Chemistry and Materials Science

Lawrence Livermore National Laboratory

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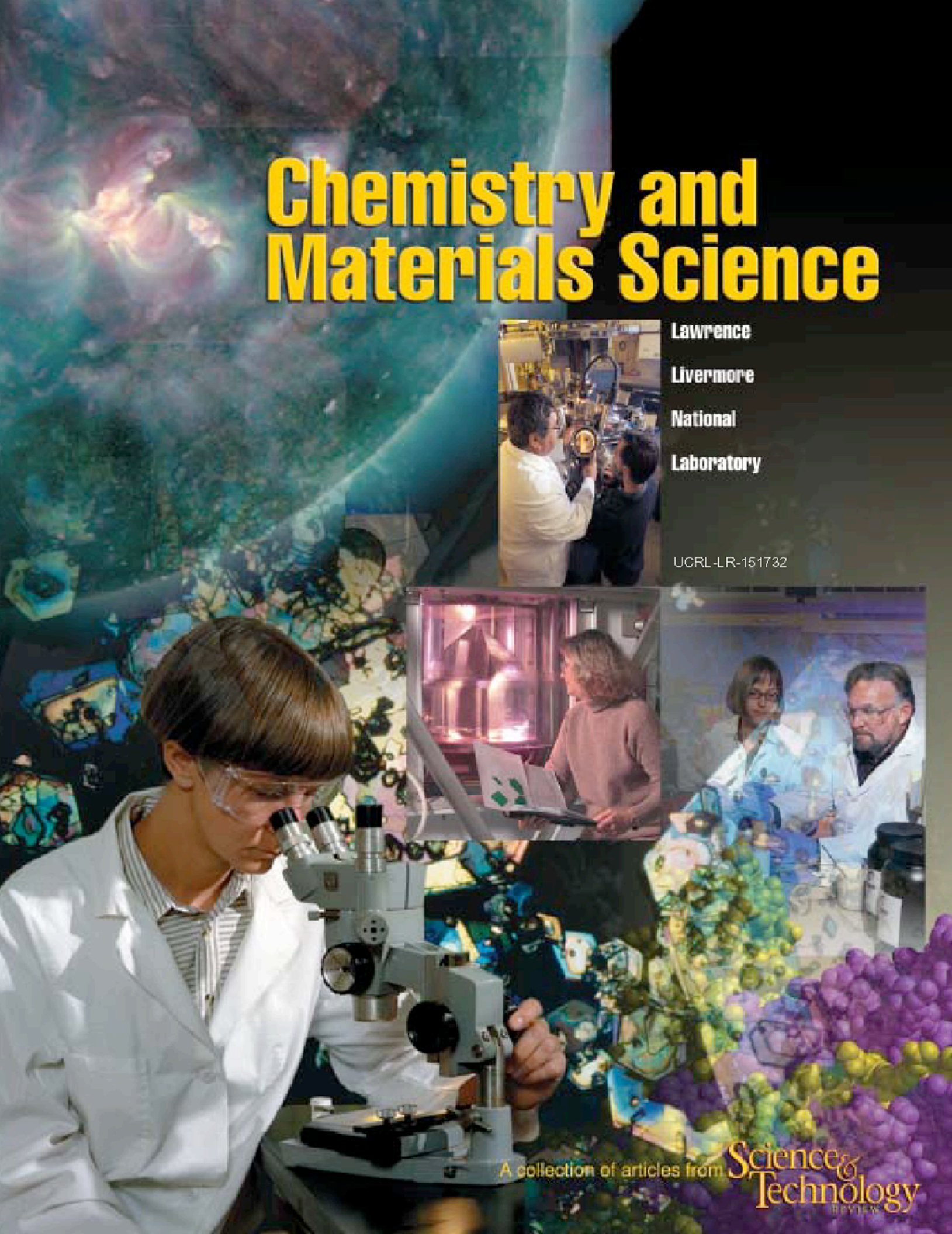
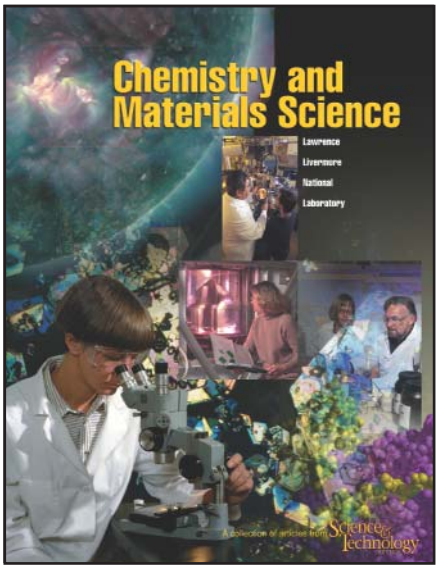


A collection of articles from Science & Technology Review

About the Cover

The Chemistry and Materials Science Directorate (CMS) at Lawrence Livermore performs a diverse body of research, which is demonstrated by the articles included in this publication. That diverseness is also depicted in the cover collage of images of various CMS projects. The round object in the background is the Sun's corona as seen through multilayer optics developed by CMS. In the foreground, from left, a researcher examines high-explosives crystals through a microscope; another researcher looks at a very large potassium dihydrogen phosphate laser crystal grown for Livermore's National Ignition Facility; and two researchers assemble an experimental carbon conversion fuel cell.



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National Nuclear Security Administration

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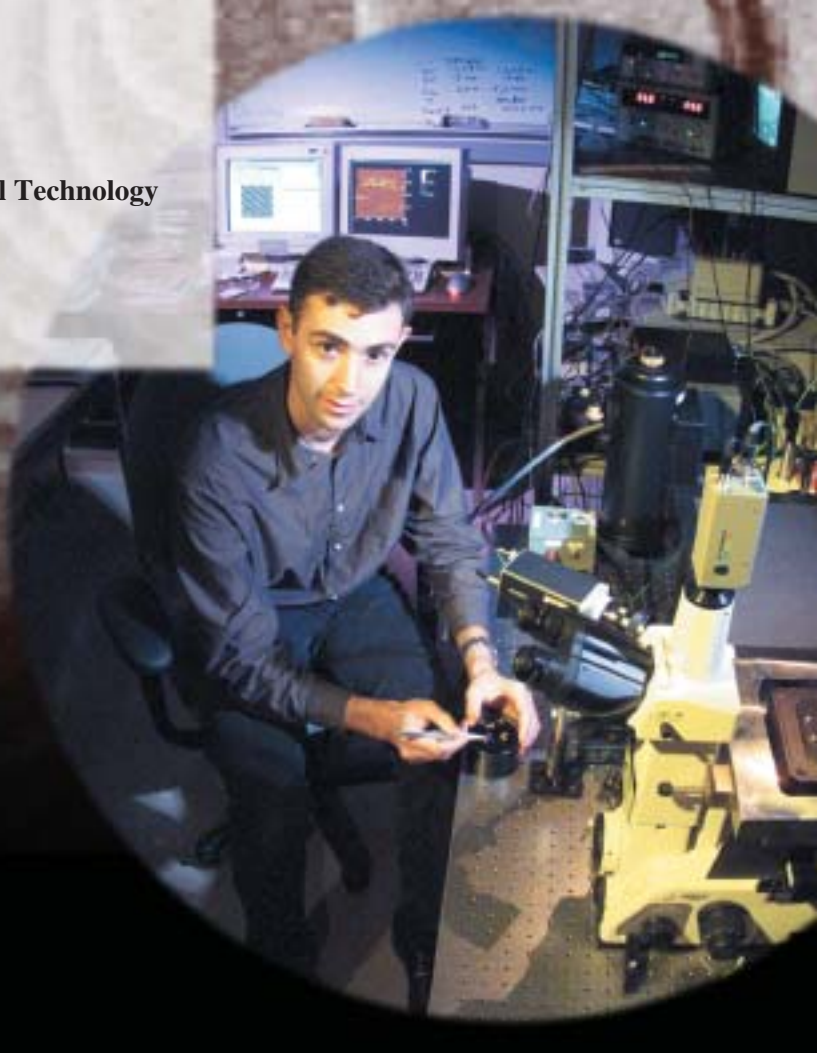
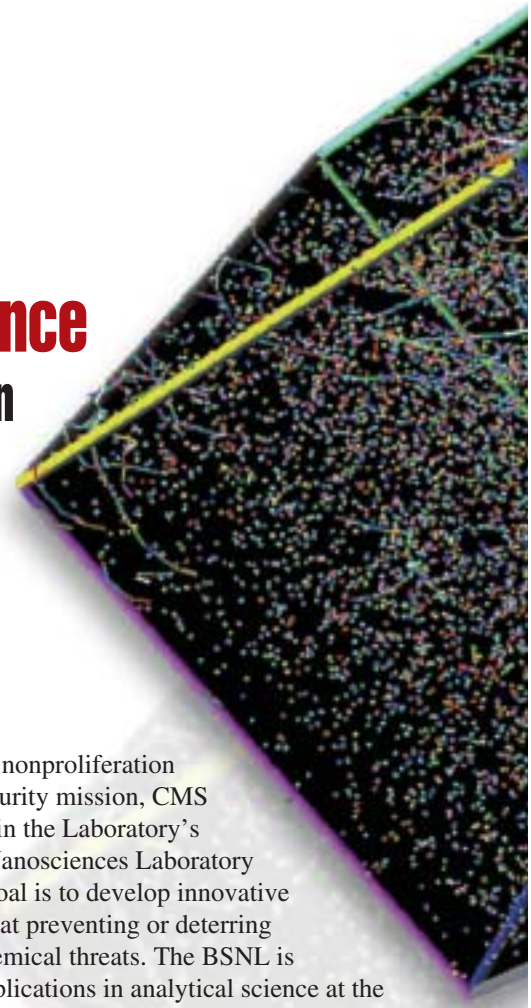


Acknowledgment

The Chemistry & Materials Science Directorate thanks *Science & Technology Review* for the excellence of the articles that represent the directorate and the cutting-edge science performed by it.

Chemistry and Materials Science
Serving the Laboratory and the Nation



THE articles in this publication, reprinted from Lawrence Livermore's *Science and Technology Review* magazine, demonstrate the breadth and depth of scientific research performed in the Chemistry and Materials Science Directorate (CMS). Nationally recognized as a science leader, CMS works to serve national security—Lawrence Livermore's primary mission—both by supporting Laboratory programs and forging ahead in unique areas of chemistry and materials science research.

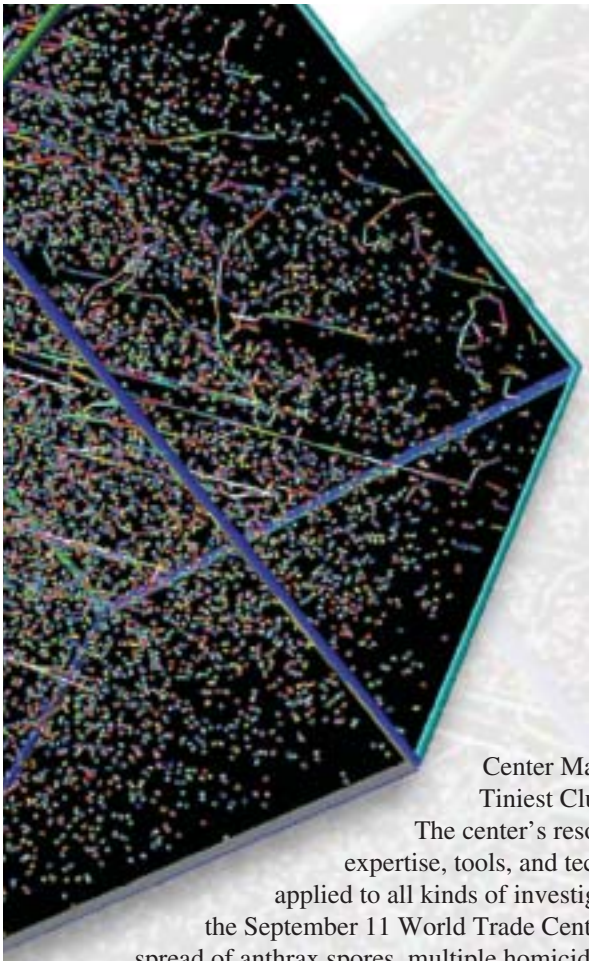
The directorate is an integral part of the Laboratory whose work tradition derives from E. O. Lawrence—performing large-scale science in multidisciplinary teams solving problems that matter to the nation. Now, in an era in which chemical and biological terrorism threaten the globe, compounding the challenges of guarding against nuclear proliferation, CMS is continually advancing and evolving research to deliver on important commitments to other Laboratory programs, thereby continuing its support of an evolving national security mission.

The culture of CMS encompasses state-of-the-art technologies, the best and brightest talent, and a can-do spirit that is unfazed by unexpected challenges while looking forward to future opportunities. This spirit is captured in "Chemistry—50 Years of Exploring the Material World" (beginning on p. 4), which summarizes the growth, opportunities, and evolution of the CMS organization. According to Laboratory Deputy Director Hal Graboske, "For the past half-century, [CMS] goals have been to provide the right people for the Laboratory's programs and a research environment that fosters growth. The people have always risen to the challenge, meeting the changing needs and seizing emerging opportunities over the decades."

How some of those people come to work at the Laboratory is described in the article beginning on p. 11, "The Best and the Brightest Come to Livermore," about Livermore's postdoctoral program that invites the best Ph.D. graduates to apply to be a Lawrence Fellow. Only 1 in 100 applicants is accepted, but many of the fellows become affiliated with CMS and produce remarkably creative research during their tenure as they work alongside more seasoned CMS scientists to develop their skills and talents.

To support the nonproliferation and homeland security mission, CMS researchers work in the Laboratory's Biosecurity and Nanosciences Laboratory (BSNL), whose goal is to develop innovative techniques aimed at preventing or deterring biological and chemical threats. The BSNL is exploring new applications in analytical science at the molecular scale, discovering how to rapidly identify, image, and detect pathogens in new and innovative ways. Similarly, at the Glenn T. Seaborg Institute, they are focused on applying these same techniques to important questions in human health and environmental science. Three articles here explore these technologies. "A Two-Pronged Attack on Bioterrorism" (p.18) discusses how Livermore scientists are designing tiny synthetic molecules to detect biological warfare agents and fight cancer. For cancer therapy, the goal is to use these small, exceptionally high-affinity molecules to deliver a lethal radiation dose directly to a tumor. "Small Science Gets to the Heart of Matter" (p. 26) shows CMS researchers' efforts to find the best ways to detect biological warfare agents. The challenge is in detecting a few molecules of a toxin or a few bacteria or viruses to provide the early warnings of a biological attack. "Machines from Interlocking Molecules" (p. 34) describe CMS scientists exploring ways to control molecules to possibly make sensors that can detect infinitesimal traces of chemicals or biological agents or an on–off switch for molecular computers.

CMS scientists participate in the projects of Livermore's Forensic Science Center, which has a stellar reputation among law enforcement, intelligence, and emergency response agencies and is described in "Forensic Science



Center Maximizes the Tiniest Clue" (p. 38). The center's resources, expertise, tools, and techniques are applied to all kinds of investigations, from the September 11 World Trade Center attack to spread of anthrax spores, multiple homicide case work, and nuclear materials smuggling.

In support of stockpile stewardship, the work discussed in "Nanoscale Chemistry Yields Better Explosives" (p. 46) on sol–gel chemistry and modern-day energetic materials research shows how scientists are designing new materials at the nanoscale to meet exacting performance requirements for explosives. "Plutonium Up Close…Way Close" (p. 49) explores the complexity of plutonium's electronic structure and unique properties. To better understand plutonium, CMS microscopists and materials scientists use state-of- the-art transmission electron microscopy and other tools to investigate microstructure features at the atomic scale.

"Present at the Creation" (p. 52) describes how our nuclear chemists have worked with Russian scientists to discover new elements in the periodic table. They recently synthesized elements 114 and 116, confirming decades-old predictions of the existence of superheavy elements with comparatively long lifetimes. Now, the researchers are studying the chemical properties of elements 112 and 114 and continue their efforts to discover additional new elements.

For Livermore scientists, predicting the performance of advanced materials is essential to success in countless research programs in national security, lasers, energy, and biotechnology. Computational materials science is one of the fastest growing areas within the field of chemistry and materials science. Simulations on massively parallel supercomputers are helping researchers understand how and why materials change and ultimately fail. "Following Materials over Time and Space" (p. 60) illustrates the dynamic presence that Livermore has established in this scientific field.

Livermore has a vital interest in knowing all it can about welding. Dependable welds are important for maintaining the performance and safety of nuclear weapons. Welds will also play a key role in the success of the Department of Energy's planned repository for long-term storage of nuclear wastes, which will potentially be located at Yucca Mountain in the Nevada desert. "Welding Science, A New Look at a Fundamental Technology" (p. 68) examines what occurs during welding.

The National Ignition Facility (NIF), a 192-beam laser that is making tremendous progress toward completion, will allow Livermore scientists to carry out high-energy-density science research unique in the world. A streamlined process to manufacture large pieces of laser glass of high quality is necessary to the success of the NIF. "Big Glass for a Big Laser" (p. 76) highlights a Livermore team and their method of continuous glass melting to make laser glass that meets the exacting standards of NIF.

CMS scientists are supporting the long-term energy and environmental future of the U.S. "Turning Carbon Directly into Electricity" (p. 78) describes a breakthrough technology that pushes the efficiency of using fossil fuels for generating electricity far closer to theoretical limits than ever before. Direct carbon conversion, if adopted on a large scale, would help conserve precious fossil resources by allowing more power to be harnessed from the same amount of fuel.

At CMS, our past is the foundation for a dynamic future, and our workforce is the core that will make this future happen. We are committed to continuing our scientific excellence in support of the Laboratory's national missions. Future compendia of the science being performed at CMS will describe our continuing progress.

■ Tomas Diaz de la Rubia is the associate director for the Chemistry and Materials Science Directorate.

Chemistry—50 Years of Exploring the Material World

OF the 70 or so people who came to work at the Livermore branch of the University of California Radiation Laboratory in September 1952, nearly a third were chemists, chemical engineers, and material scientists, hired to support the Laboratory's fledgling nuclear weapons program. These personnel had two immediate tasks. At the front end of a weapon's development, Livermore chemists had to be able to form parts out of unusual materials such as plutonium and uranium for nuclear test devices. Then after each device was tested, they had to be able to analyze the radioactive components of the leftover debris and gases to help determine the weapon's performance.

Livermore's chemists wasted no time setting up a processing laboratory in the only available room equipped with running water: the women's restroom of the bachelor officers' quarters of the former naval air station that was the home of the new "Rad Lab." By spring 1953, they had also put a laboratory in the former dispensary and set up a chemical fabrication capability in the assembly hall. The women's restroom and the assembly hall were merely temporary measures. The first permanent building at the Livermore site, completed in 1954, was built for the chemistry organization.

As the Laboratory grew and evolved, so did its chemistry organization. From studies of isotopes—particularly in the actinide group of elements—Livermore chemists built a first-class institute to study heavy elements and helped discover new elements. They developed high explosives that were safer but still delivered the power needed by weapons designers, and they tailored other special materials for specific applications. Chemists were the first at the Laboratory to use computers to automate laboratory processes. And their involvement with the computational world didn't stop there. With the explosion in computational abilities and sophisticated experimental capabilities of the past decade, chemists and material scientists are gaining a more complete and fundamental understanding of the behavior of materials as esoteric as aging plutonium and as common as the surface of water.

> *Nothing in life is to be feared.*
> *It is only to be understood.*
>
> *—Marie Curie, physicist and winner of the Nobel Prize for physics (1903) and chemistry (1911)*

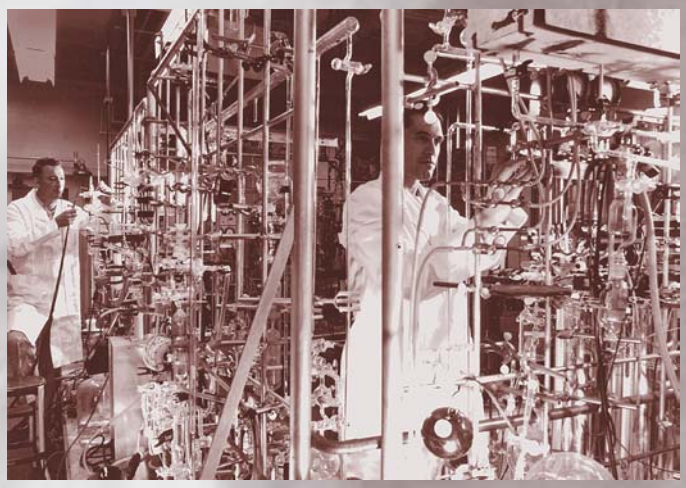
Of Yields, Isotopes, and Heavy Elements

In his preliminary plan for the Laboratory, Herb York, the young physicist whom Ernest O. Lawrence designated to get the Livermore project up and running, made specific note of the need for a radiochemistry group. Radiochemistry, a fairly new field in 1952, is the study of radioactive substances and is closely tied to nuclear chemistry, which is the study of the atomic nucleus, including fission and fusion reactions and their products. Radiochemical diagnostics were crucial to determining how well a device performed in a test. An exploding device produces large neutron fluxes. Those neutrons interact with the device materials, creating different isotopes and other elements. By determining the differences between the materials in the weapon before the explosion and those produced by the explosion, scientists can deduce what happened during the test.

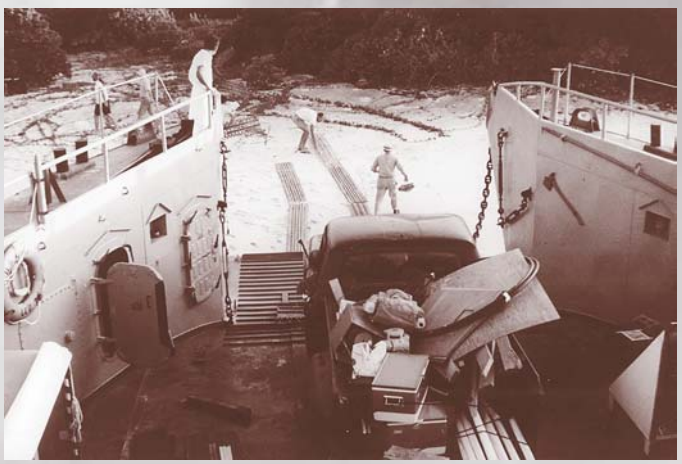
Obtaining those results was a long, extremely complex process, and not without its hazards. (See the box on p. 7.) Livermore conducted nuclear experiments for nearly four decades, at first in the atmosphere and later underground. Throughout that time, radiochemists examined fission products, heavy elements, products resulting from neutron capture, products from other neutron interactions, and short-lived gases. Their results—when combined with results from nonchemical diagnostics (such as those described in *S&TR*, April 2002, pp. 22–24)—gave weapon designers a picture of how well the device worked.

For example, to determine the fusion yield of a device, chemists would add detectors—small quantities of specific elements, such as yttrium—to various parts of a device as it was being made. Radiochemist David Nethaway, who started his Laboratory career during the early days of atmospheric testing, explains, "Certain reactions between neutrons and detector materials such as yttrium only occur when the neutron energies are above a particular threshold." For instance, the reaction that converts an atom of yttrium-89 to an atom of yttrium-88 plus two neutrons only occurs when a neutron with an energy greater than 12 megaelectronvolts (MeV) smashes into the yttrium-89 atom. "By measuring the amount of yttrium-88 in debris samples recovered from the test, we could determine the fluence of 14-MeV neutrons, and from that we infer a fusion yield," says Nethaway. (See *S&TR*, May 2002, pp. 16–21.)

Over time, Livermore's radiochemical expertise was applied to other projects as well. In the early 1970s, radiochemists performed radiological surveys of Enewetak Atoll in the Pacific Ocean to prepare for the islanders' return after the atmospheric tests of the 1950s. The initial focus was on elements of particular use to nuclear weapons research and testing, including the set of elements known as actinides. This work led to the establishment of the University of California's Glenn T. Seaborg Institute for Transactinium Science at Livermore in 1991. Since the Laboratory's early days, Livermore chemists have also been involved in searches for new elements to add to the periodic table. This work includes detailed studies of debris from the Hutch Event, a 1969 underground test specifically designed to produce superheavy



A 1957 photo of Livermore's chemists setting up equipment in a gas analysis laboratory. Rare gases such as krypton and xenon were regularly analyzed as part of the chemical diagnostics for nuclear weapon tests.



In the mid-1950s, inhabitants of Enewetak Atoll in the South Pacific relocated when the U.S. began conducting atmospheric nuclear tests nearby. When the islanders were preparing to reinhabit Enewetak, Livermore led a research force, members of which are pictured here, drawn from 19 federal and scientific organizations to perform a radiological survey of the soils, plants, and marine environment of the islands.

elements, and culminates with the recent synthesis of elements 114 and 116. (See *S&TR*, January/February 2002, pp. 16–23.)

After a decade of underground testing at the Nevada Test Site, Livermore's radiochemists began studying the movement in groundwater of radioactive elements from those tests. Using both radioactive and stable isotope tracers, these scientists investigated groundwater sources, ages, travel times, and flow paths. Having proved their usefulness at the Nevada Test Site, isotope tracer methodologies have since been applied to other water resource projects, including one for the Orange County Water District in southern California. (See *S&TR*, November 1997, pp. 12–17.)

Today, radiochemists and nuclear chemists are also contributing their skills in radiation detection, gamma-ray spectrometry, and mass spectrometry to programs aimed at preventing nuclear proliferation. For example, sophisticated codes originally developed to analyze the complex gamma-ray emissions from nuclear explosion debris now form the standard for analyzing samples collected by the International Atomic Energy Agency (IAEA) and other international organizations. Nuclear chemists are also developing gamma-ray imaging technology that can be applied to a range of counterterrorism applications.

Developing Safe Explosives, New Polymers, and More

In the division assigned to develop and design thermonuclear weapons and testing devices, York also sketched in spots for chemists and metallurgists, noting, "[C]ertain unusual mixtures of materials are very frequently needed . . . and are normally unobtainable outside." Over the years, Livermore's material specialists have dealt with nearly every element in the periodic table. Sometimes they created new materials, and sometimes they synthesized existing materials in unusual or exotic ways or combinations.

At the start, new materials development was strictly related to nuclear weapons and mostly involved unusual alloys (including a corrosion-resistant "stainless" uranium) and plastics. About those earliest days, chemical engineer Barney Rubin recalled, " A major activity was becoming expert in making plastic parts or fabricating components out of weird exotic materials that used plastics as binding agents. We also got heavily into metallurgy. We weren't material scientists in the sense that they are known now. We were sort of kludging things together as best we could—sometimes by intuition and black art, sometimes by science, and sometimes by a combination of the two."

In the area of high explosives (HE), Livermore started pretty much from scratch. The chemists turned for assistance to the centers for HE expertise —Los Alamos and certain Department of Defense laboratories. Livermore's chemists worked closely with weapon designers to develop an HE program that made sense for the design effort, eventually creating the LX series of explosives for Livermore's weapons.

"We had a general goal of trying to get more bang per unit volume," says Gus Dorough, an early leader of the chemistry organization. "It was a point that clearly interested the nuclear

A collaboration with Lawrence Berkeley researchers resulted in the discovery of element 106 in 1974. A separate collaboration (pictured above) with the Joint Institute for Nuclear Research in Dubna, Russia, that began in 1989 led to the discovery of several new isotopes in the early 1990s and in the recent synthesis of superheavy elements 114 and 116.

Fran Foltz examines crystals of the insensitive high explosive triamino-trinitrobenzene (TATB) under the microscope. The background shows TATB crystals at high magnification.

designers, and it turned out to be a very sophisticated and subtle subject. It's not just a matter of more potential energy per unit volume; it's a matter, for instance, of how that energy is released, what kind of chemical detonation products are formed, and the equations of state of those products. Just developing a good technique to measure energy release so we could screen new compounds was no simple matter."

Several empirical tests for measuring HE energy and sensitivity were developed, including the Susan Test (named after Dorough's daughter), which measured safety properties of explosives under simulated accident conditions. Livermore also developed insensitive HE that met the designers' requirements while significantly improving the safety and survivability of munitions, weapons, and personnel. One such, triamino-trinitrobenzene (TATB), is nearly invulnerable to significant energy release in plane crashes, fires, and explosions or to deliberate attack with a small firearm. (See *S&TR*, November 1996, pp. 21–23.)

Polymers—substances made of giant molecules formed by the union of simple molecules—have long been of interest to the Laboratory. In the 1980s, a low-density lightweight polymer called aerogel, first invented in the 1930s, caught the attention of Livermore chemists who went on to create superlight silica aerogels and organic aerogels for the Strategic Defense Initiative. (See *Energy & Technology Review*, November 1994, pp. 16–17.)

Since then, Livermore has developed and improved aerogels for national security applications and synthesized electrically conductive inorganic aerogels for use as supercapacitors and as a water purifier for extracting harmful contaminants from industrial waste or for desalinating seawater. Recently, chemist Glenn Fox led a desalinating project to bring atomic-level control to the design and synthesis of organic aerogels. (See *S&TR*, June 2000, pp. 23–25.) A team headed by chemist Randy Simpson created aerogellike energetic materials with structures that can

Samples from the Sky—Radiochemistry in the Era of Atmospheric Tests

The atmospheric tests of nuclear weapon devices presented unique challenges in data gathering for radiochemists. Right after an atmospheric test, much of the material—radioactive particulates and gases—resides in the signature mushroom cloud. The objective of researchers was to get representative samples of this cloud for analysis.

In an interview conducted nearly 20 years ago, the late Harry Hicks, one of the early radiochemists at Livermore, described what was involved in collecting and processing the samples. The first step was to look at the expected yield of an upcoming test to estimate the size of the cloud and its altitude. "Then you look at the mix of fission and fusion," said Hicks. "The fission products tell you what the radiation level is in the cloud. What you want to do is to send the aircraft in to get your samples, but you don't want to overexpose the crews."

A plane with a Laboratory chemist would be in the air before shot time. After the shot went off, the chemist would observe the cloud and its formation. "If you saw a wisp of cloud or a likely spot," said Hicks, "you'd go over and find out whether it was radioactive or not by flying through to see if you wanted to sample the thing." If the cloud appeared promising, an Air Force sample plane would fly in and obtain a sample. Particulates were captured on large filter papers mounted in pods on each wingtip. Short-lived gases were drawn through the filter, compressed, and stored in 30-centimeter spheres.

Radioactive elements decay constantly, so time was of the essence. Planes landed immediately after obtaining samples, and the samples were removed, packaged, and rushed back to Livermore by courier plane. The samples from Pacific tests normally came in at seven or eight o'clock at night, and the chemical analysis—which took place inside gloveboxes in a building without air-conditioning—began. First, a chemist dissolved the filter papers, a nasty business involving beakers, hot plates, red fuming nitric acid, and hot perchloric acid. Once the papers were dissolved, each desired chemical element had to be completely separated out and completely cleaned of other materials. "Our procedures were relatively new," noted Hicks, "and they weren't exactly reliable, so we would do everything in quadruplicate, hoping we got three, or two, to agree. It just took a long time to be able to say, 'I'm sure that there's nothing but that element there.'"

As the shots got larger, the test clouds got larger and higher, so planes could only sample the tail end of the cloud. In the early 1960s, Livermore researchers had the unique idea of using rockets to determine how representative such samples were. "With remotely controlled rockets, we were able to get samples from higher up and earlier than we could with planes flown by pilots," says retired Livermore chemist John Kury. Results from the rocket tests showed that plane samples—taken later and lower—were indeed representative of the clouds. "At the time, this project made a real difference in our understanding of the radiochemistry needed to analyze device performance," notes Kury, "and it made a real difference for years after, by validating the samples done in earlier tests."

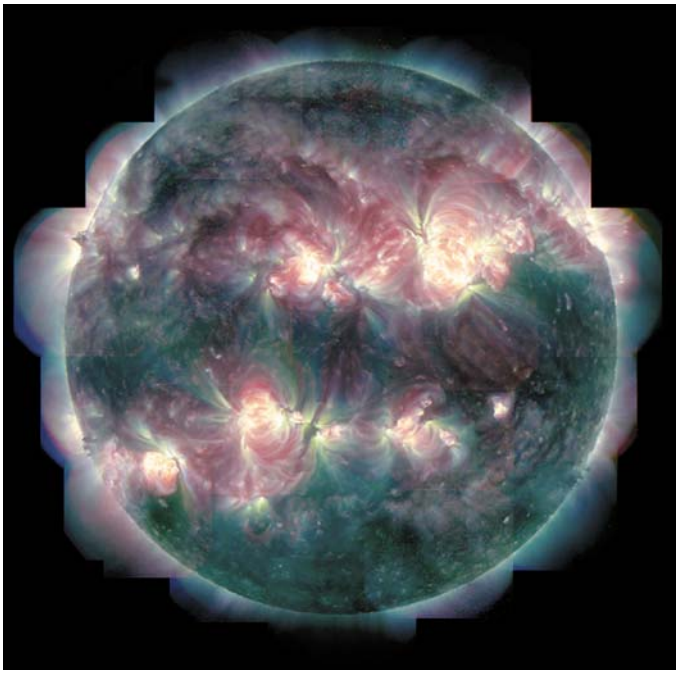
Chemist Harry Hicks ready to board an Air Force RB-57 sampling plane.

be engineered at the nanometer scale. (See *S&TR*, October 1999, pp. 19–21.)

Aerogels aside, polymers have long been used by Livermore's material scientists to create smooth, spherical thin-walled shells or coatings for targets used in laser fusion experiments. (See *S&TR,* June 1997, pp. 22–24.) Another organic polymer, Mercaptoplex, was originally developed at Livermore for use in processing nuclear fuel rods. Mercaptoplex has found another application in removing toxic mercury from industrial waste streams and public water supplies. (See *S&TR*, November 1999, pp. 17–19.)

Multilayers—exceedingly thin alternating layers of materials—are another example of the Laboratory taking an existing material, developing it further, and expanding its applications. First demonstrated more than 50 years ago, multilayers offer extraordinary strength, hardness, heat-resistance, and unexpected new properties. In 1987, chemist Troy Barbee led a team that designed and synthesized multilayer optics for the soft x-ray and extreme ultraviolet regions of the spectrum. Telescopes with these multilayer x-ray optics were used to capture high-resolution, wide-field x-ray images of the Sun. (See *S&TR*, December 1997, pp. 12–19, and December 1999, pp. 11–13.) Multilayer optics are also used in electron microprobes, scanning electron microscopes, and particle beamlines in accelerators. Multilayer optics are crucial to the current collaboration among Livermore, other Department of Energy laboratories, and private industry to develop extreme ultraviolet lithography for manufacturing the next generation of microcomputer chips. (See *S&TR*, November 1999, pp. 4–9.)

A piece of extremely lightweight aerogel poised on soap bubbles. Aerogels have the highest internal surface area per gram of material of any known material and also exhibit the best electrical, thermal, and sound insulation properties of any known solid.



The Sun's corona seen with x-ray optics designed at Livermore.

Delving into Material Behavior and Properties

"Exploratory, basic scientific research is key to the Laboratory's success in fulfilling its missions," explains Hal Graboske, former associate director for Chemistry and Materials Science (C&MS). "In all of our work, we are pushing the frontiers of science and often must know the basics beforewe can proceed with the more complex." To meet the Laboratory's programmatic needs, Livermore's chemistsand material specialists have often returned to the basics, investigating the behaviors and properties of elements and various materials in ever-increasing detail and at more encompassing scales.

Nuclear weapons include highly reactive metals—plutonium and uranium—as well as organic compounds that degrade over time from exposure to radiation, high temperatures, and accumulated gases. In the past, scientists at Livermore studied how various materials aged and interacted under stockpile conditions to guide the selection and use of the best available materials for new weapons. They developed accelerated aging tests, subjecting small samples of candidate materials to elevated temperatures for a day to several months. These tests measured gas evolution, weight loss, and chemical reactions with contacting materials. Materials that passed this screening were assembled into configurations that modeled the material interfaces in the weapon design and tested at temperatures appropriate to service conditions for months or even years.

With the advent of stockpile stewardship in the 1990s, material scientists looked for ways of predicting the lifetime of key weapon materials and developing "age-aware" material

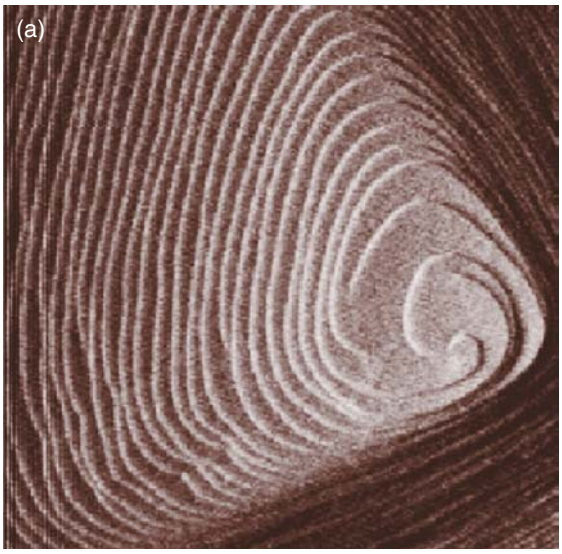
models for use in codes that predict the lifetime of the overall weapon system. (See *S&TR*, September 1999, pp. 4–11.) For example, metallurgist Adam Schwartz is part of a team conducting experiments to measure the structural, electrical, and chemical properties of plutonium and its alloys and determine how these materials change over time. (See *S&TR*, March 2001, pp. 23–25.) "Plutonium is a complex and perplexing element," notes Schwartz. "For instance, it has seven temperature-dependent solid phases—more than any other element in the periodic table. Each phase has a different density and volume and its own characteristics." Instruments such as the transmission electron microscope image the microstructure, allowing researchers like Schwartz to see not just the surface, but the internal structure of the material at the atomic scale, providing the measurements needed for Livermore's material models.

It's not just exotic materials such as plutonium that get the close scrutiny. Water, for instance, was the subject of a recent collaboration between Lawrence Livermore and Lawrence Berkeley chemists. (See *S&TR*, November 2001, pp. 20–23.) Any system involving liquid water—hemoglobin in blood, proteins in water—is affected by the way that hydrogen bonds to the oxygen atoms. The researchers developed a technique using synchrotron radiation to determine for the first time the distance of bonds between hydrogen atoms and oxygen atoms at the surface of liquid water.

