

SEARCH AND DISCOVERY

Theorists Take Steps Toward Understanding Ladder Compounds

Whatever causes superconductivity above 40 K, it seems to involve the layers containing copper and oxygen atoms, which are common to all compounds exhibiting a high critical temperature, T_c . Hoping to gain insight into the mechanism for superconductivity in these complex structures, some theorists have looked at systems as simple as one-dimensional chains of copper and oxygen atoms. More recently they have turned to copper oxide ladders—that is, pairs of copper oxide chains linked by additional oxygen atoms between the coppers. So far, the theorists have predicted a number of physical properties of such ladders, including the possibility that the ladders can go superconducting.

The ladders are not just theoretical constructs: Experimentalists have found a few compounds that are physical realizations of the ladders, and, more strikingly, they have found that these ladder compounds exhibit some of the expected behavior.¹ This past summer, a team in Japan even reported² superconductivity in one such

Theorists toying with a simple model of copper and oxygen atoms joined in a ladder-like structure have predicted some behavior that has been seen in real ladder-like compounds. Will their prediction of superconductivity also hold?

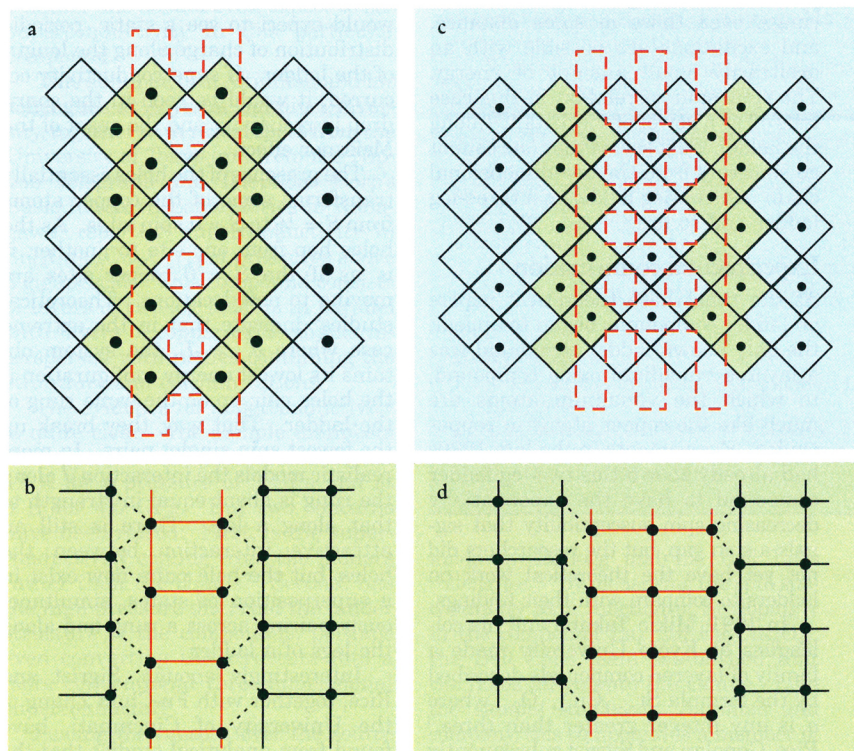
compound, at temperatures up to about 12 K. However, this superconducting compound—made of strontium, calcium, copper and oxygen—is quite complex, having both chains and ladders; the researchers are still working to establish more conclusively that the superconductivity can be attributed to the compound's ladder structures.

None of the so-called ladder compounds is known to be a high-temperature superconductor. It remains to be seen whether one can approximate the copper oxide planes seen in the proven high- T_c compounds by assembling an arbitrarily large number of copper oxide chains into ladders, and—what is more important—whether such an assembly exhibits superconductivity.

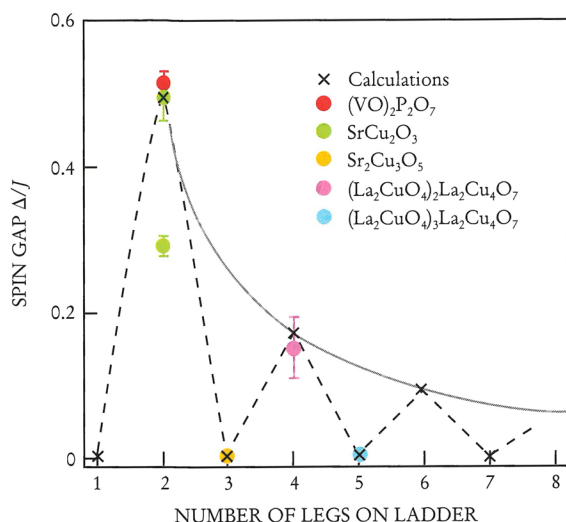
Ladders, legs and rungs

How can a real material be made up of a number of discrete ladders? One way is for a double chain to cross a copper oxide plane and break it into a certain number of individual ladders, outlined in red in the figure below. In the top half of that figure, the dots are the copper atoms, each surrounded by four oxygen atoms, located at the intersections of the lines. The bottom half of the figure shows only the copper atoms and the bonds between them. The left half of the figure depicts a two-leg ladder, and the right half, a three-leg ladder.

