



Surprises on the Way from One- to Two-Dimensional Quantum Magnets: The Ladder Materials

Author(s): Elbio Dagotto and T. M. Rice

Source: *Science*, New Series, Vol. 271, No. 5249 (Feb. 2, 1996), pp. 618-623

Published by: American Association for the Advancement of Science

Stable URL: <http://www.jstor.org/stable/2889679>

Accessed: 18-09-2016 05:58 UTC

JSTOR is a not-for-profit service that helps scholars, researchers, and students discover, use, and build upon a wide range of content in a trusted digital archive. We use information technology and tools to increase productivity and facilitate new forms of scholarship. For more information about JSTOR, please contact support@jstor.org.

Your use of the JSTOR archive indicates your acceptance of the Terms & Conditions of Use, available at <http://about.jstor.org/terms>



American Association for the Advancement of Science is collaborating with JSTOR to digitize, preserve and extend access to *Science*

Surprises on the Way from One- to Two-Dimensional Quantum Magnets: The Ladder Materials

Elbio Dagotto and T. M. Rice

To make the transition from the quasi-long-range order in a chain of antiferromagnetically coupled $S = 1/2$ spins to the true long-range order that occurs in a plane, one can assemble chains to make ladders of increasing width. Surprisingly, this crossover between one and two dimensions is not at all smooth. Ladders with an even number of legs have purely short-range magnetic order and a finite energy gap to all magnetic excitations. Predictions of this ground state have now been verified experimentally. Holes doped into these ladders are predicted to pair and possibly superconduct.

The unexpected discovery of high-temperature superconductivity (1) in lightly doped antiferromagnets has sparked renewed interest in low-dimensional quantum magnets. The parent cuprate insulators are now considered the best examples of planar spin-1/2 antiferromagnets with isotropic and predominantly nearest-neighbor coupling. They show simple long-range antiferromagnetic (AF) order at low temperatures in agreement with theory, which predicts an ordered ground state for the $S = 1/2$ AF Heisenberg model on a two-dimensional (2D) square lattice (2). The 1D AF Heisenberg chain is also well understood. A famous exact solution found by Bethe many years ago (3) showed that quantum fluctuations prevent true long-range AF order, giving instead a slow decay of the spin correlations at a rate that varies essentially inversely with the separation between the spins. Therefore, it came as a great surprise when numerical calculations found that the crossover from chains to square lattices, obtained by assembling chains one next to the other to form "ladders" of increasing width, was far from smooth. Although there is no apparent source of frustration, quantum effects lead to a dramatic dependence on the width of the ladder (given by the number of coupled chains).

Ladders made from an even number of legs have spin-liquid ground states, so called because of their purely short-range spin correlation. An exponential decay of the spin-spin correlation is produced by a finite spin gap, namely, a finite energy gap to the lowest $S = 1$ excitation in the infinite ladder. These even-leg ladders may therefore be regarded as realizations of the unique, coherent singlet ground state proposed some years ago by Anderson in the

context of 2D $S = 1/2$ AF Heisenberg systems (the so-called resonance valence bond state) (4).

A ladder with an odd number of legs behaves quite differently and displays properties similar to those of single chains at low energies, namely gapless spin excitations and a power-law falloff of the spin-spin correlations, apart from logarithmic corrections. This dramatic difference between even-leg and odd-leg ladders predicted by theory has now been confirmed experimentally in a variety of systems.

Two-leg $S = 1/2$ ladders are found in vanadyl pyrophosphate $(VO)_2P_2O_7$ and in some cuprates like $SrCu_2O_3$ (Fig. 1) (m -leg ladder denotes m coupled spin-1/2 chains). Measurements of the spin susceptibility show that it vanishes exponentially at low temperature, a clear sign of a spin gap. Neutron scattering and muon spin resonance measurements are consistent with short-range spin order in the 2-leg ladders, although as we stressed before, they are unfrustrated spin systems that classically should order without a spin gap. Further nuclear magnetic resonance (NMR) measurements have confirmed the large spin gap in the excitation spectrum.

Three-leg ladders ($Sr_2Cu_3O_5$) by contrast show longer range spin correlations and even true long-range order at low temperature because of weak interladder forces. There is excellent agreement between theory and experiment, confirming that there is a dramatic difference between even- and odd-leg $S = 1/2$ Heisenberg AF ladders.

Doped chains have long fascinated theorists because they form unusual quantum liquids, so-called Luttinger liquids, with many unique properties (5). Although doping experiments in ladder compounds are just starting, extensive theoretical studies have been made of doped ladders. Again, a clear difference between even- and odd-leg ladders is predicted. Even-leg ladders are especially interesting because a variety of techniques reveal hole pairing in a relative

" d -wave" state, which places them in a different universality class of 1D systems than the Luttinger liquids found in single chains and odd-leg ladders.

Theoretical Aspects of the $S = 1/2$ Heisenberg Model on Ladders

The properties of $S = 1/2$ Heisenberg AF models defined on 1D chains or on 2D square lattices are well-known. The model is defined by the Hamiltonian

$$H = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j$$

where i is a vector labeling lattice sites where spin-1/2 operators \mathbf{S}_i are located, $\langle i,j \rangle$ denotes nearest-neighbor sites, and $J (> 0)$ is the AF exchange coupling that provides the energy scale in the problem. This scale is material dependent and ranges from a few millielectron volts to, in the case of high-temperature superconductors, about 0.1 eV. On 2D square lattices, the Heisenberg model has a ground state with long-range AF order, whereas in 1D chains, the spin-spin correlation decays slowly to zero as a power law. Neither system has a spin gap, that is, there is no cost in energy to create an excitation with $S = 1$.

