

New candidate emerges for a quantum spin liquid

A newly synthesized mineral is perhaps the most promising material yet to realize a hypothetical state with exotic behavior.

Nature sometimes surprises us with intriguing material behavior. Witness the fractional quantum Hall effect or high-temperature superconductivity. More rarely, theorists conceive of novel systems and then set out to look for them in nature. One such novel system is the spin liquid,¹ postulated in 1973 by Philip Anderson for an antiferromagnetic insulator. In particular, he considered a material featuring planes of spin-carrying atoms arranged in triangular lattices. The atoms are fixed in position but the spins interact antiferromagnetically with their neighbors. Because the triangular lattice frustrates attempts of the spins to order, the spins will not freeze into a fixed configuration, even at the lowest temperature. Thus the system is called a spin liquid.

The spin-liquid concept spurred many theorists to study a variety of magnetic materials in which frustration prevents the development of an ordered state. Lured by the prospect of finding unconventional new phases of matter, experimentalists also began looking for real materials that embody such behavior. Unlike a conventional antiferromagnet, a spin liquid does not develop any magnetic order. In a spin liquid, no single atom carries a spontaneous time-averaged dipole magnetic moment in the low-temperature limit. While such behavior has been demonstrated in one-dimensional magnets and in systems where spins form clusters, it has not yet been seen in extended two- or three-dimensional networks of spins.

If a spin liquid remains disordered down to absolute zero, the system is then sufficiently coherent that quantum effects should come into play. Such a quantum spin liquid is expected to adopt some kind of subtle quantum order. The mystery lies in what kind of subtle order that might be. One example is the topological order underlying the fractional quantum Hall effect. A quantum spin liquid might have exotic excitations, perhaps with fractional quantum numbers, and it might exhibit unusual correlations.

The discovery of high- T_c superconductivity renewed interest in spin liquids because copper oxide materials are antiferromagnetic insulators before they are doped to become superconductors. Anderson and others have used the concept of a resonating-valence-bond, which underlies the prediction of a spin-liquid state, to try to explain the behavior of the high- T_c materials.²

Despite the heightened interest, experimental realizations of a spin liquid have been scarce and remain controversial. Two materials have emerged in recent years as possible candidates; both embody spins arranged on a 2D lattice of edge-sharing triangles (see figure 1a).

The system that is most expected to be a quantum spin liquid, however, is a 2D array of spin- $1/2$ particles on a lattice of vertex-sharing triangles. Such a lattice is known as a *kagome* lattice, from the Japanese for a bamboo basket with a woven pattern of interlaced triangles (see figure 1b and PHYSICS TODAY, February 2003, page 12). Although experimenters have found a number of systems with kagome lattices, the lattices either contained spins greater than $1/2$ or had less than perfect kagome structures.

In 2004, after a two-year effort, Daniel Nocera and a team of chemists

at MIT were able to synthesize a rare mineral known as herbertsmithite.³ (The small amounts found in nature are not sufficiently pure.) It's a member of the paratacamite family characterized by the formula $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$, where $x = 1$ for herbertsmithite. As pictured in figure 2 and confirmed by crystallography, the spin- $1/2$ copper atoms form a kagome lattice.

Recently, Nocera and his team joined Young Lee and others from MIT, the University of Florida, the National High Magnetic Field Laboratory, the University of Maryland, College Park, and NIST in Gaithersburg, Maryland, to study the mineral's behavior using neutron scattering, magnetization, and thermodynamic measurements.⁴ Nocera's group also collaborated with Amit Keren's group at the Technion-Israel Institute of Technology in Haifa to perform nuclear magnetic resonance measurements and take muon spin resonance data at the Paul Scherrer Institute in Switzerland.⁵ Independently, Philippe Mendels of the Université de Paris-Sud and CNRS and Andrew Harrison's group from the University of Edinburgh performed muon spin resonance measurements at the UK's Rutherford Appleton Laboratory and at the Paul Scherrer Institute.⁶ The