In the copper oxide plane, the copper atoms are connected through the oxygen sites by 180° bonds, such as those between the rightmost pairs of copper atoms in each panel of the figure. By contrast, in the double chains (shaded in green), the copper atoms are diagonal to one another; they are linked through an oxygen atom by 90° bonds.³ These bonds are magnetically weaker than the 180° couplings, so that the ladders of copper and oxygen at-



FORMATION OF LADDERS in a copper oxide plane. **a:** Schematic representation of copper atoms (dots) surrounded by oxygen atoms (at intersections of the lines). When a double chain (green) interrupts the plane, the magnetic coupling of the copper atoms within the double chain is weaker than that of its binding across a rung or down a leg of a ladder (red dashed lines). So the ladder is coupled only weakly to the rest of the plane. **b:** Another representation of the ladder in **a**. Strong magnetic bonds between copper atoms are shown with solid lines; weak magnetic bonds with dotted lines. The ladder is shown in red. **c** and **d:** Same as **a** and **b** but for a three-leg ladder. (Adapted from refs. 3 and 5.)



PREDICTED AND MEASURED SPIN GAP in compounds containing ladders with varying numbers of legs. Colored dots indicate measured values; dashed lines connect theoretically expected values. The solid line is a guide to the eye. Most data confirm the expectation that a spin gap develops only for even-leg ladders. There are two green dots because the spin gap for SrCu_2O_3 is measured in two ways, one of which gives a result below the expected value. (Courtesy of Bertram Batlogg and Robert Cava.)

oms, while chemically connected to the other atoms in the plane, are only loosely linked to them in terms of magnetic couplings. In the ladders, each copper atom has a spin- $\frac{1}{2}$ magnetic moment and has an antiferromagnetic interaction J with the neighboring copper sites.

Elbio Dagotto of Florida State University, José Riera of the National University of Rosario in Argentina and Douglas Scalapino of the University of California, Santa Barbara, started thinking about ladders in the early 1990s.⁴ They reasoned that there would be a spin gap if the interaction along the rungs, called $J_{\perp}$, was much larger than the coupling along the legs, $J_{\parallel}$. The spins would then pair in singlets with total spin $S = 0$ and interact very little with adjacent rungs. It would take a finite amount of energy, known as the spin-gap energy, to excite each pair to a spin triplet. In this case, the spin-spin correlation length falls off exponentially with distance along the ladder. The spin gap should show up as an exponential decrease in the spin susceptibility below a certain temperature.

While it is fairly straightforward to reason that there is a spin gap when $J_{\perp} \gg J_{\parallel}$, it is not so obvious what happens when the couplings are about equal, much less when their relative strengths are reversed. By numerical calculations Dagotto, Riera and Scalapino predicted that a spin gap,

$\Delta = J/2$, occurs even when $J_{\perp} \approx J_{\parallel}$. Subsequent calculations have shown that the spin gap persists as long as there is even the slightest coupling across the rung. The argument can be extended to ladders with any number of legs—provided the number of legs is even.

In one of the most striking twists of the ladder scenario, it seems that only ladders with even numbers of legs have a spin gap; odd-leg ladders do not. That conclusion was reached⁵ in 1993 by T. Maurice Rice, Sudha Gopalan and Manfred Sigrist, all then at the Swiss Federal Institute of Technology, Zurich (ETH), based on suggestions by R.

Hirsch, at that time a student at the University of Cologne, and Hirokazu Tsunetsugu, then at ETH Zurich. The odd-even discrepancy occurs because, in the ground state, the total spin of an odd number of copper atoms across a rung is $S = \frac{1}{2}$. Each rung then couples antiferromagnetically to other rungs, even those at some distance, and excitations are possible with an arbitrarily small amount of energy. The spin-spin correlation in this case falls off as a power of the distance along the ladder. So it seems that one cannot go smoothly from the one-dimensional chain to a two-leg ladder to a three-leg ladder and so forth.