The field of ladder systems started when Dagotto *et al.* (6) [see also (7, 8)] found evidence that 2-leg ladders have a finite spin gap, because a finite energy is needed to create a $S = 1$ excitation. They started with the simple limit obtained by generalizing Eq. 1 so that the exchange coupling along the rungs of a 2-leg ladder (denoted by J') is much larger than the coupling J along the chains. This idealization has the advantage that rungs interact only weakly with each other, and the dominant configuration in the ground state is the product state with the spins on each rung forming a spin singlet. The energy in this limit is approximately $E_{gs} = -3/4J'N$, where N is the number of rungs and $-3/4J'$ is the energy of each rung singlet state $|\Psi\rangle_S = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$ (\uparrow and \downarrow are the spin-up and spin-down eigenvectors of the spin operator in the z direction). The ground state has a total spin $S = 0$ because each rung is in a spin singlet. To produce a $S = 1$ excitation, a rung singlet must be promoted to a $S = 1$ triplet $|\Psi\rangle_T = [|\uparrow\uparrow\rangle, (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}, |\downarrow\downarrow\rangle]$. An isolated rung-triplet has an energy J' above the rung singlet. The coupling along the chains cre-

E. Dagotto is in the Department of Physics and National High Magnetic Field Lab, Florida State University, Tallahassee, FL 32306, USA. T. M. Rice is with AT&T Bell Laboratories, Murray Hill, NJ 07974, USA, and Theoretische Physik, Eidgenössische Technische Hochschule, 8093 Zürich, Switzerland.

ates a band of $S = 1$ magnons with a dispersion law $\omega(k) = J' + J(\cos k)$ in the limit $J' \gg J$ (k is the wave vector). The spin gap is the minimum excitation energy $\Delta_{\text{spin}} = \omega(\pi) \approx J' - J$, which remains large in this limit (9). Concurrently, the spins are mostly uncorrelated between rungs because the spin correlations decay exponentially with distance along the chains, leading to the spin-liquid nature of this state. Note, however, that the spins are not disordered but are in an isolated quantum-coherent ground state.

In the other extreme, $J'/J = 0$, the two chains decouple, but isolated spin-1/2 Heisenberg chains do not have a spin gap and excitations with $S = 1$ and $k = \pi$ are degenerate with the ground state in the bulk limit. To reconcile the different behavior in the limits $J'/J \gg 1$ and $J'/J = 0$, it was conjectured (6) that the spin gap should smoothly decrease as J'/J is reduced, reaching $\Delta_{\text{spin}} = 0$ at some critical value of the coupling. Later, Barnes *et al.* (9) observed that the power-law decay of the spin correlation in an isolated chain implies that a chain is in a critical state and thus small perturbations can qualitatively alter its properties. They predicted that the spin gap would vanish only at $J'/J = 0$, so that $\Delta_{\text{spin}} > 0$ at all $J'/J > 0$, including the values of experimental interest, $J'/J \sim 1$. The ladder spin system would always be in a spin-liquid state, in contrast to the more familiar cases of the 1D and 2D Heisenberg models, which are gapless.

Physical realizations of ladders like SrCu_2O_3 or $(\text{VO})_2\text{P}_2\text{O}_7$ correspond to $J' \approx J$. However, at $J' = J$ there is no small parameter to guide a perturbative calculation, nor is an exact solution known. Nu-

merical techniques can handle the region $J' \approx J$, and exact diagonalization of small clusters and quantum Monte Carlo techniques have been used (6, 9) to study Δ_{spin} as a function of J'/J . The techniques used are not essential to this discussion, so the reader is referred to (10) for details.

Numerical calculation of Δ_{spin} (9) (Fig. 2A) shows that indeed $\Delta_{\text{spin}} > 0$ for all $J'/J \neq 0$. At the realistic coupling $J' = J$, the gap is $\Delta_{\text{spin}} \approx 0.5J$. More recently, White *et al.* (11), using a renormalization group (RG) technique suitable for static properties of 1D systems, reported $\Delta_{\text{spin}} = 0.504J$ at $J' = J$, in excellent agreement with predictions (6, 9). There are AF spin correlations at short distances along the chains and across the rungs, but even at $J' = J$, the latter are somewhat stronger (11), showing that the rough picture of a ground state dominated by rung singlets (6) is robust. The closely related one-band Hubbard model at half-filling also shows a spin gap for all interaction strengths (12, 13).

A useful intuitive approximation is to visualize the ground state of a 2-leg ladder as mostly rung singlets supplemented by weak AF correlations along the chains. Gopalan *et al.* (14) suggested that a good variational description of the ground state could be obtained using the short-range resonance valence bond state proposed by Anderson (4) and Kivelson *et al.* (15) with mostly adjacent rung singlets but including resonance between two adjacent rung singlets into two nearest-neighbor singlets along the chains (12).

Determining what happens if we increase the number of "legs" in the ladder is not a purely academic pursuit: Materials such as $\text{Sr}_{n-1}\text{Cu}_{n+1}\text{O}_{2n}$ contain ladder

structures with a number of legs that depends on the value of n (16). The large J'/J limit allows us again to make predictions for the behavior of the m -leg ladder. Let us begin with the even-leg ladder. At $J'/J \gg 1$, the rungs decouple, and at each level there are 2^m states instead of the four states of the 2-leg ladder, apparently complicating the problem. However, the ground state of the m -spins rung is also a $S = 0$ singlet separated by a finite gap from the first excited state. Thus, as in the case of the 2-leg ladder, the even-leg ladder at $J' \gg J$ has a finite spin gap proportional to J' . Taking the analogy with the 2-leg ladder further, it is plausible to assume that a spin gap exists in the even-leg ladder for any $J'/J \neq 0$. Early numerical calculations on 4-leg ladders are in agreement with this picture (8). By evaluating exactly the 4×6 and 4×8 clusters with periodic boundary conditions and extrapolating the results to the bulk limit using an exponential form, Poilblanc *et al.* (17) obtained a spin gap $\Delta_{\text{spin}} = 0.245J$, which is about half the size of the gap for the 2-leg ladder. Hatano and Nishiyama (18) found $\Delta_{\text{spin}} = 0.27J$ using a similar analysis. A reduction in the size of the gap is natural because as the width of a ladder grows, the limit for the 2D square lattice is approached and $\Delta_{\text{spin}} \rightarrow 0$. White *et al.* (11), using a RG technique on larger $4 \times N$ clusters but with open boundary conditions, which amplify the finite size effects, reported $\Delta_{\text{spin}} = 0.190J$ extrapolated to $N \rightarrow \infty$, with a spin correlation length $\xi_{\text{AF}} \sim 5$ or 6. Finally, a mean-field approach (14) predicted $\Delta_{\text{spin}} = 0.12J$. The presence of a finite spin gap in the 4-leg ladder seems by now well established theoretically, but some discrepancies on its value remain to be clarified.