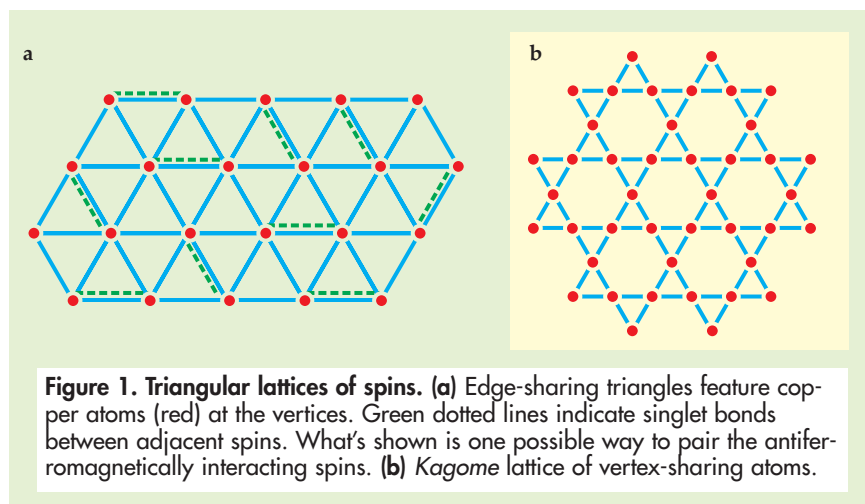


Figure 1. Triangular lattices of spins. (a) Edge-sharing triangles feature copper atoms (red) at the vertices. Green dotted lines indicate singlet bonds between adjacent spins. What's shown is one possible way to pair the antiferromagnetically interacting spins. (b) Kagome lattice of vertex-sharing atoms.

Mendels group's samples were prepared at Edinburgh and at CEMES-CNRS, Toulouse, France.

The experiments all show fairly conclusively that the spin- $\frac{1}{2}$ kagome lattice behaves as a spin liquid: Its spins do not develop conventional antiferromagnetic order down to temperatures as low as 50 mK. The jury is still out, however, on whether the putative quantum spin liquid shows any exotic behavior. Interpretation is difficult first of all because only microcrystalline samples are available; researchers have not yet been able to grow crystals larger than a few microns. Furthermore, even small amounts of impurities can affect the low-temperature behavior and prevent ordering that might otherwise have occurred.

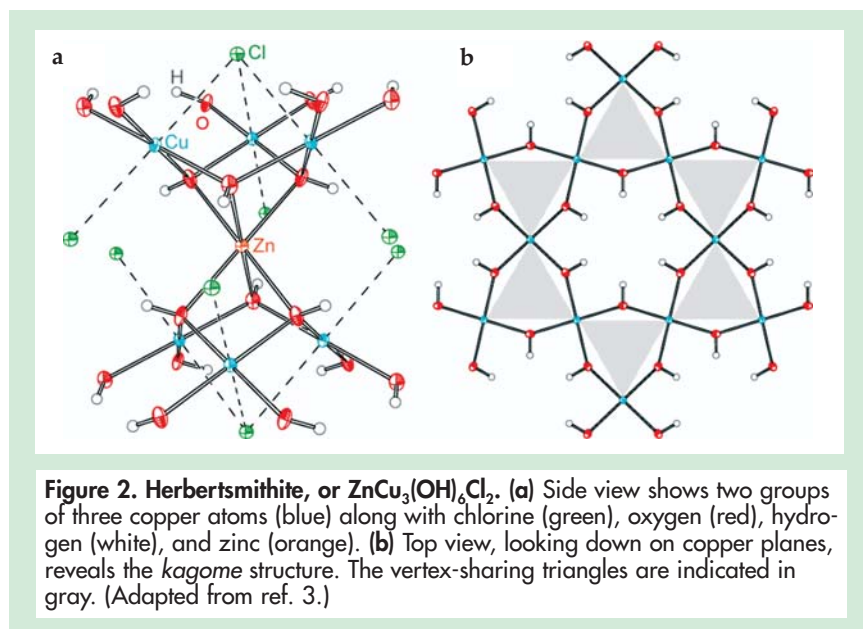
Lee comments that his group and others are still in the early stages of studying this material. With more experience, they hope to have a better handle on impurities and begin to define more precisely the low-temperature physics of the spin- $\frac{1}{2}$ kagome materials.