Experimental confirmation

At the time these theoretical papers on ladder compounds began to appear, the only known ladder compound was a layered vanadium oxide compound, in which the vanadium atoms are much like the copper atoms in copper oxides. Experiments in the late 1980s had already shown this two-leg ladder compound to have the exponentially decreasing spin susceptibility that signals a spin gap, but the researchers did not yet have the theoretical work on ladders to compare with their findings.

In 1991, Mikio Takano and his colleagues at Kyoto University made a family of layered compounds described by the formula $\text{Sr}_{n-1}\text{Cu}_{n+1}\text{O}_{2n}$, where n is any integer greater than three.³ Rice, Gopalan and Sigrist subsequently

recognized that these compounds contained ladders.⁵ For $n = 3$ and 5, one gets, respectively, SrCu_2O_3 , having two-leg ladders, and $\text{Sr}_2\text{Cu}_3\text{O}_5$, with three-leg ladders. In 1994, Takano and his coworkers found that the two-leg compound had a spin gap of the predicted magnitude, whereas the three-leg ladder compound had no spin gap at all.⁶ (See the figure at left.)

The same contrast between even and odd-leg ladders was found for wider ladders by Bertram Batlogg, Robert Cava and their colleagues, then all at AT&T Bell Labs, who were studying the compounds $\text{La}_{4+4n}\text{Cu}_{8+2n}\text{O}_{14+8n}$. The members of this family of compounds with four-leg ladders had a spin gap, although it was smaller than that for two-leg ladders; the five-leg ladder compounds had no spin gap.

Doping the ladders

In the high- T_c compounds, superconductivity results when the materials are doped with holes. What happens when one starts to add holes to these ladder structures? Dagotto, Riera and Scalapino noted in their 1992 paper⁴ that the attractive correlations between holes—in even-leg ladders—create either charge density waves or superconductivity, depending on the degree of doping and the relative strengths of the magnetic coupling J and the electron charge transfer t . Rice and his ETH colleagues subsequently bolstered that conclusion with additional calculations.⁷ If a charge density wave were created, one would expect to see a static, periodic distribution of charge along the length of the ladder. If superconductivity occurred, it would be seen in the sharp drop in resistivity and the onset of the Meissner effect.

The presence of the holes essentially transforms some of the copper atoms from $S = \frac{1}{2}$ to $S = 0$ spin sites. As the holes hop from one site to another, it is as if the $S = 0$ copper sites are moving to new locations. Theoretical studies⁴ indicate that in the extreme case where $J_{\perp} \gg J_{\parallel}$, the system obtains its lowest energy configuration if the holes pair up on the same rung of the ladder. That way, they break up the fewest spin singlet pairs. In more realistic models the interaction J along the rung is about equal in strength to that along a leg. There is still an attractive interaction between the holes, but the hole pairs now exist in a superposition of states, simultaneously pairing across a rung and along the legs of a ladder.

Interestingly enough, Sigrist and Rice, together with Fu-Chun Zhang of the University of Cincinnati, have found from analytical studies that the

amplitude for coupling along the legs has the opposite sign from that for coupling along the rungs.⁸ Such behavior is reminiscent of the d-wave nature of the wavefunction describing the Cooper pairs in the high- T_c materials. (A d-wave function has four lobes; the two lobes along the x -axis are opposite in sign from the two lobes along the y -axis. See PHYSICS TODAY, January 1996, page 19.) The same behavior is seen in numerical calculations performed by Scalapino, Reinhard M. Noack of the University of Würzburg and Steven R. White of the University of California, Irvine.⁹

To test the predictions of superconductivity the experimenters first had to figure out how to dope the ladder compounds. That was not a trivial problem; the holes seem to resist going onto the ladders. Nevertheless researchers have managed to get the holes to leak from the chains onto the ladders in some compounds. Paradoxically, Takano notes, the very materials that would be easiest to understand theoretically— SrCu_2O_3 and its family—have not yet been successfully doped.