Rice *et al.* (16) and Gopalan *et al.* (14), quoting arguments by Hirsch and Tsunetsugu, made the interesting observation that

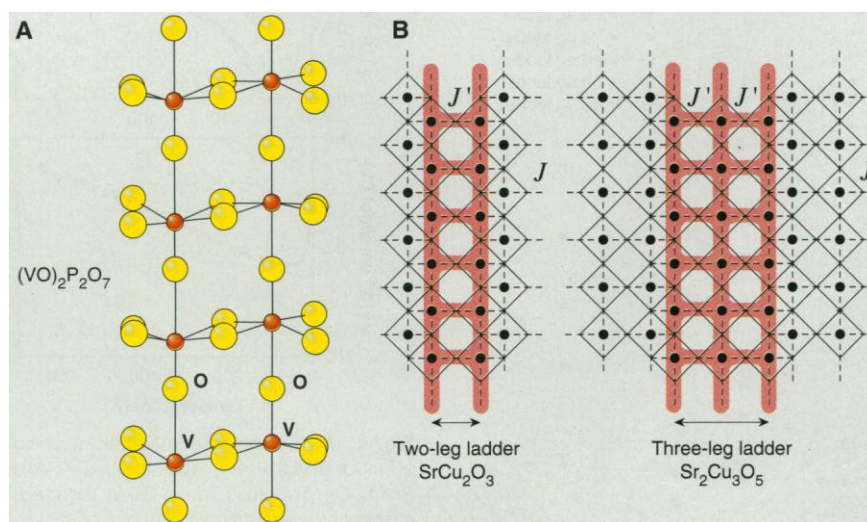


Fig. 1. (A) Ladder compound $(\text{VO})_2\text{P}_2\text{O}_7$; O and V ions are indicated. [Reprinted from (31).] (B) Schematic representation of the 2-leg compound SrCu_2O_3 and the 3-leg compound $\text{Sr}_2\text{Cu}_3\text{O}_5$. The black dots are Cu atoms, and the intersections of the solid lines are O locations; the dashed lines are Cu-O bonds. The 2- and 3-leg structures are highlighted, J is the coupling along the chains, and J' is the coupling along the rungs. [Reprinted from (34).]

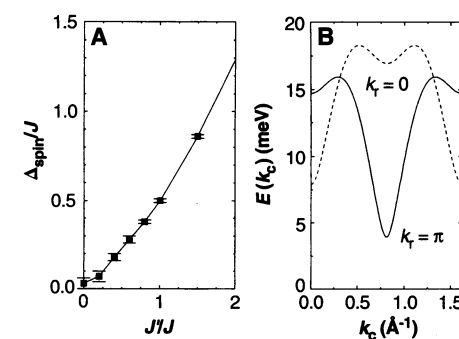


Fig. 2. (A) Spin gap Δ_{spin} versus J'/J for the 2-leg ladder. The results are extrapolations to the bulk limit using numerical results obtained on finite $2 \times N$ clusters. [Reprinted from (9).] (B) Triplet spin-wave excitation spectra for the isotropic point $J' = J$, with $J = 7.79$ meV and the $(\text{VO})_2\text{P}_2\text{O}_7$ lattice spacing; k_x and k_y denote momentum along the rungs and chains, respectively. [Reprinted from (24).]

odd-leg ladders should behave quite differently from even-leg ladders and display properties similar to single chains at low energies, namely gapless spin excitations and a power-law falloff of the spin-spin correlations. The simplest way to visualize this difference is again by analyzing the large J'/J limit (19). Consider, for example, 3-leg ladders. At large J'/J , each rung can be diagonalized exactly, leading to a doublet ground state and doublet and quadruplet excited states. The rung doublet of lowest energy will be the dominant configuration in the ground state at low temperature, which thus consists now of $S = 1/2$ states (doublets) in each rung. The interrung coupling J generates an effective interaction between these $S = 1/2$ rung states, which by rotational invariance must be of the Heisenberg form with an effective coupling J_{eff} as energy scale. Thus, the ground-state properties of the 3-leg ladder at large J'/J should be those of the spin-1/2 Heisenberg chain with a coupling J_{eff} instead of J , and thus with a vanishing spin gap. The argument can be trivially generalized to all odd-leg ladders. Because there is no spin gap for the odd-leg case at both $J'/J \gg 1$ and $J'/J = 0$, it is reasonable that the gap vanishes at intermediate values of J'/J , in contrast to even-leg ladders. A recent numerical RG calculation (11) verified these intuitive ideas.

Khvashchenko (20) explained the qualitative difference between even- and odd-leg ladders on the basis of an argument used by Haldane for the 2D square lattice (21). For odd-leg ladders, a topological term governing the dynamics at long wavelengths appears in the effective action, whereas for

even-leg ladders, it exactly cancels. This topological term is similar to the one that causes the well-known difference between integer Heisenberg spin chains, which have a finite spin gap, and half-integer spin chains, which are gapless. The direct analogy with the Haldane state of the $S = 1$ chain is realized in ladders with a ferromagnetic coupling $J' < 0$ on the rungs: In this case, in the $|J'/J| \gg 1$ limit the rungs become spin triplets rather than singlets (22). More work is needed to clarify the relation of the Haldane state of the integer spin chains and the spin liquid of the AF spin-1/2 even-leg ladders (23).

The single-magnon spectrum $\omega(k)$ of the 2-leg ladder evolves from a simple cosine dispersion at $J' \gg J$, dominated by $S = 1$ rung states (9), to a more linear dispersion around the minimum $\omega(\pi) \approx 0.5J$ at the isotropic coupling value $J' = J$ (Fig. 2B) (9, 14). This change can be traced to a spreading of the two parallel spins in the triplet over more than one rung as J'/J is reduced, which in turn modifies the dispersion relation through longer range transfer processes. The magnons near $k = \pi$ remain as well-defined modes separated from the two-magnon continuum (24), which starts at energy $\sim J$ near $k = 0$ (25, 26). The magnon dispersion should in principle be directly measurable through inelastic neutron scattering experiments on single crystals, but only powder spectra are available at present.

