Physical Sciences and Neutron Science and Technology

ORNL has long been a leader in nuclear physics, atomic physics, and solid-state physics, as well as chemistry, in support of energy technologies. In 1997 the first experiment was performed at our unique Holifield Radioactive Ion Beam Facility (HRIBF). Our physicists refined HRIBF experiment stations, improved a proton source, and developed radioactive ion beams for studies of nuclear structure and nuclear astrophysics. In nuclear astrophysics research involving our Oak Ridge Electron Linear Accelerator, we collected and analyzed neutron capture data for use in computer models; the data are improving our understanding of the origin and nature of flecks of "red giant" stardust in meteorites. In the area of chemistry, we are developing a second-generation mass spectrometer for the U.S. Army to detect chemical and biological warfare agents. And some important findings have come out of our chemical studies to better understand why it's so difficult to convert low-rank coals to clean liquids.

Stemming directly from the Laboratory's original mission, ORNL's strengths in neutron-based science and technology include the design and operation of neutron sources (reactors and accelerators) and the use of neutrons in science and technology (neutron scattering, isotope production, neutron activation analysis, materials irradiation, and molecular structure determination). A more detailed understanding of magnetism and superconducting materials is one of our achievements using neutron scattering. ORNL's High Flux Isotope Reactor provides the world's highest thermal neutron flux, the only domestic source of heavy transuranic isotopes, and specialized neutron activation analysis for sensitive measurements of trace elements. Capabilities in this area support fundamental nuclear physics research, studies of material properties, nuclear materials management, development of materials for nuclear fusion and fission, isotope production for industrial and medical applications, and environmental protection.

First Experiment Performed at Unique Radioactive Ion Beam Facility

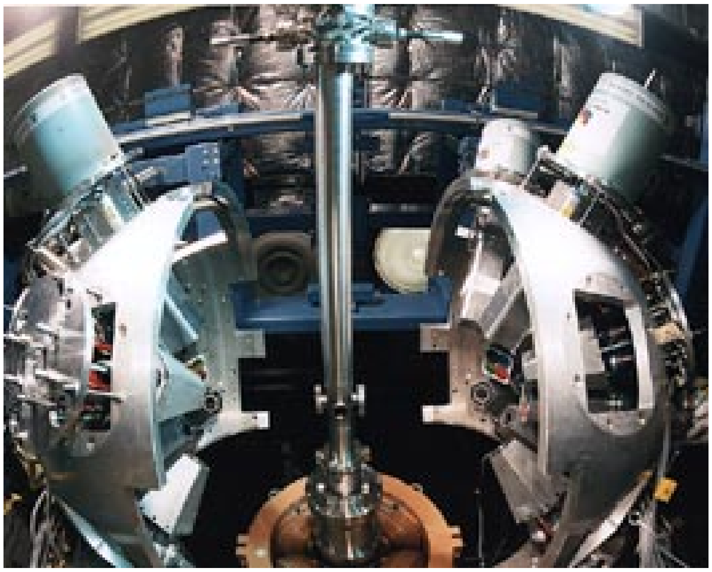
ORNL physicists and engineers refurbished and improved existing accelerators and designed and built a beam preparation system to provide a new and unique research capability—accelerated radioactive ion beams for research in nuclear structure and nuclear astrophysics.

Experiments under way at ORNL's new Holifield Radioactive Ion Beam Facility (HRIBF) will provide valuable data on the formation of heavy elements in stars and the peculiar structure of nuclei that have neutron and proton numbers far from those of stable nuclei that form most matter on earth. HRIBF, a unique tool for research in nuclear astrophysics and nuclear structure physics, began operation in March 1997, shortly after construction and commissioning of the facility were completed. The first experiment was run then at HRIBF by scientists from Yale University, Clark University, and Brookhaven National Laboratory.

HRIBF, which has been under construction since late 1992, is a part of the rapidly expanding new field of radioactive ion beam (RIB) research. Major projects are being developed in Europe and Japan, but, for the time being, HRIBF is unique in the range of radioactive species and beam energies it offers for research in nuclear structure physics and nuclear astrophysics.