The properties and behaviors of materials are also greatly affected by the processes they undergo—whether the process is welding metals or growing crystals. Livermore metallurgist John Elmer has researched details of the welding process since the early 1990s. Dependable welds are important for maintaining the performance and safety of nuclear weapons and play a key role in the long-term storage of nuclear wastes. Recent experiments using x-ray synchrotron radiation have revealed second-by-second changes in a metal's microstructure during welding, providing the first real-time look at the welding process. (See *S&TR*, November 2001, pp. 4–11.)

In the mid-1980s, C&MS researchers began to investigate ways to rapidly grow the crystals used for optical switching and frequency conversion on high-power laser systems. (See *Energy & Technology Review*, November 1994, pp. 3–5.) With the advent of the powerful atomic force microscope in the 1990s, Livermore researchers began to clarify on the nanometer scale the growth mechanisms and three-dimensional structures of widely different solution-based crystals. (See *S&TR*, November 1996, pp. 12–20.)

In the past, advances in materials were accomplished by extensive laboratory testing combined with a healthy dose of guesswork, a time-consuming and often costly approach. As experimental tools such as microscopes have become increasingly powerful, so have the computers used to model and predict material behavior. At Lawrence Livermore, home to some of the most powerful massively parallel computers in existence, C&MS researchers are linking computer simulations to laboratory experiments. (See the box on p. 10.) Codes are now so sophisticated that Livermore researchers are beginning to predict what scientists will see when imaging materials through electron microscopes.



(a) An 8- by 8-micrometer scanned image of the face of a potassium dihydrogen phosphate (KDP) crystal. The morphology and dynamics of crystal growth are relevant to the National Ignition Facility (NIF) as well as to projects that study biomaterials. (b) An example of a large KDP crystal grown for the NIF laser.

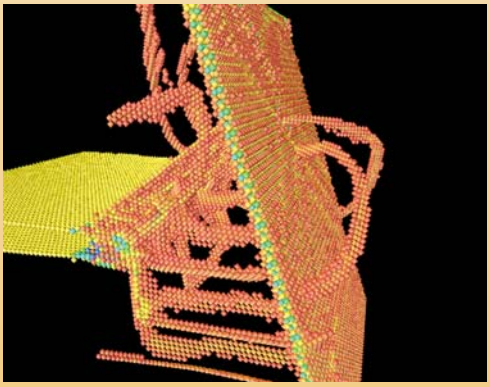
Tools of the Chemistry Trade

The tools of Livermore's chemists and material scientists extend beyond the typical array of glassware and general chemistry apparatus to include nuclear radiation counting instruments, accelerators, vapor deposition equipment, a variety of microscopes and mass spectrometers, and, of course, computers.

Chemists were the first at the Laboratory to integrate computers with laboratory equipment using a PDP-7 in the gas-analysis laboratory in 1965. By 1971, the computer was simultaneously controlling an assortment of experimental equipment including a vacuum-fusion device, a mass spectrometer, an emission spectrograph plate reader, and an automatic sampling atomic absorption system.

As computers evolved, so did the chemistry organization's applications of them. In the mid-1970s, chemistry designed the first completely computerized triple-quadrupole mass spectrometer, a marvel of its time. The system allowed chemists to detect and measure less than 1 nanogram of a sample and was used to analyze trace sulfur compounds in processing oil shale and to investigate the thermal decomposition kinetics of high explosives.

Today, massively parallel computers are a mainstay of efforts to understand material properties and behaviors. For instance, computer simulations of energetic material properties led theoretical chemist Riad Manaa to propose a novel energetic material consisting of a nitrogen analog of the familiar carbon buckyball. (See *S&TR*, June 2001, pp. 22–23.) Chemists are also supporting efforts to model chemical warfare agents by developing kinetic models for surrogate and actual agent chemicals, which could then be used in atmospheric dispersion and other accident and terrorist scenarios. As part of this effort, chemists recently developed the first detailed kinetic model for the agent sarin and modeled comparisons of the chemistry of sarin and its surrogates.



Kinetic model for the agent sarin.

Chemistry's Future Grows with the Laboratory

It's been a long journey for Livermore's chemistry organization from the women's restroom in the old barracks to today's highly sophisticated state-of-the-art laboratories and equipment, from analyzing radiochemical diagnostics for weapon tests to simulating the behavior of materials at the atomic level using supercomputers.

"For the past half-century, our goals have been to provide the right people for the Laboratory's programs and a research environment that fosters growth," says Graboske. "The people have always risen to the challenge, meeting the changing needs and seizing emerging opportunities over the decades." From continued support of the weapons program to dealing with the nation's recent threat of terrorism, the Laboratory's chemistry and materials science experts remain at the cutting edge of scientific discovery.

—Ann Parker

Key Words: actinides, aerogels, atmospheric tests, chemistry, computer simulation, crystal growth, high explosives, isotopes, materials aging, material science, metallurgy, multilayers, multiscale modeling, plutonium, polymers, radiochemistry, radiochemical sampling, welding.
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For more information about the Chemistry and Materials Science Directorate:

www-cms.llnl.gov/

For more about the history of the chemistry organization at Livermore:

www-cms.llnl.gov/50_year_anniversary/

For further information about the Laboratory's 50th anniversary celebrations:

www.llnl.gov/50th_anniv/

The Best and the Brightest

Fewer than 1 percent of applicants become Lawrence fellows at Livermore.

Come to Livermore

Shea Gardner

Wei Cai

Andrew Williamson

WOULD you apply to be a Lawrence fellow, knowing your chances were less than 1 in 100 of being accepted? For the applicants, the stakes are high. But the payoff is great for both the fellows and the Laboratory.

This postdoctoral program is formally known as the Lawrence Livermore Fellowship Program. Informally, it is called the Lawrence Fellowship in tribute to Ernest O. Lawrence, the cofounder of the Laboratory, who cultivated creativity and intellectual vitality in the scientists who worked with him. Lawrence Livermore National Laboratory strives to do the same.

The Laboratory has always been a place where postdoctoral fellows thrive. They can work on state-of-the-art equipment with leaders in their field, performing research in areas of high demand. While all postdoctoral fellows pursue independent research, most are hired by a particular program, usually to perform research for a specific project. Lawrence fellows have no programmatic responsibilities and are given the opportunity to select the group in which they want to work. The allure of freedom and an atmosphere that cultivates creativity, coupled with a competitive salary and Livermore's extensive resources, make the Lawrence Fellowship Program a prestigious opportunity. In exchange, it brings to Livermore some of the most sought-after Ph.D.s in the world.

The fellows produce remarkably creative research during their tenure. Many stay on as full-time career employees, continuing their work. Some leave Livermore to take positions at other institutions. But, as one fellow says, "The ones who leave are ambassadors for Livermore for the rest of their careers."

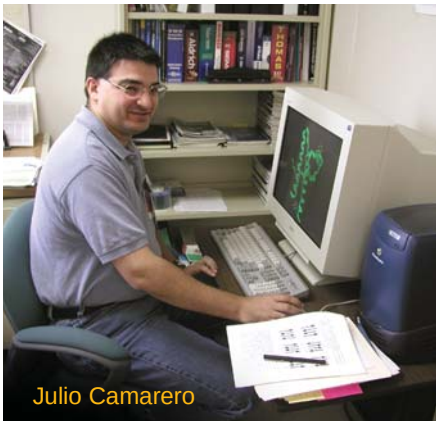
Solution to a Challenge

The Lawrence Fellowship Program was the brainchild of Jeff Wadsworth, former deputy director for Science and Technology. He initiated the program in 1997 in an effort to reverse the effects of the "dot-com" boom, which was leading many young scientists to choose the remuneration offered by private industry over employment with Department of Energy laboratories.

To help persuade the best and the brightest to come to Livermore, the Lawrence Fellowship offers an attractive salary and considerable research freedom. It was modeled after the J. Robert Oppenheimer Postdoctoral Fellowship Program at Los Alamos National Laboratory. In both programs, non-U.S. citizens may apply. Lawrence fellows are hired by the Director's Office, in cooperation with Livermore's University Relations Program.

The new program was first announced in the fall of 1997. Although some Lawrence fellows learn about the program through contacts with Laboratory employees, most applicants find out about it through advertisements in journals such as *Science* and *Nature* or on the Web at either fellowship.llnl.gov/ or www.llnl.gov/postdoc/.

"We are interested in finding people who weren't necessarily thinking about coming to Livermore or who didn't know about Livermore initially," says Harry Radousky, chair of the Lawrence Fellowship Program committee.


Julio Camarero

The fellows are chosen for 3-year appointments by a selection committee consisting of a representative from each of the Laboratory's scientific directorates. The criteria for acceptance are rigorous. Out of 1,849 applicants in the first 4 years of the program, only 15 have been accepted. More recently, 282 applications were received for the program's fifth year, and 2 applicants have been invited to participate.

Each application is read by the selection committee, which looks primarily for leadership of stellar research projects. Applicants must have received their Ph.D. within the last 5 years. The applicant pool is eventually reduced to 6 individuals who undergo a 2-day interview. On the first day, the fellowship finalist gives a seminar on his or her area of interest; has lunch with the committee, which serves as a question-and-answer session; and then meets with current fellows in the afternoon. On the second day, applicants have the opportunity to talk to Laboratory scientists with whom they might be interested in working.

The goal of this process is to find people who will succeed at the Laboratory. The likelihood of success is measured in several ways: by matching an applicant's field of interest with those of the Laboratory, examining the applicant's academic record and publications, and analyzing the research projects the applicant has initiated and the level of innovation those projects represent.

"We're not looking for management skills but at scientific leadership," says Radousky. "The object of the fellowships is to encourage intellectual vitality at the Lab and to recruit the best people in the world," he continues. "What we've discovered is that the application process is an excellent way to attract people to all kinds of positions. Many applicants who don't get into the Lawrence Fellowship Program are awarded postdoctoral fellowships to work in Laboratory programs or are hired as full-time employees."

Olgica Bakajin

Of the 15 individuals who have received Lawrence Fellowships thus far, 3 are now career employees, 2 left to become professors at the Massachusetts Institute of Technology (MIT), 1 went to the National Institute for Standards and Technology, another returned to his native Belgium, and the remaining 8 are still Lawrence fellows.

The Results of Freedom

Freedom to work on projects and with mentors of their choice is what most current Lawrence fellows say attracted them to the program. This freedom, coupled with the Laboratory's interdisciplinary atmosphere, also permits many fellows to move outside their initial area of specialization and investigate other scientific fields.

Wei Cai, for instance, a current Lawrence fellow from China, earned his Ph.D. from MIT. Midway through his graduate work, mentor Vasily Bulatov left MIT for the Laboratory. Bulatov encouraged Cai to apply for the program. Cai was a successful fellowship applicant and has worked not only with Bulatov but also with Malvin Kalos, the father of quantum Monte Carlo simulations. With Kalos, Cai has been investigating how to use Monte Carlo simulation codes more efficiently for modeling the microstructures of materials. Cai has

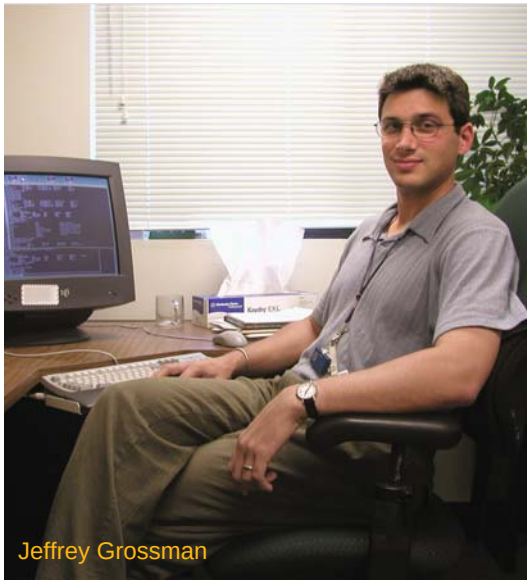
amended some of Kalos's techniques and applied them to small-scale problems with great success. Now, together with Kalos, Bulatov, and other Livermore researchers, Cai is working on a project funded by the Laboratory Directed Research and Development (LDRD) program to apply these techniques to larger, more complex systems. Cai has also been working on a new massively parallel computer code for modeling dislocation dynamics. "What happened here has a lot to do with the academic freedom the fellowship provides," Cai attests.

This freedom also allowed Cai to work on a particularly exciting project far removed from his usual line of research. At the suggestion of Giulia Galli, leader of the Quantum Molecular Dynamics Simulations Group, Cai tried to solve a problem that Galli's group was facing: adding a means of modeling a magnetic field to the electronic structure simulation codes regularly used to model condensed matter systems. Cai devised a code that successfully modeled in two dimensions the behavior of small systems, such as isolated hydrogen atoms and molecules, under an arbitrary magnetic field. The next step will be to apply this method with the more powerful electronic structure codes used for large-scale calculations, such as the modeling of magnetic field effects on the dynamics of fluid hydrogen.

Cai notes that the freedom allowed in the Lawrence Fellowship Program can be almost disconcerting at times. "You need discipline and must be able to make decisions at critical times about what you want to study."

Working at the Nanoscale

Two computational physicists became a team as Lawrence fellows. Jeffrey Grossman, a Ph.D. from the University of Illinois at Champaign-Urbana, and Andrew Williamson, a Ph.D. from the University of Cambridge in England, had known each other for years and both were interested in working with Giulia Galli. Almost immediately after arriving at Livermore as fellows, they applied for LDRD funding to use quantum Monte Carlo simulations to learn more about the characteristics of nanostructures, atomic-scale dots 1,000 times smaller than the width of a human hair. (See *S&TR*, April 2002, pp. 4–10.)

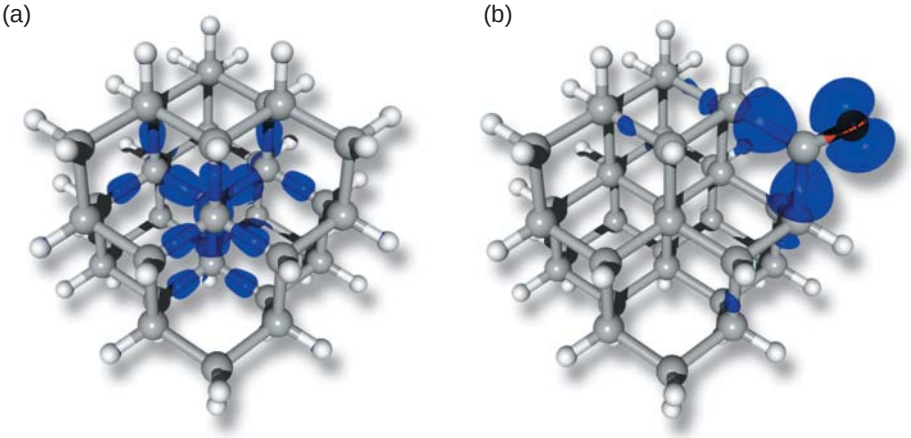

Jeffrey Grossman

"Scientific interest in nanotechnology centers around one very simple concept," says Grossman. "When you make something really small, its characteristics change. At the nanoscale—just a few hundred atoms—a material's properties start changing and become really interesting. Those differences and the ability to control the size of the structures mean that all kinds of new devices could be made—new ways to deliver drugs, storage systems for hydrogen fuel, detectors that can recognize microscopic amounts of anthrax in the air."

Livermore's supercomputers were a major draw for this duo because quantum Monte Carlo simulations are computationally intensive. With Livermore's computers, they can do work that they couldn't do at most places.

Another selling point was that Galli's group was beginning a new project on nanoscience when Grossman and Williamson joined the Laboratory. "Part of what makes the Lawrence Fellowship Program so attractive," says Williamson, "is the opportunity to create something new and shape the direction that research takes, rather than

(a) (b)



Lawrence fellows Jeffrey Grossman and Andrew Williamson are using quantum Monte Carlo simulations to research the characteristics of nanostructures such as these silicon quantum dots. (a) A 71-atom silicon quantum dot. Hydrogen atoms (white) bonded to the surface make the material less reactive. (b) When a more reactive oxygen atom replaces two hydrogen atoms, the electron charge cloud (purple) is drawn toward the oxygen atom, dramatically changing the optical properties (wavelength) of the silicon quantum dot.

trying to come in and fit into a slot that was shaped by someone else."

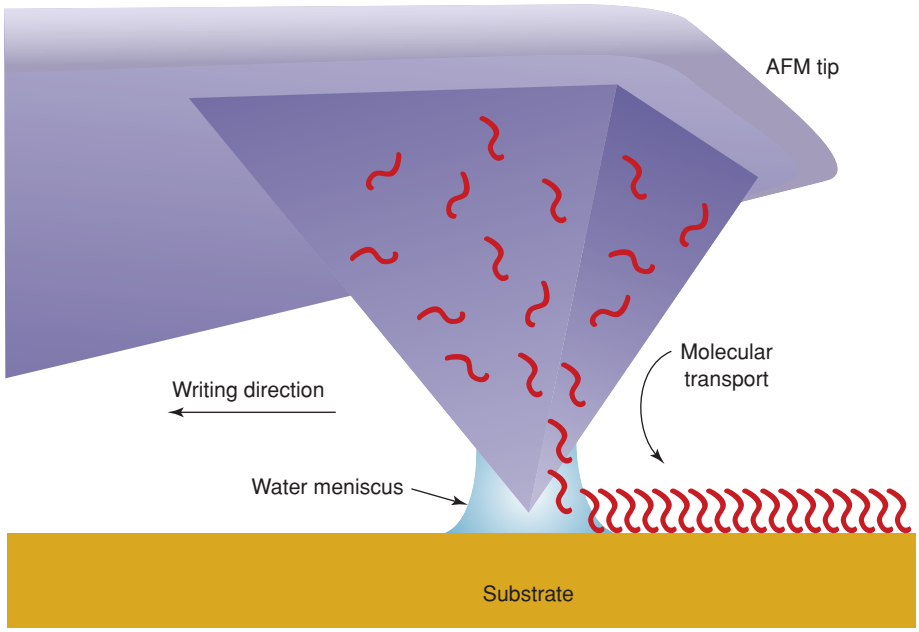
Experimental biologist Julio Camarero, who is also working at the nanoscale, saw the Lawrence program advertised in *Science* and *Nature* while a postdoctoral fellow at Rockefeller University in New York City. Camarero received his Ph.D. from the University of Barcelona.

At Livermore, he started out in the Biology and Biotechnology Research Program (BBRP) but moved to the Chemistry and Materials Science Directorate, where he continues to perform biological experiments. He is a member of a team that aims to use dip-pen nanolithography to create and probe ordered arrays of proteins and colloids. One of the many uses for dip-pen nanolithography is to create tiny sensors that will detect biological warfare agents.

"The Lab is interested in applying science and technology to create tools for national security," notes Camarero. "I think that the technology we have developed is very powerful and has many applications, not the least of which is protecting us from biological terrorism."

In dip-pen nanolithography, the tip of an atomic force microscope is dipped into either an organic or inorganic substance (the "ink") and then is used to "write" on the surface of an inorganic substrate. (See *S&TR*, December 2001, pp. 12–19.) As the tip moves across the surface, it creates a precise, orderly pattern, or template, of material that is in chemical contrast to the substrate surface.

The goal of Camarero's research is to form specific chemical patterns less than 10 nanometers wide on silicon dioxide and gold surfaces. The chemicals in this template will react with proteins, thus making the template a sort of "molecular Velcro" to which the proteins bind in ordered arrays. Use of these templates allows for total control over the orientation of the proteins.



Lawrence fellows Julio Camarero and Aleksandr Noy—now a full-time Laboratory employee—are pursuing research using dip-pen nanolithography. This technology uses the tip of an atomic force microscope (AFM) dipped in molecules to "write" on an inorganic substrate. The molecules react with the substrate to create a pattern of nanostructures attached to the substrate. These nanostructures have a variety of scientific uses.

Small, Complex Systems

Kenneth Kim was at the University of Cambridge as a Wellcome Trust fellow in the Applied Mathematics and Theoretical Physics Department when he learned about the Lawrence Fellowship Program from colleagues at the University of California at Berkeley and from Livermore's Web site. Kim works in BBRP's Computational and Systems Biology Division, led by Michael Colvin. "Traditionally, biology has been a qualitative discipline," Kim says. "But mathematics can play an important role in the biological sciences by providing a precise and powerful language to clarify underlying mechanisms and reveal hidden connections between seemingly disparate systems. Mathematical modeling may allow biology to become a predictive science alongside physics and chemistry."

Kim is applying the mathematical methods of statistical mechanics to the study of the astonishingly complex interactions and collective behavior of biological systems. He has studied the collective behavior of interacting bodies (inclusions) in an elastic medium (a cell membrane). The mathematical model that describes this behavior can be used to investigate the mechanism that causes protein inclusions in cellular membranes to distribute themselves into large, stable aggregates as a function of their global shape. This research illustrates the rich interplay between geometry and statistical mechanics that underlies biological and other complex systems.

Kim is also developing a mathematical model for gene regulatory networks. In a gene network, the protein encoded by a gene can regulate the expression of other genes, which in turn

control other genes. A protein can also regulate its own level of production through feedback processes.

"This network of interacting genes is another concrete example of collective behavior exhibiting an amazing degree of complexity at many spatial and temporal scales," says Kim.

Olgica Bakajin of Yugoslavia is yet another fellow working at the nanoscale. Bakajin had completed her Ph.D. at Princeton University and was on her way to the National Institutes of Health (NIH) when Livermore called to inform her that she was a successful Lawrence fellow applicant. Since arriving at Livermore, she has worked on several projects related to the development of novel microstructures and nanostructures. She is designing and fabricating a fast microfluidic mixer for the study of proteins. Just 10 micrometers wide—a human hair is 80 micrometers wide—the mixer can cause proteins to fold and unfold when solution conditions in the mixer are changed quickly and precisely. Bakajin will be using the mixer to examine the kinetics of fast protein folding reactions (an LDRD-funded project) and to investigate the kinetics of the folding of single-protein molecules (a collaboration with NIH scientists).

Robert Heeter

Working with former Lawrence fellow Aleksandr Noy, Bakajin is using carbon nanotubes in microfabricated devices to separate biological molecules. In the future, these microdevices could be used as detectors of chemical and biological warfare agents. "The interdisciplinary atmosphere at the Lab has provided me with lots of research opportunities," says Bakajin. "Right now, I have more ideas for interesting projects than I have time to pursue them."

Here to Stay

Three former fellows are now full-time Laboratory employees, having exchanged some of the freedom of the Lawrence Fellowship for a staff position.

Theoretical biologist Shea Gardner, who studied population biology at the University of California at Davis, worked initially on several computational biology projects, one of which was a mathematical model to tailor chemotherapy treatments for individual cancer patients. Treatment strategies are based on the kinetics of the patient's particular tumor cells. Gardner has filed a provisional patent for this modeling approach and has been contacted about commercially developing the software.

Gardner also worked on biostatistics for the analysis of gene microarrays. A microarray is a glass microscope slide covered with "spots," each occupied by a different gene. (See *S&TR*, March 2002, pp. 4–9.) The entire slide is exposed to a stimulus such as a chemical or a change of temperature, and scientists note how each gene responds to the stimulus. "With microarrays, you can see the expression of over 12,000 genes at once, in a single run," Gardner notes. "Previously, you could look at just one gene at a time."

Gardner is now participating in bioinformatics work for the National Nuclear Security Administration's Chemical and Biological National Security Program, computationally identifying DNA signatures that could be used to detect biological pathogens. She hopes to continue with this research. "Mathematical modeling, biostatistics, and bioinformatics are really different," she says. "Where else would I have had the opportunity to work on all three?"

Aleksandr Noy, a physical chemist from Harvard University, came to Livermore in 1998 to work on high-resolution microscopy. To that end, he developed a new microscope system that combines the topographic capabilities of the atomic force microscope with the spectroscopy capabilities of a confocal microscope. (See *S&TR*, December 2001, pp. 12–19.)

"My interests morphed from just looking at tiny things to fabricating them and using them for nanoscience applications," he says. "Shifting focus like that would not have been possible if I had not been a Lawrence fellow." Noy has worked on several nanoscience projects, including some that use carbon nanotubes in unique ways. Much of his research requires his new microscope to make the results visible.

He now leads a group that is fabricating electroluminescent nanostructures by dip-pen nanolithography. The researchers "write" with a conjugated polymer that emits light when a voltage is applied. Nanowires made of conjugated polymer poly [2-methoxy, 5-ethyl [2´ hexy(oxy)] para-prenylene vinylene], or MEH-PPV, may some day serve as light-emitting nanodiodes. MEH-PPV nanowires are also highly sensitive to light and can serve as tiny optoelectric switches, which today are typically 1,000 times larger than tomorrow's MEH-PPV nanowires will be.

Plasma physicist Robert Heeter heard about the Lawrence Fellowship Program from Paul Springer, a group leader in Livermore's Physics and Advanced Technologies Directorate,

who performs laboratory astrophysics experiments. Heeter has been working with Springer since coming to Livermore in 1999.

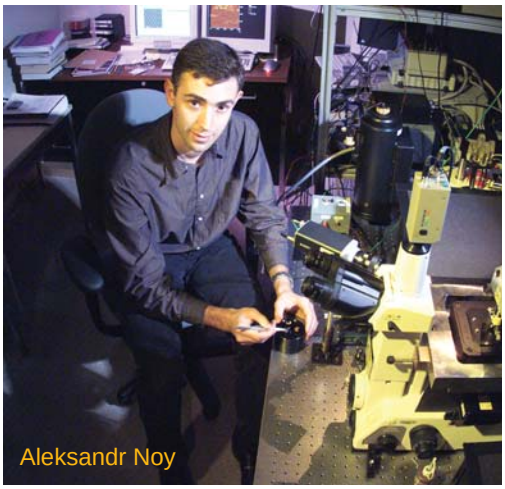
While at Princeton University earning his Ph.D., Heeter worked in England at the Joint European Torus, a magnetic fusion energy facility. But because of funding cuts, magnetic fusion research had fewer opportunities when Heeter was about to graduate. He was also interested in astrophysics, so he decided to apply for a Lawrence Fellowship at Livermore, which had active programs in both astrophysics and fusion energy.

Heeter became a Lawrence fellow and almost immediately got involved in photoionization experiments on Sandia National Laboratories' *Z* Accelerator in Albuquerque, New Mexico. Today, he continues his photoionization research. "I've also been doing other experiments in high-energy-density plasma physics," he adds. "I've stayed in the same group and in the same field that I was in as a fellow. High-energy-density physics experiments have numerous applications: in stockpile stewardship, in inertial fusion, and in astrophysics. And there's a lot of fundamental science to explore that hasn't been done before."

Laboratory Ambassadors

Not all Lawrence fellows stay on as full-time Laboratory employees. The most recent one to depart was metallurgist Christopher Schuh, who left in the summer of 2002 to become a professor at MIT. After completing his Ph.D. at Northwestern University, he came to Livermore to work on grain boundary engineering, in which conventional metallurgical processing is tailored to produce better metals. Grain boundaries—where crystals with different orientations come together—are the weak link in any material. Schuh examined ways to manipulate the orientation of crystals at grain boundaries to create metals with desirable properties such as less cracking, corrosion, and cavitation.

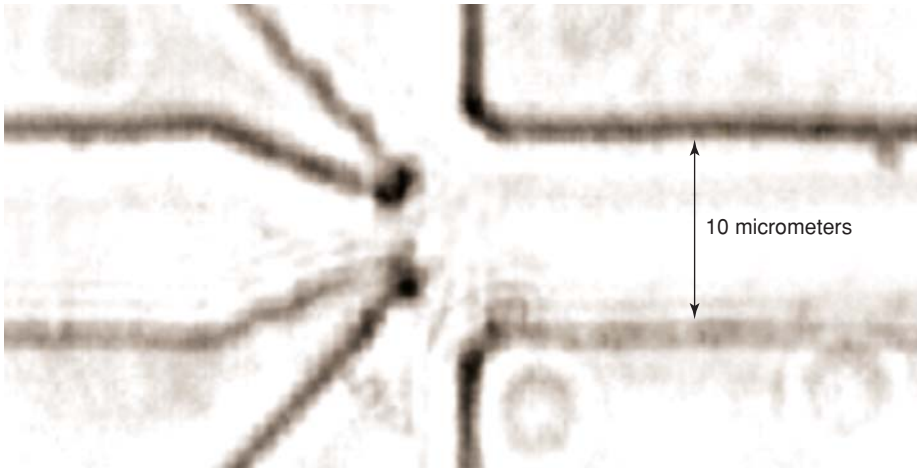
Schuh's research also took him beyond grain boundaries to the individual atoms in the crystals. "If you disturb the atoms in metals so much that the crystal structure no longer looks anything like that of traditional metals, the metals will have very different properties," says Schuh. "We're trying to understand how these changes affect the physics of the metal."


Aleksandr Noy

Schuh notes that postdoctoral fellows typically join a program with the understanding that they have been hired to work with someone on a certain project. "For Lawrence fellows," he says, "there's no such obligation. That gives you complete freedom and a lot of latitude."

Nicolas Hadjiconstantinou received his Ph.D. from MIT and immediately joined Livermore as a Lawrence fellow, deferring a teaching appointment at MIT for a year. While at Livermore, he helped to develop a code that extended the use of direct Monte Carlo calculation from the simulation of dilute gases to the simulation of dense fluids. With this code, Livermore researchers can simulate for the first time the phase change characteristics of a van der Waals fluid.

Joel Ullom, who completed his Ph.D. at Harvard, focused on the development of cryogenic detectors, which are small electrical circuits that produce a current or voltage pulse when hit by a photon or particle. The detector



Olgica Bakajin is designing and fabricating this fast microfluidic mixer used for researching the kinetics of protein folding.

must be cooled to temperatures between 0.1 and 1 kelvin, so that the energy of a single photon will produce measurable heating. Ullom used cryogenic detectors to weigh the protein fragments dislodged from bacterial spores by a pulse of laser light. He also developed refrigeration technology to produce the ultralow temperatures needed for cryogenic detectors. Ullom became a Laboratory career employee before leaving for a position at the National Institute of Standards and Technology.

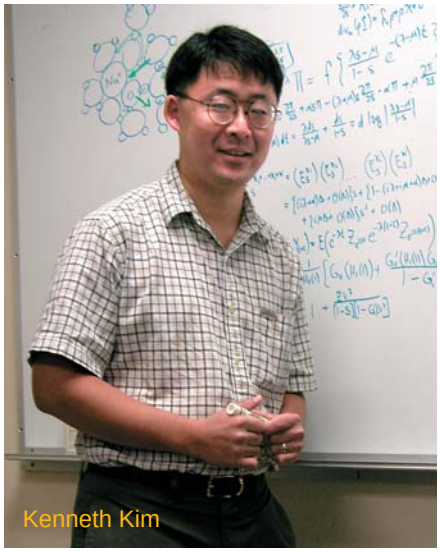
Luc Machiels, a native of Belgium, received his Ph.D. from the Swiss Federal Institute of Technology. After a postdoctoral position at MIT, he came to the Center for Applied Scientific Computing, where he solved problems in continuum mechanics. With colleagues at MIT, he developed a new finite-element error control strategy for the version of the Navier–Stokes equation that describes the motion of an incompressible fluid. The technique, which is both accurate and efficient, calculates lower and upper limits for the output of a system, such as the temperature bounds at the surface of an electronic device. Before leaving Livermore, he also developed new techniques for the solution and modeling of partial differential equations.

One of the research interests Shea Gardner pursued as a Lawrence fellow, which she continues today as a Laboratory employee, is modeling the DNA signatures of viral pathogens. These simulations contribute to technologies for detecting agents of biowarfare.

A Resounding Success

Radousky has only good things to say about the Lawrence Fellowship Program. "We've learned that we can attract really top people to the Laboratory," he says. "This program has attracted the best young scientists to the Lab and promoted university collaborations. It is also an excellent way to do general recruiting."

When the program first started, more fellows were engaged in traditional physics research, while today more are studying biology and nanoscience. This shift is consistent with changes throughout the scientific community. Biological research leaped to the foreground with the success of the Human Genome Project. Many experts predict that the 21st century will be remembered for a revolution in biotechnology and medicine comparable to the advances made during the last century in physics.



Kenneth Kim

Nanoscience is a similarly "hot" research topic. As all kinds of devices in our world become smaller and smaller, nanostructures of all types will find many uses.

All in all, the Lawrence Fellowship Program has been a resounding success in bringing new talent to the Laboratory and encouraging creativity and exciting science.

—Laurie Powers and Katie Walter

Key Words: Lawrence fellows, Lawrence Fellowship Program, postdoctoral positions.

For further information contact Harry Radousky (925) 422-4478 (radousky1@llnl.gov).

For information on the Lawrence Fellowship Program and other fellowship opportunities at the Laboratory, see these Web sites:

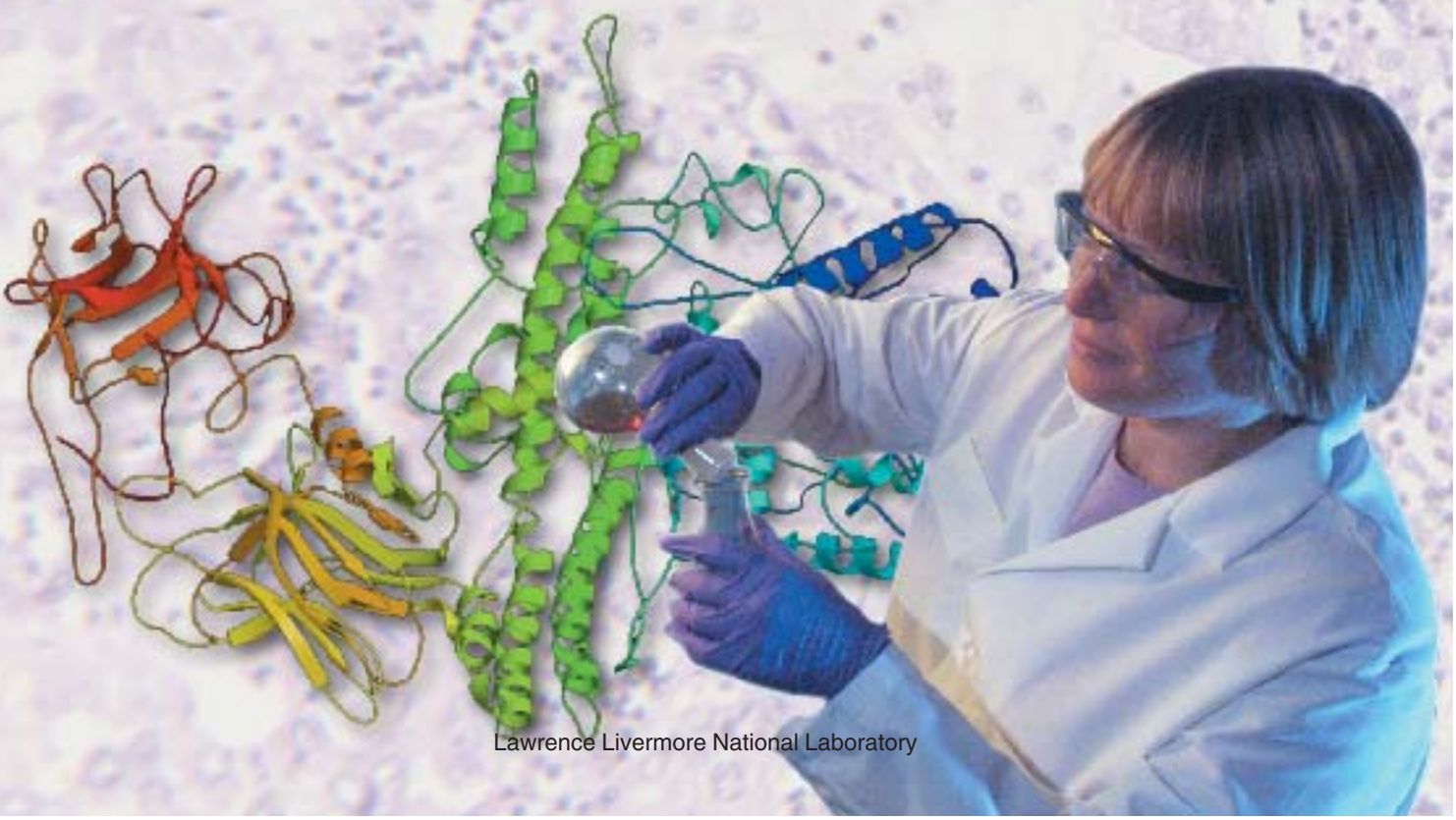
fellowship.llnl.gov/
www.llnl.gov/postdoc/

A Two-Pronged Attack on Bioterrorism

Livermore scientists are designing tiny synthetic molecules to detect biological warfare agents and fight cancer.

NEWLY designed molecules that bind to and capture biowarfare agents are on the drawing board at Livermore. The goal is for these molecules to quickly and efficiently detect such deadly pathogens as botulinum toxin, anthrax spores, or smallpox. Using synthetic chemistry, scientists produce these new molecules that bind to unique sites on the surface of the toxin or organism. Their two-pronged, or bidentate, structure is critical. When a small molecule binds to a protein, the attachment is usually weak, and the interaction between the two is short-lived. If, however, two or more small molecules that bind to the protein are linked together, their binding to the same protein may be thousands, even millions, of times stronger. By targeting specific proteins, the synthetic molecules will mimic some of the behavior in our immune system where antibodies recognize molecular foreign entities in our bodies and abnormalities such as cancer cells.

A single detector armed with many of these synthetic targeting molecules could simultaneously recognize an equal number of harmful biological agents that might be used in a terrorist attack. Assays using antibodies, known as immunoassays, are widely used to identify pathogens in the laboratory and form the basis for many biowarfare detection systems fielded to date.



However, only seven good antibodies are currently available for pathogen detection. Other detectors depend on recognizing the bioagent's DNA. "But some pathogens, such as viruses, require human exposure to only a small number of organisms to be acutely toxic," says Livermore biochemist Rod Balhorn. "With so little DNA present in each virus and given the rapid variation that occurs in the base sequences that make up the DNA, those pathogens are typically very difficult to detect."