Recently, thermodynamic properties of $S = 1/2$ ladders have also been studied by several groups. Troyer *et al.* (27) used a quantum transfer-matrix method on 2-leg ladders to obtain reliable results down to

temperature $T \approx 0.2J$. The correlation length of the short-range AF order is $\xi_{\text{AF}} \approx 3$ to 4 (in units of the lattice spacing), in agreement with calculations of $\xi_{\text{AF}} = 3.19$ at zero temperature (11). The magnetic susceptibility $\chi(T)$ (24, 27, 28) crosses over from a Curie-Weiss form $\chi(T) = C/(T + \theta)$ at high temperature to an exponential fall-off $\chi(T) \sim \exp(-\Delta_{\text{spin}}/T)/\sqrt{T}$ as $T \rightarrow 0$, reflecting the finite spin gap (29). Recently, the results were extended to lower temperatures and to ladders of up to six legs in width (30) (Fig. 3).

Experimental Results on Ladder Compounds

At present, two types of ladder compounds are known. The first to be identified was vanadyl pyrophosphate $(\text{VO})_2\text{P}_2\text{O}_7$ (Fig. 1A). The V ions are in oxidation state V^{4+} , or equivalently, in a state $3d^1$ with the single electron occupying a nonbonding t_{2g} orbital. The superexchange interaction occurs through the $dp\pi$ -overlap of V $3d$ and O $2p$ orbitals. The magnetic susceptibility $\chi(T)$ (Fig. 4A) (31) shows an activated

Fig. 3. Magnetic susceptibility $\chi(T)$ calculated with Monte Carlo techniques on m -leg ladders with $J' = J$ on clusters of $m \times 100$ sites. For even-leg ladders, $\chi(T)$ shows at low temperature the exponential suppression caused by the spin gap, whereas the odd-leg ladders extrapolate to a finite number as $T \rightarrow 0$ [Reprinted from (30).]

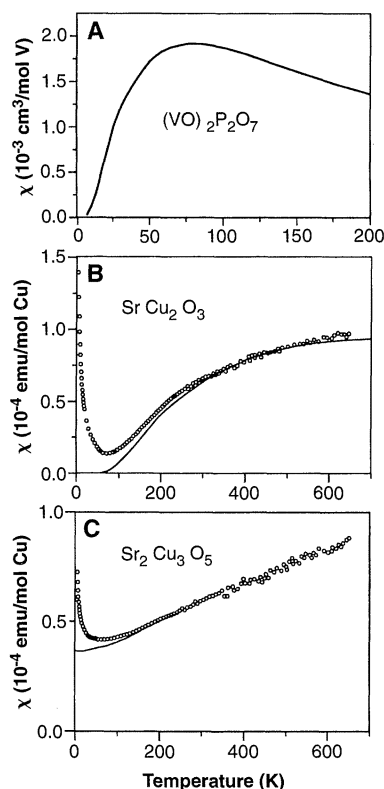
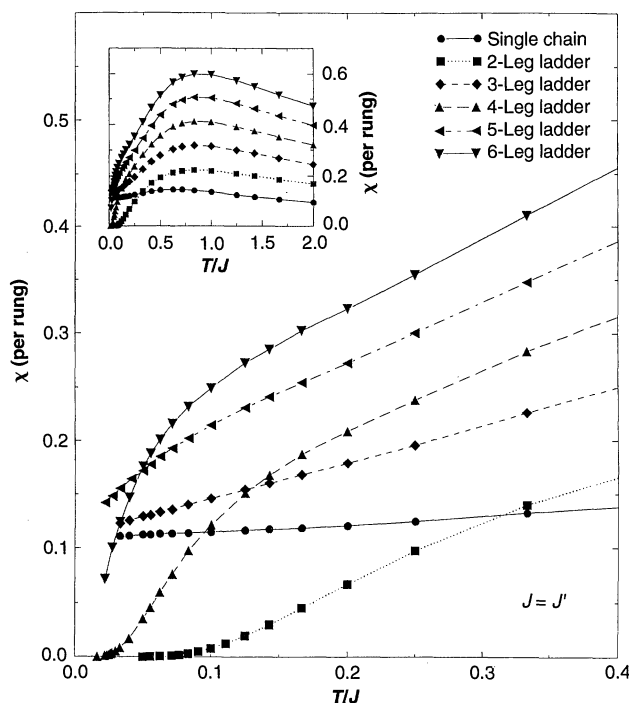


Fig. 4. (A) Experimental magnetic susceptibility $\chi(T)$ for $(\text{VO})_2\text{P}_2\text{O}_7$, (B) SrCu_2O_3 , and (C) $\text{Sr}_2\text{Cu}_3\text{O}_5$. The solid line in (B) is the calculated susceptibility assuming a spin gap of 420 K, from the equation $\chi(T) \propto T^{-1/2} \exp(-\Delta/T)$ (27). The solid line in (C) is the corrected susceptibility after subtraction of the low-temperature Curie component from the raw data. [(A) is reprinted from (31), and both (B) and (C) are reprinted from (34).]

behavior at temperatures $T < 100$ K crossing over to Curie-Weiss form at higher temperature. By fitting $\chi(T)$, Barnes and Riera (24) found almost equal values $J = 7.76$ meV and $J' = 7.8$ meV for the exchange along the chains and rungs, respectively. Recently, Eccleston *et al.* (32) used a powder time-of-flight neutron scattering technique to obtain the inelastic spectrum. The powder average of the dynamic magnetic structure factor (Fig. 5) shows clear evidence of a spin gap: at a wave vector π , $\Delta_{\text{spin}} \approx 3.7 \pm 0.2$ meV, a value that agrees well with the theoretical prediction of $\Delta_{\text{spin}} = 0.5J = 3.9$ meV (6, 9). The data do not allow a unique determination of the magnon dispersion relation but are consistent with the form illustrated in Fig. 2B.

Cuprates with modified copper-oxygen planes and other structures form a second type of ladder compound. The key is the configuration of the CuO_4 squares. The high-critical temperature (high- T_c) cuprate families are all based on CuO_2 planes with CuO_4 squares that are all corner-sharing. This leads to 180° Cu-O-Cu bonds. Because the Cu^{2+} ion has a $3d^9$ configuration with the single hole occupying an antibonding e_g orbital, there is an exceptionally strong superexchange interaction ($J \approx 0.13$ eV) through $dp\sigma$ overlap with the O $2p$ -orbital common to both CuO_4 squares. In the ideal CuO_2 plane, the O ions form a square lattice and the Cu ions occupy the centers of exactly one half of the O_4 squares, also forming a square lattice. If a line defect is introduced in the Cu occupation so that different left and right sets of

O_4 squares are occupied, then along this line the coordination of the CuO_4 squares is edge-sharing (Fig. 1B). However, the superexchange path for two CuO_4 squares sharing an edge is very different and involves primarily an intermediate state with two holes on orthogonal orbitals on the same O ion. Hund's rule then favors parallel spin alignment, and as a result, the Kanamori-Goodenough rules give a weak ferromagnetic coupling between Cu^{2+} ions that are edge-sharing.

