Antiferromagnetism Observed in La_2CuO_4

Magnetism and superconductivity are usually mutually exclusive, but they seem to be intimately related in the new high-temperature superconducting compounds

"SUPERCONDUCTIVITY and antiferromagnetism are the Jekyll and Hyde of [the lanthanum-copper-oxygen] system—they are intimately related," says David Moncton of the Exxon Research and Engineering Company. Moncton is one of a group of Exxon researchers who have found antiferromagnetism in the compound La_2CuO_4. The current revolution in superconductivity began last year with the discovery that substituting small amounts of the alkaline earths barium, strontium, or calcium for lanthanum turn this compound into a superconductor with a critical temperature of, in the best cases, 40 K. Other researchers now have some evidence that the pure compound itself may be superconducting in certain circumstances.

In any case, it is clear that the observation of antiferromagnetism places a strong constraint on any theory of superconductivity in these materials. Theorist Michael Schlüter of AT&T Bell Laboratories told *Science* that the result is a very important one. Moreover, the restriction may also apply to the more recently discovered but related family of rare earth–barium-copper-oxygen compounds with critical temperatures from 90 to 100 K that have been widely hailed as finally opening the way for superconductors to crack the world of high-tech commerce in a big way. It is not yet clear to what extent superconductivity in the two families of compounds is governed by the same mechanism.

Some commonality is suggested by the belief of theorists that the superconducting electrons in both families are those in copper and oxygen orbitals. As it happens, the antiferromagnetism in La_2CuO_4 is also due to the magnetic moment on the Cu^{2+} ions. Presumably, sorting out exactly why the new compounds remain superconducting at what only a few months ago would have been considered astoundingly high temperatures could lead researchers to the Holy Grail of the field, if it exists—a room-temperature superconductor.

The antiferromagnetism finding was reported by Exxon's David Johnston at the spring meeting of the Materials Research Society (MRS), held last month in Anaheim, California. It is an interesting turn of history that Johnston helped open the era of oxide superconductors with a 1973 report of a 13 K critical temperature in a strontium-titanium-oxygen spinel material when he was at the University of California at San Diego.

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Actually, the Exxon researchers began by looking at the effect of oxygen on the structure of the compound, whose composition is more accurately written as La_2CuO_{4-y}, where y is a small number between 0 and 0.1 or so. At high temperature, the crystal structure is tetragonal. At lower temperature, the compound makes a small switch to a very similar orthorhombic structure. The investigators found that the transition temperature rose rapidly from 450 K to 530 K as y increased from 0 to 0.1; that is, a full complement of oxygen atoms made the tetragonal structure more stable.

Be that as it may, the Exxon group also noticed anomalous maxima in the magnetic susceptibility that occurred below room temperature. Such susceptibility anomalies suggest to researchers the possibility of a transition to a magnetically ordered phase at a nearby temperature. The anomalies were also fully in the spirit of the experiment because the temperature at which they occurred depended strongly on the oxygen concentration parameter y. In particular, the temperature rose from a nominal 0 K to 295 K as y increased from 0 to 0.1. Conversely, the anomaly disappeared when 10% of the lanthanum was replaced by strontium.

To investigate the magnetic properties, the Exxon researchers went to the reactor at Brookhaven National Laboratory to do neutron diffraction experiments. The magnetic moment of the neutron allows the neutrons to be scattered by magnetic moments on the ions in the material. If the moments are ordered, a diffraction pattern is generated with reflections that are in addition to those due to the crystal structure itself.

Upon cooling a sample with y equal to 0.03, the investigators indeed did see new but weak so-called superlattice reflections that did not appear in x-ray diffraction patterns. They interpreted the appearance of the reflections below about 220 K as signaling the transition to an antiferromagnetic state at that temperature. In this antiferromagnetic state, the magnetic moments of the Cu^{2+} ions are aligned, but half are in one direction and half in the other, giving a net magnetization of zero.

In more recent experiments, the Exxon group has collaborated with researchers at Brookhaven, at Bell Laboratories, and the University of Pennsylvania. In one test of the antiferromagnetism interpretation, the investigators repeated their experiment with spin-polarized neutrons whose magnetic moments are predominantly in the same direction. By this means it was possible to separate magnetic from nonmagnetic reflections and thereby confirm the existence of a magnetic ordering. In a second experiment, they tested the sensitivity of the antiferromagnetism to the oxygen concentration parameter y by measuring two samples, one with y nominally zero and one that was annealed in a vacuum to remove oxygen. In agreement with the magnetic susceptibility anomalies, the antiferromangetic ordering temperature determined from neutron diffraction rose from 50 K to 150 K with the heat treatment.

What it all means is hardly clear. There are several threads to tie together involving the structure, orthorhombic or tetragonal, and the apparently contrary roles of alkaline earth substitution and oxygen removal. For example, researchers thought early on that the addition of the alkaline earths stabilized the tetragonal structure and that this structure was associated with the superconductivity. At the MRS meeting, however, R. Moret of the Laboratory of the Physics of Solids in Orsay, France, showed x-ray data suggesting that both structures were superconducting. Bell Labs researchers have similar evidence. Moreover, Paul Grant of the IBM Alamaden Research Center discussed experiments suggestive of superconductivity in La_2CuO_{4-y} that could be reversibly removed or restored by heating the material in argon or oxygen with no need of an alkaline earth at all. All in all, there are lots of questions and few answers. ■

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