A conventional nuclear physics facility accelerates beams of stable nuclei and directs them onto targets to generate nuclear reactions for further study. However, many of the most interesting questions in nuclear science can be answered only with beams of nuclei that are unstable, or radioactive. At HRIBF, unstable nuclei are produced in hot, thick targets by intense beams of protons, deuterons (proton-neutron combinations), or helium ions delivered from the Oak Ridge Isochronous Cyclotron (ORIC). These radioactive atoms are diffused out of the target, formed into an ion beam, purified by mass selection, and injected into ORNL's 25-million-volt (MV) tandem accelerator, which accelerates the beam to energies up to several hundred million electron volts. This high-energy beam is then directed to a target for physics experiments.

For the March 1997 nuclear-structure experiment, two radioactive ion beams were produced—arsenic-69 (^{69}As) and gallium-67 (^{67}Ga). Each beam was directed at a carbon target, which was used as a source of virtual photons to excite the low-lying states of the projectile nuclei. When the excited ^{69}As or ^{67}Ga nuclei returned to their lowest energy state, they gave off gamma rays, which were detected by a Yale instrument.



The target position gamma-ray detector array of the Recoil Mass Spectrometer, the flagship piece of new experimental equipment for HRIBF. ***Photograph by Lynn Freeny.***

During 1997, ORNL physicists and other staff conducted many stable beam experiments to commission and refine several million dollars' worth of new research equipment for physics studies. This equipment comprises the nuclear structure end station (Recoil Mass Spectrometer) and the nuclear astrophysics end station (Daresbury Recoil Separator). In one of these experiments, a new isotope of the element thulium (^{145}Tm) was identified. This isotope, which is very "proton-rich" (69 protons and 76 neutrons) for such a heavy nucleus, decays by a rare decay process, the emission of a proton from its ground state. The measured half-life of 3.5 microseconds for the ground state of ^{145}Tm makes it the shortest-lived proton emitter known.

ORNL staff accelerated three different radioactive ion beams (^{69}As, ^{70}As, ^{67}Ga) and developed low-energy, proton-rich beams of fluorine-17 and fluorine-18 (which have not yet been accelerated in the tandem) for use in 1998 for nuclear astrophysics experiments. They also are developing nickel-56 and copper-58 beams for nuclear structure experiments. Neutron-rich RIBs will also be produced by inducing fission in uranium and other heavy actinide targets. One neutron-rich RIB, tin-132 (^{132}Sn), is of great interest to nuclear structure experimenters because of its closed neutron and proton shells of 50 protons and 82 neutrons. The heaviest stable isotope of tin is ^{124}Sn, which has only 74 neutrons.

The development of HRIBF was a major technical achievement, carried out at very low cost. The RIB injector (target, ion source, mass selection, etc.) was designed and implemented from scratch. Two existing accelerators, the ORIC and the 25-MV tandem, have been adapted for radioactive ion beam production and acceleration. Finally, two state-of-the-art experimental stations were developed to support the very complex, difficult experiments that will be carried out at HRIBF in the years to come.

HRIBF is supported by DOE's Office of High Energy and Nuclear Physics, Division of Nuclear Physics.

Stardust with Red Giant Fingerprints?

ORNL neutron capture data aid understanding of the origin and nature of stardust in meteorites.

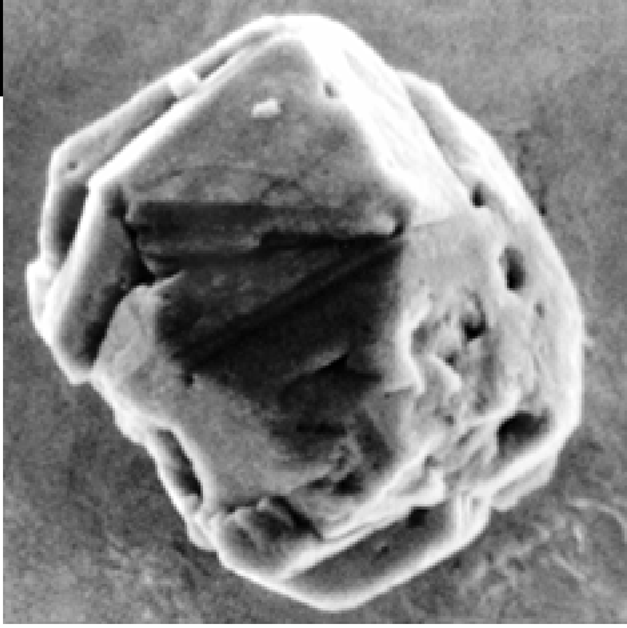
Stardust—tiny particles from stars that rode to the earth on meteorites—is thought to contain the fingerprints of a red giant star. These fingerprints tell something about how elements were synthesized inside a very large, bright, low-mass star near our solar system around the time of its birth roughly 4.5 billion years ago. This red giant cast off its outer layers during recurrent flashes of violent helium burning before shrinking to a white dwarf, a whitish star that is very small, dense, and low in luminosity. Among the ashes churned out by the burning were microscopic grains of silicon carbide (SiC) whose existence could lead to new insights about the inner life of such stars, the origin of chemical elements and their isotopes, and the formation of our solar system.