Hiroi *et al.* (33) were the first to synthesize the family of layer compounds $\text{Sr}_{n-1}\text{Cu}_n\text{O}_{2n}$, which have arrays of parallel line defects (Fig. 1B). Nearly ideal ladder compounds should result (16): The pattern of strong AF 180° Cu-O-Cu bonds makes a ladder, and the interladder coupling is very weak both because of weak ferromagnetic 90° Cu-O-Cu bonds and the resulting frustration. The first member ($n = 3$ or SrCu_3O_3) has 2-leg ladders, the second ($n = 5$ or $\text{Sr}_2\text{Cu}_3\text{O}_5$) has 3-leg ladders, and so on.

Magnetic susceptibility measurements of the 2-leg and 3-leg ladder compounds (34) (Fig. 4, B and C) reveal striking differences between the two compounds. A spin gap is indicated by a precipitous drop in $\chi(T)$ for $T < 300$ K in the 2-leg compound. A fit to the low-temperature form $\chi(T) \sim T^{-1/2} \exp(-\Delta_{\text{spin}}/T)$ yields $\Delta_{\text{spin}} = 420$ K (34). This compound should have exchange constants close to the isotropic limit $J = J' \approx 1300$ K, so that theory predicts a larger value for an isolated ladder $\Delta_{\text{spin}}^{\text{theory}} \sim 650$ K. However, in SrCu_2O_3 there is substantial exchange coupling J_c along the c axis. This should lower Δ_{spin} and may account for most of the discrepancy. However, NMR investigations (34, 35) showed not only the activated behavior in the relaxation rate T_1^{-1} at $T < 300$ K, as expected, but also an activation energy (680 K) that was substantially larger than the value deduced from $\chi(T)$. At present, the origin of the discrepancy is unclear.

For the 3-leg ladder compound $\text{Sr}_2\text{Cu}_3\text{O}_5$, $\chi(T)$ approaches a constant as $T \rightarrow 0$ (34), as expected for the 1D AF Heisenberg chain. Furthermore, muon spin resonance measurements by Kojima *et al.* (36) indicate a long-range ordered state with Néel temperature $T_N = 52$ K, which we attribute to the interlayer coupling J_c along the c axis. No sign of long-range ordering was observed in the 2-leg compound. These results confirm explicitly the drastic difference between ladders with even and odd numbers of legs.

Ladder structures occur also in other cuprates, for example, the family of compounds $\text{La}_{4+4n}\text{Cu}_{8+2n}\text{O}_{14+8n}$, which, as special cases, contain 4- and 5-leg ladder elements. These are complex structures that contain other Cu sites only weakly coupled to each

other. These latter spins dominate $\chi(T)$ below room temperature. However, by examining the difference in $\chi(T)$ between the two compounds, Batlogg *et al.* (37) identified a substantial spin gap in a 4-leg compound ($\Delta_{\text{spin}} \approx 300$ K). In these compounds, only weak interladder coupling is expected, and a value of $\Delta_{\text{spin}} \approx J/4$ (≈ 325 K) is predicted theoretically, which agrees quite well with the experiment. Recently, Hiroi and Takano (38) synthesized $\text{LaCuO}_{2.5}$, which contains 2-leg ladders weakly connected in a 3D structure.

Hole Doping of Spin-1/2 Ladders

In general, it is difficult to dope transition metal oxides and produce a highly conducting state, but the cuprates are exceptional in this regard. Early reports of doped cuprate ladder materials are starting to appear (38, 39). Apart from the realization of doped ladders, their behavior is of interest to theorists because they are examples of unusual Fermi liquids that can be carefully analyzed. Hole doping of a cuprate introduces effective Cu^{3+} sites. This oxidation state also favors square planar O coordination similar to that with Cu^{2+} ions, and in this coordination, a $S = 0$ Cu^{3+} ion is formed, which corresponds to a bound state of a $S = 1/2$ Cu^{2+} ion and a hole residing mainly on the four surrounding O $2p$ orbitals (Zhang-Rice singlet) (40). Transfer of electrons between nearest-neighbor sites allows a $S = 1/2$ Cu^{2+} and $S = 0$ Cu^{3+} ion to exchange positions. The canonical model describing the motion of the effective $S = 0$ Cu^{3+} ions in a background of Heisenberg coupled $S = 1/2$ Cu^{2+} ions is known as the t - J model (41).

The properties of a hole-doped single chain have been studied in great detail. It is an example of a Luttinger liquid, so called to distinguish it from the Landau Fermi liquid state that is ubiquitous for interacting fermions at low temperatures in higher dimensions. The simple alternating AF spin pattern of the parent insulator changes its period to an incommensurate value that depends on the doping. The exponent of the power-law decay increases, but magnetic correlations still dominate. The most striking feature of Luttinger liquids is spin-charge separation, whereby the charge and spin parts of an added hole move at different velocities and become spatially separated from each other (5). All of these properties are fascinating but do not give a sign of impending superconductivity.

The 2-leg ladder starts from a very different parent state characterized by a spin gap and exponentially decaying spin correlations. A key question is how these features evolve with doping. Mean-field studies (42) found an increase in the gap upon doping, but numerical studies of finite length lad-

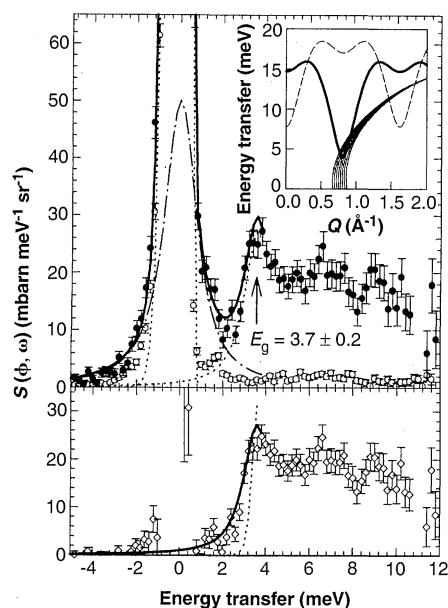


Fig. 5. Neutron scattering data for $(\text{VO})_2\text{P}_2\text{O}_7$ showing the finite spin gap E_g . $S(\phi, \omega)$, dynamical spin structure factor; ϕ , angle; ω , frequency. [Reprinted from (32).]

