange, in H, as defined in Eq. (1). *Any Hamiltonian with arbitrary competing interactions will give the same asymptotic behavior, provided only that it renormalizes to the same fixed point.* Moreover, the results of Cross and Fisher [7] may be used with little change other than inclusion of the logarithmic corrections, since they did not take account of umklapp scattering and worked with the fixed point Hamiltonian. In particular, the scaling of the energy gap with the dimerization and the phase diagram in the presence of a weak magnetic field would not suffer any change.

On the other hand, the physical picture changes radically when α exceeds α_c: the umklapp interaction is a relevant variable and the spectrum develops a gap. A clear picture of this regime can be obtained by examining the properties of the system at the special value $\alpha = \frac{1}{2}$, where the exact ground state is a product of near-neighbor singlets and is twofold degenerate [17,18]. Translation invariance is spontaneously broken, and the two ground states are simply related by translation through one lattice spacing. There is a gap in the excitation spectrum and the spin correlations are very short ranged. The spin system exhibits [19] long-range order in the correlation function $\langle(\mathbf{S}_{i-1} \cdot \mathbf{S}_i)(\mathbf{S}_{l-1} \cdot \mathbf{S}_l)\rangle$. In the presence of a small interaction of the form $J\delta\sum(-1)^i\mathbf{S}_i \cdot \mathbf{S}_{i+1}$, the gap would scale linearly with δ. The same qualitative behavior is to be expected for more general models with competing antiferromagnetic interactions.

Previous studies using different methods have estimated [20–23] $\alpha_c \approx 0.24-0.30$ for the Hamiltonian of Eq. (1). We have obtained the value of α_c by following the method proposed in Refs. [13] and [16]. The idea is to recognize that, in a fermion system with a fixed number of particles, umklapp scattering is the only interaction that splits the degeneracy of the two lowest excited states, which have momenta $\pm 2k_F$. Thus, the difference of their energies provides a precise measure of the magnitude of the umklapp interaction, and it is zero when $\alpha = \alpha_c$. We have used the Lanczos algorithm to determine the critical value α_c for lattice sizes varying between $N = 8$ and $N = 22$ sites.

As shown in Fig. 1, the gap varies as N^{-2}, as predicted by scaling [16], and extrapolation to $N \to \infty$ yields $\alpha_c = 0.2412 \pm 0.0001$, which agrees very well with the result of Ref. [23], obtained using conformal field theory methods.

In applying these ideas to $CuGeO_3$, the first step is to examine the question of whether the gap in the energy spectrum at low temperatures is a consequence of frustration, i.e., that $\alpha > \alpha_c$. Very recently, Harris *et al.* [5] have used neutron scattering to measure the intensity I of superlattice peaks resulting from the lattice dimerization. They used a Landau order parameter theory to argue that $I \sim \delta^2$ and, therefore, $\Delta \sim I^{1/3}$, provided the behavior is controlled by the Heisenberg fixed point, with Cross-Fisher scaling, as described above. They find that the data for $I^{1/3}$ and Δ as functions of T lie on the same curve down to $T = 4$ K, with no sign of a gap due to frustration. Furthermore, the low-temperature values of Δ (which was measured down to 2 K) fall below the extrapolated values of $I^{1/3}$ (which was measured down to 4 K). Thus the experimental data are in accord with the assumption that $\alpha \leq \alpha_c$ and that there is no contribution to the gap from frustration.

In order to fix the value of α for $CuGeO_3$ more precisely, we now consider the susceptibility and the spin wave spectrum. The calculation of the susceptibility is straightforward, and it shows that a relatively large value

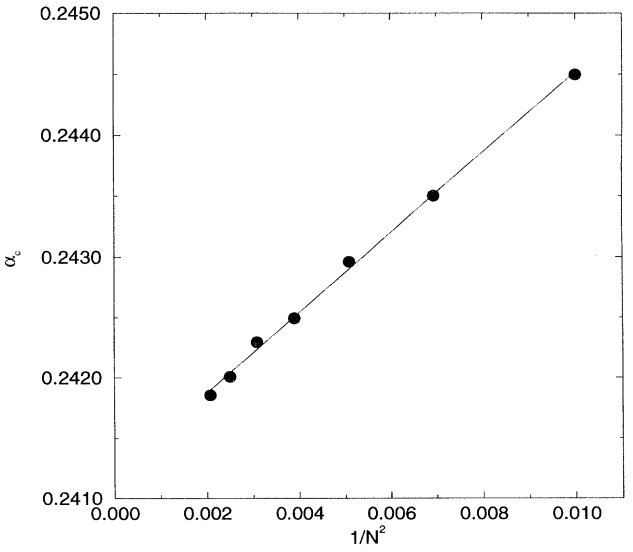

FIG. 1. $\alpha_c(N)$ vs $1/N^2$. The linear fit gives the intercept $\alpha_c = 0.2412$.

of α gives a better agreement with experiment. The physical reason for this is that the hopping along the chain of oxygens may give rise to third, fourth, and so forth nearest-neighbor interactions. Thus α must be understood as an effective coupling that quantifies the effect of the frustration.

Figure 2 shows the susceptibility for $\alpha = 0.24$, together with the susceptibility data for $CuGeO_3$ from Hase, Terasaki, and Uchinokura [1]. The theoretical curve was obtained by calculating the susceptibility for lattices varying between 8 and 14 sites. As in Ref. [9], the calculated susceptibility shows an odd-even alternation at low temperatures. We have used the method of Padé approximants to extrapolate to low temperatures [24]. A value of $J = 150$ K gives a good fit, especially in the high-temperature region. Though reasonable, the agreement is poorer in the region close to the spin-Peierls transition, where other factors such as the phonon degrees of freedom and the interchain coupling are expected to assume a more decisive role. In contrast, the fit corresponding to $\alpha = 0$ and $J = 88$ K is quite poor [1].