Quantum spin liquid

Anderson's 1973 paper looked at a model in which one spin- $\frac{1}{2}$ particle (an electron in the outer orbit of a magnetic atom) is fixed at each vertex of a triangular lattice and interacts antiferromagnetically with its neighbors. On a square lattice, such spins order into a Néel state, freezing into a spin solid with alternating spins. But the triangular lattice frustrates the attempts to order (see the article on geometrical frustration by Roderich Moessner and Arthur Ramirez in *PHYSICS TODAY*, February 2006, page 24).

Anderson proposed an alternative state. He pictured a state consisting of singlet-bond pairs, such as the configuration shown in figure 1a. That configuration is far from unique because each spin has an equal probability of forming singlet pairs with any of its neighbors. Anderson defined a resonating-valence bond state as a linear combination of all the configurations that one can get by different pairings.

Since Anderson's work, a team led by Claire Lhuillier from the Pierre and Marie Curie University in Paris found that a triangular spin- $\frac{1}{2}$ lattice with only nearest-neighbor interactions can reach an ordered state with spins on any given triangle oriented at 120° to one another.⁷ Still, triangular lattices with more complicated interactions remain candidates for a quantum spin liquid. Most promising of all is the 2D spin- $\frac{1}{2}$ kagome lattice because its vertex-sharing geometry



gives it a higher degree of frustration than a triangular lattice and because quantum fluctuations are particularly strong for a low spin.

The excitations in the spin-liquid picture result from breaking spin pairs. This creates two single spins (spinons, with spin $s = \frac{1}{2}$) that move around independently of one another, much as electrons move in a metal—even though the material is still an insulator. By contrast, the fundamental excitations in a magnetically ordered Néel state are $s = 1$ spin waves, known as magnons.

Theorists have studied two types of spin liquids: those with an energy gap and those without. In most of the former types of spin liquid, singlet bonds form between nearby spins, and these cost energy to break. Studies indicate that such gapped excitations behave much like particles, although they may have fractional quantum numbers. The system may have a topological order, such as that found in the fractional quantum Hall states.

In gapless spin liquids, there are singlet bonds connecting pairs of spins that can be spatially well separated, as well as shorter-range pairs. Since it costs much less energy to break the bond between widely separated spins, the spin liquid may be gapless. This possibility, only appreciated in recent years, is quite intriguing. Normally, one expects a system with a spontaneously broken symmetry, such as an antiferromagnet, to be gapless: It costs little energy to excite spin waves in the system. But a spin liquid would be a gapless system with no broken symmetry. What protects such a system from developing a gap?

Gapless spin liquids have been called critical or algebraic spin liquids because their properties are expected to exhibit some of the same power-law dependencies as those found near a critical point. The excitations might be described by an extended wavefunction rather than as a single particle. Theorists are just starting to explore what the properties of such a system might be.

For the spin- $\frac{1}{2}$ kagome lattice with nearest-neighbor interactions, Lhuillier's group, joined by Hans-Ulrich Everts and colleagues from the Leibniz University in Hanover in Germany, numerically calculated the energy spectrum and predict that there is a continuum of low-lying singlet states and a very small gap (if any) to a spin triplet continuum.⁸ The big question for experimentalists is whether this prediction is verified in real materials.

Experimental signatures

The initial experiments on the newly synthesized kagome material primarily addressed two questions: Does the system remain disordered down to low temperatures and does it have a spin gap?