ders (6, 12, 17, 43) indicate a decrease. Another detailed study (44) showed that it was necessary to distinguish two different types of magnetic excitations. Again, the limit $J' \gg J$ is useful to gain intuition. As remarked by Dagotto *et al.* (6), in this limit holes form pairs on the same rung in a $S = 0$ and zero-momentum state to reduce the cost in magnetic interactions. One type of magnetic excitation is the promotion of a singlet pair of spins spatially separated from the hole pairs to form a $S = 1$ triplet; this excitation evolves smoothly from the magnon discussed earlier in the undoped case. However, a different type of spin excitation is possible (44): It involves the separation of the hole pair into a state with the holes on two spatially separated rungs, each of which then contains an unpaired spin. This excitation still requires a finite energy so the spin gap and the exponential decay of the spin-spin correlations remain, but its appearance at a lower energy than the magnon mode leads to a discontinuity in the spin gap upon doping. Because these excitations require holes, their number vanishes as the undoped insulator is approached.

The early calculations of Dagotto *et al.* (6) supported a continuous evolution of the doped system from the anisotropic limit $J' \gg J$, where strong pairing correlations signaling superconductivity were observed, down to the isotropic case $J' = J$. This continuity is similar to the smooth connec-

tion observed in the undoped Heisenberg models. The mean-field calculations of Sigrist *et al.* (42) were in agreement and suggest that holes were paired in a state of approximate d -wave symmetry, although the lack of rotational invariance of the lattice prevents an exact symmetry classification. Calculations (45) confirmed that this " d -wave" paired state for holes persists down to the limit $J' = J$ (46, 47). The size of the hole pair is now larger than a single rung, but they are spread only over a few lattice spacings. The excitation spectrum of the doped 2-leg ladder contrasts with the Luttinger liquid in that the low-energy sector of the ladder contains only the collective sound mode of the bosonic liquid of hole pairs and a finite energy is needed to make a triplet excitation. These features are similar to the case of attractive fermions in a single chain (48), rather than the repulsive case, the Luttinger liquid. Another interesting aspect of lightly doped 2-leg ladders is the way in which they combine features of lightly doped insulators with those of metals with large Fermi surfaces. The former behavior dominates in the energy dependence of the spectral function to add electrons, but metallic behavior appears in the momentum dependence of added quasi-particles (26, 45, 49, 50).

Binding pairs of holes gives them a bosonic character, which in turn is a necessary step on the way to superconductivity. However, this alone does not suffice because a ground state with a crystalline order of hole pairs is also possible (6). Actually, in a quasi-1D system like a ladder, true long-range order will be prevented by quantum fluctuations, but a power-law falloff will persist. In the doped ladder, such a situation occurs both in the channels corresponding to crystalline ordering of hole pairs and in those with superfluid or a Bose condensation of hole pairs. The balance between the two and the question of which dominates by means of a smaller exponent depends on the parameters of the model and more generally on residual interactions between hole pairs. This is hard to predict accurately (45, 51). The first experiments on $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{2.5}$ (38), a doped 2-leg ladder system, showed substantial decreases in the resistivity upon doping and evidence of metallic behavior in resistivity versus temperature at the highest value of $x = 0.2$ (Fig. 6). There are signs that the spin gap persists upon doping at least initially, but there are no signs of superconductivity. More experiments will be needed to determine if hole pairing exists and if the disorder suppresses superconductivity. Nonetheless, conceptually the relation of the paired hole state of the doped 2-leg ladder to the superconducting state of the planar cuprates is much closer than the relation to the single chain or Luttinger liquid state.

Conclusions

The study of low-dimensional quantum antiferromagnets has emerged as a central problem in condensed matter physics since the discovery of high- T_c superconductivity in lightly doped cuprates with planar structures. Quantum effects are largest in a $S = 1/2$ system and with isotropic Heisenberg coupling. A square lattice still has an ordered ground state, although with a substantial reduction of the sublattice magnetization as a result of quantum effects. In the 1D analog, namely a Heisenberg $S = 1/2$ chain, the quantum effects overwhelm the long-range order, but the ground state has quasi-long-range order with a decay in the spin-spin correlation function as an inverse power in the separation, apart from logarithmic corrections.

One might expect that a 2-leg ladder should be intermediate between a chain and a plane, thus the discovery that quantum effects are much stronger in such a ladder and lead to purely short-range order with an exponential decay in spin-spin correlations came as a great surprise. This result, first found in numerical simulations, has been verified by a variety of techniques and more importantly has experimental confirmation in $(\text{VO})_2\text{P}_2\text{O}_7$, SrCu_2O_3 , and $\text{LaCuO}_{2.5}$. This difference between a single chain and 2-leg ladder extends to all odd- and even-leg ladders, and the difference can be traced to the absence in even-leg ladders of the topological term that appears in the low-energy action of the single chain. This term is also absent in integer spin chains, which also display exponentially decaying spin-spin correlations and a spin-gap.

The various families of high- T_c superconductors all have a unique structural element, namely CuO_2 planes composed of a square lattice of Cu ions separated by O ions. The local coordination is characterized by CuO_4 squares, which in turn are all corner sharing in the CuO_2 planes. The ladder cuprates again have the same local CuO_4 coordination, but the pattern of the CuO_4 squares is changed, which in turn changes the pattern of magnetic exchange interactions. For example, in $\text{Sr}_{n-1}\text{Cu}_n\text{O}_{2n}$, line defects break the plane into weakly coupled ladders. The many ways of assembling CuO_4 squares illustrates the richness of cuprate chemistry, which is only now beginning to be explored, and various possibilities for novel quantum ground states remain to be studied.

