CONDENSED MATTER PHYSICS

Quantum Magnetism and Its Many Avatars

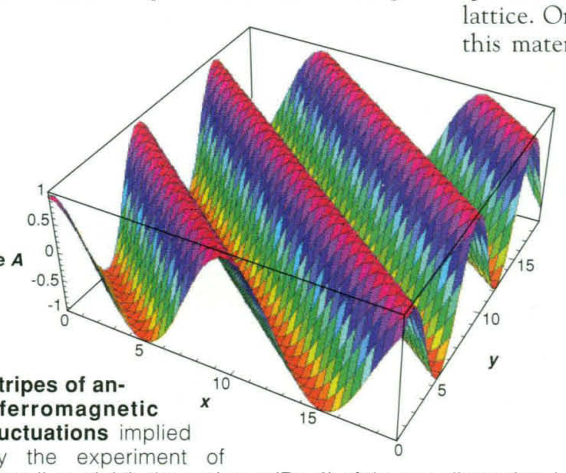
Sudip Chakravarty

The challenge posed by high-temperature superconductors remains as poignant as ever. On the one hand, the striking presence of antiferromagnetism in the phase diagram is unmistakable; on the other, the materials with the highest transition temperatures show little evidence of magnetic fluctuations. It is as though antiferromagnetism abhors superconductivity and vice versa, yet they are mysteriously intertwined. It is common to confront such a situation with the Cheshire cat principle; the cat is gone, but its smile is there. This situation would be intolerable were it not for clever and difficult experiments that periodically shake up our perceptions. The experiment reported on page 1432 of this issue by Aeppli and co-workers (*1*) is an example. It hints at a novel state of matter related to a quantum critical point and finds the existence of unusual magnetic scattering in one of the high-temperature superconductors, $La_{1.86}Sr_{0.14}CuO_4$, with a transition temperature of 35 K.

The cuprate high-temperature superconductors are derived from insulating parent compounds by the addition of charge carriers in a process known as doping. The model that successfully describes the magnetic properties of the parent compounds is the quantum spin-Heisenberg model, in which only the nearest neighbor spins situated on a square lattice interact, with an antiferromagnetic exchange constant J, which in temperature units is about 1500 K. That is, there is a tendency of the nearest neighbor spins to be antiparallel.

In the early days of this field, there was much excitement that such a two-dimensional Heisenberg model might not order in an antiferromagnetic state at zero temperature. The quantum fluctuations of the spin would destroy its ordering tendency, and it would be a spin liquid, just like liquid ^4He is a liquid, as opposed to a crystal, owing to zero-point quantum fluctuations. This hope has not materialized. Instead, it is now known, both from experiments (*2*) and theory (*3*), to be otherwise, and the concept of a spin liquid has evaporated. The wave-like excitations arising from the ordered state, called spin waves, determine its properties.

With doping, as long as the insulating antiferromagnetic state survives, the description remains essentially unchanged. Beyond this, there are strong phenomenological reasons to believe that the system does not evolve into a conventional metal, known as a Fermi liquid. What replaces Fermi liquid is a non-Fermi liquid with its own set of robust laws (*4*). Most strikingly, in a non-Fermi liquid, the electron is not a fundamental particle, but a composite object.



Stripes of antiferromagnetic fluctuations implied by the experiment of Aeppli *et al.* (*1*): the real part (Re *A*) of the two-dimensional plane wave with the incommensurate vector $\mathbf{Q} = (\pi[1 - \delta]/a, \pi/a)$, with a = 3.8 Å and δ = 0.245; x and y denote coordinates in angstroms.

The charge and spin degrees of freedom are too many. So, it may be desirable to remove one set of degrees of freedom, or to technically "integrate them out." The result, if we are fortunate, may be a simpler model. An attempt to construct a spin-only model led to the importance of the notion of the quantum critical point in this context (*3*). The model consists of an interaction parameter that measures the strength of the quantum fluctuations of the spins. One can envisage tuning this parameter at zero temperature to move from the antiferromagnetically ordered state to a state disordered by zero-point quantum fluctuations by way of a quantum critical point. The zero-temperature quantum critical point has a number of unusual properties (*3*, *5*), and remarkably, its effect can extend to experimentally measurable temperatures.