To check for long-range magnetic order, the group led by MIT's Lee looked in the neutron-scattering spectrum for Bragg peaks. As noted by Collin Broholm of the Johns Hopkins University, however, it's not always easy to see Bragg peaks from a spin- $\frac{1}{2}$ magnet in a powder. To address this concern, the MIT team showed that they could see Bragg peaks in a powder sample of a cousin of herbertsmithite that is known to have magnetic order, but did not see them in a similarly prepared powder of

herbertsmithite at a temperature $T = 1.4$ K. See figure 3a.

Another measure of long-range order is magnetic susceptibility. Figure 3b shows a plot of the inverse magnetic susceptibility versus temperature, measured by Young Lee's team. (Keren's group extended the susceptibility measurements down to 60 mK.) The plot of the Lee group's data is linear at high temperatures, as one would expect for randomly fluctuating spins. The linear fit yields an estimate of the Curie-Weiss temperature T_{CW} , which is related to the spin-spin interaction strength J . The MIT-led group finds T_{CW} to be about 300 K. Unlike an ordered antiferromagnet, the $s = \frac{1}{2}$ kagome system appears to resist ordering at temperatures that are more than 1000 times lower than T_{CW} .

Still another way to check for magnetic ordering is to use muon spin resonance, in which muons are embedded in the material to sample the local field. Using μ SR, Mendels and his collaborators found no evidence for magnetic order down to 50 mK.

Regarding the question of a spin gap, the experimental evidence so far is consistent with a gapless state. Based on inelastic neutron scattering, Lee and his team estimate that the spin gap is smaller than 0.1 meV. Keren's group measured the nuclear spin-lattice relaxation time T_1 of chlorine atoms, which are sensitive to the magnetic spins of the copper atoms. The group says that the slow decrease of T_1^{-2} with decreasing temperature also suggests the absence of a spin gap.

To learn even more about a spin liquid, one can look at such properties as the variation of specific heat with temperature. Ramirez of Alcatel-Lucent's Bell Labs says that in all the frustrated magnets he's looked at, the specific heat goes as T^2 . Such a dependency can stem from known excitations such as magnons, or spin waves, which are described by classical wavefunctions, but they could also come from an excitation with no classical analogue. It would be a big deal, says Ramirez, if the power law deviated from T^2 . Such behavior would almost certainly be a harbinger of an exotic state.

The MIT-led team reports a specific heat that goes as T^α , where $\alpha < 1$. That result is already being tested by theorists. Recently, MIT theorists found the lowest energy state of a spin- $\frac{1}{2}$ kagome

lattice to consist of spin- $\frac{1}{2}$ spinons obeying a Dirac spectrum.⁹ They predict that the specific heat will go as T^2 . Taking a different approach to the same problem, theorists from the University of California, Santa Barbara, and Caltech have found a different state but still predict a T^2 specific heat.¹⁰

Further experiments will have to determine how much the specific heat and other low-energy measurements might be affected by impurities. Radu Coldea of Bristol University in the UK would like to see measurements of the kagome system at higher energies, closer to the energies of the spin interactions.

Other spin-liquid candidates

Two other systems are also promising candidates for a spin liquid. One is an organic antiferromagnetic insulator given by the formula κ -(ET)₂Cu₂(CN)₃, where ET stands for a specific organic molecule. The symbol κ specifies a particular packing pattern of the ET molecules within layered planes. This material has been extensively studied by an experimental group led by Kazushi Kanoda of the University of Tokyo. The researchers have seen no evidence for

magnetic long-range order down to 32 mK.¹¹

The organic material has an interesting phase diagram. For example, one can take the material from an antiferromagnetic insulating phase directly into an unconventional superconductor not by doping but by applying pressure. The spin liquid appears to be close to a Mott transition between insulator and metal. This proximity makes charge fluctuations more important and strengthens certain spin interactions such as a ring exchange around the four corners of two adjoining triangles.^{12,13} Patrick Lee of MIT has proposed that the spinons in this system form a Fermi surface.¹⁴

Kanoda says that recently performed measurements of specific heat and thermal conductivity have shown peak anomalies at the same temperature, which may be an indication of some hidden order. He asserts that the Heisenberg model, which has no charge degrees of freedom, may not be the most apt model for studying the spin liquid near the Mott transition. Unfortunately, κ -(ET)₂Cu₂(CN)₃ does not lend itself to neutron-scattering measurements.