The SiC grains appear to contain traces of the elements formed in the star by the "slow neutron capture process." In this so-called "s" process, heavy elements are synthesized (starting from iron "seed" nuclei produced by a previous generation of stars) through a chain of nuclear reactions involving the capture of neutrons by nuclei until a radioactive isotope is reached. At this point, beta decay (a process in which a neutron in the nucleus decays into an electron and a proton) transmutes the nucleus from one element to another. The "s" process, together with the "p" process and the "r" process (which are thought to occur in supernovae explosions), are responsible for the formation in stars of the elements between iron and uranium.

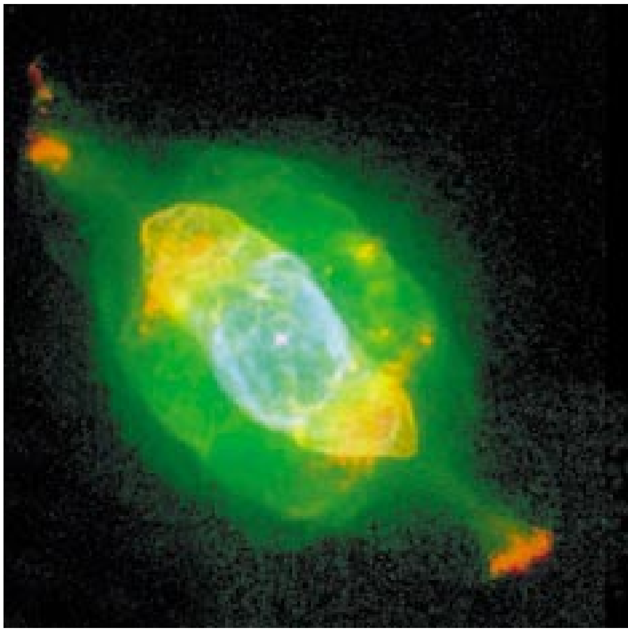
Since the 1970s, scientists at the University of Chicago and later Washington University in St. Louis have been measuring the pattern of abundances of trace elements and their isotopes captured in SiC grains found on the Murchison meteorite (which fell on Australia in 1969). The relative amounts of the various isotopes of several different elements determined from the analysis of the meteorite grains were found to be different from the patterns found in average solar system material. The hypothesis: the grains reflect the chemical and isotopic composition of a single star, but average solar system material is a mix from several different sources and processes.

The precision of the analysis of the SiC grains has improved in the past few years because of the availability of more sensitive techniques. In the same period, a new computer model of nucleosynthesis processes in red giant stars has been developed at the University of Turin in Italy. The stellar model is being refined by its developers to predict accurately isotopic abundances in red giant stars by comparing its results with the meteorite data. To make its predictions, the red giant model must have the best possible neutron capture data, which are being supplied by researchers at Karlsruhe, Germany, and ORNL's Oak Ridge Electron Linear Accelerator (ORELA).

The new red giant model predicts that the temperature at which the s process produces elements in stars is around 70 to 90 million degrees, a factor of five lower than the originally calculated 350 million degrees. ORELA is ideally suited to provide precise determinations of the neutron capture rates at these lower temperatures.



