Advances in Unconventional Iron-Based Superconductors

Landmark research about a newly discovered superconducting material will lead to more efficient, less-expensive products in fields such as energy, transportation, and medicine.

In mid-March 2008 Pengcheng Dai, researcher in the Neutron Scattering Science Division (NSSD) and joint professor of condensed matter science at the University of Tennessee, attended a conference in his native China. He asked a fellow scientist familiar with a paper in the February 23, 2008, issue of the *Journal of American Chemical Society* why he and his colleagues were so excited. The scientist called the paper "fantastic" and said that the paper reports the discovery in Japan of a new iron-based superconducting material.

After reading the paper, Dai shared their excitement. After obtaining some "made in China" samples of the superconductor's iron-based parent compound, he returned to ORNL to analyze the material's magnetic structure using neutron scattering. The experiments employed instruments at HFIR and the National Institute of Standards and Technology (NIST) research reactor in Maryland.

At about the same time, ORNL staff Michael McGuire and Athena Safa-Sefat became the first team in the United States to report that they had synthesized powders and crystals made of the iron-based material. In addition, ORNL's Mark Lumsden and Andy Christianson, both in NSSD, were performing neutron scattering experiments on ORNL-made samples.

The original discovery of superconductivity in an iron-based material was made in February 2008 by Japanese scientist Y. Kamihara and colleagues. They initially reported that an iron-based material can conduct electricity without resistance at 4 Kelvin (4 degrees Celsius above absolute zero). The elements in the first known iron-based superconducting material are iron, arsenic, oxygen, and the rare earth lanthanum. When LaFeAsO was doped with fluorine, the Japanese discovered that the new material became superconducting at 26 K. Since then several different families of iron-based superconductors have been discovered. The common element is the presence of layers of iron atoms arranged in a square lattice.

Any material that is superconducting at more than 50 K is considered a high-temperature superconductor (HTS). The first high-temperature superconductors discovered and the most explored to date are the copper oxides, or cuprates. The cuprates have been carefully studied for more than 20 years, but condensed matter scientists still lack a complete understanding of how they work. The highest known temperature at which a cuprate turns into a superconductor is 130 K, achieved more than 15 years ago. Scientists throughout the world are excited about the iron-based superconductors because now they have an opportunity to study the electrical and magnetic properties in a new and different system in the high-temperature superconducting class, hopefully gaining crucial insight into the mechanism for superconductivity in these materials.

Clues to how both types of HTS materials work will lead to designs of new superconducting combinations of elements that come close to conducting electricity with zero resistance at room temperature. Such materials would be practical for use in electricity generators, underground electrical transmission in tight spaces, cheaper medical imaging scanners, and extremely fast levitating trains. The reason: these high-temperature, or unconventional, superconductors would not require expensive coolants to chill the

Mark Lumsden (left) and Andy Christianson (right) at HFIR's Triple-Axis Spectrometer.

materials to the critical temperature (Tc) at which they become superconducting. Low-temperature, or conventional, superconductors work only if chilled to very low temperatures using expensive liquid helium. HTS materials can be cooled by helium gas or much less costly liquid nitrogen. Unconventional cuprates with yttrium and barium are already being used for superconducting wires and tapes.

The famous BCS theory, formulated in 1957, explains how the conventional superconducting materials discovered in 1911 actually work. BCS stands for the last names of the theorists—John Bardeen, Leon Cooper, and Robert Schrieffer—who received the Nobel Prize in Physics in 1972 for their theory.

In March 2001, magnesium diboride was discovered to have superconducting properties at its critical temperature of 39 K. This material's superconductivity can be explained by the BCS theory, making magnesium diboride a conventional superconductor. The two unconventional superconducting materials—the cuprates discovered in 1986 and the oxypnictides discovered in 2008—possess superconducting and magnetic properties that cannot be explained by BCS theory. The theory explains that in a conventional superconductor crystal, the negatively charged electrons attract the positively charged nuclei in the lattice, leaving a wake of positive charges that attract a second electron. The net effect is that the moving, positively charged nuclei, which constitute a phonon or measurement of vibrational energy, provide an attractive interaction to make a pair of electrons, known as Cooper pair. These electron pairs are able to flow more easily between the oscillating atoms in lattice walls, which normally resist the flow of single-file, unpaired electrons in a current. This easier flow creates superconductivity.

Lumsden and Christianson studied the samples synthesized at ORNL using the Triple-Axis Spectrometer at HFIR and the Wide Angular-Range Chopper Spectrometer (ARCS) at SNS (see sidebar on page __).

Using ARCS, Lumsden and Christianson compared the lattice vibrations in the conventional superconducting material with those in the iron arsenates. "The phonons we measured in the iron arsenates should induce superconductivity only at a temperature of 2 K using a conventional phonon mechanism, " Christianson said. "Yet measurements show the material's critical temperature is 26 K."

Some scientists predict that magnetic properties of the iron arsenates might make them superconducting at a relatively high temperature. To find out if magnetic fluctuations are the missing piece of the puzzle, Dai's team and Lumsden's team both studied the magnetic structure, or arrangement of electron spins, in the iron arsenates.

In materials that exhibit antiferromagnetism, the magnetic moments of atoms or molecules are the manifestation of ordered magnetism that exists at low temperatures and then disappears at and above a specific temperature. The existence of the antiferromagnetic structure is easily detected by neutrons because, like electrons, neutrons are small magnets, positive at one end and negative at the other.

Undoped iron arsenates, like the parent compound LaFeAsO, are antiferromagnetic materials when chilled to a low temperature. Using both a powder diffractometer at NIST and HFIR's Triple-Axis Spectrometer, Dai and his collaborators observed very weak magnetic peaks in LaFeAsO, suggesting weak magnetic interactions between layers of iron arsenate molecules (FeAsO). When doped with fluorine and chilled to its critical temperature, LaFeAsO becomes superconducting.