Similarly designed targeting molecules could zero in on defective or overactive proteins in our bodies and poison them, just as our natural antibodies do. These antibodylike molecules can lock on to cancer cells or other pathogens and kill them—and only them. By targeting unique sites on other proteins that cause disease—for example, the proteases that cause inflammation in arthritis or enable HIV to function—the synthetic molecules would block the activity of the protein without entering its active site. The active site is a cavity on the surface of a protein that is used by the protein to perform its function. Similar active sites can be present in many proteins, both those that are essential to cell function and others that cause disease.

The pharmaceutical industry has already begun using this approach to develop drugs that function as intended without blocking the activity of healthy cells or proteins. Molecules that target unique sites on the surfaces of specific proteins may soon lead to a new generation of drugs that have minimal side effects.

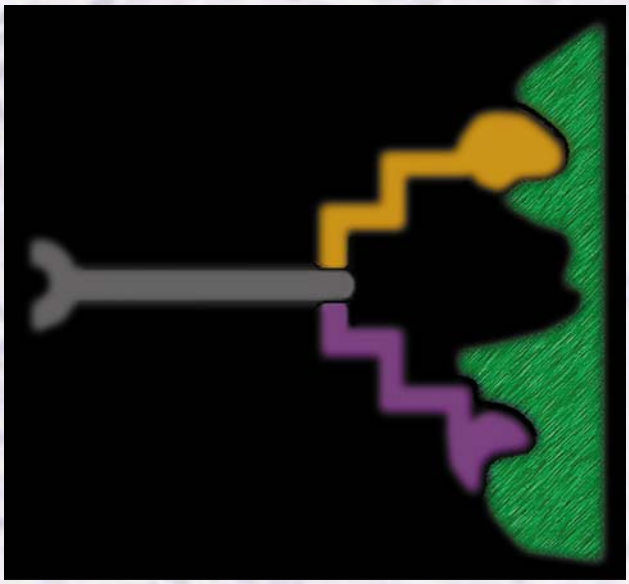
Balhorn is leading the program at Livermore to design synthetic molecules for bioagent detection and cancer treatment. He and a team of Livermore investigators are collaborating with scientists at Brookhaven and Sandia national laboratories and the University of California at Davis Cancer Center. Together, they are developing the methods needed to produce the first of these synthetic antibodylike molecules.

"Terminology is a little tricky," he notes. "It is tempting to call our new molecules 'synthetic antibodies.' But we are designing small molecules that function like antibodies, not large proteins that are synthetic versions of antibodies. So we use the term 'high-affinity ligands' to describe our molecules."

"Ligand" is a general term used to describe a small molecule that binds to proteins or other large molecules. The higher the affinity a ligand has for a specific protein, the more tightly it binds to it. Research by others has demonstrated that bidentate ligands have a vastly increased affinity for the target protein, anywhere from thousands to millions of times greater. Polyvalent ligands—molecules that bind to multiple sites on the surface of a protein—are observed in many biological interactions that require very tight binding. The seek-and-destroy antibodies of our immune system, which normally operate quite successfully, are one example.

"What we're doing is searching for two molecules that bind to two sites next to each other on the surface of a protein," says Balhorn. "Then our synthetic chemist joins them together using a third molecule, called a linker. The linker must be both flexible and robust, or the new molecule will fall apart. This new synthetic ligand will then behave pretty much like an antibody, binding tightly to the protein."

The new bidentate molecules, called high-affinity ligands (HALs), will have several advantages over naturally occurring antibodies. They can be totally inorganic (nonprotein) and can be synthesized in large quantities using methods to ensure that each batch is structurally and functionally identical. They will also be stable over a long period, making them excellent candidates for long-term deployment in detectors for agents of biological warfare.



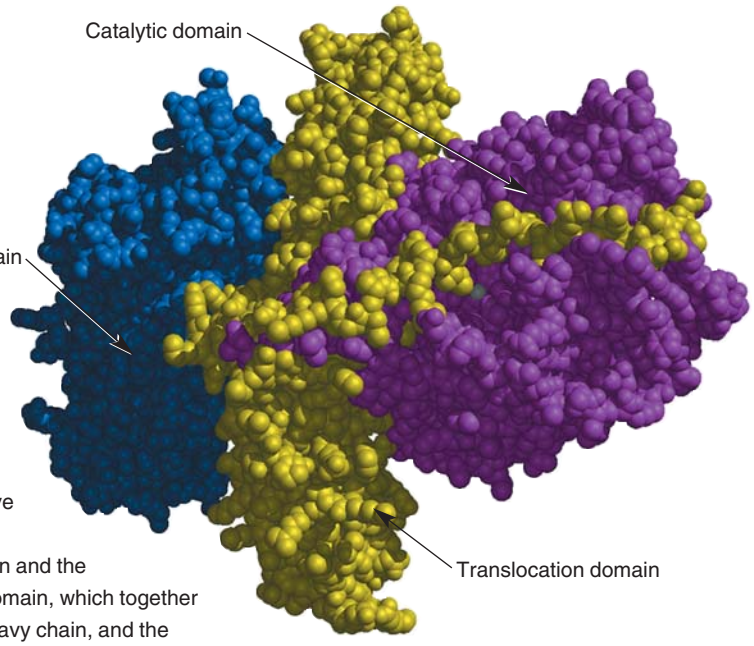
This schematic diagram shows how a linker molecule will connect molecules that bind to two sites on a protein. The goal is to develop a process for designing and producing high-affinity ligands for any structured surface. When two molecules are connected with a linker, they bind with up to a million times higher affinity than does each molecule alone.

The Toxic Targets

As bioagent detectors, HALs can be designed to target protein toxins produced by pathogens as well as any major protein component of pathogenic organisms. For the National Nuclear Security Administration's Chemical and Biological National Security Program, work is under way to develop HALs that bind to the *Clostridium* neurotoxins, which include botulinum and tetanus, the most toxic substances known. The *Clostridium* toxins attack the central nervous system and cause spastic paralysis in the case of tetanus and flaccid paralysis in the case of botulinum.

Balhorn's team is laying the groundwork for future development of HALs to target the *Staphylococcus* enterotoxins, which cause acute intestinal symptoms such as those associated with food poisoning, and ricin, a residue of castor bean processing that causes major intestinal or respiratory complications. The body's response to toxic quantities of either of these substances is swift and often fatal.

Work is also scheduled to begin in the near future on HALs that bind to proteins in the spores of *Bacillus anthracis* (anthrax) and in *Yersinia pestis* (plague). Once these HALs are completed, efforts will focus on the next highest priority agents: smallpox, *Francisella tularensis* (a plaguelike illness), and *Brucella melitensis* (an organism whose infections, often called Mediterranean fever, cause spontaneous abortions). Creating synthetic ligands even for proteins with a known structure is still a research project. Work began in 2000, and Balhorn estimates that high-affinity ligands for these eight bacterial toxins and threat organisms can be delivered in about 2005.



Clostridium neurotoxins have three parts: the targeting domain and the translocation domain, which together make up the heavy chain, and the catalytic domain, which makes up the light chain and is the toxic part of the molecule.

Got Structure?

If the structure of the target protein is known, the team uses that structure to develop a HAL. Work on these molecules is a logical progression from Livermore's protein structure and computational biology effort, with which Balhorn has been involved since its inception. (See *S&TR*, April 1999, pp. 4–9.) Using x-ray crystallography and nuclear magnetic resonance (NMR) spectroscopy, high-resolution structures for many proteins have been determined at laboratories around the world, including Livermore. These include several types of *Clostridium* toxins (botulinum and tetanus) and the *Staphylococcus* enterotoxins.

All toxins in the *Clostridium* family have three parts. The targeting (or binding) domain, which binds to receptor molecules on the nerve cell membrane, and the translocation domain, which makes a pore in the cell through which the toxin passes, together make up what is known as the heavy chain. The light chain, which contains the catalytic domain, is a protease that is injected into the nerve cell and disrupts its functioning.

For the *Clostridium* neurotoxins, the team is developing a HAL to bind to the targeting domain, that fragment of the protein that recognizes and binds to motor neurons. Of these neurotoxins, botulinum is considered a greater threat than tetanus, but tetanus is easier to work with. Fortunately, its targeting domain is sufficiently similar in structure to botulinum's that it serves as a model for botulinum.

In 1998, Livermore's x-ray crystallography group completed a high-resolution structure of the binding domain of the tetanus toxin. Researchers then computationally calculated the molecular surface of the protein to identify sites where binding is likely to occur. "We look

for pockets on the surface of the folded protein, places where another molecule would be able to fit tightly," says computational chemist Felice Lightstone. For the tetanus toxin, Lightstone found two appropriate sites adjacent to one another on the binding domain.

For a HAL to be effective, the sites designated for binding must be on a part of the toxin that is "conserved," meaning that these regions remain essentially identical across all strains of a toxin. When bioagents are being genetically engineered, areas such as these are difficult to modify without altering the toxicity of the agent. Ideally, a high-affinity ligand for tetanus toxin will be able to recognize engineered and other unknown or related *Clostridium* toxins.

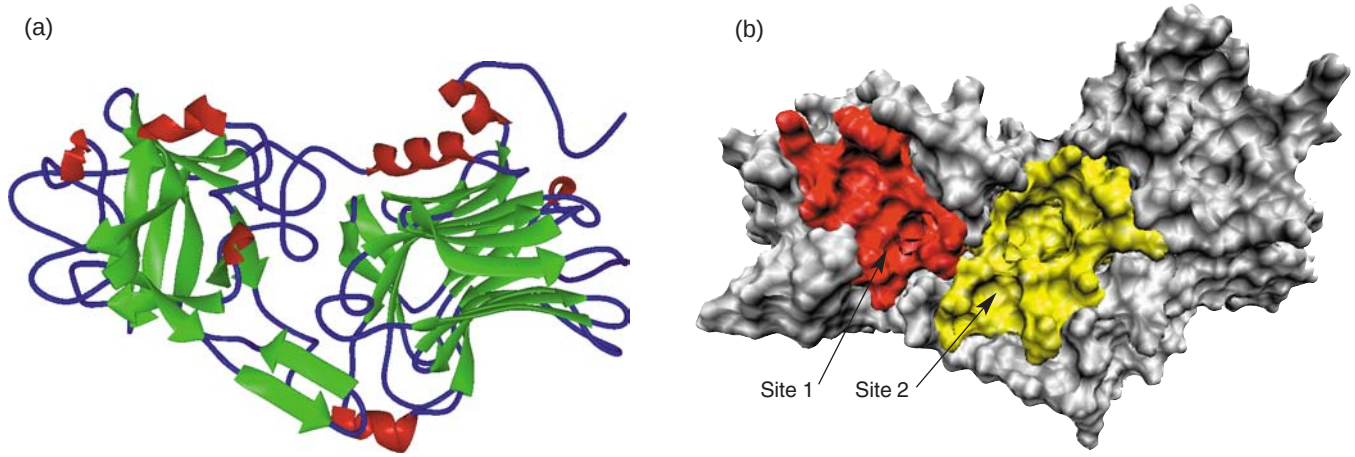
The next step involved selecting compounds that might fit into the two sites. All of the 300,000 compounds in the Available Chemicals Database, a listing of all commercially available compounds, were computationally inserted (docked) into each site. The potential fit and interactions were then assessed. The top 1,000 compounds were run again using a range of structures for each compound representing the different bond orientations and shapes, known as conformations, that each molecule is likely to adopt. In this manner, the top 100 compounds were identified. The calculations for each site took about 3 weeks on a Linux cluster of 40 dual-processor personal computers.

Sandia National Laboratories in Livermore has recently written new programs to expedite this time-consuming process. Each compound is tested in 10 different conformations to see which fits best into the rigid protein. This provides a more realistic test of binding, because many of these small molecules are not rigid and can adopt different conformations. "Computational docking projects typically have success rates of anywhere from 10 to 40 percent," says Lightstone. "Even before we started using our new version of this program, our success rate of identifying molecules that actually bind to the protein was in the 40- to 65-percent range. Now, the likelihood of getting a fit may be even greater."

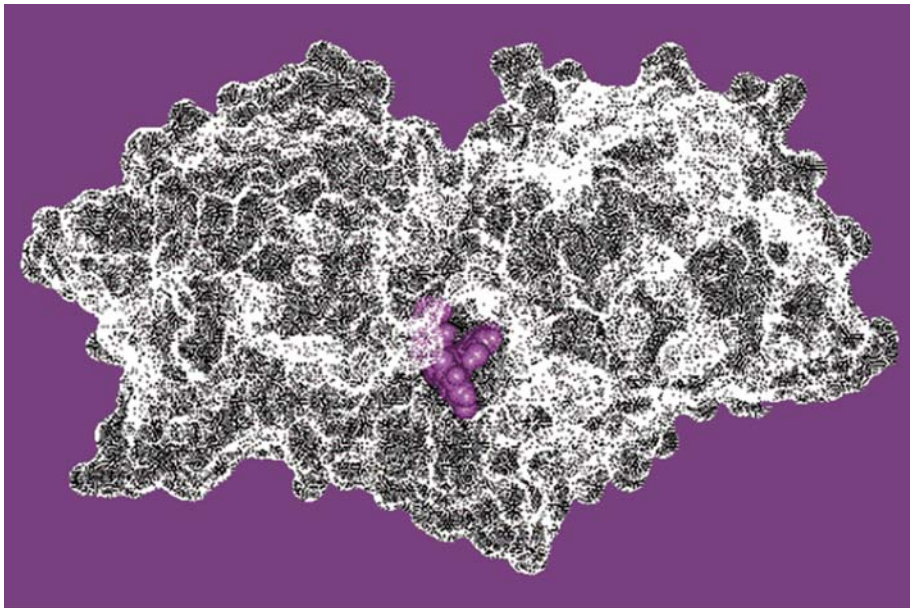
Into the Laboratory

Once possible ligands have been identified computationally, they must be tested in the laboratory to see whether binding actually occurs. Mass spectrometry (MS) and NMR spectroscopy are both effective for testing ligand–protein binding. NMR examines binding in the solution state, while MS looks at binding in the gas phase. MS typically requires much smaller samples, but it cannot handle certain compounds or chemical buffers. NMR can examine mixtures of compounds more easily and determine which combinations bind best in solution. Both techniques can identify where on the target protein binding is occurring.

The initial computational screening process to find new compounds that bind to tetanus neurotoxins resulted in 100 possible ligands that were predicted to bind to one of two sites (site 1 and site 2) on the tetanus neurotoxin's targeting domain. Experiments using electrospray ionization–mass spectrometry (ESI–MS) suggested that



(a) The x-ray crystal structure for the tetanus toxin showing how the amino acid chain is folded and (b) its calculated molecular surface showing sites 1 and 2, predicted binding sites for ligands.



The predicted structure of the tetanus–lavendustin A complex. Lavendustin A is shown in purple binding to site 2.

7 of the first 13 tested compounds bound to the toxin. With ESI–MS, ligand binding is confirmed when a new mass peak appears at the expected mass-to-charge ratio for the ligand–tetanus complex.

The antitumor drug doxorubicin was discovered to be the best fit at site 1. The binding of this ligand to site 1 was later confirmed by x-ray crystallography of doxorubicin–tetanus toxin and doxorubicin–botulinum toxin complexes. For site 2, the same MS method was used to screen 1 of 100 compounds, six of which were observed to bind. The figure above shows one of these ligands, lavendustin A, docked into site 2 in the predicted structure of the tetanus–lavendustin A complex.

The six ligands predicted to bind to site 2 were then screened for binding to the targeting domain using NMR. The six molecules were tested individually, as mixtures of different combinations of the compounds, and in the presence or absence of the known site 1 binder, doxorubicin.

When examined by NMR, small molecules exhibit weak, negative signals referred to as NOEs (nuclear Overhauser effects). Large molecules such as proteins exhibit strong, positive NOEs. When small molecules bind to proteins, the characteristics of the NOE for the large molecule are transferred to the small molecule. Thus, strong NOEs are detected for ligands that bind to the protein.

The NMR screening of mixtures containing the six predicted site 2 ligands confirmed that four bind to tetanus toxin in solution. Using a novel transfer NOE (trNOE) competition assay, researchers have determined that three of these ligands bind in the same site, presumably at site 2. The fourth ligand was determined to bind in a third site distinct from site 1 and site 2.

NMR experiments were also performed to evaluate how possible structural changes induced by the binding of one ligand in site 1 could influence the binding of the second ligand in another site. In these experiments, doxorubicin, which was added first, remained bound to site 1 throughout the additions of all six of the predicted site 2 ligands. The mixture containing doxorubicin and lavendustin A produced the strongest positive trNOE signal in the presence of the tetanus toxin. This experiment confirmed that both lavendustin A and doxorubicin bind simultaneously to the toxin, indicating that each must bind to a different site.

"Unfortunately, this assay cannot define the location of the binding site," says physical chemist Monique Cosman, leader of the NMR group at Livermore. "But since doxorubicin is known to bind to site 1, we know that lavendustin A must bind to a different site, which may be site 2.

By performing these trNOE binding experiments with pairs of molecules that were determined to compete for binding to the same site, Cosman developed a new NMR method for identifying the relative strength of binding of each ligand to a particular site on the protein. MP-biocytin, another molecule that binds to site 2, did so with a relatively lower affinity than lavendustin A. The affinity of the third ligand is similar to that of lavendustin A, but it was not studied further because it is too perishable.

Mass spectrometry was then used to verify where the molecules are binding. Chemist Sharon Shields developed a new method that combines MS with proteolysis, a process in which a protein is digested by enzymes. "This is unique," she notes. "Now we can study solution-phase biological processes using a gas-phase mass spectrometric method."

She first treated the targeting domain of tetanus toxin with proteases that make clips in the amino acid chain either alone or on the tetanus–

doxorubicin complex using various ratios of doxorubicin to the neurotoxin. Then she used matrix-assisted laser desorption ionization and ESI–MS to determine the pattern of enzymatic degradation that had occurred. In the tetanus–doxorubicin combinations, doxorubicin prevented the enzyme from digesting the protein at the binding site by limiting access to the amino acids located in that region.

The figure below shows a map of peptides (amino acid chains) produced by digesting the tetanus–doxorubicin complex compared to the tetanus toxin alone. In this experiment, Shields used the enzyme trypsin. The decreased abundance of peptides indicates the location where binding is occurring. That location contains amino acids 299–304, 351–376, and 394–434. Molecular docking calculations had predicted that doxorubicin would reside near amino acids 356, 358, 359, 407, 409, 419, 427, and 437. These predictions are a close match to MS results. Comparable locational experiments using other enzymes had similar results.

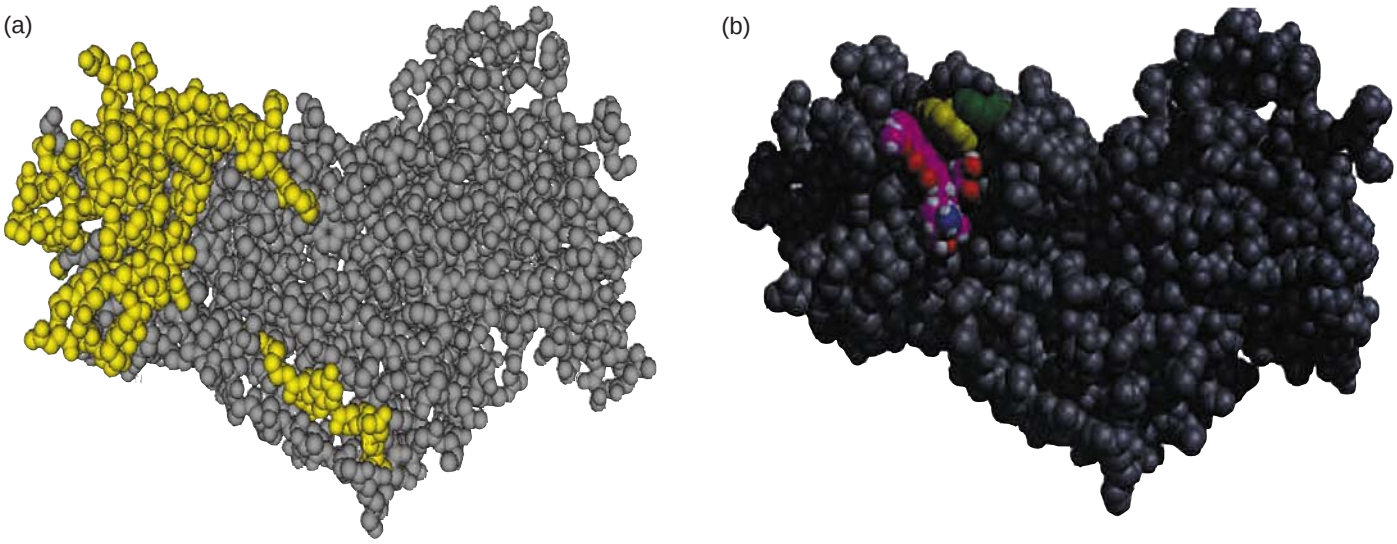
Shields also found that the presence of doxorubicin induces subtle changes in the tetanus toxin's three-dimensional structure, suggesting that the protein may envelope, or wrap around, doxorubicin when it binds. Further experiments are needed to confirm these results.

Creating a New Molecule

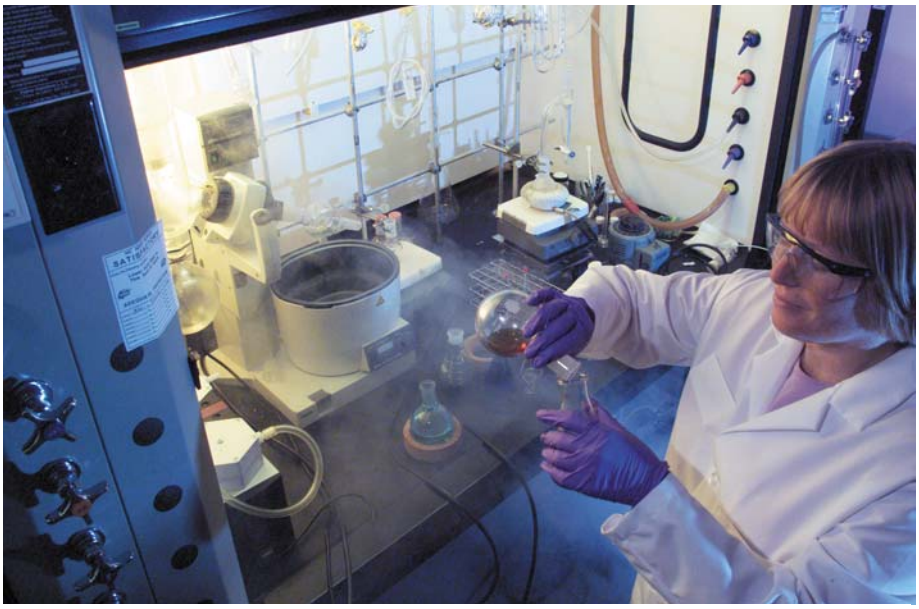
Synthetic chemist Julie Perkins has the job of linking the two molecules that bind to sites 1 and 2 to create a new HAL. This is the critical step. She is experimenting with linkers that will connect doxorubicin and MP-biocytin as well as doxorubicin and lavendustin A. "We know that each of these compounds binds individually to sites 1 and 2, but because they bind weakly, they can also float away," Perkins says. "When the compounds are linked together, they are much more likely to stay bound.

She is starting with the amino acid lysine as a linker. Lysine is an ideal building block because it has three distinct functional groups upon which she can perform synthetic chemistry experiments. Many derivatives of lysine are commercially available as well. The molecules that have been identified to bind into site 1 and site 2 can either be attached directly to lysine, resulting in their close proximity, or with a linker, which increases the distance between them. Increasing the distance between the two compounds with a flexible chain may also help increase the affinity of the ligand for the protein.

"To achieve maximum affinity of the ligand for the protein, we have to find the optimal length and rigidity of the linker," says Perkins, "and that can only be done experimentally." She is experimenting with a flexible glycol chain that can be attached to the lysine to increase the distance separating the two ligands.



(a) This map of peptides (amino acid chains) compares the doxorubicin–tetanus toxin complex to the tetanus toxin alone. Amino acids in yellow represent the peptides that showed a decreased abundance, which indicates that binding is occurring. (b) Computational docking studies predicted that binding would occur at the location shown. The two match quite well.



Synthetic chemist Julie Perkins works to link two molecules, each of which binds to two protein binding sites. The new molecule will bind more strongly and securely to a specific toxin protein than the individual molecules can.

Once she has synthesized each new compound containing the two linked ligands, conventional binding studies will identify the highest affinity and most selective ligand combinations. These studies will determine how tightly the HALs bind and confirm that they selectively bind only to *Clostridium* neurotoxins.

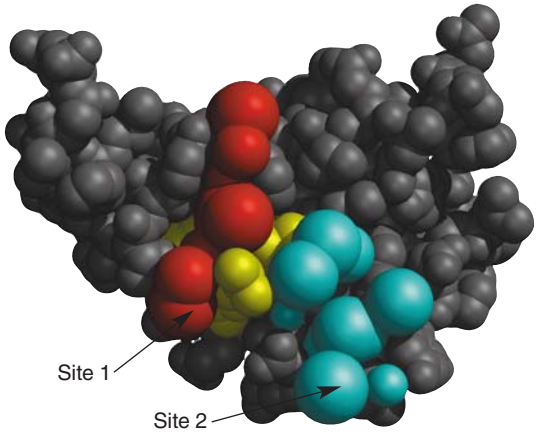
Targeting Cancer

For cancer therapy, the challenge is to synthesize molecules that bind with high affinity to each cancer cell without themselves generating an immune reaction from the body. Targeting molecules therefore must be smaller and more specific and have higher affinities than natural antibodies. They should also not be made of proteins, which elicit an immune response from the body.

The goal is to use these small, exceptionally high-affinity molecules to deliver a lethal radiation dose directly to a tumor. In this case, the HALs would be tagged with radioactive isotopes and introduced into the body. Research all over the world is focused on this new technique, known as isotopically enhanced molecular targeting.

To create new HALs for cancer treatment, Livermore is using the same process developed for producing HALs that bind to toxins and pathogens. The first project will be a HAL for a receptor protein found on the surface of non-Hodgkin's lymphoma, HLA-DR10. The crystal structures of four HLA-DR molecules are known, and unique binding sites on the HLA-DR10 protein have been identified using computer models of the protein generated by computational biochemists Adam Zemla and Daniel Barsky. Computational docking experiments are under way.

The HAL developed for binding HLA-DR10 and targeting human lymphomas will be designed to rapidly pass through the liver and kidney and thus minimize the systemic damage that can occur when antibodies carry radionuclides. "We are striving to convert the meaning of the word 'cancer' from 'fear, pain, suffering, and death' to 'just another treatable disease,'" says Balhorn.



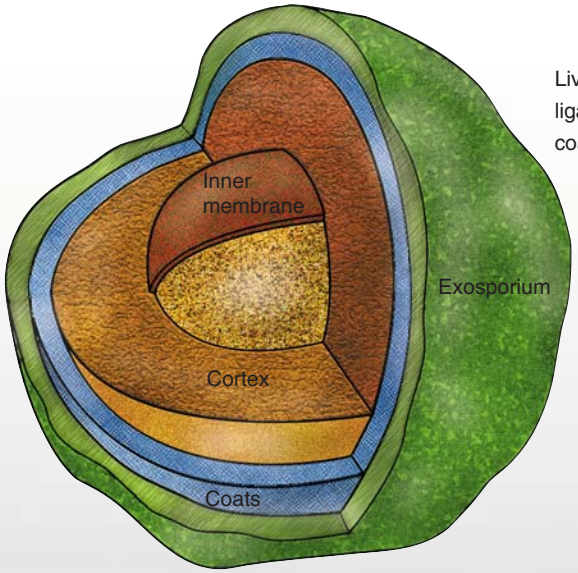
Sites 1 and 2 on the HLA-DR10 molecule (a protein receptor for non-Hodgkin's lymphoma) have been identified.

Targets of Unknown Structure

When a target protein's structure is not known, the team will use a different route to design and synthesize HALs. Computers cannot be used to predict the binding of molecules to

sites on these proteins. But NMR and MS processes that are being developed and fine-tuned now for identifying ligands that bind to known protein structures will identify ligands that bind to unknown structures.

Libraries of molecules will be experimentally screened for their ability to bind to the protein using a combination of Cosman's NMR technique and mass spectrometry methods being developed by chemist Lori Zeller. The molecules that bind will be segregated into sets that bind to different sites. Perkins will then synthesize all possible combinations of pairs of these small molecules using a series of different-size linkers. With Livermore's new Fourier transform ion cyclotron resonance mass spectrometer, mixtures of the HALs and protein can be quickly screened to identify the particular combination of ligands and linkers that produce HALs that bind to the protein. This approach should work well for creating detection reagents for pathogens. In collaboration with groups at Porton Down Defense Science and Technology Laboratory in England, Livermore researchers will design the first HAL for a protein with an unknown structure to bind to a protein on the coat of the anthrax spore.



Livermore will design a high-affinity ligand to bind to protein in the spore coat of *Bacillus anthracis* (anthrax).

Measuring Success

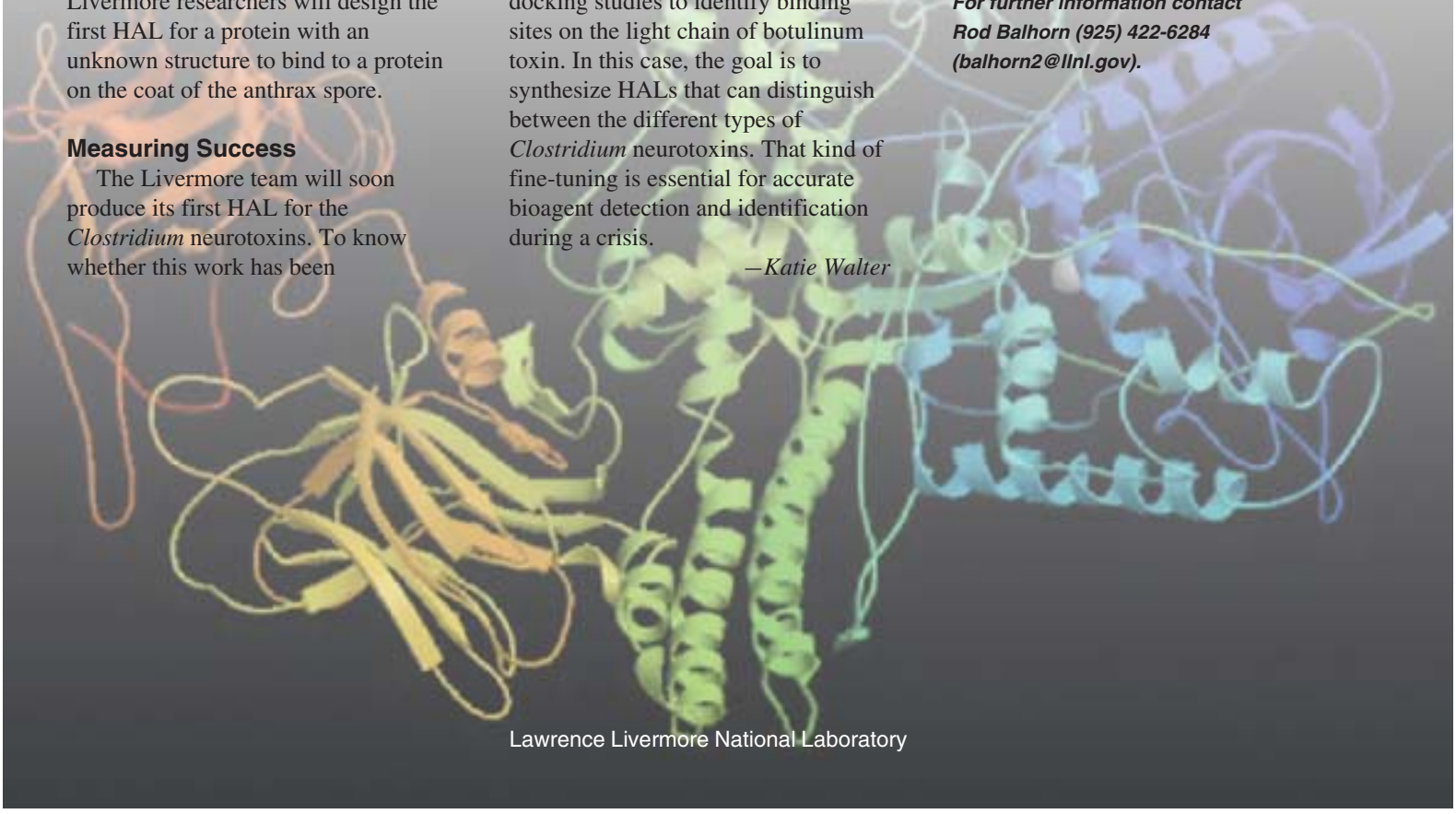
The Livermore team will soon produce its first HAL for the *Clostridium* neurotoxins. To know whether this work has been successful—whether the ligand works as designed in a bioagent detector—the team will send its results to the Department of Defense's Critical Reagent Program to be assessed for quality and specificity.

In the war against bioterrorism, the best defense begins with having the best possible data. Work has begun on docking studies to identify binding sites on the light chain of botulinum toxin. In this case, the goal is to synthesize HALs that can distinguish between the different types of *Clostridium* neurotoxins. That kind of fine-tuning is essential for accurate bioagent detection and identification during a crisis.

—Katie Walter

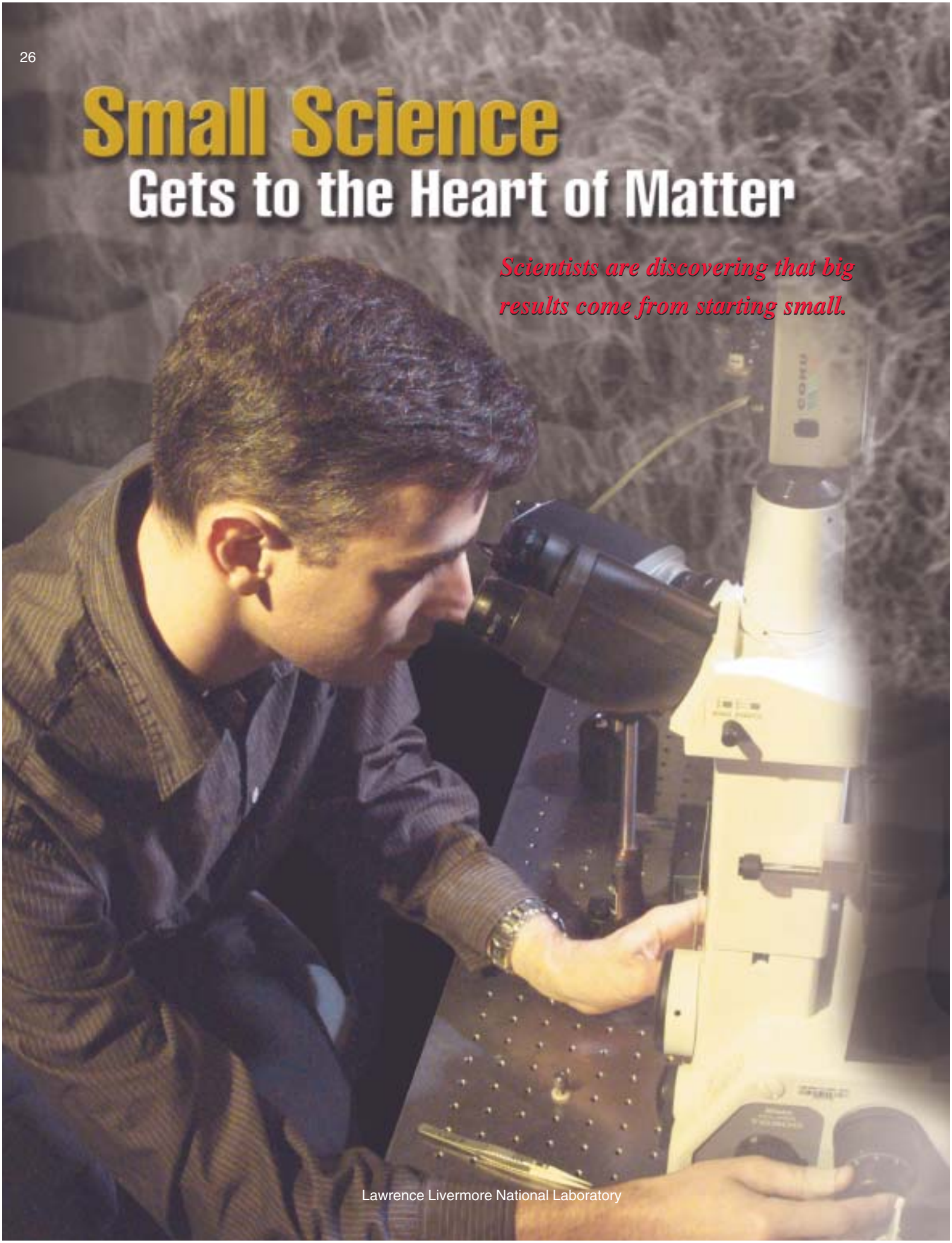
Key Words: antibodies, bioterrorism, botulinum toxin, cancer treatment, *Clostridium* neurotoxins, high-affinity ligands (HALs), mass spectrometry (MS), nuclear magnetic resonance (NMR), protein structure, synthetic chemistry, tetanus.

For further information contact Rod Balhorn (925) 422-6284 (balhorn2@llnl.gov).