Magnetic neutron scattering measures how the spin at a given lattice site at a given instant of time is correlated with another at another site at another instant of time. The sharp features that rise above the background indicate intrinsic excitations of the system.

The measurements in (*1*) are surprising. The antiferromagnetic order of the undoped parent compound La_2CuO_4 is rather simple. If you move along a row or a column of a square lattice, the average orientation of the spins alternate from up to down periodically. The periodicity can be expressed by a two-dimensional plane wave $e^{i\mathbf{Q}\cdot\mathbf{R}}$, where the ordering vector $\mathbf{Q}$ is $(\pi/a, \pi/a)$, and a is the spacing between the sites of the square lattice. The vector $\mathbf{R}$ labels the site of a square lattice; this is called commensurate order, as the arrangement of the spins is commensurate with the underlying lattice. One would expect that as we dope this material with charge carriers to turn them into superconductors, the antiferromagnetic fluctuations would be peaked at this ordering vector, even though long-range order is absent. Indeed, nuclear magnetic resonance experiments are commonly analyzed on this premise. What is found instead is that the magnetic scattering is strongly peaked at incommensurate vectors $\mathbf{Q} = (\pi[1 \pm \delta]/a, \pi/a)$ and $\mathbf{Q} = (\pi/a, \pi[1 \pm \delta]/a)$, where δ = 0.245 at low temperatures. To see how striking this incommensuration is, I plotted (see figure) the real part of the plane wave with $\mathbf{Q} = (\pi[1-\delta]/a, \pi/a)$, for a = 3.8 Å, with smooth interpolation between the lattice points. There is an unmistakable pattern of stripes not commensurate with the underlying crystalline lattice. There is growing evidence that these stripes may be present in other superconducting materials as well. These stripes are not fully understood theoretically. One of the theories (*6*, *7*) is based on the idea of frustrated phase segregation, in which the material breaks up into alternating regions of antiferromagnetic domains. It may also be that this is due to the special topology (near nesting properties) of the Fermi surface. In this regard, it is worth noting that this incommensuration does not require a Fermi liquid. Even a non-Fermi liquid has the usual Fermi surface, and the topological features are the same. The distinction between a Fermi and a non-Fermi liquid lies in the actual frequency, momentum, and tempera-

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ture dependencies of the magnetic neutron scattering at these incommensurate wave vectors, which may be stronger in a non-Fermi liquid.

The second striking feature of this experiment is that significant magnetic scattering at these incommensurate wave vectors or nearby exists for a range of frequencies. This scattering means that these magnetic excitations are not elementary, but are composite objects. Spin-flip neutron scattering couples to spin-1 excitations, composite or elementary, because neutron scattering flips a spin of $^1/_2$, from up to down or from down to up. If the excitation is elementary, for example, a spin wave, a given momentum transfer will lead to a given frequency or energy transfer and not a range of frequency transfers. Thus, it is unlikely that these magnetic fluctuations give rise to pairing in a simple way. These excitations could arise from a nearby quantum critical point, but the theory of the quantum critical point (*3*, *5*) has to be generalized appropriately to include incommensurate fluctuations.

To me, the very same observations that have led Aeppli *et al.* to suspect quantum criticality seem to negate its existence. They have found that the amplitude of the magnetic scattering rises strongly as the temperature is lowered, and the widths of peaks at the incommensurate momenta scale in a simple way, where frequency and temperature can be interchanged almost exactly. So far, so good; these are indeed the characteristics of a quantum critical point. But if we look more closely, we discover that in the limit as frequency and temperature go to zero, the length scale is finite, about 30 Å, instead of infinity. So, in the zero-temperature limit, we are in a quantum (as opposed to thermally) disordered state (*3*, *5*). This state would imply an energy scale of order 6 meV (70 K in temperature units) or greater [in this estimate, I have used the only quoted scale, approximately equal to $(1/3)Ja$]. For quantum criticality as we understand it, scattering should disappear below this energy transfer. This does not seem to be the case, and it is not contained in the functional form of the scattering function chosen by the authors.

There are many avatars of quantum magnetism, including spin liquid, magnetic stripe phases, and quantum critical points. It remains to be seen if any of them are useful in solving a problem that has occupied a sizable fraction of the physics community over the last decade.