Another spin-liquid candidate found in recent years is cesium copper chloride. Coldea and his fellow experimenters from Oxford University, Oak Ridge National Lab, and the UK's Rutherford Lab, have done neutron scattering studies of large Cs₂CuCl₄ crystals.¹⁵ Coldea has collaborated with other groups to measure additional properties of the crystals. Between 0.62 K and 2.65 K, the 2D layers of this crystal are decoupled and the material has no long-range order, but the material does order below 0.62 K. That fact has damped the interest of some theorists. Moreover, although the copper atoms in this material lie on a triangular lattice, the lattice is distorted, with the bonds along one leg being stronger than those along another, so that some researchers think the material is more 1D than 2D.

Yet another material with a triangular lattice is the compound NiGa₂S₄.¹⁶ It lacks magnetic order, but the spins have $s=1$. Theorists question whether the integer spin makes it a fundamentally different system from a spin liquid.

The diversity of materials has presented many challenges to theorists, and much work has been done with toy models. Theorists still hope that exper-

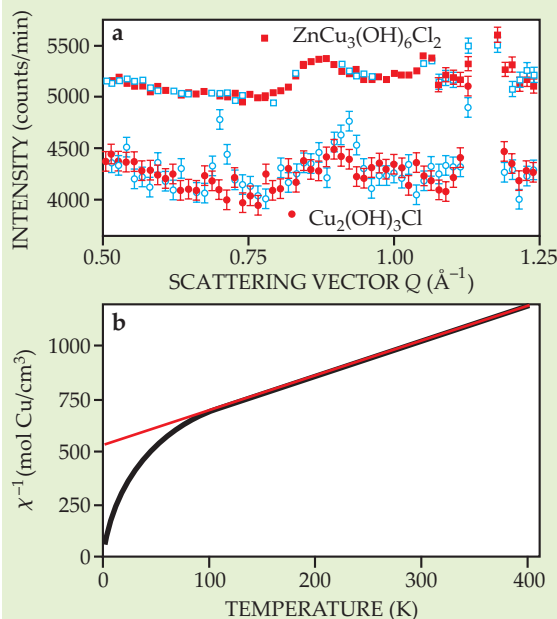


Figure 3. No evidence for magnetic order is seen in either elastic neutron scattering or susceptibility measurements on the spin- $\frac{1}{2}$ kagome lattice. (a) For $\text{Cu}_2(\text{OH})_3\text{Cl}$ (circular data points) at a temperature $T = 1.4$ K (open blue points), Bragg scattering peaks are seen at $Q = 0.70 \text{ \AA}^{-1}$ and at $Q = 0.92 \text{ \AA}^{-1}$. No such peaks appear for its cousin, $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$, the spin-liquid candidate (square points), nor at $T = 20$ K (solid red points). (b) Inverse susceptibility data (black) follow a straight line at high temperature. The linear fit (red line) gives a Curie-Weiss temperature of about 300 K. (Adapted from ref. 4.)

iments will be able to probe deep enough into these promising materials to reveal the exotic behavior they expect to be there. As Matthew Fisher of the University of California, Santa Barbara, sees it, spin liquids are the cleanest example of a strongly correlated quantum system that has qualitatively different behavior from Fermi liquids and other simple, well-understood phases.