Small Science
Gets to the Heart of Matter

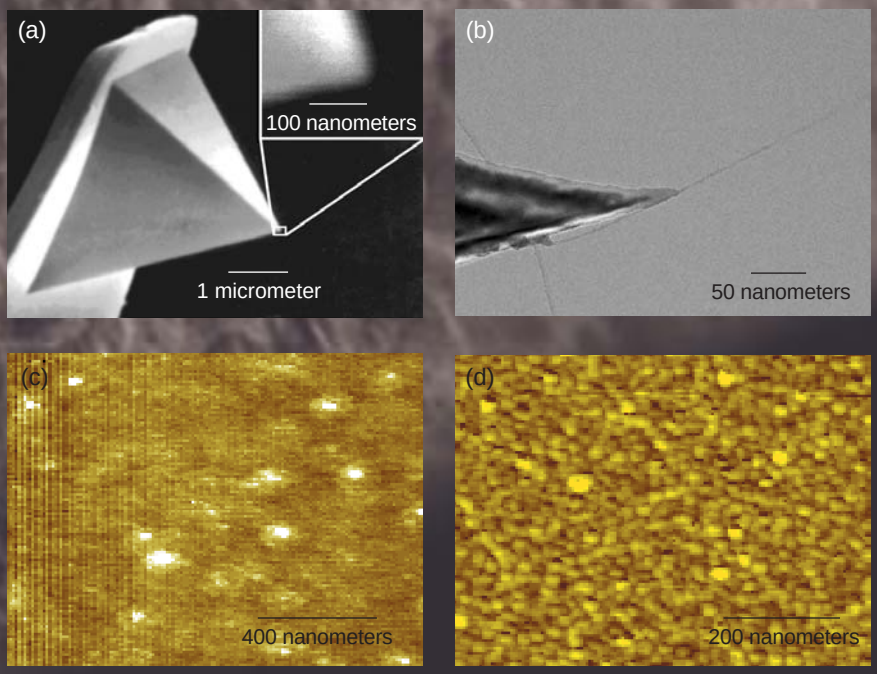
Scientists are discovering that big results come from starting small.



FINDING the best ways to detect biological warfare agents is one of Lawrence Livermore's missions today. Detecting large quantities of a biological pathogen is not difficult. The challenge is in detecting a few molecules of a toxin or a few bacteria or viruses to provide the early warnings of a biological attack.

Physicist Christine Orme and colleagues in the Chemistry and Materials Science Directorate are helping to understand some of the fundamental issues that underlie biodetection as well as fulfilling other Laboratory goals. They are performing research at minute scales in a field known as nanoscience, which takes its name from nanometer, a billionth of a meter. The team is examining, on an atom-by-atom and molecule-by-molecule basis, the organization of materials on surfaces and learning how that organization affects material properties. "One of the keys to working in nanoscience is controlling the surface and then being able to detect what is there," says Orme.

At the nanoscale, experimental results can be viewed only with the most powerful imaging tools. The atomic force microscope (AFM) has been used since the mid 1980s to produce topographic maps of nanostructures. Today, Orme's colleagues are developing new microscopic techniques based on use of the AFM that give even higher resolution and supply more than just topographic data. They are also refining the spectroscopic techniques that identify chemical bonds and supply fingerprints of molecules.



(a) Typical atomic force microscopy (AFM) tip and (b) nanotube tip. With the smaller nanotube tip, it is possible to obtain much more detailed information about a surface. AFM images of titanium grains obtained using (c) a typical AFM tip and (d) a nanotube tip.

The current research builds on pioneering Livermore work in crystal growth and thin multilayers, both of which depend on a keen understanding of material behavior at the atomic level. Livermore has a long-standing effort in crystal growth and characterization, born out of the need for large, ultrapure crystals in Livermore's lasers. Multilayers—exceedingly thin alternating layers of materials—were first demonstrated more than 50 years ago. But improved fabrication technologies developed by Livermore's Troy Barbee have prompted their use as highly reflective mirrors for telescopes as well as in a variety of optical applications, including electron microprobes, scanning electron microscopes, and particle beamlines in accelerators. (See *S&TR*, December 1999, pp.11–13.)

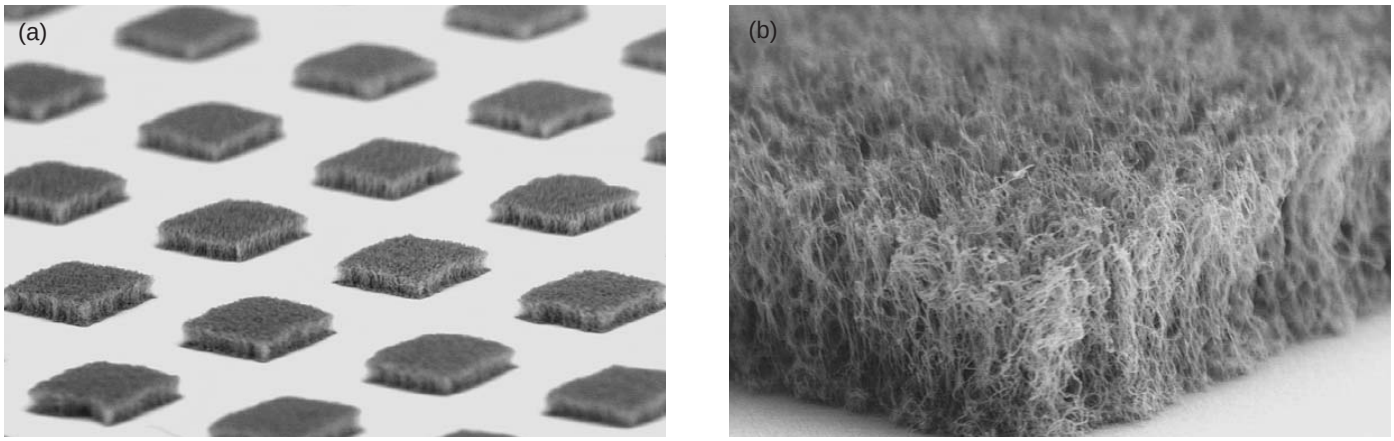
Seeing Is Believing

In atomic force microscopy, an extremely sharp tip senses the atomic shape of a sample while a computer records the path of the tip and slowly builds up a three-dimensional image. The AFM tip is positioned at the end of an extremely thin cantilever beam and touches the sample with a force of only 1/10 millionth of a gram, too weak to budge even one atom. As the tip is repelled by or attracted to the sample surface, the cantilever beam deflects. By imaging a larger or smaller area, researchers can vary the level of magnification of an AFM image. The

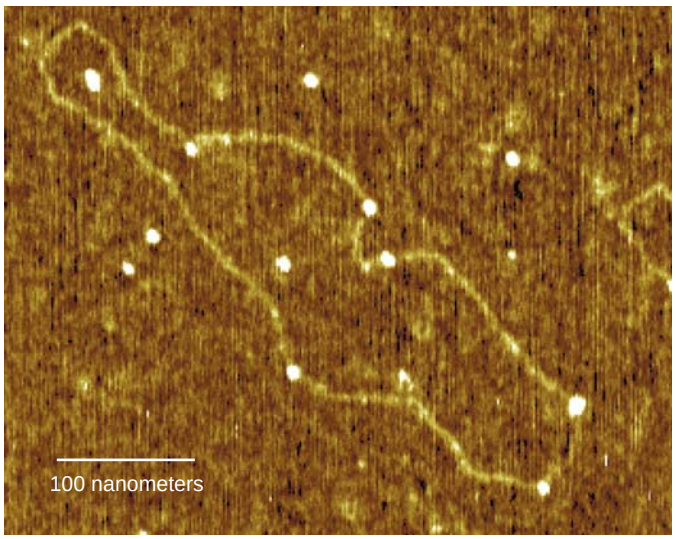
AFM can also be adapted to sense a range of forces including attractive or repulsive interatomic forces, electrostatic forces, and magnetic forces.

But even the sharp tip of the AFM is sometimes not tiny enough for the small scale at which the research team is working. Physical chemist Aleksandr Noy is growing carbon nanotubes that can be used to replace the standard AFM tip. The figure on the previous page compares a typical AFM tip and a carbon nanotube tip. Carbon nanotubes are built of carbon hexagons that are arrayed in a configuration resembling chicken wire. They are 1/50,000th of the width of a human hair but a hundred times stronger than steel at one-sixth the weight. Noy can make many kinds of nanotubes—single wall, multiwall, thick, thin, single isolated, or large arrays. The smaller, lighter nanotube tip tracks the shape of an object more accurately to provide more detailed information about its surface.

Noy used the nanotube-tipped AFM to image the cucumber mosaic virus and reveal its structure fairly clearly. AFM images contain less information than structures revealed through x-ray diffraction techniques, but Noy's image was captured in minutes, whereas the same structure took over a year to resolve from diffraction data. "In principle, this technology could be used to image a single virus," says Noy. "Emergency workers could compare its image with a



(a) "Farms" of carbon nanotubes and (b) a closeup of one farm. Livermore is exploring the potential of such nanotube arrays for detection applications.



One of the first images of DNA repair proteins bound to DNA.

Aleksandr Noy with the atomic force–confocal optical microscope.

computerized database of known virus structures to identify it very quickly."

With the nanotube tip on the AFM, a team led by Noy also obtained the first unambiguous visualization of a DNA repair protein bound to DNA. By incorporating a synthetic mutagenic molecule into DNA and tagging a repair protein with a fluorochrome, they will be able to study the repair process in situ.

Another imaging technique being used by physicist Thomas Huser and others is confocal microscopy. It is based on a fluorescence microscope augmented with a pinhole that limits the volume being probed to get rid of extraneous background "noise." Its beam can be focused to 500 nanometers. The confocal microscope efficiently collects fluorescence emitted from fluorescent molecules that have been excited by laser light. With this spectroscopic technique, Huser has been able to detect single molecules.

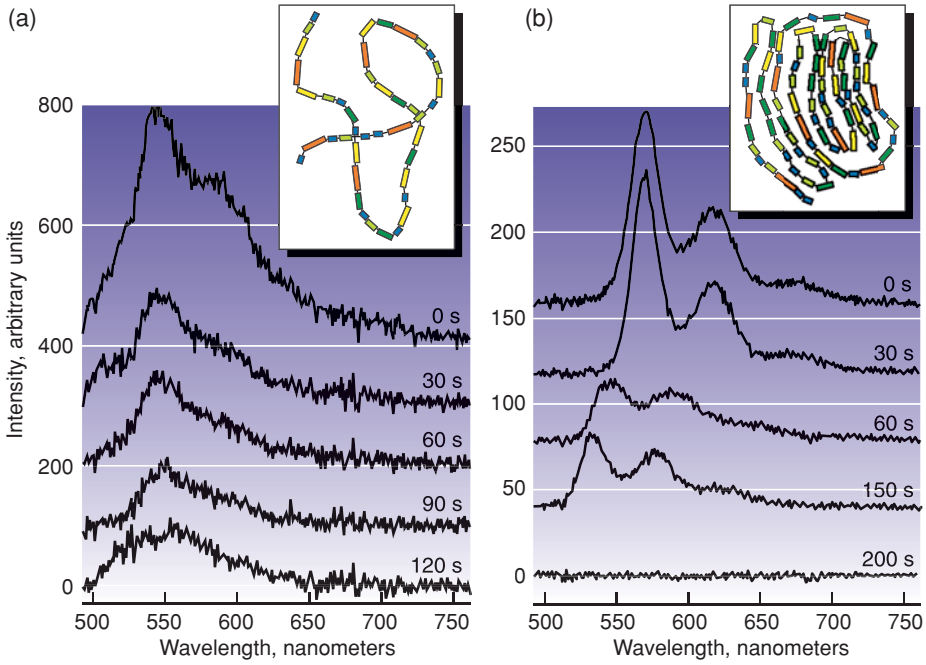
The confocal microscope is ideal for studying conjugated polymers, a new material that may be used to fabricate the next generation of light-emitting diodes (LEDs). Known as 2-methoxy, 5-(2′-ethyl-hexyloxy)-p-phenylene-vinylene, or MEH-PPV, the polymers are composed of a chain of benzene rings that emit light when linked by electrodes to which voltage is applied. The advantages of these polymers over the inorganic semiconducting materials of today's LEDs are many: They are easier to process on a large scale, they can be used to create ultrathin and flexible devices, and their power consumption is lower. Last year's Nobel Prize in Chemistry was awarded for the development of conjugated polymers.

Huser has learned that the physical configuration of the MEH-PPV molecules affects their fluorescence. "The photoluminescence of conjugated polymers depends strongly on how they are shaped," says Huser. When they fold up into a well-organized pattern in toluene, their shape enhances efficient energy transfer within the molecule. As conjugated polymers begin to be used as LEDs in electronics, some LED applications will take advantage of the high-energy-transfer configuration while others will benefit from the less ordered pattern for low energy transfer.

In experiments, Huser exposed MEH-PPV to two solvents, toluene and chloroform. In toluene, the MEH-PPV molecules curl up tightly because, says Huser, "they don't like toluene. They try to avoid it." Spectrographic data collected every 5 seconds show a slight flicker as the molecules die off with exposure to oxygen and the light they emit shifts from red to blue. In chloroform, the polymer spreads out. There is no blue shift, the light spectrum is broader, and the light intensity simply decays slowly with time.

Huser recently began experiments with the confocal microscope to examine the dynamics of single molecules of DNA. Fluorescent labeling of DNA, RNA, enzymes, and proteins is common laboratory practice to illuminate the interactions and functions of these important biomolecules.

At the same time, Noy has built a whole new microscope system that combines the topographic capabilities of the AFM and the spectroscopy of the confocal microscope. He will be using this system to obtain even better information about DNA repair as well



The development of photoluminescence over time in the conjugated polymer MEH-PPV, a material with multiple fluorophor segments on a chain. (a) MEH-PPV exposed to chloroform forms an open, irregular coil (see inset) that leads to luminescence from multiple sites, hence the broad spectral emission. (b) MEH-PPV exposed to toluene forms a tight coil (see inset) with strong overlap between segments. In this conformation, only the segments with the lowest transition energy emit light. Thus, the emission is narrow and more structured. Once all the red fluorophors are photodestructed, the segments with the next lowest energy begin to emit light at slightly blue-shifted wavelengths.

as new information on how DNA is packaged.

Identifying a Single Molecule

Another tool for identifying molecular species is Raman spectroscopy, a form of light scattering similar to fluorescence. Although Raman-scattered light is much less intense than fluorescence, the technique is a powerful analytical tool because the changes in wavelength of the weakly scattered light are characteristic of the scattering material. Raman spectroscopy can identify chemical bonds and obtain the unique fingerprint of a molecule. Every molecule has a unique Raman spectrum, but not every molecule fluoresces. Raman spectroscopy is one of the few optical techniques that can identify a molecular species and determine its chemical bonding by observing its distinct molecular vibrational frequencies.

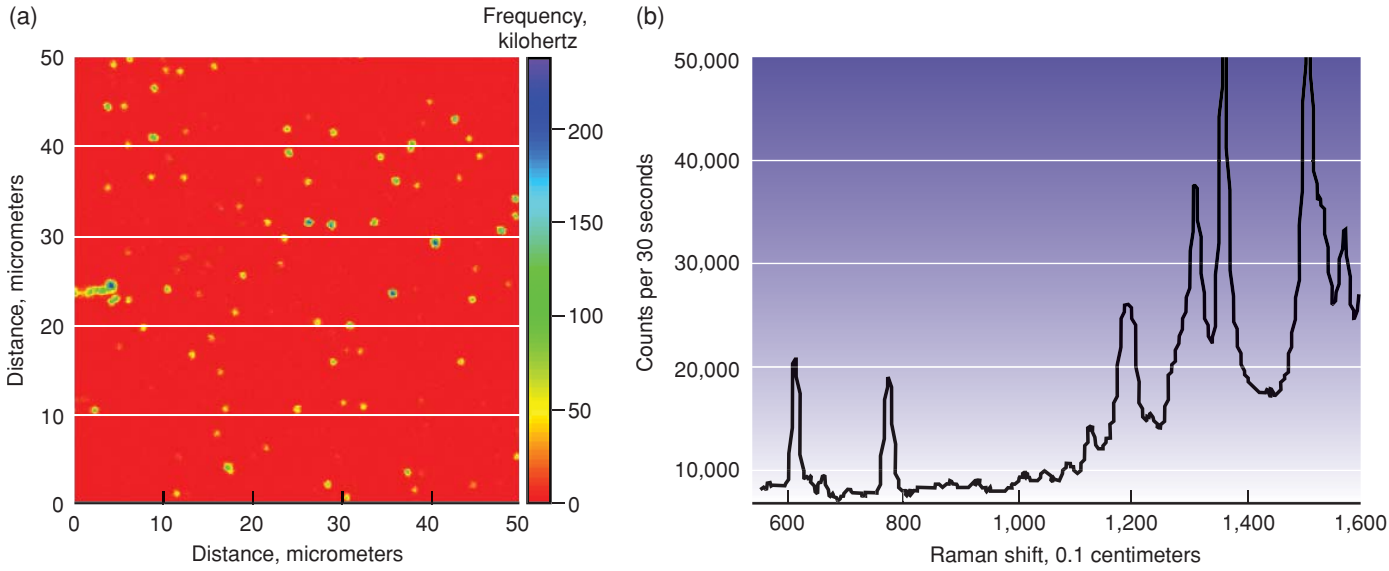
To increase the brightness and thus the resolution of Raman-scattered light, Huser has introduced nanometer-size gold crystals to the tip of a scanning probe microscope in a technique known as surface-enhanced Raman spectroscopy. The gold is negatively charged and attracts positively charged materials such as amino acids to adhere to kinks in the crystals. Electron density waves radiate from the corners of the gold crystals and increase the Raman signal by a factor of a quadrillion. At the same time, the scanning probe produces an image of the physical structure of the sample. The combined data allow for identification of single molecules. Unlike fluorescence, which fades with exposure to oxygen, the increased energy from the gold particles persists.

"Being able to characterize materials and chemical bonds at the level of a single molecule is a whole new capability for Livermore," says Huser. It is possible to perform Raman spectroscopy on single DNA molecules or proteins and to look for differences between individual cells. Using this technique, scientists also can detect and identify the byproducts or precursors of chemical agents such as the nerve gas sarin. This capability is important in the development of sensors for chemical warfare agents.

Controlling Biomolecules

Some nanoscience projects require the careful design of surfaces to collect and organize atoms, molecules, nanocrystals, colloids, cells, and spores. These surfaces are known as templates or, as Noy describes them, "landing pads" for toxins, proteins, and other biomolecules.

Livermore is exploring several techniques for creating templates. Physicist Jim De Yoreo is developing one method based on dip-pen nanolithography, which dips the tip of the AFM into an "inkwell" of organic molecules to "write" on an inorganic surface. As the tip moves across the surface, it makes a pattern that has almost no topographic relief but exhibits chemical contrast with the surrounding region. It is even possible to create multiple ink patterns with this method. The feature size is controlled by such factors as tip coverage, humidity, and contact time with the substrate, or, in the case of lines, tip



An example of the benefit of surface-enhanced Raman spectroscopy. (a) Confocal optical micrograph of 60-nanometer-diameter gold nanocrystals loaded with just a few molecules of the laser dye rhodamine 6G. (b) Surface-enhanced Raman spectrum of one of the gold particles in (a) easily identifies the adsorbed rhodamine by its characteristic Raman signature.

speed across the substrate. Examples of patterns created using a gold-coated mica surface for the substrate and 16-mercaptohexadecanoic acid for the ink are shown in the figure at right. This method has been used to deposit patterns of antibodies that would attract toxins and viruses, a first step in the development of nanostructured biosensors.

Another major area of research at Livermore's Biology and Biotechnology Research Program (BBRP) and elsewhere is in proteomics, the study of proteins. Cells produce particular proteins either all the time or as needed to prompt gene expression, that is, to turn a specific part of the genetic code on or off. Without proteins, our DNA could not operate properly. One of the best ways to examine the structure of a protein is to crystallize it and then subject it to x rays to obtain its unique diffraction pattern. During the crystallization process, molecules come together and separate (in a process known as nucleation) until a critical size is reached. Reaching that critical size can take a long time, and sometimes it does not happen at all. One goal of current proteomics work is to speed up the nucleation process and make it more likely that proteins will crystallize.

Dip-pen lithography, using a chemical that would prompt protein nucleation, is an option. "But," says Orme, "the size scale is a challenge. Proteins are extremely small, typically from 1 to 10 nanometers."

"If we make the pen's lines smaller, they won't be visible," adds Noy. So he and researchers in BBRP are developing a fluorescent ink for drawing lines with the density of a single molecule. In initial tests, a single-molecule line of the human chorionic gonadotropin (HCG) antibody has been successfully drawn. The next step will be to attract the HCG protein.

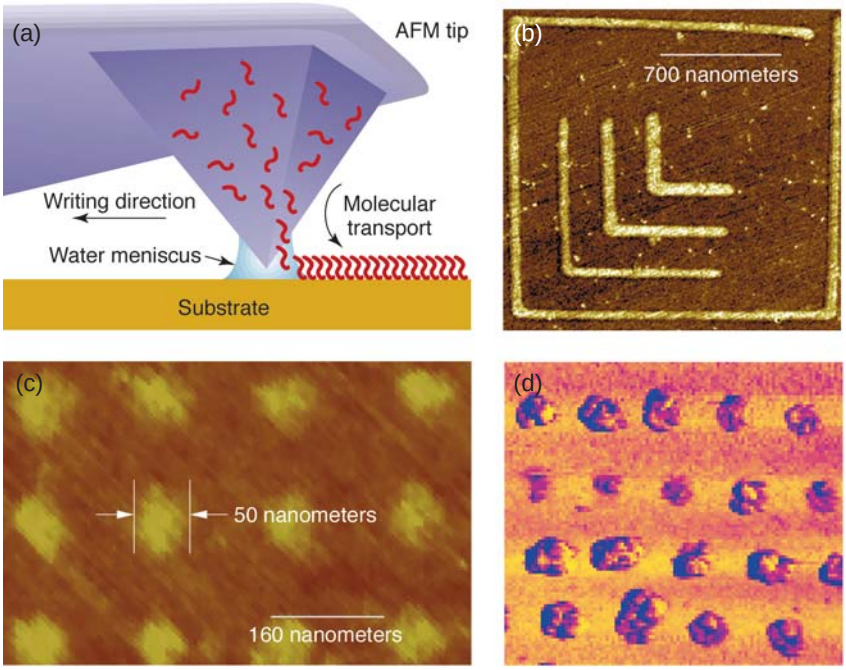
Nanolaminates, the next generation of multilayers, are also being explored as a way to accelerate the nucleation and growth of ordered proteins. Nanolaminate structures have been successfully synthesized with layers that are the same small size as typical proteins. The alternating layers have different surface charges, which prompt the proteins to adsorb in ordered rows. In the example shown in the top figure on p. 32, a nanolaminate was dipped into a solution of the protein ATCase. The nanolaminate was then removed, rinsed, air-dried, and imaged with AFM using a carbon nanotube tip. The resulting extremely high resolution of the image makes nonspherical proteins individually distinguishable on silica stripes. An image of the same deposition onto a homogeneous silica surface is very different, lacking any linear order. This set of experiments was the first step in accelerating nucleation and growing protein crystals that are suitable for x-ray diffraction.

Mimicking Natural Growth

Nanoscience is finding another application in the hands of Orme, De Yoreo, and colleagues whose research on the growth of calcite crystals sheds new light on the formation of bones, eggshells, and seashells.

The natural growth of organic crystals is known as biomineralization. Biomimetics is the term for mimicking nature's building methods to make a synthetic material. "We can only learn to make better bones and teeth if we first understand how the materials grow and interact with biological molecules," says Orme. "While there is a big step between this fundamental research and synthesizing materials that are truly similar to the real thing, we are part of the process to create better materials that affect health."

Pure calcium carbonate in the mineral form called calcite grows only in a symmetrical, six-sided rhombohedral-shape crystal. But that does not explain the intricate shapes found in nature, such as that of seashells. Researchers have known for a long time that organic

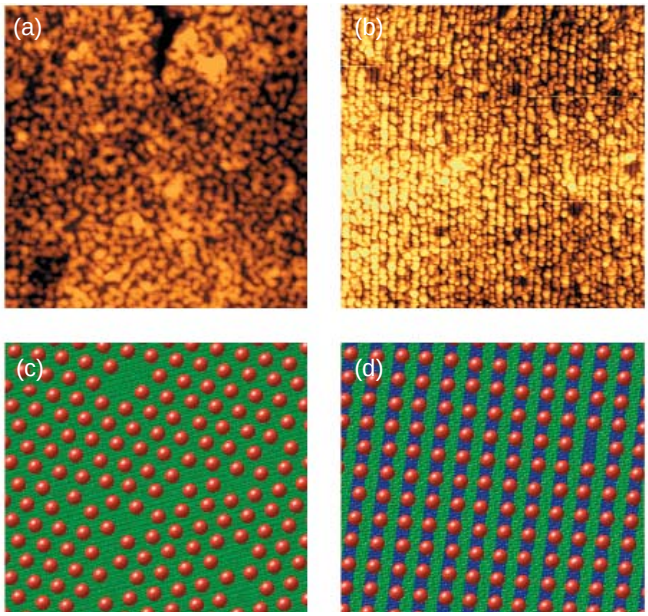


(a) Schematic of dip-pen nanolithography technique. Friction force images of (b) logos, (c) dots drawn on gold, and (d) colloid particles adsorbed preferentially on the dots. Features are composed of 16-mercaptohexadecanoic acid. The lines are 40 to 50 nanometers wide.

molecules can influence the shape of a growing mineral crystal by attaching themselves to it. But it took experiments at Livermore to demonstrate the process in detail, showing how amino acids work at the molecular level to change a growing crystal.

In the experiments, the team added aspartate, one of the more abundant amino acids found in the proteins of shellfish, to calcite crystals growing in solution. Aspartate is typical of many amino acids in that it exhibits handedness, or chirality. As the researchers monitored crystal development, they found that the left-handed and right-handed form of the molecule attached more strongly to opposite atomic steps. The results were crystals that were mirror images of one another. The figure below illustrates how a chiral amino acid influences a growing calcite crystal. By knowing which steps the amino acid interacted with and using the symmetry relations of the crystal and the amino acids, the team was able to predict the binding position of the amino acid to the calcium carbonate step.

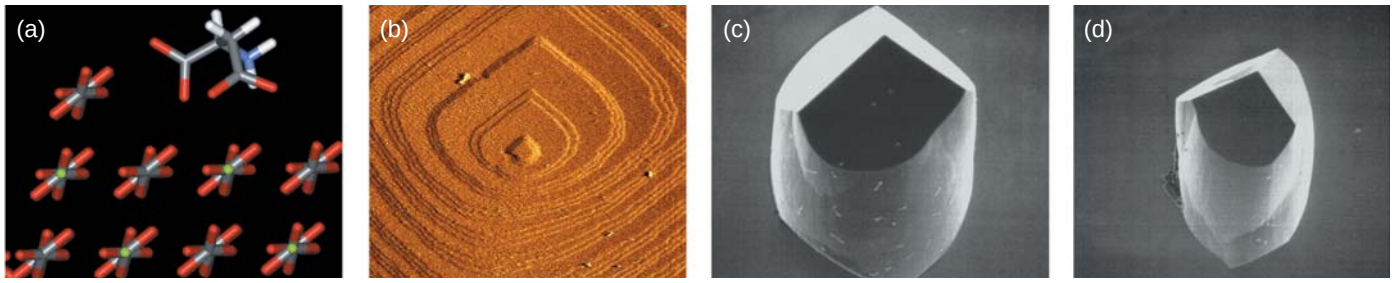
Comparable experiments are just beginning on calcium phosphate, the material used by animals to grow bones. Ultimately, experimental results may be put to myriad uses, from potential laboratory growth of human and animal bones to prevention of scale formation in pipes to the manufacture of toothpaste—any situation in which calcium-based crystals grow naturally or are used.



(a) A homogeneous silica substrate and (b) a nanolaminate of alumina and silica were dipped into a solution of the protein ATCase. Models show that (c) the deposition on the silica surface lacks any linear order, but (d) proteins adsorb to the nanolaminate in ordered rows, indicating the likelihood of growing ordered protien crystals suitable for x-ray diffraction.

Fundamental Science at Work

A nanostructured device is also finding its way into tests for the Yucca Mountain project, the nation's candidate



The interaction of D-aspartic acid (D-Asp) with a calcite mineral surface. (a) Model illustrating the binding of Asp to a calcite step. (b) An atomic force microscope image of calcite steps (0.32 nanometers high) in a solution containing D-Asp. The steps of pure calcite are rhombohedral, but when an Asp-bearing solution is flowed into the fluid cell, the two lower steps interact with Asp and become curved. L-Asp binds more strongly to the left step, and D-Asp binds more strongly to the right step. These differences were used to deduce the binding motif. (c) An electron microscopy image of an approximately 10-micrometer-diameter calcite crystal nucleated on micropatterned, self-assembled monolayers in the presence of D-Asp. The atomic step structure in (b) is reflected in each of the three caps. (d) Crystals nucleated in the presence of L-Asp are mirror images of those nucleated with D-Asp.

for a repository for long-term storage of nuclear wastes. Tests of corrosion-resistant materials are being developed that use patterns formed by "writing" with voltage rather than with chemical inks. A voltage is applied between the AFM tip and a metal or semiconductor substrate to grow oxide patterns under the tip. In the figure below, an oxide greeting is written into a titanium film. The dot on the "i" is made larger and broader by applying a higher voltage. If the nanopatterns blur or dissolve during testing, the change provides a very sensitive indicator that the protective oxide film is changing.

This project is typical of so much fundamental research performed at Livermore. Using funding from the Laboratory Directed Research and Development (LDRD) Program, the oxide templates were originally developed to nucleate calcium phosphate minerals and to control protein deposition onto medical implants. Now, the Yucca Mountain project is putting the template to practical use. Much of the other work at Livermore to grow and image nanostructures also started as basic research, funded either by LDRD or by the Department of Energy's Office of Basic Energy Sciences, before finding a range of applications—including sensors that may someday be a lifesaver.

—Katie Walter

Key Words: atomic force microscope (AFM), biological sensors, biomineralization, carbon nanotubes, chemical sensors, confocal microscope, genomics, nanolaminates, proteomics, surface-enhanced Raman spectroscopy.

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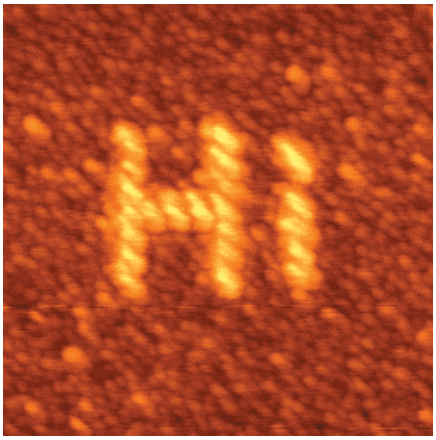


Atomic force microscope image (0.7 micrometers by 0.7 micrometers) of oxide grown on titanium using a voltage applied between the tip of the atomic force microscope and the substrate. (Image made by Livermore summer student researchers R. Sivamani and E. Bochner.)

About the Scientist

CHRISTINE ORME, a physicist in the Materials Science and Technology Division of the Chemistry and Materials Science Directorate, received a B.S. in physics from the University of California at Berkeley. She joined the Laboratory as a postdoctoral fellow after receiving her Ph.D. in physics from the University of Michigan in 1995. Her background is in experimental physics in the area of surface evolution and pattern formation during the growth of thin films. In her thesis work, she combined imaging with kinetic Monte Carlo simulations and continuum modeling to deduce diffusional processes during vapor growth. At Livermore, she uses this background to study crystal growth from solution (rather than from vapor). She is particularly interested in the area of biomineralization where organic molecules substantially change the shape of inorganic crystals; she wants to understand the formation of materials such as shells, bones, and teeth. Recently, she has become interested in the use of electrochemical driving forces to control electrodeposition and corrosive processes, particularly in their application to biomedical implants and corrosion-resistant industrial materials.

Machines from Interlocking Molecules

IMAGINE a mechanical device created from a handful of molecules. Such a device could be a sensor that can detect infinitesimal traces of chemicals or biological agents, or it could be an on–off switch, a miniature building block for creating molecular computers. These ideas are moving closer to reality because of recent work on mechanically interlocking molecules at Livermore.

Unlike molecules that are joined by covalent bonds (by sharing pairs of electrons), mechanically interlocking molecules are physically joined, in the same way as the links in a chain or the rings in the Olympic Games symbol. Mechanically interlocking molecules are of growing interest to synthetic chemists, such as Livermore's Andrew Vance, who view them as potential building blocks for future molecular-scale devices—motors, sensors, and machines on the nanometer scale.

Vance heads up an effort originally funded through Laboratory Directed Research and Development to find new mechanically interlocking molecules that will consistently attach in a single layer on a gold surface. The team, which includes Vance, physicists Anthony Van Buuren and Art Nelson, and University of California at Davis physics graduate student Trevor Willey, is focusing on molecules known as catenanes and rotaxanes. A catenane has two or more interlocking rings. A rotaxane consists of a long, straight molecule—an "axle"—ringed by a doughnut-shaped molecule. Molecular "caps" at both ends of the rotaxane's axle keep the ring from sliding off. No chemical bond holds ring to ring or ring to axle.

Vance notes, "Interlocking molecules in solution are well understood, but not much is known about them on surfaces. Questions such as which molecules attach best, what's the best way to determine how well they're attached, and how to make the attachments stable are virtually unexplored."

Looping the Loop

The team started by exploring what kind of molecules worked best for forming a loop on a gold surface. Forming loops is the first step toward creating a monolayer of catenanes, in which

Chemist Andrew Vance working in his laboratory.

each attached loop would thread a ring. Vance explains, "We started at the most fundamental level, looking at how different molecules attached to the surface and how well they attached." The challenge was to come up with a molecule that would consistently attach at not just one but both ends.

The team first tried a linear dithiol monomer. (A thiol is a molecule that has an atom of sulfur bound to an atom of hydrogen. This particular monomer had a thiol at each end; hence, it is a dithiol.) The monomer was, according to Vance, "a floppy molecule." The researchers reasoned that when the sulfur atom at one end attached to the gold surface, the molecule would flop over and the sulfur at the other end would also attach, forming a loop. But measurements taken with x-ray absorption (XAS) and x-ray photoemission spectroscopy (XPS) at the Laboratory and at Stanford's Synchrotron Radiation Laboratory revealed that only about 50 percent of the sulfur atoms had bonded to gold. (See the box, below right.) "In other words, most of the monomers had one unattached sulfur," says Van Buuren.

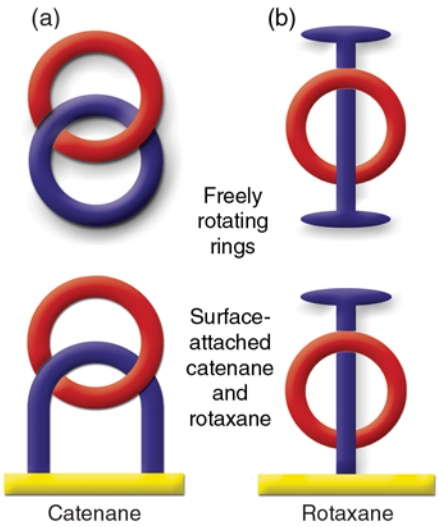
Other measurements indicated that these monolayers were disordered and had molecules that, on average, were tilted slightly more than 55 degrees from the surface. "All these data indicated that most monomers were essentially standing on end on the surface," notes Van Buuren. Because the concentration of monomers was quite high, the suspicion is that the monomers packed the surface, leaving little room for them to flop over and make a loop.

Another set of experiments used a polymer containing disulfide components. (A disulfide is two atoms of sulfur bound to each other.) In this case, the scientists expected the disulfide bonds to cleave, the sulfurs to bind to gold atoms, and the polymer to form a loop. XPS measurements showed that the resulting monolayer contained over 90 percent of bound sulfurs, evidence that nearly all the molecules had successfully formed surface-attached loops.

"The presence of a disulfide made it more likely that both sulfurs would attach to the surface," says Vance. "All this pointed out the importance of designing molecules that will bind to surfaces in a predictable manner to form monolayers. In the case of surface-attached loops, simply preparing compounds with end components that bind well to the surface doesn't guarantee loop formation. Other factors come into play, including the solution concentration and the shape of the molecule. Following these initial results, we also looked at molecules with built-in turns that encourage loop formation over single attachment."

Of Axles and Rings

Next, team members turned their attention to attaching rotaxanes to gold. As in the previous experiments, the team took two different approaches. One involved an electron-deficient, positively charged T-shaped thiol (which had the characteristic sulfur–hydrogen bond at one end and an anthracene stopper at the other) and an electron-rich crown ether ring. In solution, the two molecules are drawn to each other. The thiol threads the crown ether to form a pseudorotaxane with only one stopper. "Our question was whether the pseudorotaxane would then attach to the gold, or would the crown ether ring slip off, leaving only a thiol to attach to the surface," explains Vance. Vance also synthesized a [3]rotaxane composed of three molecules: two crown ether rings threaded by an antracene-capped thiol with a disulfide bond in the middle. "From our work with loops, we felt



(a) Catenanes are formed from two or more molecular rings interlocked like links in a chain. (b) Rotaxanes are formed from a ring molecule threaded on an "axle" molecule capped by two molecular stoppers.

X-Ray Vision

To "see" what was happening with the synthesized molecules and the gold surface, the physicists in Andrew Vance's team used two techniques—x-ray absorption spectroscopy (XAS) and x-ray photoemission spectroscopy (XPS). Both techniques use x rays from the soft end of the spectrum (with wavelengths between those of ultraviolet light and harder, medical x rays). For the photoemission measurements, the team used the soft x rays created by a beamline at the Stanford Synchrotron Radiation Laboratory as well as a newly acquired Physical Electronics Quantum 2000 scanning XPS system here at Livermore.

The two techniques enable scientists to obtain detailed and specific information about the monolayers under scrutiny. According to physicist Trevor Willey, XPS measurements reveal the chemical composition of what's on the surface as well as the nature of chemical bonds between the surface and the material. "We used XPS to determine whether the sulfur atom of the thiol was bound to gold or whether the thiol was just lying on the surface, essentially unattached," he explains. Measurements with XAS revealed the orientation of the molecule. "With XAS, we could tell whether the thiol molecules were standing up, lying down, or leaning in some direction relative to the gold surface," Willey says. "This also gave us information on how well ordered the layer was—that is, whether the attached molecules were packed together in ordered domains or leaning randomly every which way."

confident that when the disulfide bonds cleaved, we'd get surface-attached rotaxanes," says Vance.

The team's physicists took spectra of powder samples of the crown ether rings, anthracene caps, and [3]rotaxane for reference as well as a spectrum of thiol attached to gold. When the experimental results were compared to these control spectra, the spectra from the [3]rotaxane experiments did indeed show surface-attached rotaxanes. However, the spectra from experiments with the pseudorotaxane precursor were identical to that of simple thiol on gold.