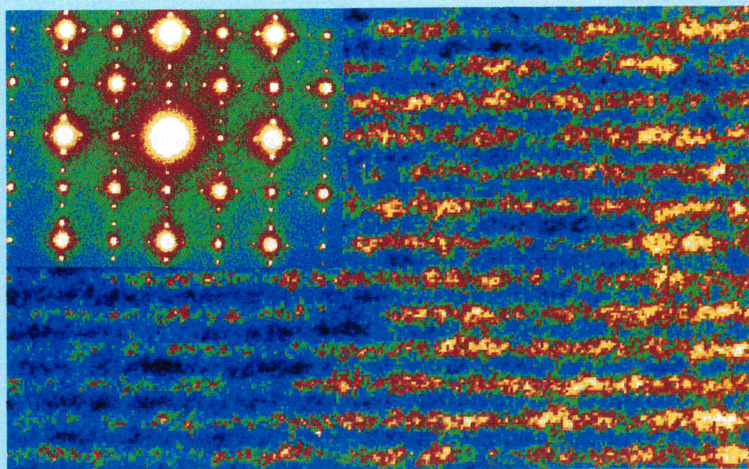
Last year, Z. Hiroi and Takano succeeded¹⁰ in doping a copper oxide ladder compound: $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{2.5}$. As the doping x increased, the material turned from an insulator to a metal. To the initial disappointment of the theorists, the compound never went superconducting. But subsequent studies have caused researchers to question whether one should even expect to see superconductivity in this particular compound.

This summer, Jun Akimitsu and his colleagues at Aoyama Gakuin University, together with researchers from the University of Tokyo and from the Nippon Telegraph and Telephone Corp's Basic Research Laboratories in Kanagawa, reported² superconductivity in $\text{Sr}_{0.4}\text{Ca}_{13.6}\text{Cu}_{24}\text{O}_{41.84}$ at pressures above 3 gigapascals. This compound consists of layers of two-leg ladders in parallel with layers of copper oxide chains interspersed with planes containing the strontium and calcium cations.

The evidence for superconductivity is quite clear. The sample manifests the signature drop in resistivity at 12 K for a pressure of 3 GPa and at 9 K for 4.5 GPa. But two concerns have been raised: First, is the superconductivity coming from the ladders rather than the chains? Second, has the high pressure distorted the ladder structure of the compounds, perhaps even converting the structure into a more conventional three-dimensional superconductor?

Fueling the concern over the source of the superconductivity are studies

Stars and Stripes in Manganese Oxide



Charge ordering in a $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$ lattice can be seen as regularly spaced stripes in this low-temperature high-resolution (0.5-nm) electron micrograph made by Cheng Hsuan Chen and Sang-Wook Cheong of Bell Laboratories, Lucent Technologies. In the strategically placed inset at the upper left, charge ordering is evidenced by the smallest stars in the electron diffraction pattern.

If one dopes antiferromagnetic insulators (especially transition metal oxides with a perovskite structure) with charge carriers, phenomena such as high-temperature superconductivity, phase separation and charge ordering can be produced. Over the last two years, a so-called colossal magnetoresistance has been found in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ when x ranges between 0.2 and 0.5. When a magnetic field of a couple of tesla is applied, the resistivity drops colossally—by several orders of magnitude. At low temperatures the material is a ferromagnetic metal in the doping range where the colossal magnetoresistance occurs; for $x > 0.5$, the ground state is an antiferromagnetic insulator. By doing transport, magnetic and diffraction studies over the last year, groups at the University of Tokyo¹ and at Bell Labs² have found indications of charge localization in manganese oxide.

In the charge-ordered state, the doped charge carriers localize along the diagonal direction of the manganese oxide square lattice and are visible as stripes. The image suggests a diagonal row of trivalent Mn ions separated by two diagonal rows of tetravalent Mn ions; the pattern repeats with a period of 1.65 nm.

What affects the ease with which electrons move through the crystal lattice from Mn site to Mn site? Correlation of the Mn 3d electrons, relative alignment of neighboring Mn spins, and interaction between the electrons and the lattice all play a role. The electron-lattice effect is especially strong when compared to nickel or copper oxides and can even impede the motion of electrons completely. In such an extreme case, the system can self-organize into a regular array such as the stripes seen here. The false colors in both the stripes and stars represent the electron beam intensity, with yellow being the highest, followed by red, green and blue.

The large magnetoresistance effect might be useful in magnetic field sensors, such as read heads for magnetic recording and position sensors.

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made by Batlogg and his Bell Labs colleagues.¹¹ By measuring the spin susceptibility as a function of Sr doping y in the compound $\text{La}_{6-y}\text{Sr}_y\text{Ca}_8\text{Cu}_{24}\text{O}_{41}$, the Bell Labs team established that the holes all go onto the chains. Like the sample studied by Akimitsu and company, this compound is a member of the general family $(\text{La}, \text{Sr}, \text{Ca})_{14}\text{Cu}_{24}\text{O}_{41}$,

but unlike the Japanese study, the Bell Labs experiment was done at ambient pressure.

Akimitsu asserts that, if one starts with $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ and dopes it with Ca, some carriers are released to the ladder sites. Cava concedes that as many as one out of every six holes could be on the ladders; their resolution is not fine

enough to detect this level of doping on the ladders.