The cuprates have another unique feature among transition metal oxides, namely the possibility of hole doping without localization to realize conducting materials. The doped chain has been the paradigm of a non-Landau Fermi liquid, and much attention has focused on the unique properties of this quantum liquid, called a Luttinger liq-

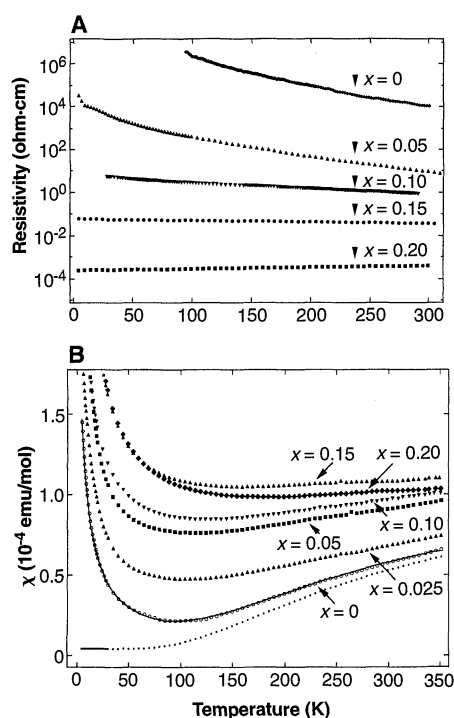


Fig. 6. (A) Resistivity versus temperature parametric with the Sr concentration x for $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{2.5}$. (B) Magnetic susceptibility versus temperature for the same compound shown in (A). [Reprinted from (38).]

uid by Haldane, such as the complete separation of charge and spin sectors into two excitation branches at low energy. The hole doped 2-leg ladder is also essentially 1D, but now the properties are radically different. The quantum liquids in lightly doped ladders retain the spin gap, show hole-hole pairing in approximate $d_{x^2-y^2}$ symmetry, and although they are lightly doped insulators, show features of a large Fermi surface that is metal-like. Doped ladders are a fascinating mixture of a dilute Fermi gas with strong attractions and a concentrated Fermi system with a large Fermi surface.

Returning to the high- T_c cuprates, we see a paradox. The parent insulating antiferromagnets show long-range order, which represents a smooth evolution or crossover from the properties of single chains but not from 2-leg ladders. Lightly doped cuprates by contrast show a spin gap and $d_{x^2-y^2}$ superconductivity, properties we can imagine evolving smoothly from the 2-leg ladders. Although much remains to be done to understand how these features fit together, it is clear that the study of ladders has given us not only surprises but valuable new insights into low-dimensional quantum systems and a new impetus to broaden our horizons and explore the rich solid-state chemistry of cuprates and related materials.