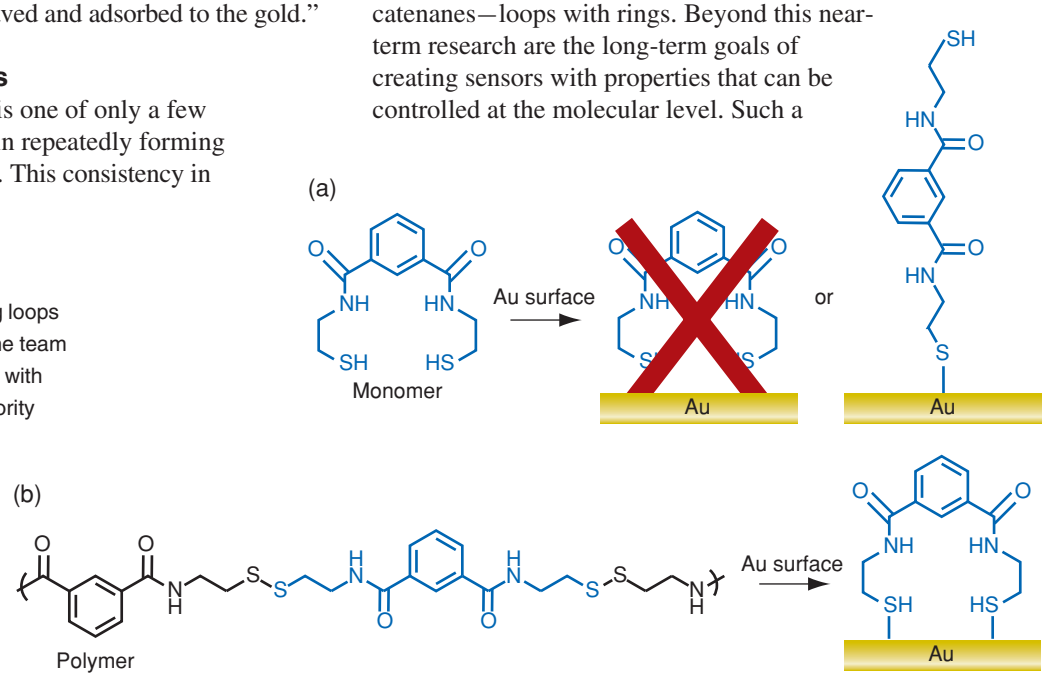
"The results confirmed that even though we'd set up a process for the thiol to thread the rings in solution, the rings came off before the sulfur could attach to the gold," says Vance. "For the [3]rotaxane, the rings were locked into place by the endcaps right up until the two sulfur atoms cleaved and adsorbed to the gold."

Links to Future Possibilities

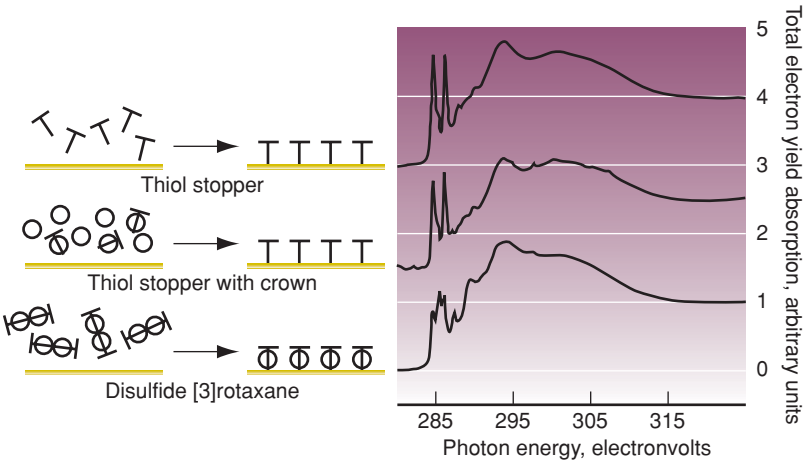
To date, the Livermore team is one of only a few groups that has been successful in repeatedly forming rotaxane monolayers on surfaces. This consistency in results is important if such surface-attached molecules are to become molecular machines of the future.

The success of Vance and his colleagues has led to a collaboration with a group from the University of California at Los Angeles (UCLA) led by chemistry professor and researcher Fraser Stoddart, one of the world's foremost experts in the synthesis of rotaxanes and catenanes. Vance's team has been taking interlocking molecules created by the UCLA group, attaching them to surfaces, and using XAS and XPS to examine the results.

In addition, the team continues its fundamental studies of surface attachment and is beginning to explore attaching molecules to other surfaces, including silicon. Furthermore, they are working on ways to create surface-attached catenanes—loops with rings. Beyond this near-term research are the long-term goals of creating sensors with properties that can be controlled at the molecular level. Such a



The team experimented with creating loops from different molecules. (a) When the team tried to attach monomers terminating with sulfur–hydrogen bonds, the vast majority attached at just one end instead of forming the hoped-for loop on gold. (b) A polymer with disulfide linkages was far more successful in attaching its sulfurs to the gold surface.



Results of surface-attached rotaxane research. Researchers started with thiols in solution (T-shaped molecules), attached them to gold, and used the resulting spectrum from x-ray absorption spectroscopy as a reference. Beginning with crown ether rings and anthracene-capped thiols in solution, researchers attempted to create pseudorotaxanes (single rings on axles capped at one end) and attach them to gold. The resulting spectrum was nearly identical to the reference, indicating that almost all the rings slipped off before the thiols attached. But using disulfide [3]rotaxane—two rings threaded on a thiol and restrained by anthracene endcaps—was effective in creating a surface-attached rotaxane. The resulting spectrum shows peaks similar to the reference spectrum for rotaxane powder.

sensor might have arrays of surface-attached catenanes with rotating rings that have tunable properties.

"By controlling the rotation of the ring, for instance, we can create an on–off switch," Vance explains. "Suppose you could create a ring that has a small hydrophobic component. In the presence of a water molecule, it would spin one way; without water present, it would spin the other way. You could also create rings that are electrochemically or optically reactive and turn them on or off by changing the charge at the surface or by the presence or absence of light. Developing these switchable features is on our list of plans for the future."

Vance believes the combination of synthetic chemistry and spectroscopy, chemists and physicists is a critical element in making this research possible. "What we're doing now," he continues, "is fundamental science that has intriguing possibilities. In the future, these surface-attached interlocking molecules could be used in molecular machines, sensors, and electronics in ways we've yet to even imagine." It all comes down to being able to understand and control these small structures on the molecular and atomic level. And it's a combination of chemistry and physics that, in the end, will make this possible.

—Ann Parker

Key Words: catananes, molecular machines, rotaxanes, Stanford Synchrotron Radiation Laboratory, surface-attached mechanically interlocking molecules, x-ray absorption spectroscopy (XAS), x-ray photoemission spectroscopy (XPS).

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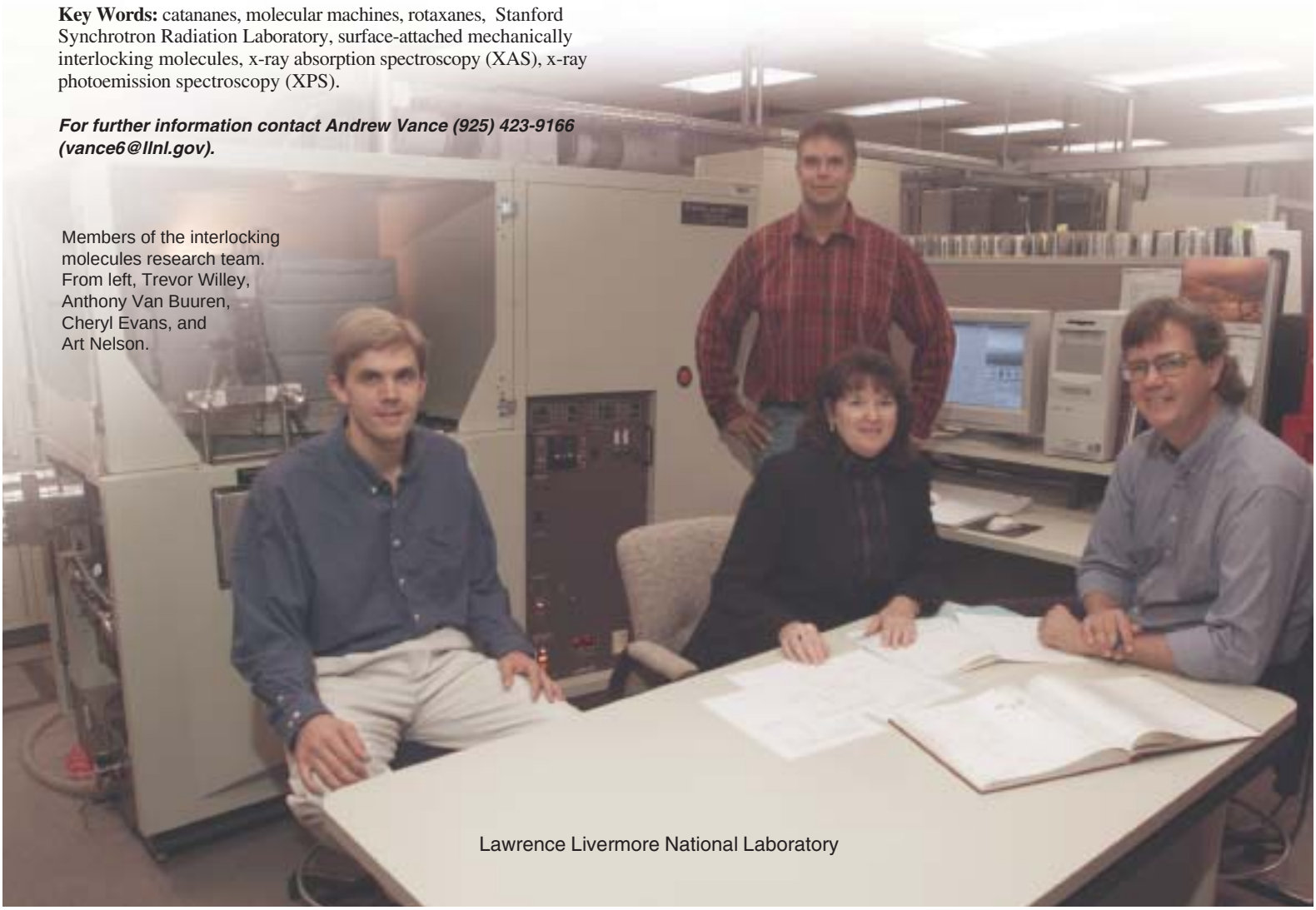
An Idea Whose Time Has Come

Nearly a century ago, Richard Martin Willstätter, a German chemist destined to win a Nobel Prize in chemistry for synthesizing complex organic molecules, raised the possibility of interlocked molecular rings. It took until the early 1960s for synthetic chemists to invent procedures for forming such molecules in the laboratory.

One such method invoked brute statistics. Mix a huge number of ring-shaped molecules with U-shaped molecules inclined to form rings in solution, and by sheer statistical chance, the linear molecule will thread the circular molecule before forming a ring. The first catenane resulted from such a threading process.

Nowadays, synthetic chemists such as Livermore's Andrew Vance use a method called template synthesis, which offers far more control over the synthesis of these structures. Template synthesis techniques use metal ions or noncovalent interactions such as hydrogen bonding, which force the stringlike molecules to thread the rings, providing a less hit-or-miss way to create catenanes and rotoxanes.



Members of the interlocking molecules research team. From left, Trevor Willey, Anthony Van Buuren, Cheryl Evans, and Art Nelson.

Forensic Science Center Maximizes the Tiniest Clue

Livermore chemists are coaxing a wealth of information from increasingly small samples.

WHILE Lawrence Livermore's national security accomplishments have received much publicity over the years, one Laboratory organization has gained such a stellar reputation among law enforcement, intelligence, and emergency response agencies that it is cited by Tom Clancy in his novel *Shadow Watch* (Berkley Books, 1999):

"I've requested assistance from the Forensic Science Center in San Francisco. It's at the Lawrence Livermore National Laboratory. I don't know if you're familiar with them."

"They did evidence analysis on the Unabomber case, the Times Square and WTC bombings in New York, probably hundreds of other investigations," Nimec said. "Uplink's had a relationship with them for years, and I've worked with them personally. The LLNL's the best group of crime detection and national security experts in the business."

Founded in 1991, the Laboratory's Forensic Science Center (FSC) offers a comprehensive range of analytical expertise to counter terrorism, aid domestic law enforcement, and verify compliance with international treaties and agreements. The center's combination of human and technological resources has made it among the best of its kind for collecting and analyzing virtually any kind of evidence, some of it no larger than a few billionths of a gram. Its resources, expertise, tools, and techniques are applied to all kinds of cases, from the September 11 World Trade Center attack to the spread of anthrax spores, from multiple homicides to nuclear materials smuggling.

FSC has a staff of 15 personnel, mostly chemists, with expertise in analytical chemistry, organic chemistry, inorganic chemistry, nuclear chemistry, toxicology, pharmacology, special coatings, and forensic instrument design and fabrication. The center also draws upon the resources of experts in Livermore's Chemistry and Materials Science and Nonproliferation, Arms Control, and International Security directorates.

The center's approach to forensic analysis maximizes the information that can be obtained from sometimes extremely small samples of explosives residue, dust particles, hair strands, blood stains, radioactive isotopes, drugs, chemicals, and clothing fibers. As Brian Andresen, until recently FSC director, says, "We're probing the lower limits of detection for many types of compounds isolated during an investigation." Even the tiniest quantities, says Andresen, are usually enough to provide compelling evidence that holds up in court. The minuscule amounts of oils remaining on fingerprints, for example, can tell the

general age of suspects, their diet, and whether they smoke. In that respect, says Andresen, "Everything someone does leaves a chemical or biological signature that we can investigate."

Many forensic research projects have required FSC personnel to develop new analytical tools, forensic techniques for analyzing trace amounts of evidence, and unique sampling procedures. Several new, portable instruments have been developed that are capable of detailed analysis in the field. These tools provide important advantages when dealing with substances that may be unstable, perishable, or too toxic to bring back to the Laboratory.

Supporting International Security

Andresen notes that the term "forensic science" used to apply only to the scientific analysis of evidence for civil or criminal law. Increasingly, however, forensic analyses done at FSC are broadening that definition to include support for monitoring or verifying compliance with international treaties and agreements, particularly those involving weapons of mass destruction, and for countering threats of terrorism. For example, the center is contributing to the National Nuclear Security Administration's (NNSA's) Chemical and Biological National Security Program to develop and field advanced technologies to better prepare for, detect, and respond to chemical or biological incidents in the U.S.

Heather King and David Chambers demonstrate Livermore's solid-phase microextraction (SPME) sampling technique for identifying and quantifying the chemical composition of physical evidence.

In light of its demonstrated capabilities to analyze minute specimens, FSC was selected by the U.S. State Department in 2000 to support the Organization for the Prohibition of Chemical Weapons (OPCW) as the second U.S. certification laboratory. (The other facility is the Edgewood Chemical and Biological Analytical Center in Maryland.)

OPCW, based in the Netherlands, is responsible for implementing the Chemical Weapons Convention, which bans the production, stockpiling, or use of such weapons as nerve agents and blister agents. OPCW-designated laboratories test samples collected by OPCW inspectors from sources around the world to determine whether the samples contain chemical weapon agents, their precursor chemicals, or decomposition products. The convention stipulates that all samples must be analyzed at the two OPCW-designated laboratories. Federal legislation requires that all samples taken from a U.S. facility be tested in a U.S. laboratory that is OPCW-certified.

FSC has established a separate chemical weapons analysis laboratory that is certified by the American Association for Laboratory Accreditation. To date, no actual samples have been officially collected from any site or analyzed at any laboratory. FSC, however, has been required to analyze and identify constituents of mock samples supplied by the OPCW as part of a series of proficiency tests.

According to FSC's Armando Alcaraz, "Passing the tests is a very challenging task because the samples might contain literally thousands of chemicals that are linked to chemical weapons manufacturing." He notes that the samples are sometimes spiked with certain materials to deliberately try to

throw the analysis teams off track. Like the test samples, the real samples will be extremely dilute (that is, parts-per-million level) so that they can be shipped commercially or sent through the mail.

Helping Law Enforcement

FSC also assists law enforcement agencies with special needs that cannot be handled by standard crime laboratories. "We're not in the business of routine police lab work," Andresen cautions. However, for cases that are particularly difficult, FSC may be a valuable resource capable of providing a conclusive analysis. In this respect, law enforcement agencies benefit from Livermore technologies that were developed initially to support counterterrorism efforts, detect nuclear proliferation activities, and advance stockpile stewardship.

Under the 1998 "Partnership for a Safer America" memorandum of understanding between the Department of Energy and the departments of Justice, Commerce, and Treasury, the center provides law enforcement agencies such as the Federal Bureau of Investigation (FBI), the U.S. Customs Service, and the Bureau of Alcohol, Tobacco, and Firearms with new crime-fighting technologies. This agreement provides a framework for formal working relationships to facilitate the transfer of DOE technology and technical expertise to law enforcement.

FSC deputy director Pat Grant notes that supporting law enforcement increases the center's expertise and shortens the turnaround times for sample analysis. "Anytime we analyze questioned samples important to a real-world investigation, we are honing our skills. It's a much more interesting and stimulating experience than participating in an exercise."

Scientists from the Forensic Science Center have miniaturized thin-layer chromatography to make it suitable for field use. The portable system includes appropriate reagents, glass plates, a digital camera, and a notebook computer.

Shrinking Instruments

Some of the center's most enduring accomplishments are new tools it has developed for intelligence, law enforcement, and health professionals working in the field. These compact, battery-powered tools provide mobile chemistry laboratories. Because they eliminate the need to ship samples back to a standard laboratory for analysis, the portable technologies greatly speed decision making.

For example, FSC scientists have miniaturized and modernized thin-layer chromatography (TLC), a well-established laboratory procedure that identifies compounds belonging to the same general chemical class. FSC chemists made TLC technology suitable for field use with a portable system that fits inside a suitcase and weighs about 23 kilograms. Although the portable system uses minimal equipment and chemical reagents, it is highly specific and sensitive. The kits can be used to analyze two sets of samples simultaneously, with

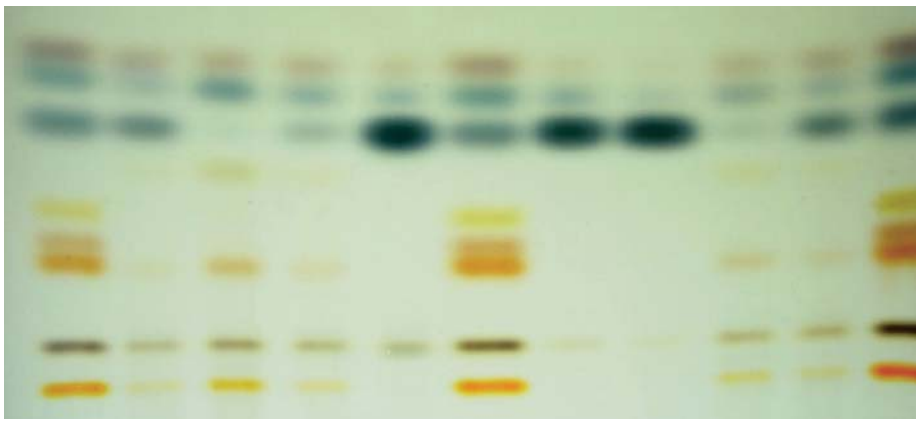
each set containing about 10 samples. Depending on the compounds being analyzed for, the entire process takes 10 to 20 minutes to complete.

TLC works by separating compounds over the distance they move up a glass plate. Tiny amounts of samples are placed just above the bottom edge of a TLC plate, the plate is placed in a small solvent reservoir, and the solvent moves up the plate by capillary action. A commercial digital camera captures the resulting patterns of dark spots that develop, which are analyzed on a notebook computer using a software program originally developed for the analysis of DNA. Based on the distance the samples have traveled, together with their color and intensity, the computer program identifies the compounds and their relative concentrations.

The center's portable TLC kits are tailored to detect chemicals indicative of chemical weapons, high explosives, propellant stabilizers, or illegal drugs. Each specialized kit includes solvents and developing reagents that are specific to the compounds of interest.

The TLC system was originally developed for the U.S. Army to quickly detect propellant instabilities within the nation's munition storage depots. Propellants (especially high explosives) require stabilizers to prevent them from spontaneously igniting. Because stabilizers are depleted by long exposure to environmental conditions, the Army needed a way to quickly determine the safety of large numbers of munitions. The center's TLC system requires only 50-milligram samples of explosive, instead of the gram quantities typically required by other methods, and 15 minutes for each group of 20 samples, allowing many more samples to be analyzed and at much lower cost than is possible using traditional methods. "Army personnel without a degree or extensive training in chemistry can do this work," says FSC chemist Jeff Haas.

Over a few days in 1998, the portable system successfully characterized the contents of more than 1,200 unearthed mortar rounds discovered in a shallow excavation site at an Army base in Massachusetts. (See *S&TR*, December 1998, pp. 21–23.) The system is now deployed at several other Army facilities as well as by National Guard units.



The portable thin-layer chromatography (TLC) system separates compounds as they move up a glass plate placed in a small solvent reservoir. Based on the distance the compounds travel, together with their color and intensity, a computer identifies the compounds and their relative concentrations. Above is a typical TLC analysis done to detect propellant instabilities by measuring the amount of stabilizer compounds.

The system is also used in instances where analysis speed is essential. In light of repeated success by a variety of users, the center is transferring the portable TLC technology to private industry for commercialization and widespread availability to federal and state law enforcement, customs, and environmental agencies.

Advanced Tools for Field Use

While TLC is effective for identifying classes of chemicals that are specifically targeted, the task of completely characterizing samples in the field requires a more sophisticated instrument such as the gas chromatograph–mass spectrometer (GC–MS). An essential tool in every major analytical laboratory, a GC–MS can detect ultratrace quantities of organic compounds weighing a billionth of a gram or less. The gas chromatograph first slowly heats a sample to about 250°C. As the sample's volatile constituents travel down a long capillary column, they separate according to their vapor pressures and chemical affinities. As they flow into the mass spectrometer, the compounds are bombarded with an electron beam that fragments molecules into ions that constitute a unique fingerprint of that compound for positive identification.

FSC staff scientists have shrunk the standard 114-kilogram laboratory GC–MS to about 28 kilograms; it now fits inside a wheeled suitcase. The self-contained portable device, comparable in sensitivity and selectivity to a standard unit, contains a power generator, vacuum pumps, and laptop computer. The result is an instrument that significantly improves on-scene investigation and evidence collection.

Because of its ability to analyze samples to parts-per-billion sensitivity

within 15 minutes, this portable GC–MS can be used to support nonproliferation activities, incident response, and law enforcement investigations. For example, the instrument can precisely identify compounds indicative of the manufacture of chemical warfare agents and illicit drugs. The instrument is currently being manufactured under license to industry.

Identification with Lasers

Although many tools used by FSC personnel depend on analyzing tiny amounts of chemicals that are found in a vapor phase above a liquid or some solid materials, most solid objects, such as human hair or clothing, do not have a significant vapor pressure and thus do not lend themselves easily to GC–MS analysis. However, center personnel can vaporize these solid samples with an extremely fine laser beam to generate wisps of product that contain identifying compounds.

The technology is called imaging laser-ablation mass spectroscopy. The process combines a laser for vaporizing extremely small amounts of material, an ion trap and time-of-flight mass spectrometer for analysis, and a high-powered microscope for viewing. In this way, forensic scientists can collect and rapidly identify suspect chemicals.

The process can be used on almost any solid material—dirt, pieces of glass, paint chips, clothing fibers, strands of hair. The samples are placed inside an ion trap mass spectrometer, irradiated with a laser, and identified within a few minutes by the mass spectrometer. The process allows an investigator to "walk down" a hair shaft by drilling consecutive holes on the same hair with the laser and analyzing each volatile sample. "Because hair grows at a standard rate, the results can reveal a history of drug use or exposure to compounds used in biological or chemical weapons manufacturing," says FSC chemist Greg Klunder. He points out that the method could also be applied to samples of clothing or soil sticking to the shoes of someone suspected of developing chemical weapons.

A similar instrument still under development is capable of detecting chemicals in air and is well suited for high-speed aircraft sampling of exhaust smoke from chemical facilities. Potential applications include identifying hazardous spills, monitoring industrial stacks for certain compounds, and surveying the environment from a remote location to detect chemical releases from a suspect facility.

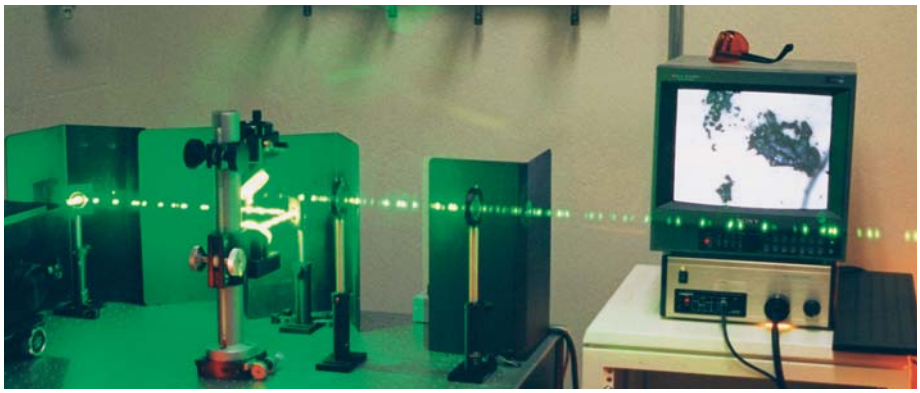
Wands of Collection

One of the center's most important developments has been the solid-phase microextraction (SPME) collection kits that use optical fibers as "chemical dipsticks" for safe and efficient sampling. "The technique has revolutionized the collection of forensic samples in the field," says FSC chemist Pete Nunes.

The technology uses commercial hair-size (100-micrometer-thick) fibers to capture organic vapors. The fiber, residing inside a syringe, is coated with a chemical polymer that, when exposed to the ambient environment for a suitable amount of time, can collect thousands of different compounds by acting as a chemical sponge. The polymer coatings are specific for different types of compounds such as chemical warfare agents, high explosives, or illegal drugs.

The collection technique requires no solvents, sample workup, or additional equipment typically associated with obtaining evidence. The fibers can be inserted directly into a portable or stationary GC–MS for immediate analysis.

Forensic Science Center chemist Del Eckels uses the 28-kilogram portable gas chromatograph–mass spectrometer that fits inside a wheeled suitcase. The portable unit, comparable in sensitivity and selectivity to much larger and heavier units, permits fast on-the-scene chemical analysis.



The imaging laser-ablation mass spectrometer combines a laser for vaporizing extremely small amounts of material, an ion trap time-of-flight mass spectrometer for analysis, and a high-powered microscope for viewing.

Nunes says that because the fibers are fragile, they had never been taken into the field. To overcome their fragility, an FSC team developed rugged aluminum transport tubes, with each tube securing one syringe and fiber. A group of five tubes is contained in each kit. The hermetically sealed tubes prevent any possibility of cross-contamination and support chain-of-custody requirements. A sampling port in the bottom of the tube permits assaying the contents in a glove box before the tube is actually opened.

SPME sampling is being put to good use by FSC weapons scientist David Chambers to monitor nuclear weapon warheads safely. This activity is part of the NNSA's Stockpile Stewardship Program to maintain the safety and reliability of the nation's nuclear stockpile.

Center Plays Role in Famous Law Enforcement Cases

The Forensic Science Center (FSC) has played a pivotal role in several well-publicized criminal investigations. For example, FSC examined the composition and structure of tiny bomb fragments containing trace metal and chemical residues in the Unabomber case.

The center provided analysis and testimony leading to the conviction of Fremont, California, bomber Rodney Blach, a former Chicago Police Department forensic investigator. Blach was convicted of planting bombs during 1998 at the homes of the police chief, a city council member, and others. Former FSC Director Brian Andresen helped investigators from the federal Bureau of Alcohol, Tobacco and Firearms (ATF) to reconstruct what Tom Rogers, assistant district attorney, characterized as "the largest as well as the most electronically sophisticated domestic pipe bombs the ATF had ever encountered." Rogers said, "The electronic aspects of the devices were beyond the expertise of anyone at the ATF."

FSC supported the Democratic National Convention in 2000 by providing a mobile forensic laboratory for the Los Angeles County Sheriff's Terrorist Early Warning Group. The center was also instrumental in interpreting factors surrounding the death of Gloria Ramirez, who made several hospital emergency room personnel violently ill in a well-publicized Southern California case.

FSC helped prosecutors in Glendale, California, rearrest Efren Saldivar, the self-proclaimed Angel of Death and alleged killer of many terminally ill hospital patients. FSC scientists performed toxicology analyses on exhumed tissues from 20 patients. They didn't expect to find anything. However, with the help of completely new techniques, including sample collection procedures developed by the center, they were able to identify the drug Pavulon in the bodies of six of the deceased patients. The rearrest of Saldivar was based primarily on the center's findings

Identifying Bullet Fragments

FSC came to the aid of Kings County, California, authorities who were stymied by an execution-style triple homicide. The evidence included a variety of bullet fragments but no weapons. Investigators found corroded, expended casings scattered around the grounds where the suspects lived. FSC personnel led by Rick Randich chemically treated the casings to remove corrosion and then used optical and scanning electron microscopes to match the crime-scene evidence with residence specimens. The staff published its restoration methods as an aid to other agencies.

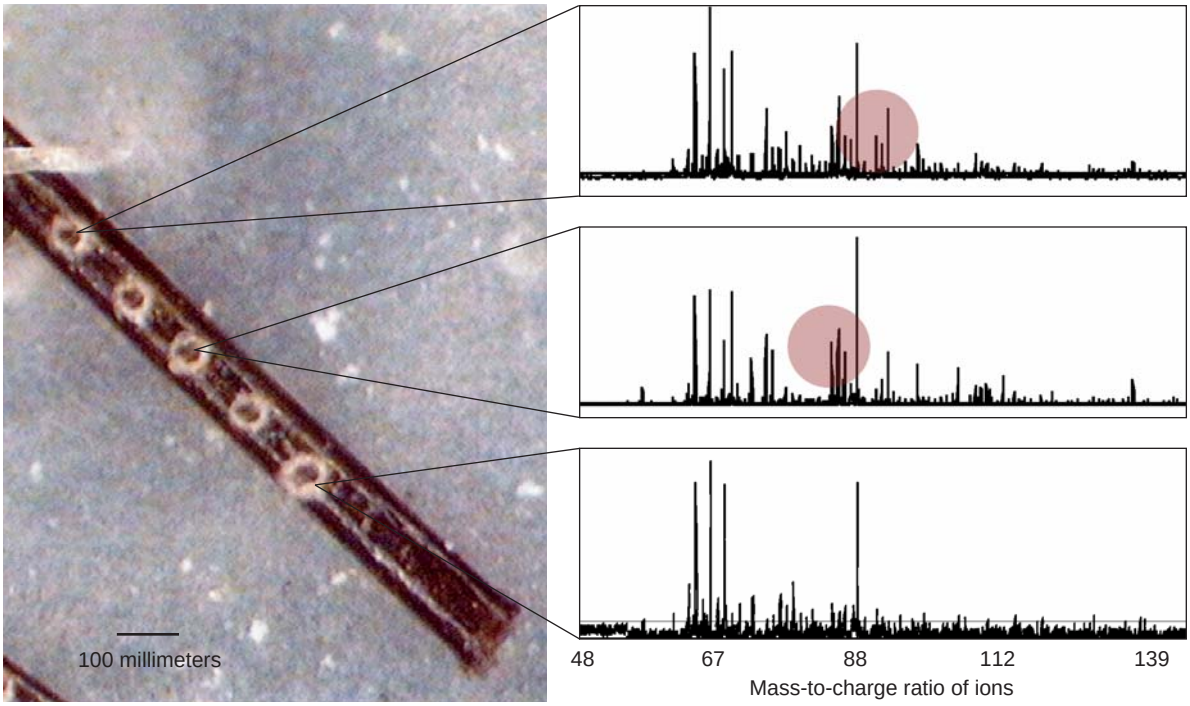
The center analyzed debris from an explosion that killed a scientist during a 1992 cold fusion experiment at SRI International in Palo Alto, California. In testing the explosion debris, FSC chemists discovered a trace amount of oil in the interior of the SRI electrochemical cell. They determined that a likely source of this oil was lubricating fluid that remained from machining the metal cell components. They concluded that the high-pressure oxygen atmosphere of the electrochemical cell possibly created the potential for an explosive reaction with the oil.

Many FSC investigations involve identifying unknown substances. One specimen brought to the center was a suspicious green liquid uncovered by the Federal Bureau of Investigation (FBI) during a search of a stolen cache of weapons. The container of the liquid was labeled "poison" and gave a dilution formula for use. FSC chemists analyzed the solution for chemical warfare agents but finally identified it as a concentrated cleaning agent.

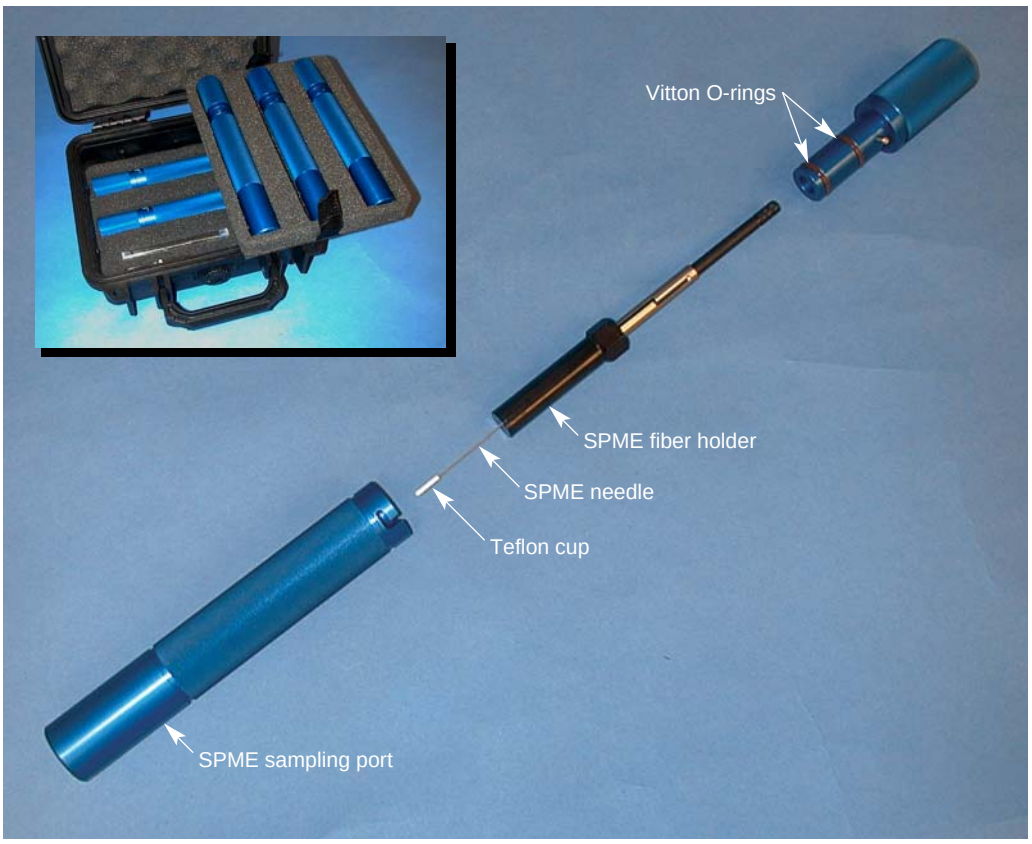
Another extraordinary analysis centered on a shipment of white crystals in ampoules from China that was thought to be heroin. The powder was interdicted by the U.S. Customs Service and subsequently investigated by the FBI. FSC analyses identified the material as tetrodotoxin, a deadly marine neurotoxin derived from puffer fish. "The definite identification of tetrodotoxin was a real success story for the center," says Andresen.

In the past several months, FSC has been helping authorities to identify samples of substances suspected of being anthrax. Several of the specimens brought to the center by law enforcement officials were from the local community, while others were from locations at the Laboratory. None was found to be real anthrax; instead, the powders were determined to be food materials, dust, dirt, cell culture medium, and powdered paper.

The imaging laser-ablation mass spectrometer allows an investigator to "walk down" a hair shaft by drilling consecutive holes with the laser on the same hair and analyzing each to obtain a volatile sample for a history of activities such as drug use or exposure to chemical weapon compounds.



The Forensic Science Center's solid-phase microextraction (SPME) collection kits use optical fibers as "chemical dipsticks" and (inset) rugged aluminum transport tubes for safe and efficient sampling. The technique has revolutionized collecting evidence in the field.



Chambers uses SPME's coated fibers to collect volatile and semivolatile molecules that are formed or outgassed from the nuclear and thermal breakdown of organic polymers and high explosives. Signs of outgassing can indicate problems such as corroded metal parts that need to be replaced. By monitoring for the presence of these chemical vapors, scientists are alerted to problems that may be developing inside the weapon.

The center has provided the FBI and other agencies with SPME field kits for the safe and rapid collection of chemical warfare agents. The kits are equally well suited for drug detection and arson investigations. FSC has also developed a new SPME transport tube that is smaller and lighter so that it can fit inside a shirt pocket. Both versions are being licensed to industry for sale to government agencies.

This solid-phase microextraction device is used to collect molecules that are formed or outgassed from the nuclear and thermal breakdown of organic polymers and high explosives contained in nuclear warheads. Signs of outgassing can indicate problems with parts that need to be replaced.

Always On Call

Although the Forensic Science Center was highlighted in a Tom Clancy novel, it is not fiction. It is a rich resource for the national security and intelligence communities and has proved itself a valuable ally to federal and state agencies alike. Just as they have for the past 10 years, FSC personnel will be on call for the next case and the next sample.