"However, the material's static magnetism disappears when superconductivity pops up," Dai says. "This phenomenon is exactly what we see with the cuprates, except the copper oxide layers becomes superconducting when the copper atoms each lose an electron."

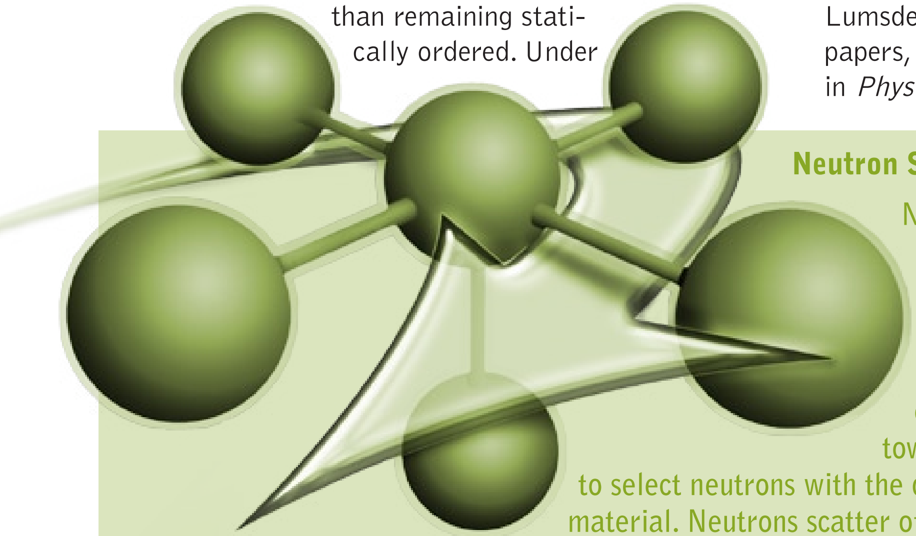
Dai and his colleagues at UT, ORNL, and NIST published a paper on oxypnictides in the May 28, 2008, issue of *Nature*. The authors have been shown to be correct in predicting the magnetic structure LaFeAsO. The experiments at ORNL and NIST produced data supporting the theory that subtle magnetism may be responsible for the high-Tc effect—the temperature at which the material exhibits superconductivity. In subsequent work using cerium, published in the October 26 issue of *Nature Materials*, Dai's team showed that the phase diagram of CeFeAsO doped with fluorine is similar to that of the doped cuprates.

In general, if the parent compound LaFeAsO is placed under pressure or doped with fluorine, the static magnetism of the compound is suppressed. The leftover magnetic moments fluctuate in time rather than remaining statically ordered. Under these circumstances, with the absence of magnetic order, the compounds tend to become superconducting.

"We think the surviving magnetic fluctuations are related to superconductivity," Christianson says. "Short-range magnetic fluctuations may be an analog to phonons. One electron enters and interacts with the antiferromagnetic lattice by flipping a spin of an iron atom's electron, causing an unhappy situation. The second electron flips it back, creating a happy situation, energetically speaking. For unconventional superconductors, magnetic fluctuations, rather than lattice vibrations, may lead to electron pairing, the key to superconductivity."

Lumsden and Christianson have published two initial papers, one in *Physical Review Letters* and the other in *Physical Review B*. They have also collaborated with scientists at Argonne National Laboratory on a study of spin fluctuations in a barium-potassium-iron-arsenic ($Ba_{0.6}K_{0.4}Fe_2As_2$) material. This paper, published in *Nature*, provides powerful evidence that weak magnetism is strongly coupled to superconductivity in iron-based materials. Since then, the two ORNL researchers and their collaborators have been studying single crystals of iron-based superconducting materials, and several more papers are in preparation. Dai and his colleagues are continuing their research on these materials and are writing additional papers for submission to scientific journals.

Other related research is in progress at ORNL. Now that ORNL researchers are producing a variety of iron-based materials in the search for a practical superconductor, Dai may be content to conduct neutron scattering studies exclusively with experimental samples made in America.



Neutron Scattering and Instrument Primer

Neutron scattering is used to examine the structure of materials. In neutron scattering, a beam of neutrons with a known energy and momentum is scattered off a sample of material. The scattered neutrons are detected with special instruments, and the energy and momentum of the neutrons are determined.

At ORNL, two types of instruments have been used to probe unconventional high-temperature superconductors. One type is the Triple-Axis Spectrometer at HFIR. A continuous beam of neutrons travel toward the triple-axis spectrometer to the monochromator, a large crystal that allows the experimenter to select neutrons with the desired energy. The experimenters are able to define the size of the beam needed to probe the sample material. Neutrons scatter off the sample and then off another large crystal called the analyzer. The analyzer is then used to measure the final energy of scattered neutrons, which is registered in a final detector.

The other instrument used extensively is ARCS, located at SNS. This instrument is a time-of-flight spectrometer with an array of hundreds of detectors. Time of flight means that the energy of neutrons is measured in terms of the time it takes for them to leave the proton-bombarded mercury target and reach an instrument detector. SNS produces pulses of neutrons; each neutron in a pulse has its own speed. To select neutrons of a desired velocity, a Fermi chopper is employed. The chopper is a curved tube that rotates at a selected speed to ensure that only neutrons arriving at the desired velocity "see" the tube as straight and shoot through it to the sample.

The capabilities of these two instruments complement each other. HFIR's triple-axis spectrometer has a single detector that measures the positions, energies, and scattering angles of the neutrons in the beam "point by point" on the diffraction pattern. With ARCS, the neutrons are scattered to a huge array of detectors that produces a pattern, making the data more meaningful.