References and Notes

1. G. Aeppli *et al.*, *Science* **278**, 1427 (1997).
2. For an up-to-date review, see M. Greven *et al.*, *Z. Phys. B* **96**, 465 (1995).
3. S. Chakravarty, B. I. Halperin, D. R. Nelson, *Phys. Rev. B* **39**, 2344 (1989).
4. P. W. Anderson, *The Theory of Superconductivity in the High-T_c Cuprates* (Princeton Univ. Press, Princeton, NJ, 1997).
5. S. Sachdev *et al.*, *Phys. Rev. B* **51**, 14874 (1995).
6. For a review, see S. A. Kivelson, in *Strongly Correlated Metals*, K. S. Bedell *et al.*, Eds. (Addison-Wesley, Reading, MA, 1994).
7. C. Nayak and F. Wilczek, *Phys. Rev. Lett.* **78**, 2465 (1997).

BIOCHEMISTRY

Methane: Small Molecule, Big Impact

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Why so much interest in methane? Each year microbes produce about 400 million metric tons of this gas, a huge mass that has a profound effect on humankind. Methanogenesis occurs in vast natural and human-made environments, but only when the conditions are anaerobic. This situation can be found inside animals (the rumen of cows or insect hindguts), in watery landscapes (natural wetlands or rice paddies), or at other human-made sites (sewage digestors, landfills, and biogas generators). Indeed, the estimated 1% annual increase in global methane is mainly attributed to human activities (*1*).

Methane-producing microbes are phylogenetically distinct from all other prokaryotes and eukaryotes. They make several novel cofactors and enzymes, and their existence has led to the present three-domain concept of phylogeny (Archaea, Bacteria, and Eukarya) (*2*). On page 1457 of this issue, Ermler and colleagues report a milestone for methane aficionados—the crystal structure of methyl–coenzyme M(CoM) reductase, a key enzyme common to all methane-producing pathways (*3*). This is the third structure reported for nickel-containing enzymes, following those of urease (*4*) and hydrogenase (*5*).

Most methane diffuses from the anaerobic to the aerobic biosphere where oxygen-requiring microbes oxidize it to carbon dioxide; thus, the microbial production and consumption of methane is a significant component of the global carbon cycle. In addition, each year about 45 million metric tons of methane escapes into the troposphere. A molecule of methane is far more effective than a molecule of carbon dioxide in absorbing and radiating energy back to Earth. Thus, methanogenesis contributes significantly to the greenhouse effect.

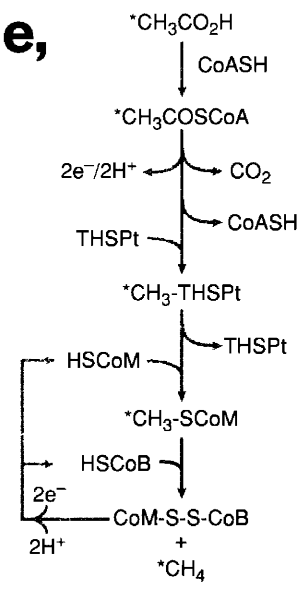

Fig. 1. Pathway for the conversion of acetate to methane by the methanoarchaea. The box highlights the reaction catalyzed by methyl-CoM reductase.

Production of methane requires a food chain of at least three interacting metabolic groups of obligately anaerobic microbes (see Fig. 2, next page) (*6*). The fermentative group decomposes cellulose and other complex molecules to volatile carboxylic acids (mainly acetate) and hydrogen gas. Only acetate, carbon dioxide, hydrogen, and formate are substrates for the methanoarchaea; thus, the hydrogen-producing acetogenic group is necessary to further metabolize butyrate and propionate. The methanoarchaea use two separate pathways in which methane derives from either the methyl group of acetate (reaction 1) (see Fig. 1) or the reduction of carbon dioxide with electrons from hydrogen or formate (reactions 2a and 2b).

$$CH_3COO^- + H^+ \bullet CH_4 + CO_2 \qquad (1)$$

$$CO_2 + 4H_2 \bullet CH_4 + 2H_2O \qquad (2a)$$

$$4HCO_2H \bullet 3CO_2 + CH_4 + 2H_2O \qquad (2b)$$

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