—Arnie Heller

Key Words: anthrax, Chemical and Biological National Security Program, Forensic Science Center (FSC), gas chromatograph–mass spectrometer (GC–MS), laser-ablation mass spectroscopy, Organization for the Prohibition of Chemical Weapons (OPCW), solid-phase microextraction (SPME), stockpile stewardship, thin-layer chromatography (TLC).

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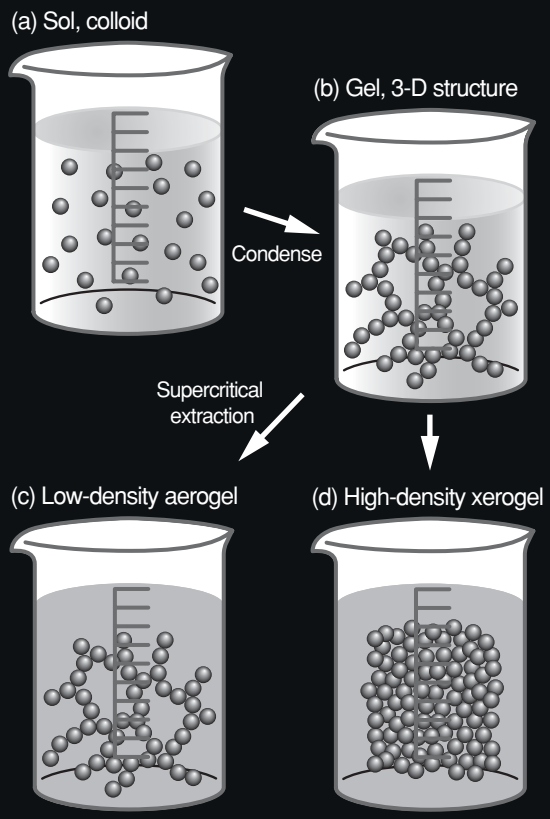
Nanoscale Chemistry Yields Better Explosives

ONE thousand years ago, black powder was prepared by grinding saltpeter, charcoal, and sulfur together into a coarse powder using a mortar and pestle. Since then, the equipment for making energetic materials—explosives, propellants, and pyrotechnics—has evolved considerably, but the basic process for making these materials has remained the same. That, however, is changing, thanks to an explosive combination of sol-gel chemistry and modern-day energetic materials research.

At Livermore Laboratory, sol-gel chemistry—the same process used to make aerogels or "frozen smoke" (see *S&TR*, November/December 1995)—has been the key to creating energetic materials with improved, exceptional, or entirely new properties. This energetic materials breakthrough was engineered by Randy Simpson, director of the Energetic Materials Center; synthetic chemists Tom Tillotson, Alex Gash, and Joe Satcher; and physicist Lawrence Hrubesh.

These new materials have structures that can be controlled on the nanometer (billionth-of-a-meter) scale. Simpson explains, "In general, the smaller the size of the materials being combined, the better the properties of energetic materials. Since these 'nanostructures' are formed with particles on the nanometer scale, the performance can be improved over materials with particles the size of grains of sand or of powdered sugar. In addition, these 'nanocomposite' materials can be easier and much safer to make than those made with traditional methods."



In sol-gel methodology, (a) chemicals in solution produce nanometer-size particles called sols. (b) These sols are linked into a three-dimensional solid network called a gel. (c) The solution can be supercritically extracted to produce aerogels, or (d) evaporated to create xerogels.

Energy Density vs Power, the Traditional Tradeoffs

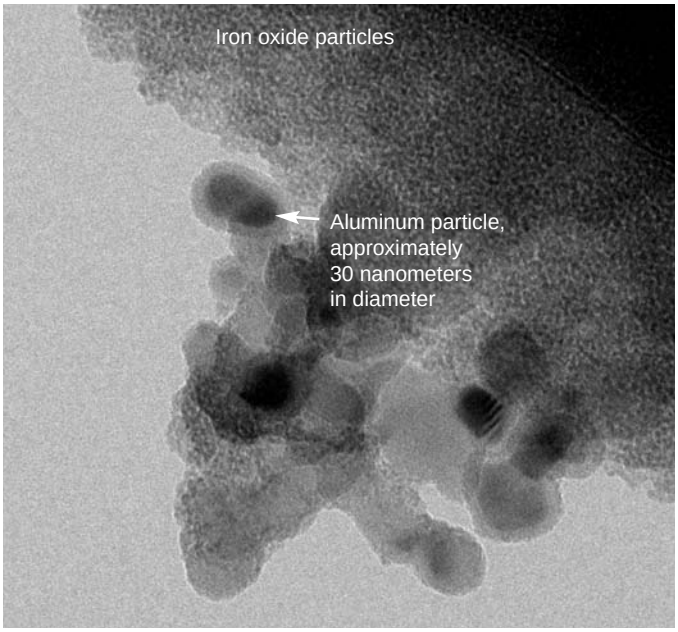
Energetic materials are substances that store energy chemically. For instance, oxygen, by itself, is not an energetic material, and neither is fuel such as gasoline. But a combination of oxygen and fuel is.

Energetic materials are made in two ways. The first is by physically mixing solid oxidizers and fuels, a process that, in its basics, has remained virtually unchanged for centuries. Such a process results in a composite energetic material such as black powder. The second process involves creating a monomolecular energetic material, such as TNT, in which each molecule contains an oxidizing component and a fuel component. For the composites, the total energy can be much greater than that of monomolecular materials. However, the rate at which this energy is released is relatively slow when compared to the release rate of monomolecular materials. Monomolecular materials such as TNT work fast and thus have greater power than composites, but they have only moderate energy densities—commonly half those of composites. "Greater energy densities versus greater power—that's been the traditional trade-off," says Simpson. "With our new process, however, we're mixing at molecular scales, using grains the size of tens to hundreds of molecules. That can give us the best of both worlds—higher energy densities and high power as well."

Energetic Nanostructures in a Beaker

To control the mix of oxidizer and fuel in a given material at the nanometer scale, Livermore researchers turned to sol-gel methodologies. Sol-gel chemistry involves the reactions of chemicals in solution to produce nanometer-size particles called sols. These sols are linked together to form a three-dimensional solid network or skeleton called a gel, with the remaining solution residing in the open pores of the gel. The solution can then be supercritically extracted to produce aerogels (highly porous, lightweight solids) or evaporated to create xerogels (denser porous solids).

"A typical gel structure is extremely uniform because the particles and the pores between them are so small," notes Tillotson. "Such homogeneity means that the material's properties are also uniform. Our main interest in the sol-gel approach is that it will allow us to precisely control the composition and morphology of the solid at the nanometer scale so that the material's properties stay uniform throughout—something that can't be achieved with conventional techniques."



Transmission electron micrograph of a thermitic nanocomposite energetic material. The material is made up of an extremely fine iron oxide xerogel (approximately 2-nanometer particles) that has approximately 30-nanometer-diameter aluminum metal spheres (the larger globules) embedded in it.

Using these sol-gel-processing methods, the team derived four classes of energetic materials: energetic nanocomposites, energetic nanocrystalline materials, energetic powder-entrained materials, and energetic skeletal materials.

Energetic nanocomposites have a fuel component and an oxidizer component mixed together. One example is a gel made of an oxidizer with a fuel embedded in the pores of the gel. In one such material (termed a thermite pyrotechnic), iron oxide gel reacts with metallic aluminum particles to release an enormous amount of heat. "These reactions typically produce temperatures in excess of 3,500°C," says Simpson. Thermites are used for many applications ranging from igniters in automobile airbags to welding. Such thermites have traditionally been produced by mixing fine powders of metal oxides and metal fuels. "Conventionally, mixing these fine powders can result in an extreme fire hazard. Sol-gel methods can reduce that hazard while dispersing extremely small particles in a uniform way not possible through normal processing methods," adds Simpson. The Livermore team has successfully synthesized metal oxide gels from a myriad elements. At least in the case of metal oxides, sol-gel chemistry can be applied to a majority of elements in the periodic table.

In energetic nanocrystalline composites, the energetic material is grown within the pores of an inert gel rather than mixed into it. One way to initiate the growth is to dissolve the energetic material in the solvent used to control the density of the resulting gel. After the gel is formed, the energetic material in the pore fluid is induced to crystallize within the pores. The Livermore team synthesized nanocrystalline composites in a silica matrix with pores containing the high explosive RDX or PETN. The resulting structures contain crystals so small that they do not scatter visible light and are semitransparent.

In the powder-entraining method, a high concentration of energetic powders (90 percent by weight) is loaded within a support matrix (for example, silica) that takes up a correspondingly small mass. Highly loaded energetic materials are used in a variety of applications, including initiators and detonators. Manufacturing this type of energetic material using current processing technologies is often difficult. Producing detonators with pressed powders is a slow manufacturing process, mixing two or more powders homogeneously is difficult, and precise geometric shapes are not easy to produce. Also, pressing powders is a hazardous process.

Many of these problems may be overcome with the sol-gel process. One result is that the sol-gel explosives formed by adding energetic powders are much less sensitive than those

produced by conventional methods. “These results were surprising because conventionally mixed powders generally exhibit increased sensitivity when silica powders are added,” says Simpson. “We’re still exploring the reasons for this decreased sensitivity, but it appears to be generally true with sol-gel-derived energetic materials.”

The final class of energetic material produced by sol-gel methods is energetic skeletal materials. Basically, the sol-gel chemistry is used to create a skeletal matrix, which is itself energetic. Satcher thinks that it might also be possible to form a nanostructure made up of a fuel–oxidizer skeleton with precise stoichiometry (the numerical relationship of elements and compounds as reactants and products in a chemical reaction). “This is something we are still looking into,” he adds. In addition to providing materials that have high energy density and are extremely powerful, sol-gel methodologies offer more safe and stable processing. For instance, the materials can be cast to shape or do not require the hazardous machining techniques required by materials that cannot be cast.

Future Looks Bright

Right now, making energetic materials using the sol-gel technique is in the basic research stage, but results look promising. “Many compositions depend on a simple, inexpensive procedure that we can basically do in an ordinary chemistry beaker,” says Tillotson. He notes that the practical advantages of these materials are encouraging. Some of the pluses are less sensitivity, safe mixing, low-temperature synthesis, safe handling, safe processing, and homogeneity leading to better performance.

“We’ve just begun to explore the possibilities for these new materials and the methodologies that produced them,” adds Simpson. “This approach is like a new baby—it has lots of potential. The ramifications are still largely unknown.”

—Ann Parker

Key Words: aerogel, energetic materials, explosives, nanocomposites, PETN, propellants, pyrotechnics, RDX, sol-gel, xerogel.

For further information contact Randy Simpson (925) 423-0379 (simpson5@llnl.gov).

In the laboratory, Alex Gash mixes a sol-gel to create an energetic material.

Plutonium Up Close . . . Way Close

STOCKPILE Stewardship, the Department of Energy's program for assuring the long-term safety and performance of the nuclear weapons stockpile without underground testing, has created a heightened focus on better understanding plutonium.

At Lawrence Livermore, a number of experiments are under way to measure the structural, electrical, and chemical properties of plutonium and its alloys and to determine how these materials change over time. The measurements will enable scientists to better model and predict plutonium's long-term behavior in the aging stockpile. (See *S&TR*, March 2001, pp. 4–12.)

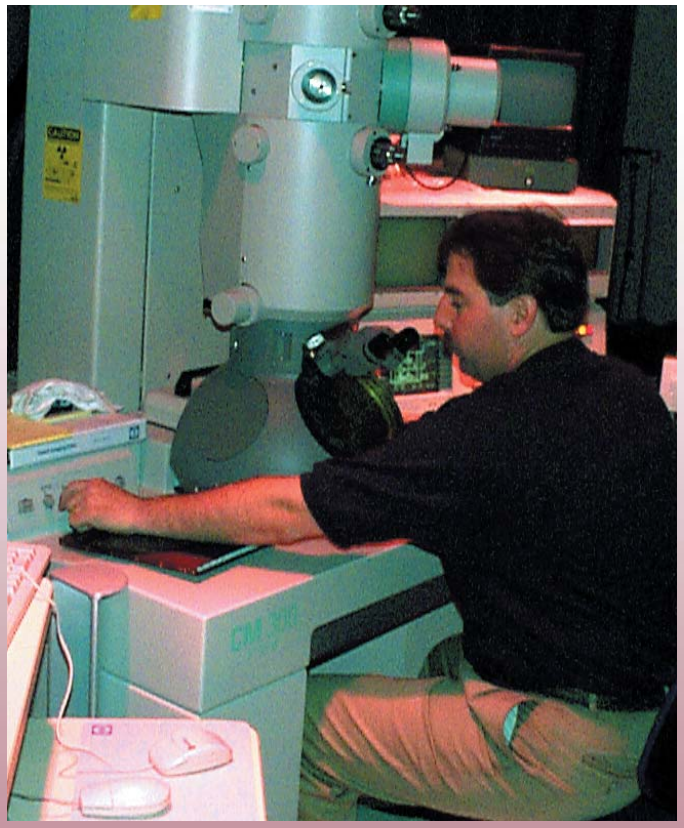
Plutonium's Peculiarities

"Plutonium is a complex and perplexing element," notes metallurgist Adam Schwartz. "For instance, plutonium has seven temperature-dependent solid phases—more than any other element in the periodic table. Each phase possesses a different density and volume and has its own characteristics. Alloys are even more complex; you can have multiple phases present in a sample at any given time."

Because plutonium is so complex, surrogate materials cannot give a complete picture of plutonium's characteristics. With the importance of stockpile stewardship, the Laboratory has seen a resurgence of interest and research in plutonium and the other actinide elements (see *S&TR*, June 2000, pp. 15–22). One area that Schwartz, microscopist Mark Wall, and physicist Bill Wolfer are pursuing as part of their stockpile stewardship responsibilities is the evolution of damage to plutonium's structure. As with the atoms of all metals, plutonium atoms form structures on scales as small as a billionth of a meter. These microstructures are constantly changing because of plutonium's radioactive nature. When an atom of plutonium-239 (the isotope of plutonium used in nuclear weapons) decays, it splits into an alpha particle—a helium nucleus with two protons and two neutrons—and an atom of uranium-235. The heavy uranium atom recoils, displacing other plutonium atoms and disrupting the surrounding microstructure. Scientists are concerned that the buildup of gaseous helium atoms combined with other elements in the weapon's environment might gradually change the properties of the plutonium metal.

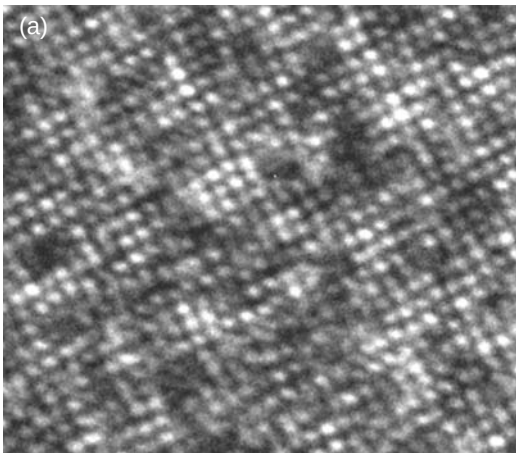
Seeing Beneath the Surface

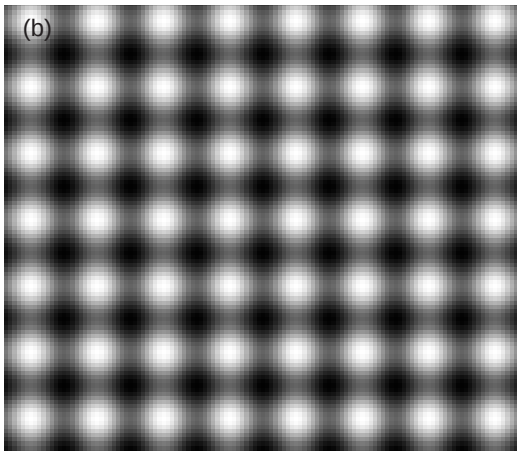
To better understand the basic nature of this complex metal and search out the long-term effects of the weapon environment, scientists must know what goes on at the atomic level. To aid this endeavor, the Laboratory acquired a 300-kiloelectronvolt, field-emission transmission electron microscope (TEM) about one year ago. This remarkable instrument uses electrons instead of light waves to "see," so features can be resolved, or viewed at the atomic scale. Where most microscopes can only probe the surface of materials, a TEM looks directly at the internal structure of materials, explains Wall.



Microscopist Mark Wall uses the transmission electron microscope to image the microstructure of plutonium.

(a) An atomic resolution image of plutonium. Such an image was created for the first time ever by the team studying plutonium properties with a transmission electron microscope. (b) A high-resolution computed image of plutonium's atomic structure.





The Inside Scoop with the Transmission Electron Microscope

According to Mark Wall, the new 300-kiloelectronvolt transmission electron microscope (TEM) leased by the Laboratory is the best of its kind in DOE's weapon complex. "Having a high accelerating voltage allows us to see through thicker specimens, facilitating more microstructural observations and better image resolution," says Wall.

The TEM is used to characterize the internal structure of a wide variety of materials, not just plutonium. It not only can image the microstructure directly, but can also identify the phases present in a specimen. The TEM characterization techniques are cataloged here under headings that describe what they do (although there is some overlap among the techniques):

Characterization of Atomic Structure

High-Resolution Atomic Structure Imaging: Directly resolves the atomic structure of crystalline materials down to individual columns of atoms.

Characterization of Microstructure, Defects, and Phases

Bright Field: Images the internal microstructure of materials, including grain and defect structures such as dislocations and voids. Can also be used to observe precipitates or inclusions.

Dark Field and Weak Beam: Allows researchers to link diffraction information with specific phase regions in the sample. Weak-beam imaging is dark-field imaging at higher resolution and is primarily used for imaging closely spaced defect structures on the nanometer scale.

Electron Diffraction (Selected Area Diffraction) and Microdiffraction: Both techniques help researchers identify internal crystal structures. Selected area diffraction allows researchers to view and record the electron diffraction pattern from selected areas as small as 0.5 micrometer. Microdiffraction allows analysis of regions as small as 1 nanometer.

Convergent Beam Electron Diffraction: Reveals diffraction details that provide additional three-dimensional crystallographic and symmetry information.

Lorentz Microscopy: Images directional variations in the magnetic field within thin samples.

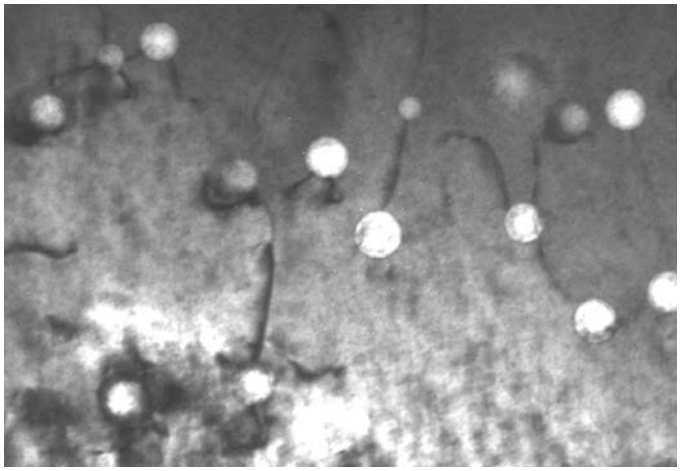
In Situ Microscopy: Allows researchers to record the evolution of a material's microstructure during heating, cooling, and mechanical deformation.

Characterization of Chemical Composition and Impurities

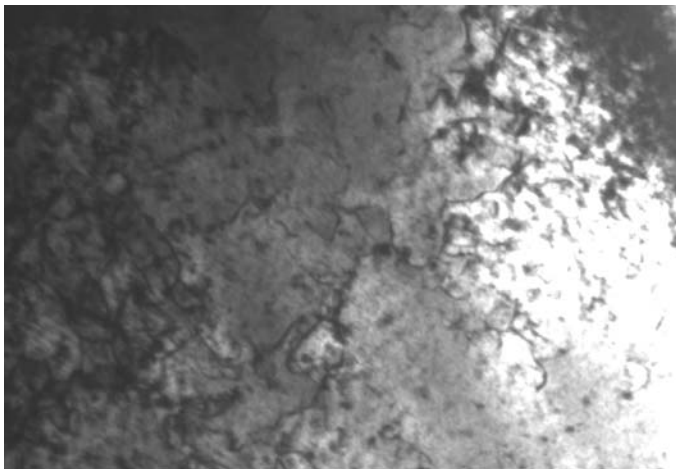
Energy-Dispersive Spectroscopy: Produces x-ray spectra that reveal the presence and amount of elements (for carbon and heavier elements).

Parallel Electron Energy Loss Spectroscopy: Complements energy dispersive spectroscopy, in that it is more sensitive to light elements, including lithium and heavier elements.

*Energy-Filtered Transmission Electron Microscop*e: Acquires real-time, quantitative chemical "maps" of a specific region with a resolution as small as 1 nanometer.



Voids or bubbles could be created by recoiling uranium nuclei and gaseous helium from alpha particles that result from plutonium decay. Here, an aged sample has been intentionally annealed to create bubbles.



A dislocation—an extra half plane of atoms—in the plutonium structure can create sinks or sources for radiation damage.

The primary strength of the instrument is that it can provide detailed characterization simultaneously over many length scales and at high resolution—from hundreds of micrometers to nanometers—and do this in either imaging, spectroscopic, or diffraction modes (see box at left). "In principle, we can observe and measure the defects and composition of microstructural features in these materials down to the nanometer level," says Wall.

Schwartz and Wall start with plutonium samples measuring less than 3 millimeters in diameter and 150 micrometers thick. They then use special sample preparation techniques to thin each sample until it is transparent to high-energy electrons, that is, to between 10 to 100 nanometers in thickness. The specimens are then vacuum-transferred to the TEM for characterization experiments. The resulting electron micrographs reveal in unprecedented detail the nature of the material and any defects in it. During this work, Schwartz and Wall produced the first-ever image of plutonium at the atomic level.

Using samples of plutonium from old, disassembled nuclear warheads and comparing their resulting micrographs to those from newly cast plutonium, the researchers can better determine the kinds and amounts of defects and changes that occur over time. In particular, they look for voids or bubbles created by recoiling uranium nuclei and the gaseous helium from alpha particles. An example from an old material annealed to intentionally form bubbles is shown in the image directly above. Dislocations—which can be described as an extra half plane of atoms—can create sinks or sources for radiation damage (see image above right).

So Far, So Good

To date, the news for the stockpile is encouraging. Schwartz sums up the results as "So far, so good. We haven't seen any issues or surprises with the pit samples we've viewed." Last year, the team began another project, looking at special plutonium alloys that have been prepared to accelerate the rate of aging. For Livermore's Enhanced Surveillance Program (see *S&TR*, September 1999, pp. 3–11), scientists have made several alloys spiked with plutonium-238, which decays much faster than plutonium-239, to try to understand what will happen with stockpiled plutonium as it ages.

Schwartz and Wall also plan to conduct in situ microscopy of plutonium. Heating plutonium samples up to 400°C will allow researchers to see helium bubbles nucleate and for the first time see the early stages of nucleation. "In essence, we'll be speeding up the kinetics of the material and increasing the diffusion rate," said Schwartz.

—Ann Parker

Key Words: plutonium research, stockpile stewardship, transmission electron microscope.

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Present at the Creation

When they synthesized elements 114 and 116, Russian and Livermore scientists confirmed decades-old predictions of the existence of superheavy elements with comparatively long lifetimes.

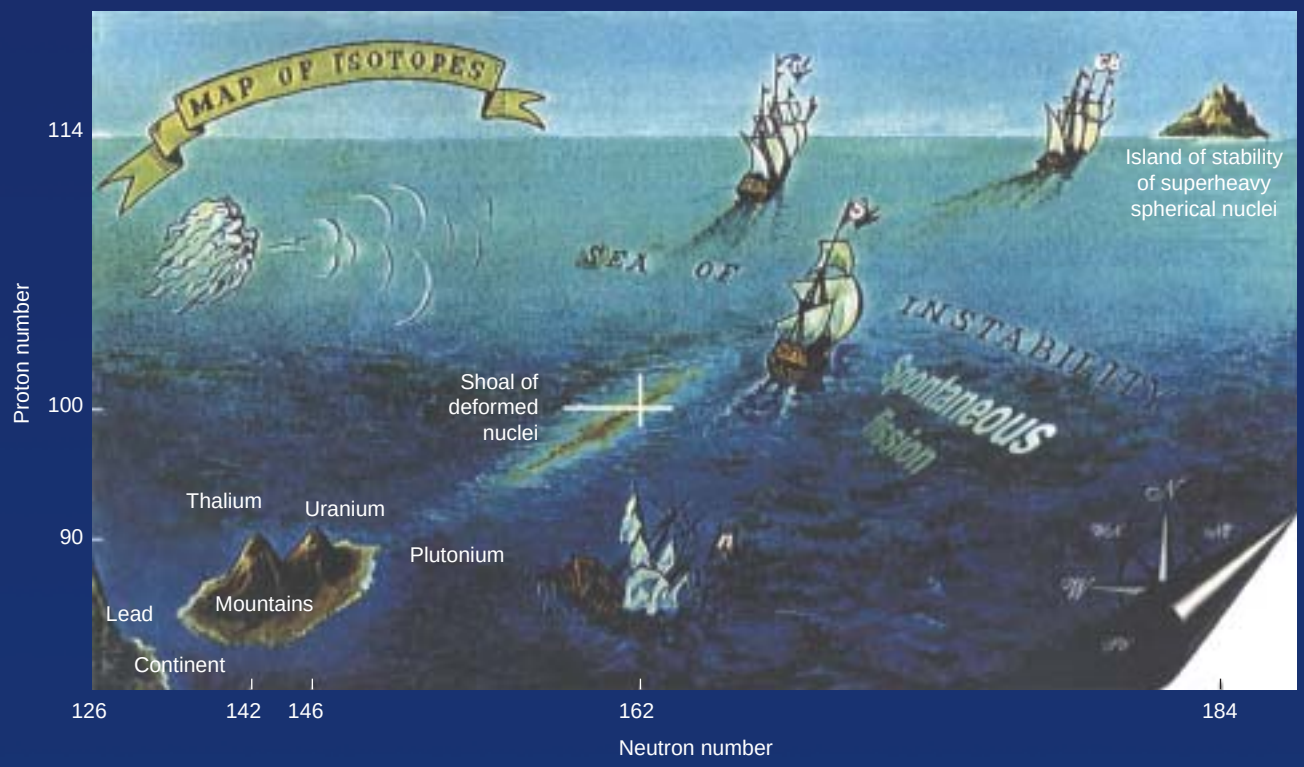
ELEMENTS that do not exist in nature—that have been created in a laboratory—are unstable. After hours or days of one element bombarding another with enough energy for both to fuse, the resulting new element typically is born and begins to decay instantly.

Neptunium and plutonium (elements 93 and 94) were the first elements created in a laboratory, at the University of California at Berkeley in 1940. Scientists have since fabricated many more elements, each one heavier and with a shorter half-life than the one before it.

In the 1960s, a few physicists predicted that some elements around element 114 would survive longer than any of their synthesized predecessors. Early estimates for the half-lives of these more stable elements were as high as billions of years. Later computer modeling reduced the anticipated half-lives to seconds or minutes before the element began to decay.

Half-lives of seconds or minutes may seem brief. But consider that various atoms of element 110 created in the laboratory have had half-lives ranging from 100 microseconds to 1.1 milliseconds. The only atom of element 112 that had been created before 1998 had a lifetime of 480 microseconds. As described further in the box on p. 57, the long-lived nuclei of elements around element 114 would comprise an "island of stability" in a "sea" of highly unstable elements.

When a collaboration of Russian and Livermore scientists at the Joint Institute for Nuclear Research in



Map of the voyage to the island of stability.

Dubna, Russia, created element 114 in 1998, the first atom survived for 30 seconds before it began to decay, a spontaneous process that leads to the creation of another element with a lower number on the periodic table. (See the box on pp. 54–55 for more information on stability and instability.) A total of 34 minutes elapsed before the final decay product fissioned, splitting in two the surviving nucleus. These lifetimes may seem brief, but they are millions of times longer than those of other recently synthesized heavy elements.

Since that groundbreaking effort in 1998, the team has created another atom of element 114. This one has a different number of neutrons and thus a different mass, thereby making it a different isotope of element 114. The team has also created several previously undiscovered isotopes of elements 112, 110, and 108 to which element 114 decayed. More recently, the team added element 116 to the periodic table with the creation of three atoms of the element in a series of experiments.

Nuclear chemist Ken Moody leads the Livermore portion of the international collaboration. “In 1998, we proved that there really was an island of stability,” he said. “We proved that years of nuclear theory actually worked.”

The collaboration began in 1989. with heavy element chemist Ken Hulet representing Livermore and Yuri Oganessian, scientific director of the Flerov Laboratory of Nuclear Reactions at the Joint Institute, leading the Russians. In the early 1990s, the U.S.–Russian team discovered two isotopes of element 106, one isotope of 108, and one of 110 at the Dubna institute.

“In 1990, when Ron Lougheed, who has since retired, and I went to Dubna, we were the first U.S. scientists to perform experiments at that institute,” adds Moody. “Remember what was happening then. The Berlin Wall had just fallen, and Eastern Europe was in turmoil. The early days of the collaboration were definitely interesting.”

Photo of Russian–Livermore team.

Forty Days and Nights

Noah's flood could have come and gone in the time it took the collaboration to create the first atom of element 114. For 40 days of virtually continuous operation, calcium ions bombarded a spinning target of plutonium in Dubna's U400 cyclotron. While the first atom of element 114 was actually created on November 22, 1998, Russian researchers discovered it in data analysis and communicated the news to Livermore on December 25, 1998—quite the Christmas present.

A Primer on Stability and Instability

Why should element 114 be so much more stable and long-lived than so many of its synthesized predecessors? The answer lies in basic chemistry.

The nucleus of an atom is surrounded by one or more orbital shells of electrons. The electron configurations of atoms of the many elements vary periodically with their atomic number, hence "the periodic table of the elements."

Elements with unfilled shells seek out electrons in other elements to fill them. These include carbon, oxygen, and all of the "reactive" elements that want to react with other elements. This is the basis of covalent bonding. The noble gases (on the far right column of the periodic table) have a completely filled outer electron shell and hence are highly stable. They are termed noble because they are "aloof," with no desire to react with other elements.

Protons and neutrons are in analogous shells within the nucleus. The proton shells of helium, oxygen, calcium, nickel, tin, and lead are completely filled and arranged such that the nucleus has achieved extra stability. The atomic numbers of these elements—2, 8, 20, 28, 50, and 82—are known as "magic numbers." These same numbers plus 126 are magic numbers for neutrons. Notice that the magic numbers are all even. No truly stable element heavier than nitrogen has an odd number of both protons and neutrons. Elements with even numbers of protons and neutrons make up about 90 percent of Earth's crust.

A nucleus is "doubly magic" when the shells of both the protons and neutrons are filled. Lead-208 has 82 protons and 126 neutrons, both of which are magic numbers. Lead-208 is thus doubly magic and seems to be virtually eternal.

A long-lived, stable element such as lead does not decay. However, all elements with an atomic number greater than 83 (bismuth) exhibit radioactive decay. Decay may happen in several ways. For heavy elements, an unstable or radioactive isotope usually decays by emitting helium nuclei (alpha particles) or electrons (beta particles), leaving a daughter nucleus of an element with a different number of protons. This process typically continues until a stable nucleus is reached. Plutonium, for example, decays ultimately to lead.

The heavy elements that have been created in the laboratory are so unstable that they decay almost immediately and have extremely

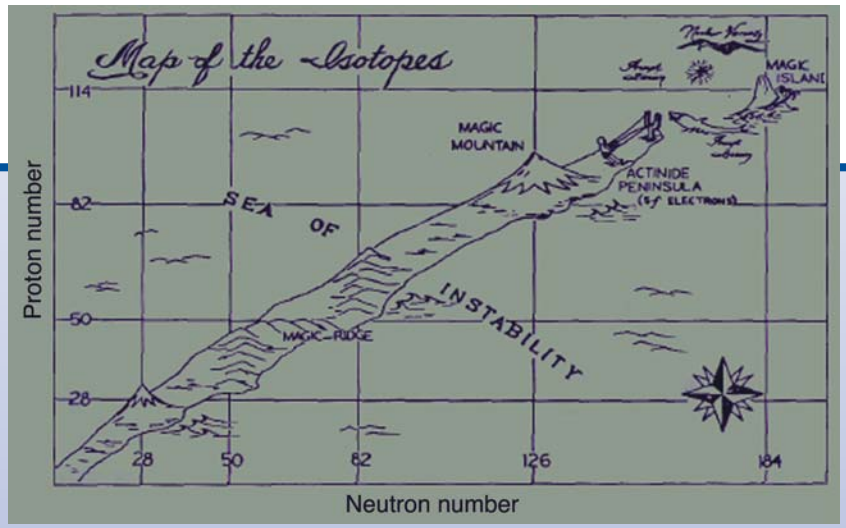
Periodic table

1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yitrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	See Lantha-nides	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	See Acti-nides	104 Rf Rutherfordium	105 Ha Hahnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 - -	111 - -	112 - -		114		116		

Lanthanides	57–71 Ln* Lanthanides	57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
Actinides	89–103 An* Actinides	89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

The box on p. 58 shows the "recipe" for the early Dubna experiments that created isotopes of element 114. Plutonium, with an atomic number, or *Z*, of 94, and calcium, $Z = 20$, add up to the necessary $Z = 114$. By fusing plutonium-244, an isotope of plutonium with 150 neutrons, and calcium-48, a neutron-rich isotope with 28 neutrons, a compound nucleus with 114 protons and 178 neutrons (150 + 28) would in theory be possible. In fact, however, when the plutonium-244 and calcium-48 nuclei collide with enough energy to overcome their mutual electrostatic repulsion, the compound nucleus has excess energy. A few neutrons evaporate to de-excite the nucleus and produce an isotope with 175 neutrons.

To discover whether new elements were created by the bombardment of plutonium, the team was interested in finding "events" comprising a series of alpha decays ending with spontaneous fission. In alpha decay, an isotope loses an alpha particle, which is two protons and two neutrons (or a helium nucleus). For example, an atom of element 114 with 175 neutrons (described as isotope 114-289) would emit an alpha particle, thereby becoming isotope 112-285, having lost 2 protons and 2 neutrons. The atom of 112-285 would become 110-281, which would become 108-277. At some point, fission would occur, ending the process.

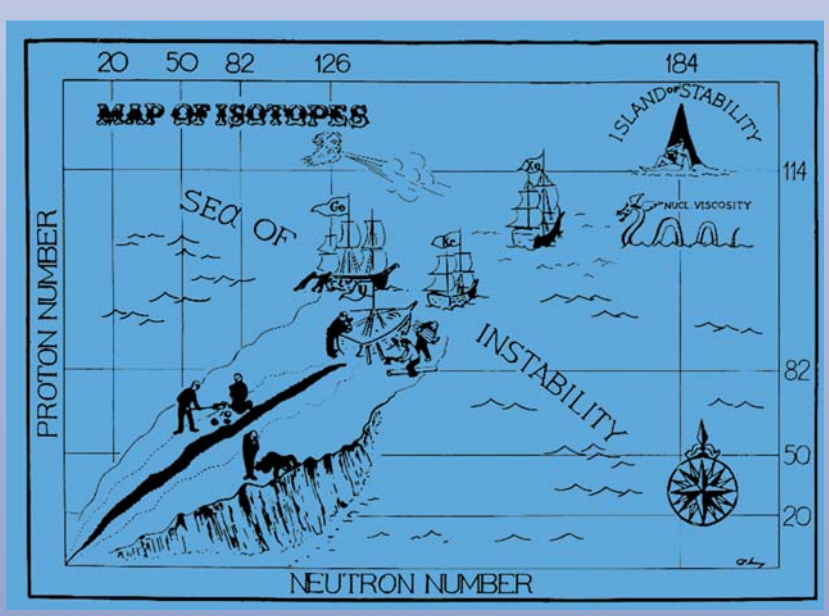


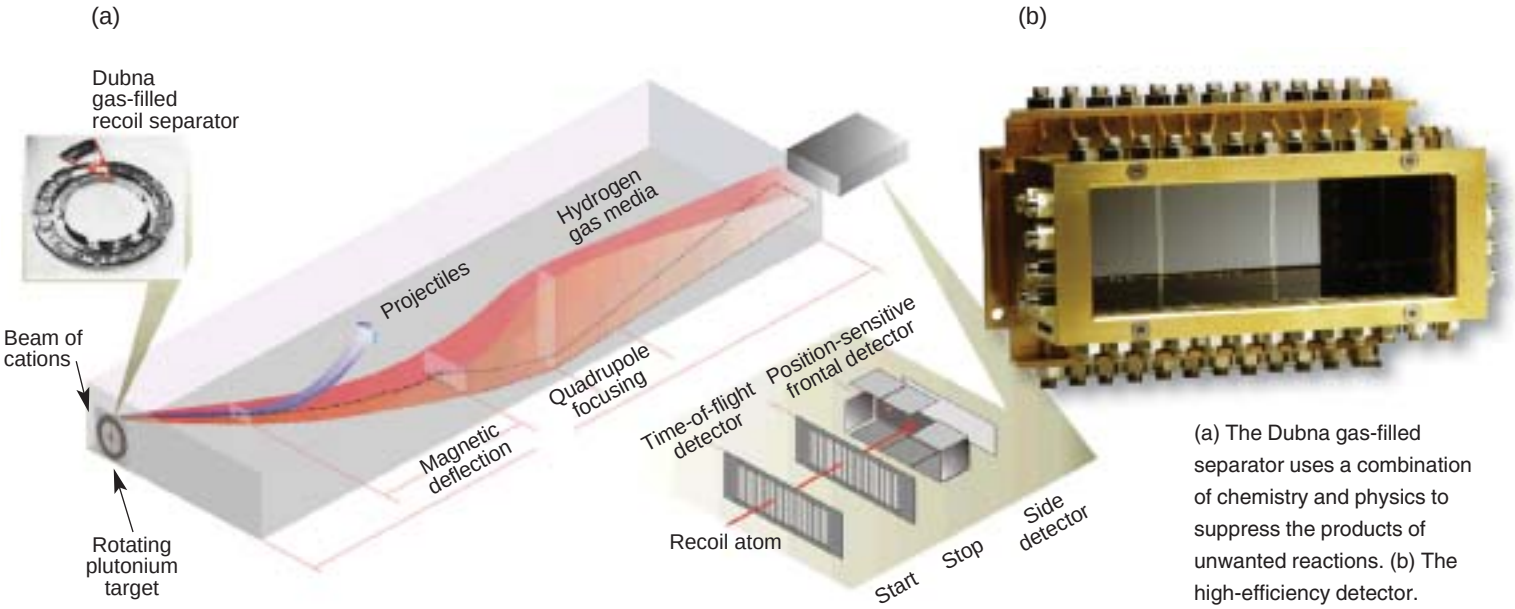
Nuclear theory (top) in the U.S. and (bottom) in Russia, in about 1969.

short half-lives and thus lifetimes. How quickly a particular isotope decays is measured by its half-life. Plutonium-239, which decays very slowly, has a half-life of about 24,000 years, while plutonium-238's half-life is just 88 years. Half-lives are a result of a statistical process. If an experiment produces only one atom, then a half-life cannot be determined. Thus, with one or a few atoms, scientists talk instead about lifetimes.