REFERENCES AND NOTES

- J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 188 (1986).
- E. Manousakis, *Rev. Mod. Phys.* **63**, 1 (1991).
- H. Bethe, *Z. Phys.* **71**, 205 (1931).
- P. W. Anderson, *Science* **235**, 1196 (1987).
- For a recent review, see H. J. Schulz, in *Proceedings of Les Houches Summer School LXI: Mesoscopic Quantum Physics*, E. Akkermans, G. Montambaux, J. L. Pichard, J. Zinn-Justin, Eds. (Elsevier, Amsterdam, in press), and references therein.
- E. Dagotto, J. Riera, D. J. Scalapino, *Phys. Rev. B* **45**, 5744 (1992).
- R. Hirsch, thesis, Universität Köln (1988).
- E. Dagotto and A. Moreo, *Phys. Rev. B* **38**, 5087 (1988).
- T. Barnes, E. Dagotto, J. Riera, E. S. Swanson, *ibid.* **47**, 3196 (1993).
- E. Dagotto, *Rev. Mod. Phys.* **66**, 763 (1994).
- S. R. White, R. M. Noack, D. J. Scalapino, *Phys. Rev. Lett.* **73**, 886 (1994).
- R. M. Noack, S. R. White, D. J. Scalapino, *ibid.*, p. 882.
- M. Azzouz, L. Chen, S. Moukouri, *Phys. Rev. B* **50**, 6233 (1994).
- S. Gopalan, T. M. Rice, M. Sigrist, *ibid.* **49**, 8901 (1994).
- S. A. Kivelson, D. S. Rokhsar, J. P. Sethna, *ibid.* **35**, 8865 (1987).
- T. M. Rice, S. Gopalan, M. Sigrist, *Europhys. Lett.* **23**, 445 (1994); see also I. Affleck, *Phys. Rev. B* **37**, 5186 (1988); D. S. Rokhsar and S. A. Kivelson, *Phys. Rev. Lett.* **61**, 2376 (1988); N. E. Bonesteel, *Phys. Rev. B* **40**, 8954 (1989); A. G. Rojo, preprint; K. Totsuka and M. Suzuki, preprint, and references therein.
- D. Poilblanc, H. Tsunetsugu, T. M. Rice, *Phys. Rev. B* **50**, 6511 (1994).
- N. Hatano and Y. Nishiyama, *J. Phys. A* **28**, 3911 (1995).
- M. Reigroztzi, H. Tsunetsugu, T. M. Rice, *J. Phys. C* **6**, 9235 (1994).
- D. V. Khveshchenko, *Phys. Rev. B* **50**, 380 (1994); D. G. Shelton, A. A. Nersisyan, A. M. Tsvelik, preprint.
- F. D. M. Haldane, *Phys. Rev. Lett.* **61**, 1029 (1988).
- For work with ferromagnetic rungs, see K. Hida, *J. Phys. Soc. Jpn.* **60**, 1347 (1991); H. Watanabe, *Phys. Rev. B* **50**, 13442 (1994); and references therein. See also K. Totsuka and M. Suzuki, *J. Phys. C* **7**, 6079 (1995).
- H. J. Schulz, *Phys. Rev. B* **34**, 6372 (1986); S. P. Strong and A. J. Millis, *Phys. Rev. Lett.* **69**, 2419 (1992); *Phys. Rev. B* **50**, 9911 (1994); Y. Nishiyama, N. Hatano, M. Suzuki, *J. Phys. Soc. Jpn.* **64**, 1967 (1995), and preprint; S. R. White, preprint; Y. Xian, Manchester preprint; H. Watanabe, preprint; D. Sénéchal, preprint.
- T. Barnes and J. Riera, *Phys. Rev. B* **50**, 6817 (1994).
- The dynamical spin structure factor $S(\mathbf{Q}, \omega)$ with $\mathbf{Q} = (\pi, \pi)$ has a sharp peak at $\omega = \Delta_{\text{spin}} \approx 0.5J$ that carries most of the weight (9, 14).
- M. Troyer, H. Tsunetsugu, T. M. Rice, Eidgenössische Technische Hochschule preprint.
- M. Troyer, H. Tsunetsugu, D. Würtz, *Phys. Rev. B* **50**, 13515 (1994).
- A. W. Sandvik, E. Dagotto, D. J. Scalapino, *Phys. Rev. B*, in press.
- In addition, the nuclear spin relaxation rate has been calculated by Troyer *et al.* (27), predicting $1/T_1 \sim \exp(-\Delta_{\text{spin}}/T)(a + \ln T)$ at low temperatures. Sandvik *et al.* (28) have also calculated $1/T_1$ using numerical techniques.
- B. Frischmuth, B. Ammon, M. Troyer, Eidgenössische Technische Hochschule preprint.
- D. C. Johnston, J. W. Johnson, D. P. Goshorn, A. P. Jacobson, *Phys. Rev. B* **35**, 219 (1987). In this paper, the experimental susceptibility for the ladder system was compared with theoretical results for spin-1/2 alternating AF chains. Note that in addition to the different geometry (chain instead of ladder), the alternating chain breaks translational invariance by one lattice spacing. Then, such a model is useful to describe a ground state with a tendency for spontaneous symmetry breaking, like a spin-Peierls system, but not the 2-leg-ladder ground state, which respects all the symmetries of the Hamiltonian.
- R. S. Eccleston, T. Barnes, J. Brody, J. W. Johnson, *Phys. Rev. Lett.* **73**, 2626 (1994).
- Z. Hiroi, M. Azuma, M. Takano, Y. Bando, *J. Solid State Chem.* **95**, 230 (1991).
- M. Azuma, Z. Hiroi, M. Takano, K. Ishida, Y. Kitaoka, *Phys. Rev. Lett.* **73**, 3463 (1994).
- K. Ishida *et al.*, *J. Phys. Soc. Jpn.* **63**, 3222 (1994); K. Ishida *et al.*, preprint.
- K. Kojima *et al.*, *Phys. Rev. Lett.* **74**, 2812 (1995).
- B. Batlogg *et al.*, *Bull. Am. Phys. Soc.* **40**, 327 (1995). Recently, hole doping in $(\text{La}, \text{Sr}, \text{Ca})_{1-x}\text{Cu}_2\text{O}_{4.1}$ compounds with CuO_2 -chain and Cu_2O_3 -ladder building blocks has been achieved (S. A. Carter *et al.*, preprint).
- Z. Hiroi and M. Takano, *Nature* **377**, 41 (1995). The band properties of $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{2.5}$ have been recently calculated by L. F. Mattheiss (preprint).
- M. Azuma, M. Takano, T. Ishida, and K. Okuda (preprint) recently presented magnetic susceptibility measurements for Zn-doped 2- and 3-leg ladders.
- F. C. Zhang and T. M. Rice, *Phys. Rev. B* **37**, 3759 (1988).
- In the case of $(\text{VO})_2\text{P}_2\text{O}_7$, it is not clear whether the $t - J$ model is suitable for describing its properties upon doping. A detailed analysis based on a many-orbital Hubbard model for V and O ions is needed.
- M. Sigrist, T. M. Rice, F. C. Zhang, *Phys. Rev. B* **49**, 12058 (1994).
- D. Poilblanc, D. J. Scalapino, W. Hanke, *ibid.*, in press.
- H. Tsunetsugu, M. Troyer, T. M. Rice, *ibid.* **49**, 16078 (1994).
- , *ibid.* **51**, 16456 (1995); see also J. A. Riera, *ibid.* **49**, 3629 (1994).
- C. A. Hayward, D. Poilblanc, R. M. Noack, D. J. Scalapino, W. Hanke, *Phys. Rev. Lett.* **75**, 926 (1995).
- Calculations of superconducting correlations for the Hubbard model were discussed in (12) and also in Y. Asai, *Phys. Rev. B* **50**, 6519 (1994), and preprint; K. Yamaji and Y. Shimoi, *Physica C* **222**, 349 (1994); R. M. Noack, S. R. White, D. J. Scalapino, *Europhys. Lett.* **30**, 163 (1995), and preprint; and Y. Munehisa, preprint. Additional information about hole binding can be found in S. Gayen and I. Bose, *J. Phys. C* **7**, 5871 (1995).
- A. Luther and V. J. Emery, *Phys. Rev. Lett.* **33**, 589 (1974).
- Note the similarities between the results for 2-leg ladders and those corresponding to models of high- T_c superconductors where the infrared Drude weight scales as the hole concentration, whereas the Fermi surface is large and electron-like (10).
- Numerical studies in odd-leg ladders beyond the single chain have not been explicitly carried out. However, the discussion linking the spin gap with hole-pair formation suggests that the tendency to superconduct in the odd-leg ladders is weaker than in the even-leg ladders. The issue of superconductivity in the 2D limit, reached when the width of the ladders increases, is subtle and is not addressed here.
- Several recent publications have addressed these issues: N. Nagaosa (Univ. of Tokyo preprint) claimed that the low-energy physics of doped ladders is described in terms of bipolarons; L. Balents and M. P. A. Fisher (ITP preprint), studying the Hubbard model ladder with a controlled RG method, found a phase with a finite spin gap and a single gapless charge mode that they interpret as the analog of a 1D superconductor or a charge density wave; and H. J. Schulz (Orsay preprint) studied two coupled Luttinger liquids, reporting a spin gap in the spectrum and either d -type pairing or orbital AF fluctuations in the ground state. The addition of a long-range Coulomb force to the $t - J$ model leads to a competition between superconductivity and charge-density wave states [see U. Löw, V. J. Emery, K. Fabricius, S. A. Kivelson, *Phys. Rev. Lett.* **72**, 1918 (1994); S. Haas, E. Dagotto, A. Nazarenko, J. Riera, *Phys. Rev. B* **51**, 5989 (1995)].
- We thank M. Azuma, T. Barnes, V. J. Emery, H. Hiroi, A. Moreo, J. Riera, D. J. Scalapino, M. Takano, M. Troyer, and H. Tsunetsugu for their help in the preparation of this review. E.D. specially thanks the Office of Naval Research for its support under grant ONR N00014-93-0495. He also thanks the National High Magnetic Field Laboratory and the Center for Materials Research and Technology (MARTECH) for additional support.