The Lanczos algorithm may also be used to calculate the energy spectrum of the lowest spin excitation for various lattice sizes. For a meaningful comparison with the experimental data, which were taken below the transition temperature, we added to the Hamiltonian of Eq. (1) a dimerization $J\delta\sum(-1)^i \mathbf{S}_i \cdot \mathbf{S}_{i+1}$. A similar term for the competing interaction is of higher order in the lattice dimerization. The value of J was chosen to be 150 K, the same as that used to fit the susceptibility.

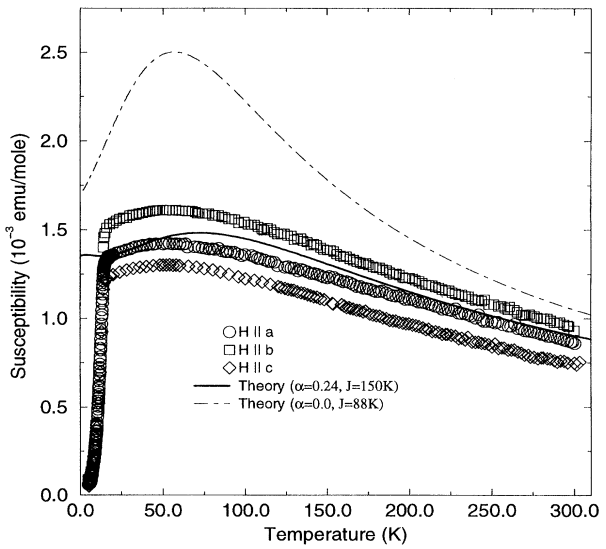

FIG. 2. Uniform magnetic susceptibility vs temperature. Following Ref. [1], we have subtracted the orbital susceptibility, estimated to be 10^{-4} emu/mole, from the experimental curves and used an isotropic g factor $g = 2.0$. The $\alpha = 0$ curve is determined so that the maximum occurs at the same temperature as the experimental curve [1].

The results for 20 sites and the experimental data of Nishi *et al.* [2] and Regnault *et al.* [3] are shown in Fig. 3. It is clear that the agreement between experiment and theory is excellent. Furthermore, from a linear extrapolation of the values of Δ for different lattice sizes, we find $\Delta \sim 2.1$ meV, which agrees well with the experimental value of $\Delta \sim 2.11$ meV of Refs. [2,3].

We also have verified numerically the intuitively reasonable idea that the gain in energy δE produced by a dimerization of the nearest-neighbor exchange integral increases substantially as α approaches the critical value α_c. Since δE drives the spin-Peierls transition, it is evident that competing exchange interactions increase the transition temperature T_{SP} [25]. In consequence, a long-range frustrating interaction may be of importance for other quasi-one-dimensional antiferromagnets, especially those undergoing a spin-Peierls transition. Torrance [26] has pointed out that, with very few exceptions, the magnetic susceptibility of organic charge transfer compounds does not follow the susceptibility expected from the spin-$\frac{1}{2}$ nearest-neighbor Heisenberg model [9]. Indeed, the susceptibility of TMPD-I, shown in Fig. 10 of Torrance's review [26], is quite similar to that of $CuGeO_3$, [1], and it may be explained in the same way by introducing a competing exchange interaction. Thus the enhancement of the spin-Peierls transition temperature by frustration may be quite common.

In summary, we have provided strong evidence that the Heisenberg model with a competing interaction $\alpha \lesssim 0.24$ and an exchange constant $J \approx 150$ K describe very well the magnetic properties of $CuGeO_3$. The experimental evidence for the scaling of Δ *imposes* a fundamental constraint on the physics of the model, which together with

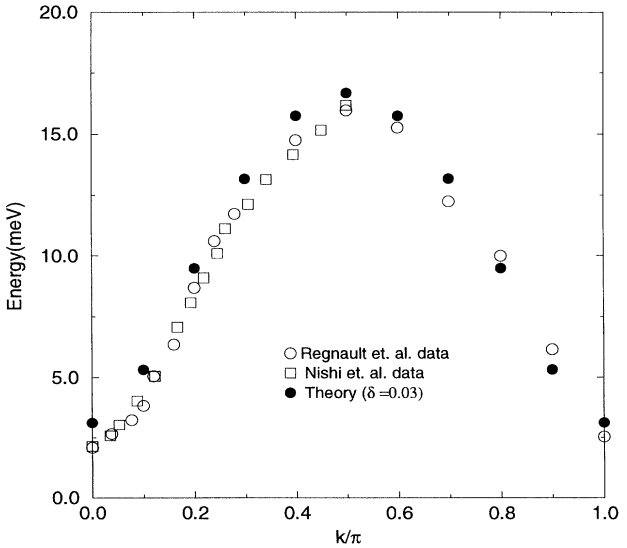

FIG. 3. Dispersion curve of the magnetic excitation along the chains. The experimental data are taken from Refs. [2,3].

the excellent fit to the spin excitation expectrum implies that the energy gap is a consequence of lattice dimerization rather than frustration. This also corroborates the idea that the spin-spin interaction between the chains has a secondary role below the spin-Peierls transition. In the case of susceptibility the theoretical results agree well with experiment except in the region where the phonon effects and the two-dimensionality of the magnetic interaction must be taken into account.

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Note added.—After this work was completed, we became aware of a preprint by J. Riera and A. Dobry, who carried out numerical calculations of χ and Δ for a competing second-neighbor interaction, following our suggestion mentioned in Ref. [27]. They concluded that $\alpha = 0.36$, which implies a gap in the absence of dimerization.

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