Electron micrograph of a silicon carbide grain, probably from a red giant. It rode to the earth on a meteorite.



Red giants form planetary nebulae (like the one in the above image captured by the Hubble Space Telescope) in which silicon carbide dust grains can be found. *Electronic file enhanced by Allison Baldwin.*

Using ORELA (whose useful neutron energies range from 0.02 electron volts to 40 million electron volts), Klaus Guber, Paul Koehler, and their colleagues for the first time experimentally determined the neutron capture reaction rates for isotopes of neodymium (Nd) at the new low temperature needed by the red giant model. When their data were used, precise agreement was obtained between the red giant model predictions and the Nd isotope ratios determined from measurements on SiC grains from the Murchison meteorite. However, more recent measurements at ORELA on barium isotopes have revealed a substantial discrepancy between the red giant model and the meteorite data. It is hoped that the discrepancy will lead to new insights into the origin and nature of this stardust. ORNL researchers are doing additional experiments at ORELA to provide more data with which to constrain and improve the red giant model.

The research is supported by DOE's Office of Energy Research, Office of Basic Energy Sciences, Division of Nuclear Physics.

Marcus Wise (left), Steve Lammert, and Cyril Thompson show the analyzer and its electronics in a testbed for evaluating systems of the new chemical-biological mass spectrometer. They are part of a 50-person ORNL team developing the instrument for the Army. *Photograph by Tom Cerniglio.*

Warfare Agent Mass Spectrometer Being Built at ORNL

ORNL is developing a second-generation mass spectrometer for the Army to detect chemical and biological warfare agents.

Seven years ago, during the Persian Gulf War, the U.S.-led multinational coalition that ousted Iraqi military forces from Kuwait used various detectors to try to determine if coalition forces were being exposed to Iraqi chemical warfare agents. Many false alarms were sounded because the chemically complex background of fumes from oil well fires, fuels, and lubricants, as well as exhausts from weapons and engines, confounded the detectors. As the health problems experienced by some veterans illustrate, the instrumentation used to detect and identify chemical warfare agents in the field has not been particularly reliable. Detection of biological warfare agents, such as toxins, viruses, and pathogenic bacteria, is even more difficult.

Because of its world-class expertise in mass spectrometry, ORNL was contracted by the U.S. Army Chemical and Biological Defense Command to design and construct prototypes and preproduction models of the next series (the Block II) of the chemical-biological mass spectrometer (CBMS) for rapid field detection and identification of chemical and biological warfare agents. This four-year, $32-million program includes 50 researchers from five ORNL divisions, three academic and commercial subcontractors, and four Department of Defense facilities or laboratories. Orbital Sciences Corporation will help design the CBMS to make it economically produceable in the commercial sector. Spin-off civilian uses of the CBMS technology may include rapid bacterial detection and identification in the health care and food processing industries, as well as environmental pollution mapping and civil defense.

The Army called for the next-series instrument to be smaller, lighter, faster, less expensive, more sensitive, more rugged, and more easily maintainable. It also should be able to detect and distinguish among a wider variety of airborne chemicals and microorganisms, as well as chemicals on the ground, than does current instrumentation. The Block II CBMS will consist of five modules; the total package will be about the size of a desktop computer and monitor. The heart of the Block II CBMS is an ion trap mass spectrometer similar to the ORNL instrument successfully deployed for field analytical measurements of hazardous chemical pollutants.