Everyone is now hoping for some independent confirmation of the Aoyama Gakuin-Tokyo-NTT result. Preliminary supporting data is starting to surface. Shin-ichi Uchida of the University of Tokyo told us about his group's measurement of the optical conductivity on a single crystal of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$. With this type of measurement, the group is able to distinguish between the contributions from the chains and those from the ladders. They find evidence that there are holes on the ladders and that their number increases as the doping level increases up to $x = 11$. (In the experiment by Akimitsu and coworkers, superconductivity sets in at $x = 13.6$.) So far, Uchida reports, his group does not see any sign of superconductivity at pressures up to 2 GPa.

Yoshio Kitaoka's group at Osaka University has done some nuclear magnetic resonance studies on these compounds with the monster-sized unit cell. His group finds that at low temperatures, the copper peaks split into several peaks, suggesting that the local electrical field is different at different sites, perhaps because of the holes. But there may also be other explanations for the observed splitting.

None of the evidence for superconductivity in a ladder compound has yet enticed all observers onto the bandwagon. They are, however, watching closely from the side of the road.

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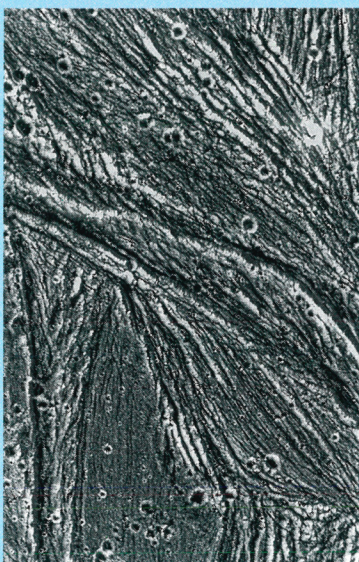
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Galileo Reveals the Light and Dark Sides of Ganymede

Following the excitement generated by the Galileo spacecraft's first Ganymede flyby on 27 June, researchers are hoping that data from the 6 September encore performance—which skimmed within 262 km of that Jovian moon—will help them understand why Ganymede is more tectonically and magnetically active than expected. The data trickling back to Earth during the next two months is expected to include the best images yet obtained (some stereoscopic) of Jupiter's and the Solar System's largest moon.

The photo on the left, taken during the 27 June flyby from a distance of 7448 km, shows some of Ganymede's complex terrain. The 55 km × 35 km portion of the Uruk Sulcus region, located at latitude 10° north and longitude 168° west exhibits networks of parallel grooves and ridges that are thought to result when tectonic activity causes extension of the region. Such features are characteristic of Ganymede's high-albedo "light terrain," which covers about half the moon's surface. Because such terrain is relatively smooth and not densely cratered, it is thought to be relatively young—that is, it may have been resurfaced in the "middle ages" of the Solar System by water "lavas" pouring over the icy crust and by subsequent tectonic activity. In this sense, such terrain resembles the next moon in toward Jupiter, Europa, whose surface seems younger and may still be active.

The photo on the right, taken from a distance of 7563 km, shows a 46 km × 64 km region of Galileo Regio, a region of "dark terrain" located at latitude 18° north and longitude 147° west. Dark terrain on Ganymede is characterized by a high density of craters, with little evidence of resurfacing (characteristics that show it to resemble the ancient surface of Callisto, the next moon out from Jupiter), and by furrows—



long, shallow troughs like those running from lower right to upper left in the photo. The furrows usually form parallel trenches and are thought to result from the collapse and relaxation of large, ringed impact structures or from large-scale tectonic activity. The crossing of the furrows near the center of the image indicates that tectonic activity has played a significant role in shaping even this ancient surface.

In addition to obtaining more detailed images, researchers very much want to see whether measurements made by the spacecraft's magnetometer and plasma wave spectrometer confirm the existence of both an ionosphere and a magnetic field, as indicated during the first flyby. The mechanism by which Ganymede could generate its own magnetic field remains mysterious. If the moon is as cold and dead as many thought before the 27 June flyby, the field could be a remanent field in a cold, solid iron core. If the source of the field is a dynamo in a molten-iron core—as on Earth, Mercury and presumably Io—Ganymede must have some unexpected energy source to drive convection in the core. Alternatively, sufficiently vigorous convection in a thin layer of salty water under the moon's icy crust could also generate a magnetic field—a mechanism postulated as the source of the magnetic fields of Uranus and Neptune. Again, however, such a mechanism would require an energy source powerful enough to drive convection with velocities on the order of a few centimeters per second. Positing such energy sources has become a cottage industry as researchers await the latest data from Galileo.

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