In the mid-1960s, a physicist in the U.S. predicted that the next magic proton number above 82 would be 114, not 126, and that an atom with a doubly magic nucleus of 114 protons and 184 neutrons should be the peak of an island of stability. Russian scientists had come to the same conclusion at about the same time.

In the years since, increasingly sophisticated computer models have indicated that element 114 would exhibit significant nuclear stability even with neutron numbers as low as 175. Note that element 114 is expected to lie in the same column (or group) of the periodic table as lead. The two elements are expected to share many properties.





(a) The Dubna gas-filled separator uses a combination of chemistry and physics to suppress the products of unwanted reactions. (b) The high-efficiency detector.

At the same time, however, unwanted nuclei generated by the experiment also undergo alpha decay and fission, mimicking the decay sequence of element 114. Trillions of these unwanted nuclei are produced every day, whereas the expected production rate for an element 114 isotope was much less than one atom per day. To deal with the problem of unwanted nuclei in earlier experiments, Dubna scientists had developed a gas-filled mass separator to separate unwanted nuclei from the desired ones. "It worked marvelously," says Moody.

Heavy-element reaction products recoil from the spinning plutonium target wheel and enter the mass separator, a chamber filled with low-pressure hydrogen gas confined between the pole faces of a dipole magnet. The magnetic field is adjusted so that, for the most part, only the nuclei of interest pass through to the detector array.

The desired nuclei are focused with a set of magnetic quadrupoles, pass through a time-of-flight counter, and are captured by a position-sensitive detector. A signal from the time-of-flight counter allows the team to distinguish between the effect of products passing through the separator and the radioactive decay of products that are already implanted in the detector. The flight time through the counter is also used to discriminate between low- and high-*Z* products, because heavier elements travel more slowly. The position-sensitive detector lowers the rate of background interference, allowing scientists to identify and ignore unwanted products.

During 40 days in November and December 1998, with ten-thousand trillion ions per hour of calcium-48 bombarding the plutonium target, the team observed the signals of just three spontaneous fission decays. Three synthesized compound nuclei had been created and passed through the separator before fissioning. Two of them lasted about 1 millisecond each and proved to be products from the decay of the nuclear isomer of americium-244.

Only one of the events involved an implant in the detector followed by three alpha decays in the detector array. This isotope of element 114 (114-289) had a lifetime of 30.4 seconds. It decayed to element 112, which, with a lifetime of 15.4 minutes, decayed to element 110. Element 110, with a lifetime of 1.6 minutes, then decayed to element 108, which decayed by spontaneous fission.

In 2000 and 2001, the collaboration performed three experiments in which a curium-284 target was bombarded with calcium-48 ions to create element 116. The team chose this combination of isotopes because they would produce isotopes of element 116 that should decay to the previously observed isotopes of element 114.

Researchers produced the super-heavy isotope 116-292 once in each of these experiments. They also created some other isotopes repeatedly. Isotopes 114-288, 112-284, and 110-280 have been found five times, lending credibility to several experimental results. However, the first atom of 114-289 with the 30.4-second lifetime has yet to be replicated.

In the Final Analysis

The recipe for element 114 on p. 58 refers to the analysis of 7 gigabytes of

A Stormy Voyage to the Island of Stability

As of November 2001, scientists throughout the world had synthesized 20 elements that do not exist in nature. The ones up to meitnerium (109) have been given official names. Elements 110, 111, 112, 114, and 116 will not be named until their existence has been corroborated with several experiments or by several different groups. Recall that one of the fundamental tenets of science is reproducibility.

In 1940, Ed McMillan and his team at Berkeley bombarded uranium with neutrons to create neptunium (element 93). Then Glenn Seaborg and his colleagues created plutonium-238, the first isotope of plutonium (element 94), through the decay of neptunium-238, which they produced by bombarding uranium with deuterium (heavy hydrogen). Elements 99 and 100 were discovered in the debris of the first hydrogen bomb test in 1952 from the simultaneous capture of many neutrons by uranium. The heavy, highly radioactive uranium isotopes decayed quickly by beta emission down to more stable isotopes of elements 99 (einsteinium) and 100 (fermium). Elements 95, 96, 97, 98, and 101 were created by irradiating heavy nuclei with beams of alpha particles to boost the atomic numbers two steps at a time.

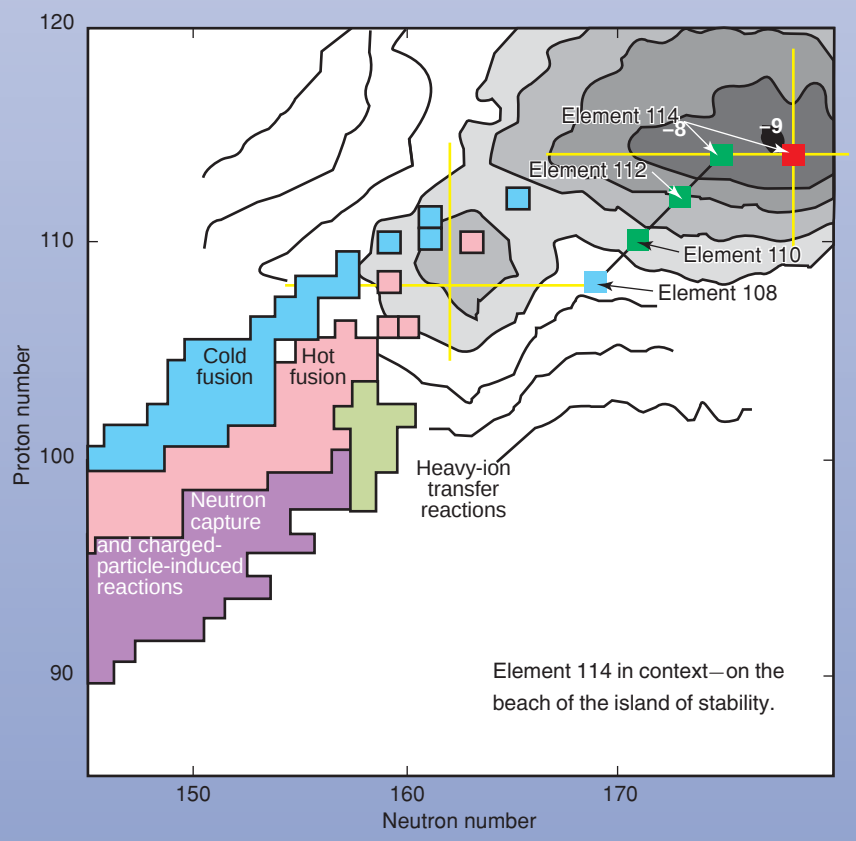
Beginning in the late 1950s, the new particle accelerators were capable of accelerating ions heavier than helium. First, ions of the lightest elements were directed at the heaviest elements. But it took excess energy to cause them to fuse, producing a very hot nucleus that tended to fission almost immediately. Known as "hot fusion," this method yielded elements 102 through 106 by 1974. Many of these experiments included Livermore scientists.

In 1974, Yuri Oganessian at the Joint Institute at Dubna found that if heavier ions are directed at lead and bismuth, less energy was needed to create new elements. These two elements are extra-stable, and thus the resulting compound nucleus has less energy and is more likely to remain intact. This process is known as "cold fusion," not to be confused with the discredited fusion energy process of the same name. Even with cold fusion, so few nuclei of the new element are produced during an experiment that existing detection techniques were not sensitive enough to find them.

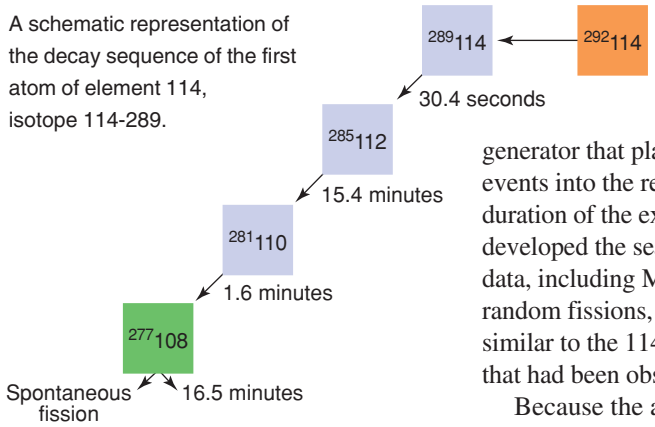
The field of synthesizing ever heavier elements went on hiatus for several years until sophisticated new separation and detection methods were developed in the early 1980s in Germany. German researchers were then able to create and detect elements 107, 108, and 109 in experiments that have since been corroborated such that these synthetic elements now have names. They also created isotopes of 110, 111, and 112, but these results have not yet been fully corroborated.

The German group, the Consortium for Heavy Ion Research at Darmstadt, Germany, has produced an isotope of element 112 that decayed into the same isotope of 110 that the Dubna–Livermore team found in 1994. This isotope had the same energy and lifetime, which is encouraging validation.

The voyage to the island of stability has been a stormy one. It took until 1998 to even reach the beach. As shown in the figure below, the island's peak is still tantalizingly just out of reach.



Element 114 in context—on the beach of the island of stability.



A schematic representation of the decay sequence of the first atom of element 114, isotope 114-289.

data from the first experiments. The team has since accumulated another 23 gigabytes of data, all requiring extensive analysis to verify the times and energies of the alpha decays. Valid decay sequences must fall within the alpha decay time and energy parameters of what is known as the Geiger–Nuttall relationship.

Scientists at Livermore and Dubna analyzed the data in parallel. Livermore gave the Dubna institute a computer workstation for the Russian scientists to use on that mountain of information. Nuclear chemists John Wild and Nancy Stoyer analyzed the data at Livermore. "These duel analyses were independent but were calibrated. In the end, our results agreed," says Wild.

The team must also confirm that the sequences they saw were not composed of random events. "The problem of randomness is real, especially for long-lived elements," adds Wild. "The longer the lifetime of a member of a decay sequence, the greater the probability that the decay could be random."

A novel Monte Carlo method to estimate the probability of whether a decay chain was random or the real thing was the brainchild of nuclear chemist Mark Stoyer. It is a pseudo-random number generator that places random fission events into the real data throughout the duration of the experiment. Nancy Stoyer developed the search code that sifted the data, including Monte Carlo–generated random fissions, for decay sequences similar to the 114-289 decay sequence that had been observed experimentally.

Because the actual decay chains end with a spontaneous-fission event, Nancy Stoyer's search algorithm looks backward from the planted fission event for candidate alpha-decay chains that match actual decay chains and end with a fission event. The number of returned "accidental" decay chains defines the probability that a decay sequence is random. For the first atom of element 114, the random probability was 0.6 percent. "If we eliminate decay chains in which all alpha events do not meet the Geiger–Nuttall relationship," says Moody, "the random probability falls to 0.06 percent. That's fantastic."

Recipe for a New Element

A Livermore chemist with a sense of humor developed this recipe to describe the creation of element 114.

Ingredients:

- 2 grams calcium-48, a rare neutron-rich isotope of calcium. Out of every 100,000 atoms of calcium, only 187 atoms are calcium-48.
- 30 milligrams plutonium-244, the most neutron-rich, long-lived isotope of plutonium. The world's supply of this isotope is only 3 grams.
- The U400 cyclotron at Dubna, Russia, to accelerate calcium ions to 10 percent the speed of light (236 megaelectronvolts).
- A gas-filled recoil separator for removing unwanted reaction products.
- A position-sensitive detector for capturing decays of reaction products.
- 2 computers, one for data acquisition and another for data analysis.
- Numerous Russian technicians and accelerator operators.
- 19 Russian scientists.
- 5 American scientists.

Directions: Combine the first seven ingredients, using 0.3 milligrams per hour of calcium-48. Add lots of patience, a dash of luck, and a dollop of inspiration. Simmer for about 6 months, 24 hours per day, 7 days a week. Use the last two ingredients to analyze 7 gigabytes of data for signature decay sequences of element 114. Garnish with several papers describing the results.

Serves: Very few. In two experiments, makes one atom of 114-289, the lifetime of which is 30 seconds, and two atoms of 114-288, each with a lifetime of 2 seconds.

New Elements Still to Come

The Livermore researchers are continuing its work to explore the southwest shores of the island of stability. With funding from the Laboratory Directed Research and Development program, they have begun efforts to add elements 115 and 113 to the periodic table. They are in the process of sending 22 milligrams of pure americium-243 to Dubna for the work on element 115.

Current exploration of the island of stability, or its beaches, is limited to stable targets and projectile beams. There exists no suitable combination of projectile and target to produce 114-298, the long-predicted highly stable isotope. The isotopes 114-289 and 114-288 require the most neutron-rich isotopes of plutonium and calcium. In the future, when radioactive beam accelerators are capable of producing intense beams of even more neutron-rich isotopes, researchers may venture farther toward the center of the island. For example, calcium-50 has a half-life of 14 seconds, far too short to gather material together to put into a conventional ion source. However, plans are for a radioactive beam facility to produce calcium-50 and accelerate it to energies required for the experiments well before it can decay. Thus, an isotope of element 114 with a mass of 290 or 291, two neutrons closer to the center of the island, may well be possible.

As scientists continue to explore for new elements, they expect that more spherical and longer-lived isotopes will be produced, which will most certainly require more sensitive detection schemes. Challenges abound.

Livermore researchers also want to study the chemical properties of elements 112 and 114. The combination of chemical and nuclear properties defines the usefulness of any nuclide. Most heavy elements exist in such small amounts, or for such short times, that no one has pursued practical applications for them. However, several heavy elements do have uses—americium is used in smoke detectors, curium and californium are used for neutron radiography and neutron interrogation, and plutonium is elemental in nuclear weapons. Although elements 114 and 116 have no immediate use, they do exist, and more of them can be manufactured when uses for them are found. Adds Moody, "Showing that the isotopes of element 114 produced by the collaboration have unique chemical properties will also provide proof that they are indeed a new element."

—Katie Walter

Key Words: element 114, element 116, heavy elements, island of stability, Joint Institute for Nuclear Research in Dubna, Russia.

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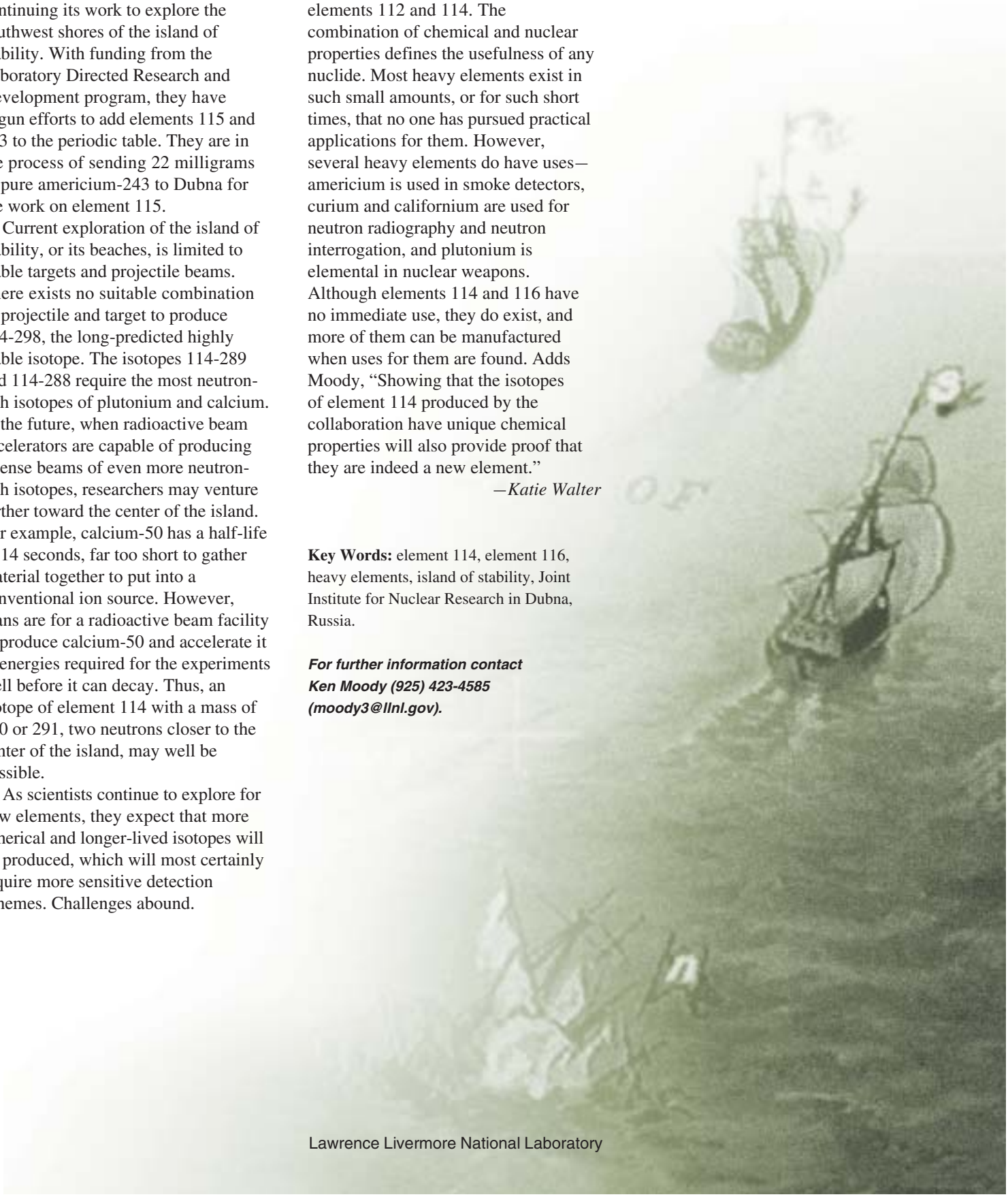


Following Materials

Simulations on massively parallel supercomputers are helping researchers understand how and why materials change and ultimately fail.

FROM breakthrough computer chips to new alloys for automobile engines, advances in materials shape our day-to-day lives and drive economic growth. For Lawrence Livermore scientists, predicting the performance of advanced materials is essential to success in countless research programs in national security, lasers, energy, and biotechnology.

In the past, advances in materials were accomplished by extensive laboratory testing combined with a healthy dose of guesswork, a time-consuming and often costly approach. Recently, a team of Lawrence Livermore scientists has begun to tap the vast computational power of Department of Energy supercomputers to simulate and accurately predict the performance of advanced materials. These simulations cover a wide range of operating environments and length and time scales.

The new field, called computational materials science, is one of the fastest growing areas within the field of chemistry and materials science. Leading the Livermore effort is materials physicist Tomas Diaz de la Rubia. He heads a team of 20 materials scientists, metallurgists, chemists, computer scientists, and physicists as well as graduate students from the United States and Europe.

The simulation research team works closely with Livermore computer scientists and collaborators from U.S. universities such as Princeton, Washington State, the University of Pennsylvania, MIT, and UCLA, and American companies such as IBM, Intel, and Applied Materials. The work is funded by Lawrence Livermore research programs, the Laboratory Directed Research and Development Program, the Department of Energy's Office of Science, and U.S. industry.

Diaz de la Rubia notes that Livermore research programs need many different classes of materials—including ceramics, glasses, plastics, and metals—and biological products. As a result, his group has assembled a broad research portfolio, one that includes simulating the mechanical properties of materials under extreme conditions, the accumulation of radiation damage in metals, the interaction of laser light with glass, the

over Time and Space

integrity of canisters for nuclear waste storage, the design and properties of advanced alloys, the actions of biomaterials such as enzymes, the dynamics of metal corrosion and cracking, and the diffusion of dopants in semiconductor manufacturing.

A Major International Presence

While helping Lawrence Livermore programs, the group is also establishing a major presence in the scientific community. The team publishes frequently in scientific journals and is prominent at international conferences. For example, Diaz de la Rubia co-chaired the spring 2001 meeting of the Materials Research Society, which attracted some 3,000 scientists from around the world to San Francisco.

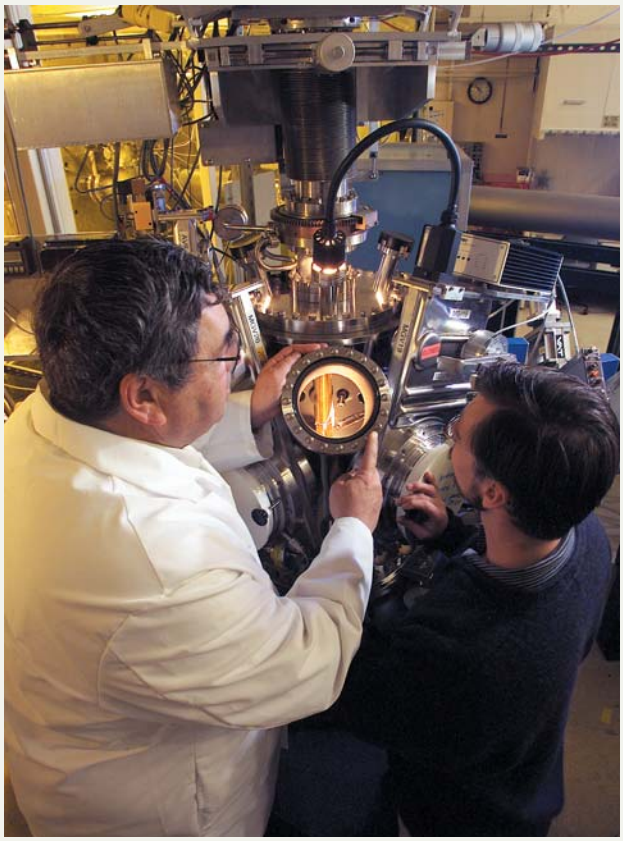
The Livermore work is part of DOE's Office of Science Computational Materials Science Network, composed of multidisciplinary scientific teams at several national laboratories. The network fosters basic materials science research within DOE and also serves to attract the best new talent to the discipline.

Diaz de la Rubia notes that scientists have long used computers to model materials and their performance. However, the newest generation of supercomputers, which employ thousands of microprocessors to tackle simulations once considered intractable, represents a significant advance. The computational materials science team works closely with members of the Laboratory's Center for Applied Scientific Computing to develop simulation tools that take advantage of multiprocessor supercomputers. The most advanced of those computers were acquired through DOE's Accelerated Strategic Computing Initiative (ASCI), a key component of the Stockpile Stewardship Program to assure the safety and performance of the nation's aging nuclear stockpile.

Writing or adapting codes for large parallel machines, in which complex problems are divided up to be jointly solved by multiprocessors, is a large effort. "The task requires people to think about software in new ways," says Diaz de la Rubia. The payoff, however, is a significant improvement in performance, as measured in the time required to run a model and the number of atoms being simulated. On Livermore's ASCI Blue supercomputer, about 350 million atoms could be simulated, but the newest computing platform, ASCI White, will track 10 billion atoms simultaneously.

The Livermore simulations are closely linked to laboratory experiments on the same materials. Experimental data ensure that the simulations accurately reflect the materials' chemical, mechanical, and thermodynamic properties as well as their manufacturing methods and the ways by which they age and ultimately fail. Only with solid experimental underpinnings, says Diaz de la Rubia, can the models help advance the understanding of how materials form, how they react under changing conditions (especially extreme environments), and how they can be improved.

The codes are so sophisticated that Livermore researchers are beginning to predict what scientists will see when imaging materials through electron microscopes. Their simulations constitute an important bridge between



Livermore materials simulations are closely coupled to a program of laboratory experiments. Researchers Mike Fluss (left) and Brian Wirth measure the atomic transport properties of radiation damage defects in metals, including plutonium; the data are used to refine codes that simulate and predict the performance of stockpiled nuclear weapons.

computer models and experiments. When a computer-generated image of calculated defects in a crystal is superimposed on an image of the same material taken with a transmission electron microscope, the results are remarkably similar. "When we see a certain image in the microscope, we now have a good idea about the mechanisms that produced it," says Diaz de la Rubia.

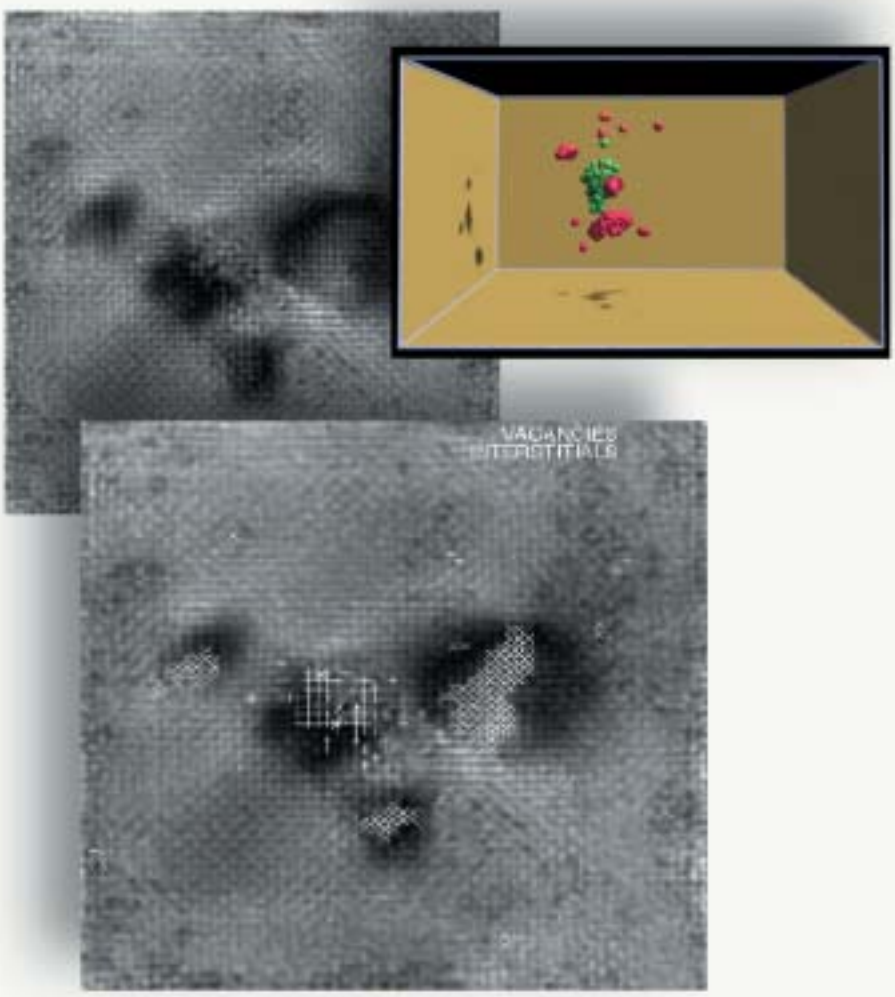
Multiscale Modeling of Materials

The Livermore codes incorporate multiscale modeling, an approach that is needed because material properties often depend on phenomena that take place at all length scales, from nanometers to meters. Multiscale modeling also incorporates a range of time scales from billionths of a second to tens of years. By combining models that cover the full range of length and time scales, scientists can simulate the evolution of mechanical and chemical changes in materials. Such changes may start with a defect occurring in a metal's crystalline lattice over a few nanometers in length and in a billionth of a second. And yet, multiplied millions of times over several years, such defects may combine to cause catastrophic failure of a computer chip, a glass optic, or a pressure vessel.

The most general approach to multiscale modeling is called information passing. In this method, which was introduced to the Laboratory by materials scientists Wayne King and David Lassila, simulations of matter at one scale are based on the results of simulations at a lower (more finely detailed) scale. The challenge is to form a coherent simulation of a material by building what Diaz de la Rubia calls "hooks between different scales."

The other approach, applicable in a limited number of cases, is called embedded multiscale modeling; its development at Livermore is being spearheaded by physicists Bernie Alder, Robert Rudd, Andrew Quong, and Vasily Bulatov. It uses the same code to solve the motion of molecules at all scales, with different physical models having different levels of approximation at each scale. For example, the way a nanometer-size crack behaves at the smallest lengths is similar to the way larger-scale cracks behave. Thus, it is a candidate for embedded multiscale modeling.

There are four major length scales: atomistic (measured in nanometers), microscale (micrometers), mesoscale (hundreds of micrometers) and



The Livermore simulations are beginning to predict the images that scientists will see when viewing materials through electron microscopes. On the upper left is a high-resolution transmission electron micrograph of a crystal of gold showing clusters of defects, namely interstitial atoms (atoms out of place, in red) and vacancies (points in the crystalline lattice where no atoms reside, in green). At the upper right is a computer simulation of how the defects should appear through the electron microscope. Superimposing the simulated image onto the electron micrograph (lower center) shows an impressive correlation between the two.

continuum (larger than 100 micrometers). In most cases, all four scales must be used to completely model a material's performance over a selected period of time. Each scale also requires a special code. For example, the microscale uses new codes such as micro3D, developed at Lawrence Livermore in collaboration with Washington State University researchers, while the continuum scale uses ALE3D, also developed at Livermore.

Simulations Begin with the Atom

The atomistic scale, which involves the properties and interactions of electrons and atomic nuclei, has been studied in great detail since the discovery of quantum mechanics. Atomistic simulations based on so-called first principles help scientists understand how atoms are arranged in crystals, how they bond to other atoms, and how impurities affect them. It is impossible, however, to use only atomistic models to simulate all material properties because of the sheer number of atoms that would be required for such a simulation.

Microscale simulations determine many materials properties, such as strength. But until the advent of ASCI machines, computers did not have the computational horsepower to perform microscale simulations with great fidelity. "People had been studying the collective behavior of dislocations in crystals for 40 years, but they couldn't simulate it until now," says Diaz de la Rubia. The microscale, he says, is the critical link between the atomistic and mesoscopic scales.

Likewise, the mesoscale links the microscale to the continuum scale. The mesoscale determines the structure of grains (a portion of a crystal in which all the atoms are oriented the same). Computer codes essential to understanding the performance of many nuclear weapons are based on this scale.

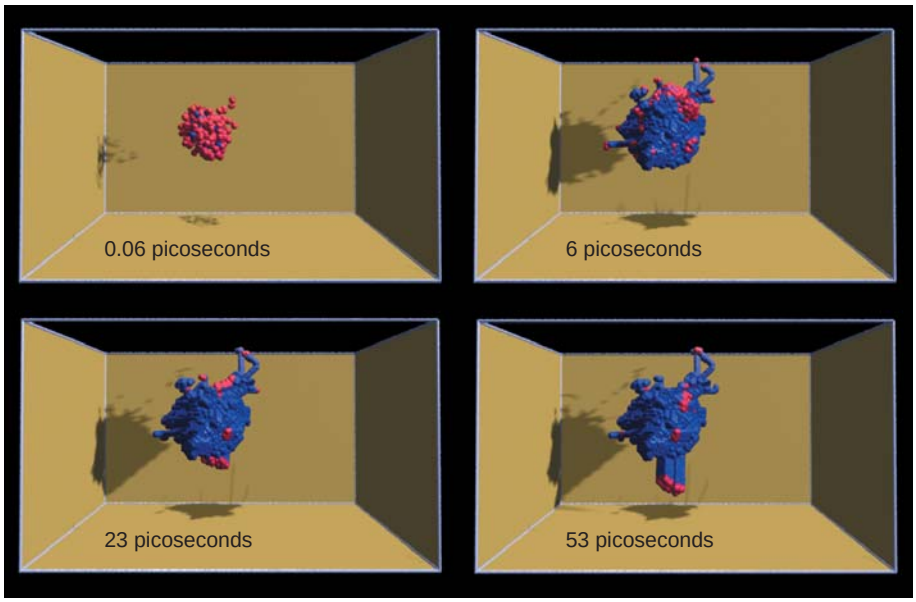
Finally, simulations on the continuum scale provide engineers with the likely behavior of materials in such areas as the damage that occurs in crash testing. At this level—visible to the naked eye—simulations using finite-element methods and experimentally derived equations model physical structures with element sizes that approach those studied individually with mesoscale models.

One essential aspect of multiscale modeling is its interdisciplinary nature. At Livermore, the effort is led by physicist Elaine Chandler and brings together scientists in the Defense and Nuclear Technologies, Physics and Advanced Technologies, Engineering, and Chemistry and Materials Science directorates to accomplish the goals of the modeling programs.

A major focus of the collaborative multiscale modeling effort is predicting the strength of metals in a variety of environments. Diaz de la Rubia notes that a general relationship between a metal's composition and its strength has been well established for decades. However, a detailed understanding of the mechanisms that confer strength based on the metal's crystalline microstructure has been lacking. Such knowledge is particularly vital to making predictions of performance under extreme conditions of pressure and temperature. "We want to predict how metals will deform under all conditions, and multiscale modeling is showing us the way," Diaz de la Rubia says.

Dislocations Are Key

He explains that in a metal, atoms are stacked in an ordered, crystalline lattice. However, there are also regions of less ordered stacking that can affect mechanical properties. These disordered areas can be caused by impurities, point defects in the crystal's lattice, or especially dislocations, which are misaligned planes of atoms that are sometimes referred to as line defects. When dislocations move through a crystalline lattice, they create plastic deformation, the ability of a material to bend without breaking. Without some plasticity, a metal becomes brittle and vulnerable to fracture and failure.



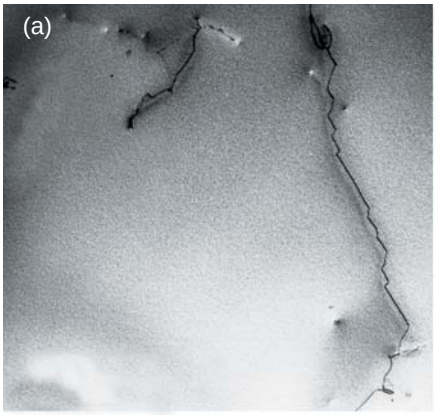
Atomistic simulations of radiation damage in copper atoms show the accumulations of defects over time, particularly those caused by clusters of interstitials (atoms that are not in their correct place in the copper crystal) or by replacements of the original atoms in the lattice. Data from atomistic simulations are used as the basis for microscale simulations.

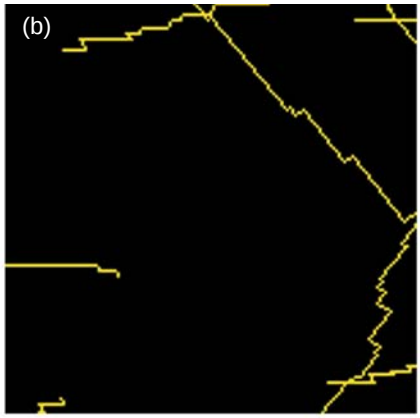
Livermore microscale simulations model the motion, multiplication, and interaction of dislocations, a phenomenon called dislocation dynamics. The simulations show the collective and complex behavior of millions of dislocations per cubic centimeter and how they determine a material's plastic deformation. The simulations are helping researchers better understand how certain manufacturing methods, such as the addition of selected impurities (alloys), harden a metal by interfering with dislocation movement.

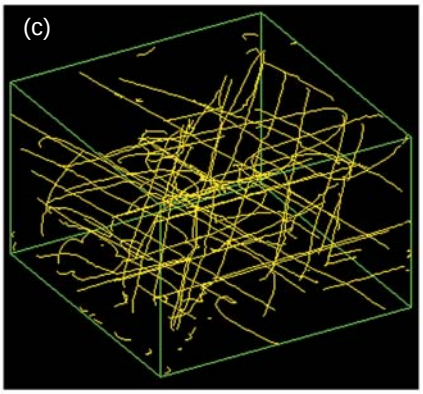
The strength simulation work is closely tied to experiments. The overall effort is headed by David Lassila and is based on the behavior of dislocations in molybdenum and tantalum crystals because these crystals are similar to materials found in many Laboratory programs and the nuclear stockpile. The experiments provide well-characterized dislocation structures to validate the results of the simulations. The experimental results are aided by directly observing dislocation mobility with transmission electron microscopes.

The current parallel version of the simulation code has been run on Livermore's ASCI Blue supercomputer using 80 processors and 260 hours of processing time. Led by Lassila and Bulatov, the researchers are revising the code to run on ASCI White. Lassila and Bulatov, together with physicist John Moriarty, are looking to extend the simulation work to areas of extreme pressure and temperature to improve the accuracy of current material models.

Predicting the strength of materials is important in almost all aspects of stockpile stewardship. Indeed, stockpile stewardship–related projects comprise the majority of the group's work. Diaz de la Rubia notes that materials are at the heart of most of the issues associated with the nation's enduring nuclear stockpile and that a central goal of ASCI is to acquire full-scale materials simulation tools to more accurately predict the lifetimes of weapon components. In particular, scientists want to improve their ability to predict the effects of aging or the performance of a remanufactured weapon part (see *S&TR*, June 1999, pp. 22–25).







(a) An electron micrograph of molybdenum under pressure determines (b) the initial conditions used in the model for simulating dislocation dynamics. (c) The simulation shows a compressed sample of molybdenum with many dislocations running through the crystalline lattice.

Radiation Damage Is Multiscale

One of the most challenging stockpile stewardship–related simulation problems is radiation damage to warhead components and materials. The problem is inherently a multiscale phenomenon. The individual events occur over a scale of 100 nanometers and a small fraction of a second, but the effects build up over decades throughout a material (see box on p. 66).