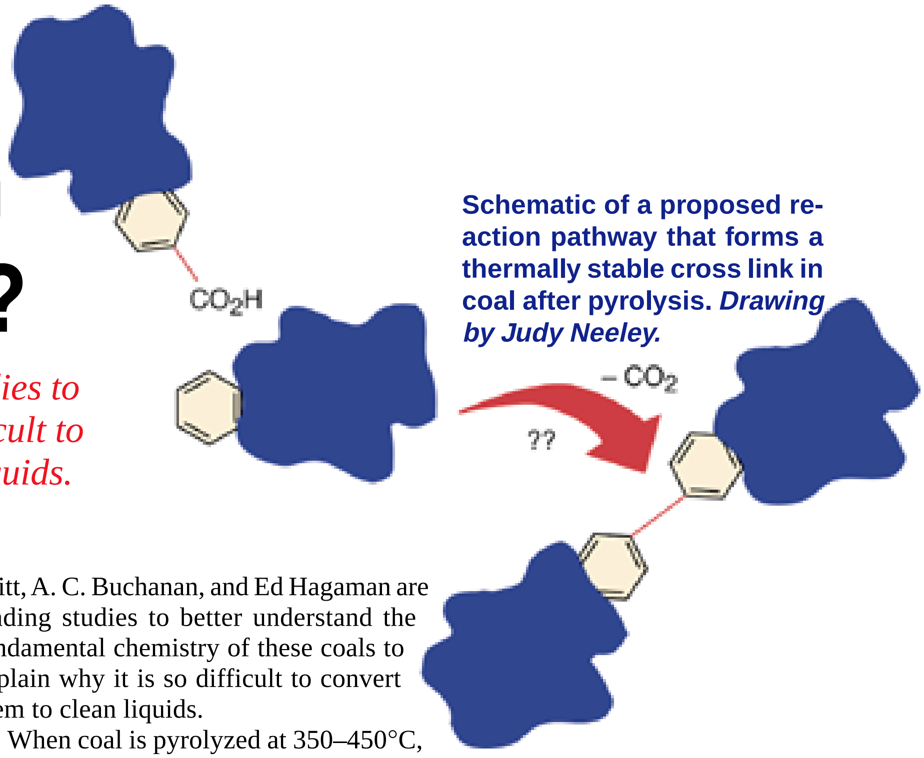
The CBMS will sample air and collect, classify, and concentrate micron-sized particles of biological warfare agents such as anthrax spores or bacterial toxins. The biomarkers in the biological agents are released and introduced into the ion trap by a combination of pyrolysis and in situ methylation. In the spectrometer, the biomarker molecules are ionized, selectively accumulated, separated in an electric field, and detected. Sophisticated identification algorithms are required to detect and identify biological agents present in a background that may include naturally occurring microorganisms, pollen, mold, and fungus. Chemical warfare agents (e.g., the nerve agent VX or blister agent HD) are much more easily detected and identified in ground surface and air samples by their known, characteristic ions.

The CBMS team's researchers have introduced several innovations to improve the instrument to meet the Army's goals. In addition to the instrumental innovations by ORNL analytical chemists, ORNL computer scientists are developing data acquisition, manipulation, and display systems. Our electrical engineers are designing the circuitry to include state-of-the-art components that can perform advanced functions and yet maintain physical ruggedness and radiation tolerance. Facilities are being established at ORNL for testing the CBMS units with very small quantities of the targeted agents before they are delivered to the Army for acceptance tests.

The final product will provide vastly improved protection to our troops. It should not sound any false alarms, but it is hoped there will be no need for real ones.

Can Fuels Be Made from Inferior Coals?

ORNL is conducting chemical studies to better understand why it is so difficult to convert low-rank coals to clean liquids.



Schematic of a proposed reaction pathway that forms a thermally stable cross link in coal after pyrolysis. ***Drawing by Judy Neeley.***

During the oil embargo of the 1970s, the temporary shortage of imported oil forced Americans to wait in long lines to fill their cars with gasoline. One proposal for bypassing unreliable oil sources was to produce an alternative fuel from coal. The idea was to pulverize coal, mix it with a solvent that donates hydrogen to it (because coal is hydrogen poor compared with oil), heat it in the presence of hydrogen to break its chemical bonds in a process called pyrolysis, and refine the resulting liquid for use as transportation fuel for vehicles. Coal liquefaction pilot plants were built in the United States, but they eventually closed because climbing oil prices later fell, making coal liquids uncompetitive.

But basic research in support of coal liquefaction is still alive at ORNL and a few other institutions. In fact, ORNL organic chemists have broadened their research effort to study oil shales and renewable resources such as lignin from waste wood. Their goal is to pin down the relationship between molecular structure and chemical reactivity in organic energy resources. Coal is particularly challenging because it is an amorphous, insoluble hodgepodge of organic materials and inorganic minerals with no repeating units as are present in crystals and in polymers.