Barbara Goss Levi

References

1. P. W. Anderson, *Mater. Res. Bull.* **8**, 153 (1973).
2. See, for example, P. W. Anderson, *Phys. Rev. Lett.* **96**, 017001 (2006).
3. M. P. Shores et al., *J. Am. Chem. Soc.* **127**, 13462 (2005).
4. J. S. Helton et al., <http://arxiv.org/abs/cond-mat/0610539>.
5. O. Ofer et al., <http://arxiv.org/abs/cond-mat/0610540>.
6. P. Mendels et al., <http://arxiv.org/abs/cond-mat/0610565>; *Phys. Rev. Lett.* (in press).
7. B. Bernu, P. Lecheminant, C. Lhuillier, L. Pierre, *Phys. Rev. B* **50**, 10048 (1994).
8. C. Waldtmann et al., *Eur. Phys. J. B* **2**, 501 (1998).
9. Y. Ran, M. Hermele, P. A. Lee, X.-G. Wen, <http://arxiv.org/abs/cond-mat/0611414>.
10. S. Ryu, O. I. Motrunich, J. Alicea, M. P. A. Fisher, <http://arxiv.org/abs/cond-mat/0701020>.
11. Y. Shimizu et al., *Phys. Rev. Lett.* **91**, 107001 (2003).
12. W. LiMing, G. Misguich, P. Sindzingre, C. Lhuillier, *Phys. Rev. B* **62**, 6372 (2000).
13. O. I. Motrunich, *Phys. Rev. B* **72**, 045105 (2005).
14. S.-S. Lee, P. A. Lee, *Phys. Rev. Lett.* **95**, 036403 (2005).
15. See, for example, R. Coldea, D. A. Tennant, Z. Tylczynski, *Phys. Rev. B* **68**, 134424 (2003).
16. S. Nakatsuji et al., *Science* **309**, 1697 (2005).

Designer materials render objects nearly invisible to microwaves

Coordinate transformations and curved spaces, the traditional tools of general relativity, are finding applications in optical engineering.

Optical design is largely a matter of choosing the right material for the job and then optimizing its geometry—say, a glass lens to form images, a metal cage to screen sensitive electronics, or a polymer film to reduce surface reflections. But the range of electromagnetic properties available to optical engineers from materials found in nature falls far short of what is theoretically possible.

In 1999 John Pendry and colleagues from Imperial College London dramatically extended the palette of realizable electromagnetic properties by proposing a variety of artificial structures—metamaterials—whose response to radiation could be custom-designed.¹ Although the field of artificial materials dates back to the 1940s, it took advances in computation and fabrication technology made in the 1990s, along with a surge of interest in negative refraction, to set the stage for engineering composite materials whose effective magnetic permeability tensor μ and electric permittivity tensor ϵ could be tailored.

Essentially miniature inductive and capacitive circuits composed of copper loops built into a repeated array of unit cells, Pendry's metamaterials owe their electromagnetic properties to subwavelength details of geometric structure rather than to chemical composition. As long as the size and spacing of circuit components are small compared to

wavelengths of interest, incident radiation cannot distinguish circuits from conventional materials. Adjusting a circuit's geometry tunes its resonant frequency and the strength of its electromagnetic response to the incident radiation.

To understand how, think of each circuit as a magnetic atom. Just as a magnetic atom produces a net magnetic dipole in response to a field, so do these metamaterials, at least in the microwave regime where metals react strongly to applied fields. A time-varying electromagnetic field induces an electromotive force that drives a current in a conducting loop. A gap in the loop introduces a capacitance into the circuit and produces a resonance at a frequency set by the loop's geometry. Similarly, the electric component of the field induces an electric dipole that oscillates with a large amplitude near its resonant frequency. Because the resonant frequency of a metamaterial can be set to virtually any value, one has tremendous control over ϵ and μ .

Armed with this powerful design flexibility, researchers have since created metamaterials with properties impossible to find in nature. If fashioned so that both ϵ and μ are negative at some frequency, for instance, metamaterials can form exotic lenses that bend light at that frequency in a direction opposite



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