U.S. reserves of high-carbon, high-energy coals—anthracite and bituminous coals—are quickly becoming depleted, so U.S. electric utilities and other industries are relying more on our cheap, abundant supplies of low-rank coal from surface mines in the western United States. These subbituminous and lignite coals are lower in carbon and hydrogen content but higher in oxygen than bituminous coals, making low-rank coals harder to liquefy than the high-carbon coals. ORNL chemists Phil Britt, A. C. Buchanan, and Ed Hagaman are leading studies to better understand the fundamental chemistry of these coals to explain why it is so difficult to convert them to clean liquids.

When coal is pyrolyzed at 350–450°C, the quality and yield of the products formed depend on the extent of chemical bond breakage to make small molecules, the donation of hydrogen to coal to make petroleum-like liquids, mass transport, and cross linking—the retrogressive process by which smaller molecules form larger molecules. Of these processes, cross linking is least understood. Therefore, ORNL chemists have focused their research on oxygen-containing heteroatom compounds (e.g., carboxylic acid, phenols, and ethers) which are thought to be responsible for the formation of thermally stable cross links in low-rank coals (requiring temperatures greater than 600°C to break).

In the mid-1980s scientists from Lehigh University, Brown University, and Advanced Fuel Research pyrolyzed samples of low-rank coal and analyzed the evolved gases, such as carbon dioxide, carbon monoxide, methane, and water vapor. For low-rank coals, cross-linking occurred simultaneously with carbon dioxide evolution. Later research results suggested that carbon dioxide was produced by pyrolysis of aromatic carboxylic acids [carbon atom linked to an oxygen atom and a hydroxyl group (OH), represented as CO_2H].

Applying the tools of organic chemistry to this problem, ORNL researchers followed reactions of their model coal compounds and a polymer analog they had synthesized and related their observations of the pyrolysis chemistry back to coal. They looked for different reaction pathways involving aromatic carboxylic acid, whose existence and abundance in coal was determined by Hagaman using solid-state nuclear magnetic resonance spectroscopy. Their studies showed that thermal decomposition of aromatic carboxylic acids produced carbon dioxide but was not responsible for the formation of the thermally stable cross links, suggesting that computer models for the pyrolysis and liquefaction of low-rank coals should be changed.

So, what was the source of the thermally stable cross links? The ORNL researchers' recent studies suggest that, during pyrolysis, two acids combine to form an anhydride cross link, and a molecule of water is released from the coal. The anhydride undergoes further reactions to form a thermally stable cross link. The chemists further suggested that coal structure researchers should look for evidence of anhydrides, and that the chemistry of coal liquefaction could be altered to stop anhydride formation, perhaps by running the process with water present.

All these findings could become valuable if the price of oil soars and coal liquids become competitive. It could happen, given the political instability of the oil-producing countries, and the first sign may be an unusually long line at the gas pumps.

The research was sponsored by DOE's Office of Energy Research, Office of Basic Energy Sciences, Division of Chemical Sciences.

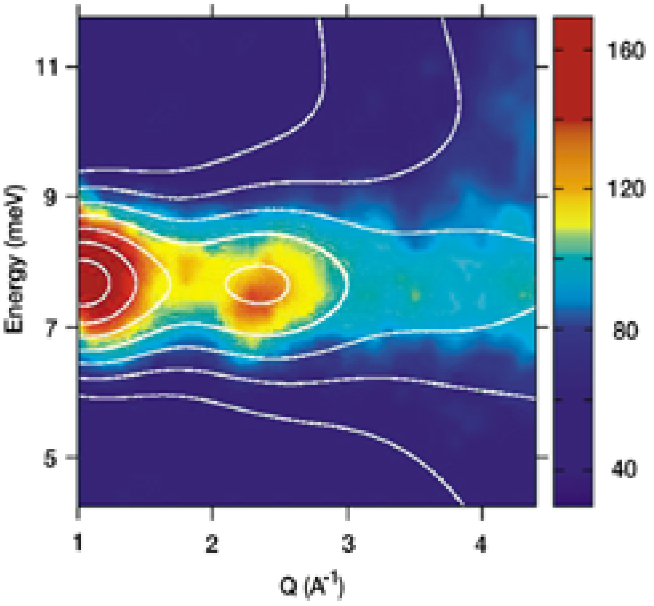
Quantum Leaps in Understanding Quantum Magnetism

ORNL neutron-scattering studies show that magnetic interactions in some magnetic chain materials are very different from what was previously believed.

When we hold a horseshoe magnet, we think of magnetism in three dimensions. Some scientists, however, view magnetism in lower dimensions. In fact, understanding lower-dimensional magnetism may lead to the design of improved superconducting materials with higher transition temperatures. In the high-temperature superconductor yttrium-barium-copper oxide (YBCO), scientists focus on copper, the material's only atom that has significant magnetic properties. Copper atoms exist in YBCO in a one-atom-thick plane (two dimensions) and in long chains (one dimension). Similar structures that have planes or chains containing magnetic atoms are found in many materials.

Physicists refer to the microscopic magnet of an individual atom as the "spin." Spins respond to one another by a mechanism known as a quantum mechanical exchange interaction. Isolated chains of magnetic atoms are referred to as spin chains. Two or more parallel spin chains together form structures known as spin ladders, which actually have a spatial dimension between one and two, which is especially interesting theoretically. Researchers in quantum magnetism are eagerly seeking to discover spin ladders and chains in materials that might lead to new families of high-temperature superconductors.

Scientists had suggested that the best example of a spin ladder found in nature was a phosphate salt containing magnetic vanadium ions, called VOPO [$(VO)_2P_2O_7$]. This idea was widely accepted until neutron-scattering studies of this material by ORNL's Stephen Nagler and colleagues showed that VOPO is really a different type of magnetic beast called an alternating spin chain. Alternating chains and ladders do have some things in common: Both can be visualized as structures composed of interacting "dimer" building blocks, which are pairs of interacting spins. In addition, both have unusual "quantum spin gaps" such as are found in many of the most interesting materials currently studied by solid-state physicists.



Neutron-scattering pattern from a VODPO. White lines are theoretical contours for spin dimer model. ***Digital image enhanced by Allison Baldwin.***

To carry out neutron-scattering experiments at ORNL's High-Flux Isotope Reactor, the group used single crystals of VOPO grown by ORNL's Brian Sales. Andrew Garrett, a graduate student of Nagler's from the University of Florida, assembled an array of roughly 200 millimeter-sized VOPO crystals to make the neutron-scattering studies possible. The other members of the team are Alan Tennant, a postdoctoral researcher who recently came to ORNL from Oxford University's Clarendon Laboratory, and theoretical physicist Ted Barnes.

The single-crystal studies allowed the researchers to determine the spectrum of elementary quantum magnetic excitations (magnons) in VOPO, giving definitive proof of the alternating spin chain model. Nagler and associates also studied isolated vanadium spin dimers in a related material called VODPO. (The sample was provided by C.C. Torardi of DuPont). Here the ORNL studies found yet another surprise: The basic V-V dimer building block had been misidentified. The strong magnetic interaction was not between the closest pair of neighboring vanadium atoms as had been thought, but rather it was between a more widely separated V-V pair with a bridging phosphate (PO_4) group mediating the pair's magnetic interaction.

A third surprise from these studies was the discovery of a new kind of magnetic excitation in the VOPO alternating chains. Instead of seeing one peak from the neutron scattering, researchers saw two peaks. The unexpected peak may arise from a two-magnon bound state. Ted Barnes, who appeared on CNN after predicting the existence of the exotic meson which was detected experimentally in 1997 by DOE's Brookhaven National Laboratory, thinks that bound magnons will be found in magnetic spin ladders as well as alternating chains. Nagler says that the spin characteristics of free and bound magnons make them mathematically similar to mesons. In a quantum spin chain each magnon is really composed of two different quantum excitations called "spinons." Thus a two-magnon bound state has four spinons.

Similarly, mesons are composed of two quarks, and particle physicists hypothesize the existence of a mesonic molecule composed of four quarks (a proton and neutron are each formed from three quarks). Pending the outcome of this research ORNL may be able to claim discovery of an exotic magnetic excitation, which to some scientists, is far more interesting than an ordinary horseshoe magnet.

The research was sponsored by DOE's Office of Energy Research, Office of Basic Energy Sciences.