The materials scientists are applying multiscale modeling to predicting the performance of nonweapons materials in nuclear radiation environments. One team led by physicist Maria Jose Caturla and materials scientist Brian Wirth is modeling materials that could be used in future fusion reactors. Another team headed by physicist Patrice Turchi is modeling the long-term performance of waste canisters manufactured from exotic metal alloys. The canisters are being considered for storage of high-level nuclear waste at Yucca Mountain, Nevada (see *S&TR*, March 2000, pp. 13–20). Livermore scientists are performing simulations to determine how the canister will react over a 100,000-year period in response to extreme conditions of high humidity, temperature, and radiation. The assignment is a huge challenge because

it involves length scales ranging from the atomistic to the entire 45,000-kilogram, 3-meter-long waste canister.

One related area of interest is stress corrosion cracking, the most common mode of failure for a wide range of materials, including not only nuclear waste containers, but also bridges, fiber-optic cables, and nuclear reactor pressure vessels. Because microscopic cracks grow slowly, it is difficult to predict when a part will fail. For the first time, Livermore scientists led by Andrew Quong and materials scientist Wayne King are making the connection between the breaking of single atomic bonds at the tip of a growing crack and the ultimate failure of a part. They are planning to further their research through collaborations with materials scientists from IBM's Almaden Research Center in San Jose, California.

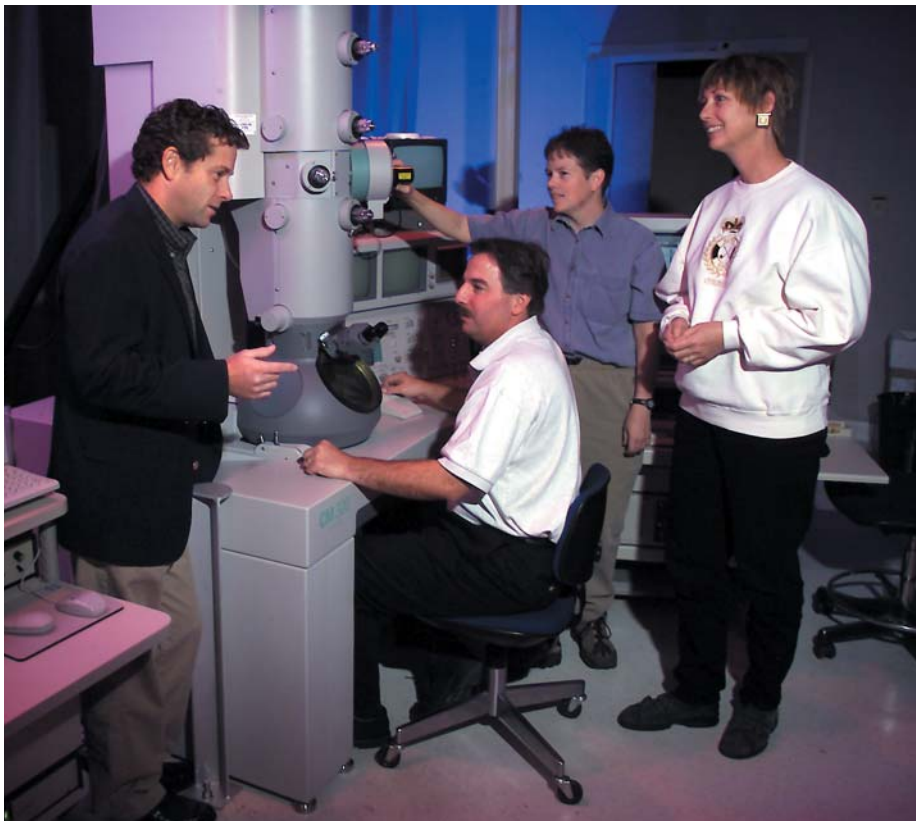
Advancing Semiconductors

An area of great potential is applying multiscale modeling to gain a better understanding of processes in the semiconductor industry. Diaz de la Rubia explains that the semiconductor industry has traditionally used simple models to explain the actions of dopants (impurities deliberately added to semiconductors to achieve a desired property) and defects. However, semiconductor manufacturing involves more than 200 steps in a process that is far too complex to be treated with these models. What's more, the industry is building increasingly smaller features on their chips, and the lack of accurate modeling, particularly on the atomistic scale, is proving to be a serious impediment to the development of next-generation devices. As a result, new atomistic-level models are required.

"Semiconductor companies want to be able to predict the outcome of a process from a given set of manufacturing conditions," says Diaz de la Rubia. To aid the manufacturers, Livermore researchers investigated the kinetics of defect and dopant migration in silicon chips, using funding from DOE's Office of Science and U.S. corporations such as Intel and Applied Materials. The approach provides a fundamental database for use in developing predictive simulations. It combines both experiments and theoretical advances and uses the same methods applied to other multiscale modeling projects.

The simulation results, when compared to results from laboratory experiments, showed the models to be very accurate. The project's success and the promise of the Livermore approach led to a Cooperative Research and Development Agreement with Intel and Applied Materials to create predictive modeling tools for semiconductor manufacturing.

In like manner, says Diaz de la Rubia, researchers are creating a family of tools for simulating biochemical processes. These tools will permit more accurate and rapid protein structure predictions. They will contribute to the study of DNA and aid predictions of protein function, drug activity, and the effects of chemical hazards such as carcinogens.



Materials scientist David Lassila, left, discusses the results of dislocation dynamics simulations with his team while they are directly observing dislocations with a transmission electron microscope. Mark Wall is seated at the transmission electron microscope, while Mary Le Blanc and R. Ann Bliss look on at right.

Simulations Reveal Damage from Radiation

Radiation damage is a ubiquitous phenomenon that affects many Lawrence Livermore research programs, the nation's nuclear weapons stockpile, and the nuclear power industry. Radiation damage can significantly degrade mechanical properties, seen most notably in increased brittleness and outright failure of a component.

The damage shortens the lifetime of pressure vessels in nuclear power plants and limits the choice of materials for fusion energy research. The problem is of particular concern for weapons materials such as plutonium. When plutonium-239 decays, it emits an alpha particle (a helium nucleus) and an atom of uranium-235. The resulting buildup of gaseous helium atoms and displaced plutonium atoms from the recoiling uranium could produce unacceptable changes in the plutonium metal. (See *S&TR*, June 2000, pp. 15–22.)

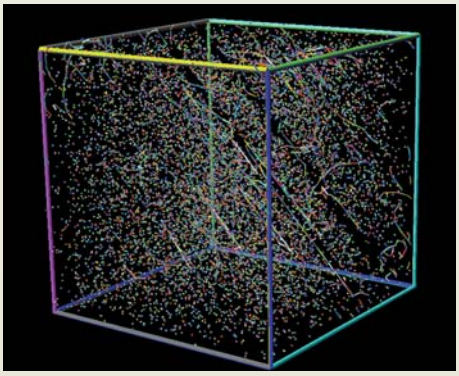
Although radiation damage has been studied for many years, the underlying mechanisms that relate damage to degradation of mechanical properties had not been clearly demonstrated until recently by a Livermore team. Headed by Diaz de la Rubia, the team reported its findings in the August 24, 2000, issue of *Nature* magazine. Because the damage evolves over a wide range of length and time scales, Diaz de la Rubia believed it could only be understood through multiscale modeling whose results are then validated by laboratory experiments.

Simulations show that some of the dislocations in irradiated copper form defect-free channels.

The team used atomistic and then three-dimensional microscale simulations of irradiated metals. The simulations showed defects (both vacancies and out-of-place atoms) accumulating at the shortest scales (nanometers and picoseconds) and quickly growing into clusters. These clusters served to pin or prevent the movement of dislocations, which are misaligned planes of atoms. The free movement of dislocations confers plasticity or strength properties on metals.

The simulations showed that as some of the dislocations moved through the metal, they annihilated any defects along their path, thereby forming 200- to 300-nanometer-wide channels along particular directions (see figure below, left). The defect-free channels resulted in plastic instability, that is, areas of reduced strength. The team then compared the simulations to images taken with electron micrographs of irradiated copper and saw a very close correlation between the two (see figure below, right). While electron micrographs had previously revealed the presence of clear channels, scientists could not explain their formation.

Diaz de la Rubia notes that in the case of modeling radiation damage in metals, length scales are not as important as the time scales and energy scales of particles (for example, neutrons) involved in causing damage. The critical information, he says, is "figuring out how fast the changes happen so we can make predictions." To accomplish that requires first simulating the evolution of the smallest changes at the atomistic scale, using kinetic Monte Carlo software, and then applying the results as input to dislocation dynamics models to determine how mechanical changes occur.



Electron micrographs of irradiated copper reveal the same clear channels predicted by the simulations. The clear channels are areas of reduced strength.

Another major area of materials simulation work is for the National Ignition Facility (NIF), which will be the world's largest laser and is now under construction at Lawrence Livermore. Because the facility will have the largest concentration of optics anywhere, scientists need a more accurate method for predicting how the extremely pure optical glass will respond to the laser's high fluence levels.

Diaz de la Rubia is embarking on an effort to predict the lifetime of NIF optics with experiments and multiscale modeling. The project focuses on the final optics system, where the frequency of each laser beam is tripled into the ultraviolet with crystals of potassium dihydrogen phosphate and then focused onto a target through a fused silica lens. "We want to be able to model the response of fused silica in the presence of high intensity laser light," he says.

The modeling effort, led by physicist Michael Feit, involves performing atomistic calculations based on the fundamental properties of silica when exposed to laser light and the methods by which cracks propagate in glass. All of the information will be passed up to continuum-level simulations using the ALE3D code to model large-scale fractures. As with other multiscale modeling work, the NIF project involves a multidisciplinary team that includes experts in optics, lasers, materials science, and mechanical engineering.

With the advent of multiprocessor supercomputers, scientists can finally execute simulations with unprecedented accuracy and with seamless integration over all length and time scales. The Livermore simulation studies will help stockpile stewardship scientists to confidently predict the performance of stockpiled weapons.

The multiscale modeling work affects much more than DOE research programs. Use of the supercomputers amounts to a revolution in the materials science community. In this new era, simulation will guide advanced materials development and will show how materials form, how they react under changing conditions, and how they can be optimized for better performance. Simulations will also provide basic information about material behavior of interest to the nation's industrial products manufacturers.

—Arnie Heller

Key Words: Accelerated Strategic Computing Initiative (ASCI), ASCI Blue, ASCI White, Center for Applied Scientific Computing (CASC), dislocation dynamics, Laboratory Directed Research and Development, multiscale modeling, National Ignition Facility (NIF), plutonium, radiation damage, stockpile stewardship, Yucca Mountain.

For further information contact Tomas Diaz de la Rubia (925) 422-6714 (diazdelarubia1@llnl.gov).

About the Scientist

TOMAS DIAZ DE LA RUBIA is associate director of the Chemistry and Materials Science Directorate. After completing his Ph.D. in physics at the State University of New York at Albany, he joined Lawrence Livermore in 1989 as a postdoctoral fellow working on supercomputing applications for fusion materials research.

On becoming full-time staff, he first developed physics-based predictive process models for semiconductor manufacturing, in collaboration with several large semiconductor corporations. Then he began developing multiscale models of materials strength and aging in irradiation environments. He has published over 100 peer-reviewed scientific articles, chaired numerous international conferences and workshops, edited conference proceedings and special journals, served on national and international panels, and is currently on the editorial board of five scientific journals and a member of the American Physical Society's selection panel for the Rahman prize in computational physics. His research interests are in applying large-scale computing to materials problems, developing predictive tools for materials performance, and designing new methodologies for multiscale modeling.

Welding Science

A New Look at a Fundamental Technology

Livermore experiments allow a second-by-second examination of what occurs during welding.

WELDS—the melting and fusing together of two pieces of material to make one—hold together much of the industrial world. Your safety while driving in a car depends in part on the reliability of more than 3,000 welds. If a weld were to fail, the results could be catastrophic. Welds make possible airplanes, metal bridges, office buildings, and high-pressure tanks as well as all sorts of high-technology devices. Welding is the most widely used method for joining metals and is typically stronger, lighter, and cheaper than other joining methods such as riveting and bolting.

Forge welding has been around almost since people began to work with metals. Then, in the late 19th century, Sir Humphrey Davy discovered the electric arc, and modern welding was born. The materials that welders use have changed over the years and today include not just metals but also polymers, ceramics, and composite and engineered materials. Lasers, electron beams, and plasma arcs supplement traditional electric and torch welding methods. Yet for all this history, basic knowledge about the welding process is surprisingly sparse. Conventional inspection techniques are not adequate

to indicate how a weld evolves in time. Welding may be old, but the science of welding is in its infancy.

Livermore has a vital interest in knowing all it can about welding. Dependable welds are important for maintaining the performance and safety of nuclear weapons. Welds will also play a key role in the success of the Department of Energy's planned repository for long-term storage of nuclear wastes, which will potentially be located at Yucca Mountain in the Nevada desert. Waste canisters will have three layers of containment: a convenience can inside an inner can inside an outer can. The lids of the inner and outer cans will be welded shut. The canistered waste must remain impervious to attack by air, moisture, and the surrounding environment for thousands of years. All told, more than 100 miles of welds will be required at the repository.

Metallurgist John Elmer, Livermore's expert on welding, has been researching details of the welding process since the early 1990s with physical chemist Joe Wong, whose specialty is synchrotron x-radiation experiments. They are currently working with another metallurgist, Todd Palmer. The three are also collaborating with colleagues at Pennsylvania State University and Oak Ridge National Laboratory.

Over the last several years, the team has succeeded in producing maps of the microstructural changes that occur in and around the weld area as a metal melts and resolidifies. More recently, their experiments have revealed second-by-second changes in a metal's microstructure during welding. In contrast, conventional diagnostic techniques can examine the material only before and after welding or can derive information about changes only indirectly and after the fact. "These experiments at Livermore have given us the first real-time look at the welding process," says Lou Terminello, division leader in the Chemistry and Materials Science Directorate.

Welds Take the Heat

When two pieces of material are being welded together, high heat rapidly melts the solid material, which quickly cools and solidifies again as the heat source moves away. Adjacent to the immediate weld area, or fusion zone, is the heat-affected zone (HAZ). As the name HAZ implies, the material there is affected by the high heat of the welding process but does not melt.

Heat causes changes in the material. The three well-known basic phases of a material are gas, liquid, and solid. But for many materials, multiple solid phases exist at various temperatures or at various combinations of temperature and pressure. At sea level—1 atmosphere—plain old H_2O may form several kinds of ice, each of which is a different solid phase. Iron undergoes three solid-state phase transformations as its temperature increases from room temperature to 1,535°C, where it melts. Carbon also has several solid phases, including graphite and diamond. No one would confuse graphite and diamond. Each one is still carbon, but their crystal structures are very different.

When a material is welded, its crystalline structure changes. It is these microstructural changes that interest

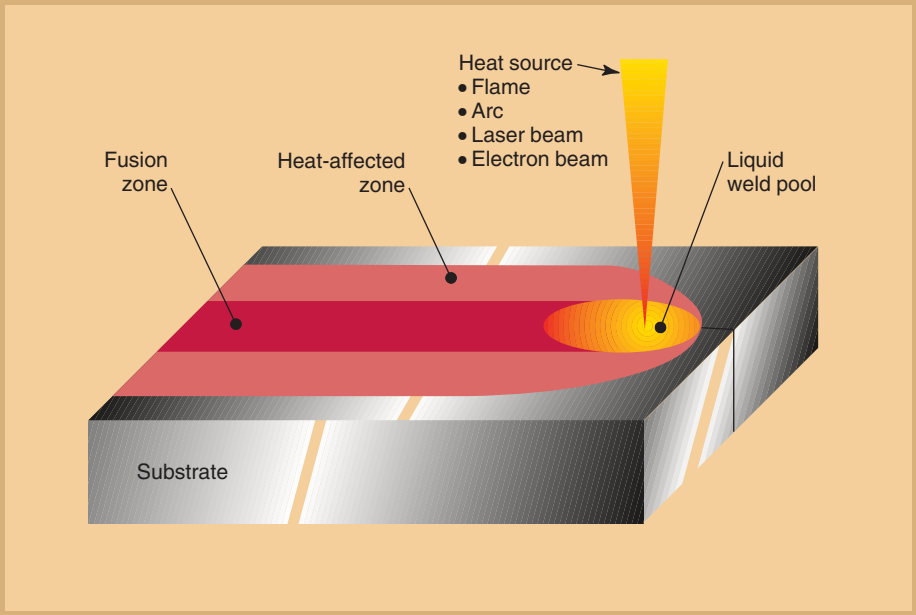


Illustration of a fusion weld. A liquid weld pool is created through the interaction of an intense heat source and the substrates being joined. Melting on the front side of the weld pool eliminates the interface between the materials, while solidification on the back side of the weld pool fuses the substrates together to create a solid joined part. Surrounding the fusion zone is a heat-affected zone, where the substrate is heated to temperatures up to the melting point of the metal being joined. Solidification in the fusion zone and solid-state phase transformations in the heat-affected zone are responsible for dramatic changes in the microstructure and properties of the welded joint.

Elmer. They can affect the strength of the material as well as its corrosion resistance, ductility, and mechanical properties. Any or all of the changes could either enhance the quality of the weld or reduce the weld's integrity. "We want to be able to understand the welding process by modeling it and then predict the changes that will occur," says Elmer. "But first, we need to gather real experimental data during welding to understand the fundamental properties of the process."

Synchrotron Is Key

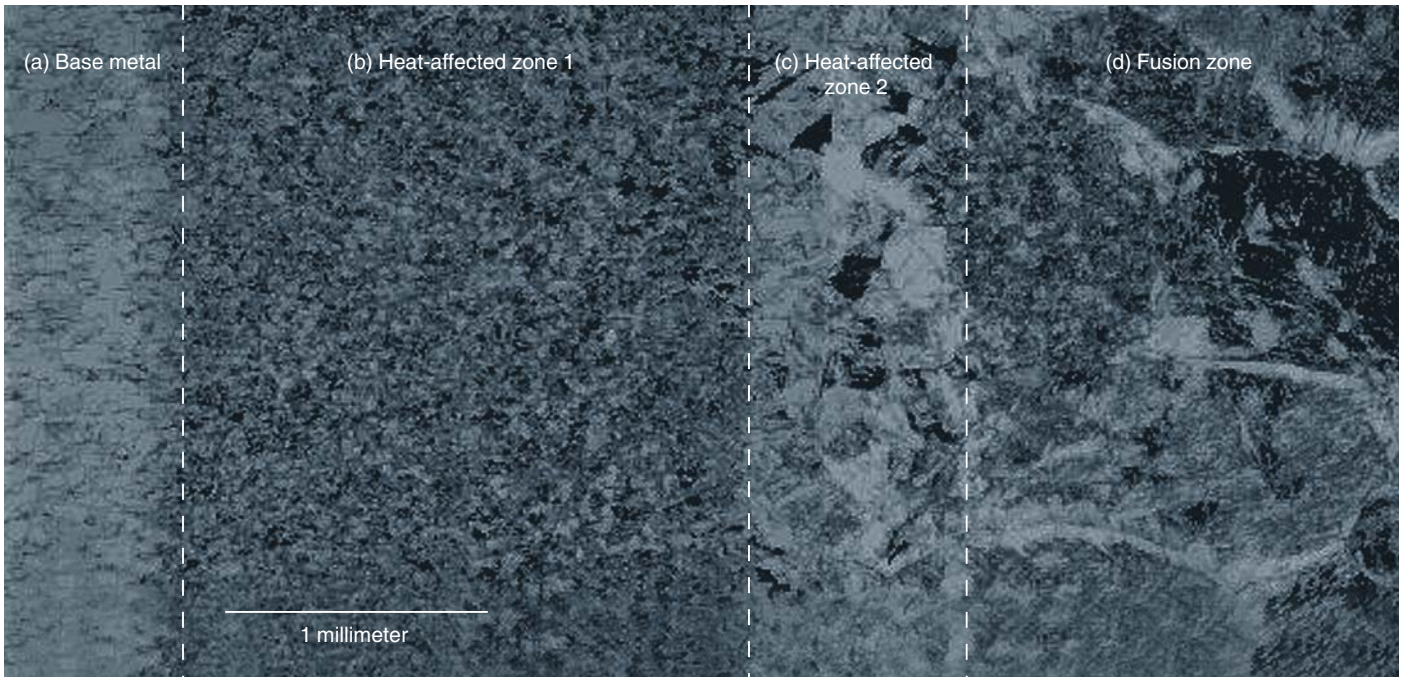
Joe Wong has been performing experiments with synchrotron radiation to examine materials for the past two decades. He and others helped to develop the experimental facility at the Stanford Synchrotron Radiation Laboratory back in 1977.

Synchrotron radiation is a particularly intense form of electromagnetic radiation. Highly energetic charged particles traveling at almost the speed of light and deflected in a magnetic field emit synchrotron radiation. This intense, highly collimated radiation—millions of times more powerful than that from a conventional x-ray tube—can probe the atomic structure and electronic states of matter. Experiments that would have taken hours with an x-ray tube source take milliseconds instead.

Synchrotron radiation spans the electromagnetic spectrum from infrared to hard x rays. X rays are ideal for probing matter because the wavelength of x-radiation is about the same size as an atom. Thus, with synchrotron x rays, the team can make direct observations of phase transformations in welds, watching microstructural changes as they evolve.

Synchrotron radiation sources at Stanford and elsewhere around the world are used by scientists working in many fields—by materials scientists like Elmer and Wong to study the dynamic properties of solid and amorphous materials, by biomedical researchers to study proteins and other large biomolecules, by medical workers for coronary angiography and other forms of imaging, and by geologists for structure characterizations and trace-element analyses of minerals.

The Livermore team is using x rays from the 31-pole x-ray "wiggler" at Stanford Synchrotron Radiation Laboratory for their experiments. In this device, an x-ray beam wiggles between an array of 31 magnetic poles, gathering intensity along the way. By carefully



Room-temperature top view of the microstructure of titanium from the fusion zone, through the heat-affected zone, and into the base metal (30 times magnification): (a) the base metal, (b) the small-grained portion of the heat-affected zone where the gamma phase has partially transformed to the beta phase, (c) the large-grained portion of the heat-affected zone where gamma-phase titanium has fully transformed into the beta phase, and (d) the fusion zone. Note the dramatic changes in grain structure.

directing this small, intense synchrotron beam at a given location in a weld, they can obtain an x-ray diffraction pattern to identify the phases present in the material at that location during the welding process. The x-ray diffraction pattern depends on the atomic structure of the material. "The diffraction pattern is the fingerprint of a material's crystal structure," says Wong. "Liquid is chaotic with no long-range order," he continues, "so there is no diffraction."

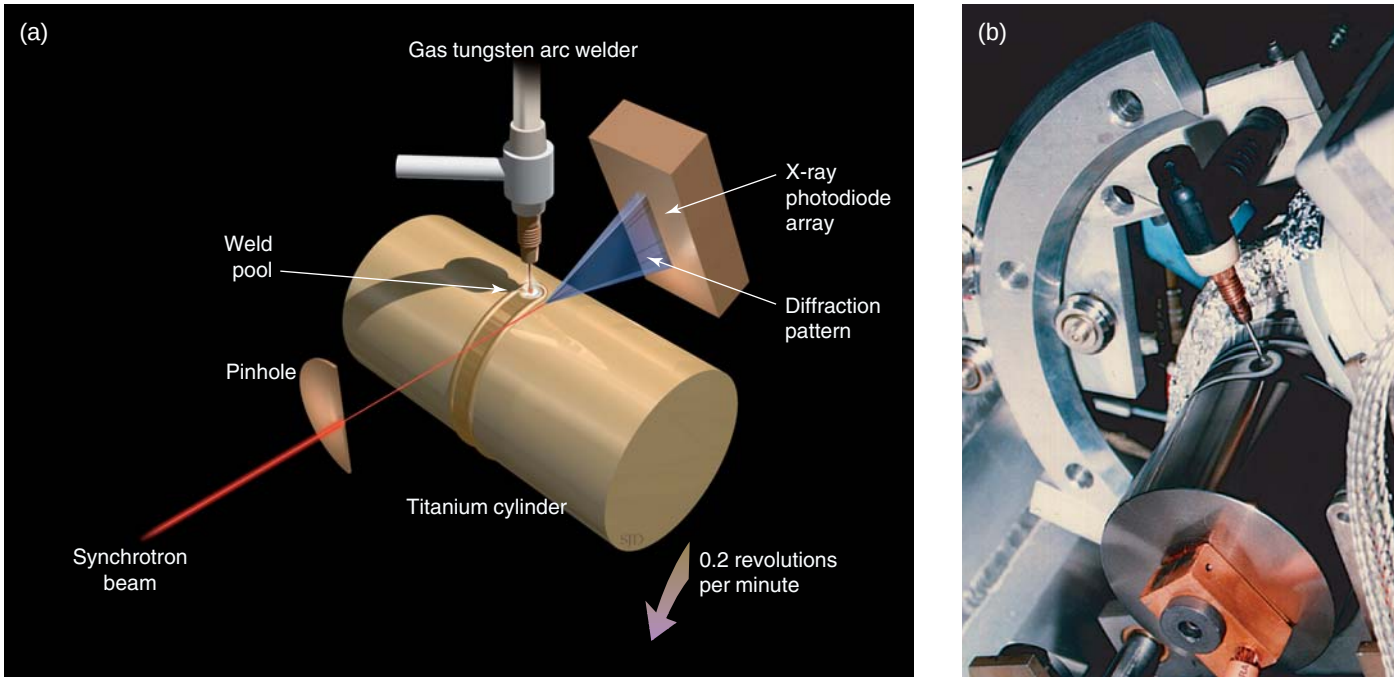
From Simple to Complex

The team's first experiments examined titanium welds. Titanium is popular in manufacturing because of its corrosion resistance and light weight. Also, titanium has two well-characterized solid-phase transitions at ambient air pressure before it melts. In pure titanium, the alpha phase exists from room temperature to 882°C. At these temperatures, titanium has a hexagonal-close-packed crystalline structure. At 882°C, pure titanium's crystalline structure changes to the beta (body-centered-cubic) phase, which it maintains until it reaches the liquid phase at 1,670°C. As the liquid titanium cools, the phase transformations are reversed. Because these phase transformations occur over such a wide temperature range, titanium is a relatively easy material to study.

Using the experimental setup shown in the figure below, a metal bar rotates under a gas tungsten arc, taking 6 minutes for a full revolution. An intense x-ray beam from the synchrotron source passes through a pinhole to allow researchers to resolve features as small as 180 micrometers. During welding, the x-ray beam is aimed at specific points around the heat source. A silicon photodiode linear array detector records the diffraction patterns during the experiment.

The team maps phase transformations by performing a series of sequential linear scans from the centerline of the weld and out into the HAZ. In every row, 30 to 40 x-ray diffraction patterns are collected, spaced 0.25 millimeters apart. Each row requires one revolution of the cylinder. After completion of the first row, the welding heat source is moved 1 millimeter from its previous position to collect data in the next row, and so on.

This spatially resolved x-ray diffraction (SRXRD) technique is unique to Livermore for the study of welding. "Spatial resolution is the key to collecting useful in situ phase transformation data during welding," says Elmer.



(a) A rendering of (b) the experimental setup for real-time investigations of welds using synchrotron radiation. The x-ray beam enters from the lower left through a pinhole to provide spatial resolution of 180 micrometers. During welding, this spatially resolved beam is aimed at a specific location of the weld where diffraction takes place. The diffracted beams are captured in real time using a silicon photodiode linear array detector. The weld is produced by a gas tungsten arc on a revolving solid bar of the material being studied.

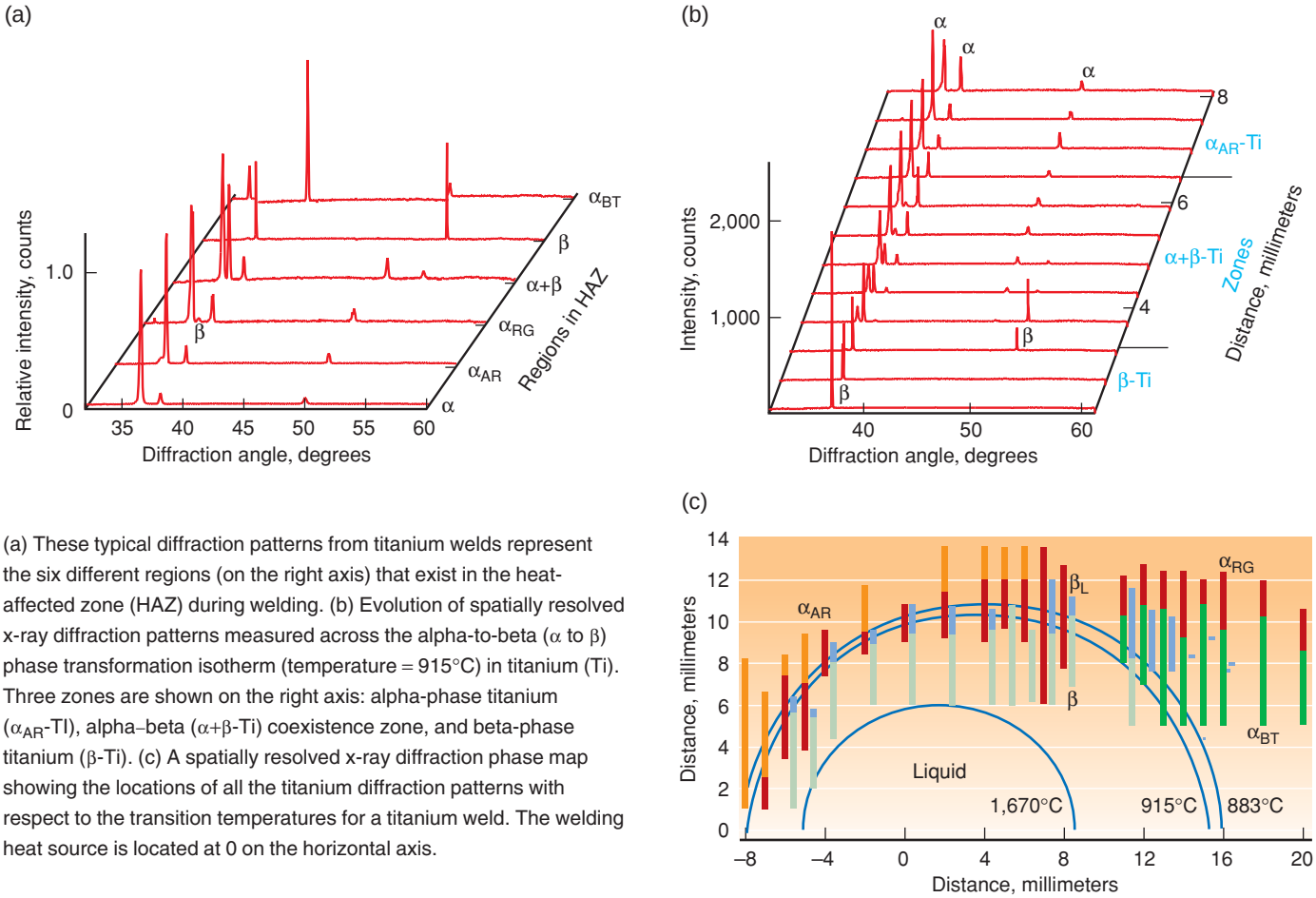
The grain structure of commercially pure titanium—or any solid material for that matter—changes during welding. It is subjected to peak temperatures hundreds of degrees higher than the melting point, followed by rapid cooling. These temperature fluctuations alter the microstructure of the material nonuniformly to create the HAZ adjacent to the weld fusion zone. Solid-state phase transformations that occur in the HAZ create gradients of both microstructure and properties between the liquid metal in the fusion zone and the unaffected base metal farthest from the weld. Within the HAZ, the most severe microstructural changes occur close to the fusion zone, where the peak temperatures are the highest.

Researchers had suspected for some time that annealing and recrystallization occur in the colder portions of the HAZ in titanium. They also knew that both partial and complete alpha-to-beta transformations take place in the hotter portions of the HAZ. But what they had not been able to determine was the exact size and location of these regions.

Using SRXRD, the Livermore team found six regions in the HAZ around the liquid titanium weld pool, each with an identifiable diffraction pattern. From their diffraction data, they could follow the evolution of the phase transformations, at various locations and at various temperatures. This research resulted in a diffraction map of the HAZ [part (c) of the figure below] that shows the location of all the phases with respect to the transition temperatures.

"Titanium was a good place to start with our experiments," says Elmer. "But steels are welded much more frequently." So their next sets of experiments dealt with carbon–manganese steel and stainless steels. While these alloys have more complex phase changes than pure metals, their phase transformations can be studied with the SRXRD technique.

Duplex stainless-steel alloys consist of austenite and ferrite solid phases, each of which has different crystal structures and magnetic properties. Here, they found five principal phase regions between the



(a) These typical diffraction patterns from titanium welds represent the six different regions (on the right axis) that exist in the heat-affected zone (HAZ) during welding. (b) Evolution of spatially resolved x-ray diffraction patterns measured across the alpha-to-beta (α to β) phase transformation isotherm (temperature = 915°C) in titanium (Ti). Three zones are shown on the right axis: alpha-phase titanium (α_{AR}-TI), alpha–beta (α+β-Ti) coexistence zone, and beta-phase titanium (β-Ti). (c) A spatially resolved x-ray diffraction phase map showing the locations of all the titanium diffraction patterns with respect to the transition temperatures for a titanium weld. The welding heat source is located at 0 on the horizontal axis.

liquid weld pool and the unaffected base metal that contribute to the final microstructure observed in the HAZ.

Changes over Time

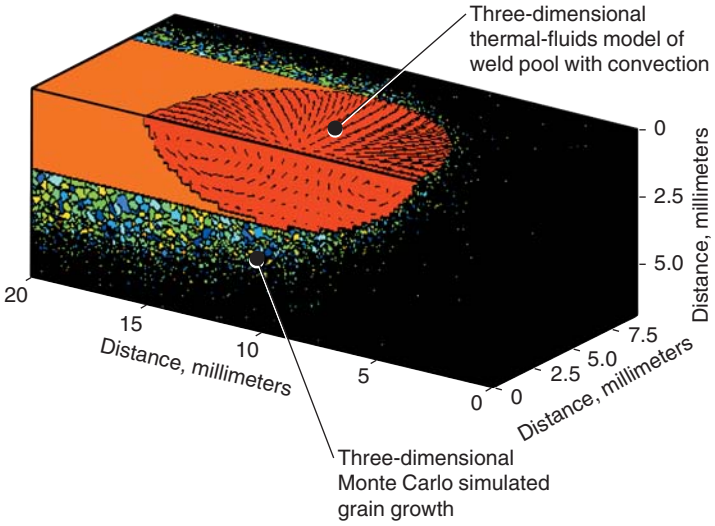
Phase mapping experiments performed using the SRXRD method are useful for observing phase changes under quasi-steady-state heating and cooling conditions. The next step was to examine the changes that occur at a single spot as a function of time. Wong developed a time-resolved x-ray diffraction (TRXRD) technique that takes a set of x-ray diffraction patterns at a single location adjacent to or within a stationary spot weld. When the detector is clocked for durations of tens to hundreds of milliseconds, phase transformation may be observed on a much shorter time scale than is possible with moving welds. Changes in the diffraction pattern show directly how phase changes are taking place as a function of time and temperature. As the temperature goes up and then down, the metal at the weld becomes liquid and then solidifies. With TRXRD, the Livermore team has been able to examine the solidification and subsequent solid-state phase transformations in a number of different materials for the first time.

For example, TRXRD has proved useful for examining the solidification behavior of austenitic stainless steels. In these stainless steels, the presence of residual ferrite in the austenitic microstructure affects the integrity of welds. Researchers have long been interested in understanding how residual ferrite in the microstructure evolves. For more than 50 years, those who work with welds have known that the composition of the weld is important and have developed methods for assuring that the austenite–ferrite ratio was appropriate for each specific need. Numerous studies have examined the rate of solidification, which affects the microstructure and relative percentage of austenite and ferrite in the final weld.

But Livermore was the first to make direct observations of the ferrite and austenite phases and the dynamics of this transformation. The Livermore team found directly, for the first time, that ferrite is the first phase to solidify from the liquid weld pool in a 304 stainless-steel alloy. The ferrite phase existed as the only solid phase for 500 milliseconds before beginning to transform into the austenite phase. The ferrite-to-austenite transformation took an additional 200 milliseconds of cooling, during which both phases coexist. The combined results showed that the majority of the ferrite phase transformed to the austenite phase by the time the weld had cooled to a temperature of 1,100°C.

Beginning to Predict

Elmer and Palmer have also worked with modeling experts at Pennsylvania State University, where a research group has spent many years developing models to predict the temperatures present throughout a weld. By combining the results of the SRXRD experiments with the modeling results, the evolution of observed phase transformations can be more fully understood. As part of their collaboration, they performed three-dimensional Monte Carlo simulations



Three-dimensional Monte Carlo simulation of grain-size evolution in welds.

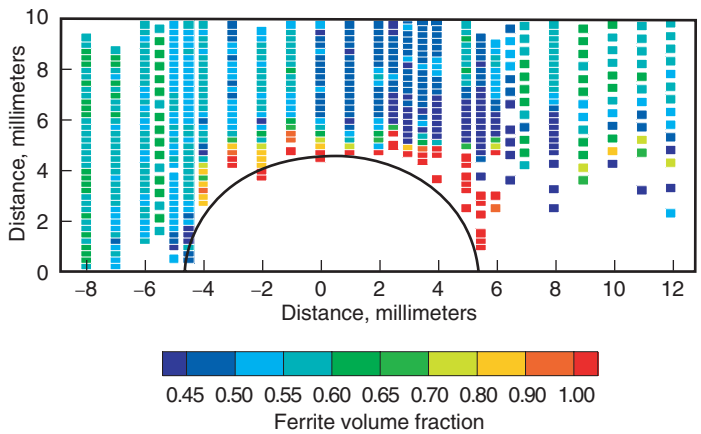
Infrared image of a duplex stainless-steel weld obtained in real time during a synchrotron experiment.

of the growth of grains during gas tungsten arc welding of titanium, shown in the figure on the left on p. 73.

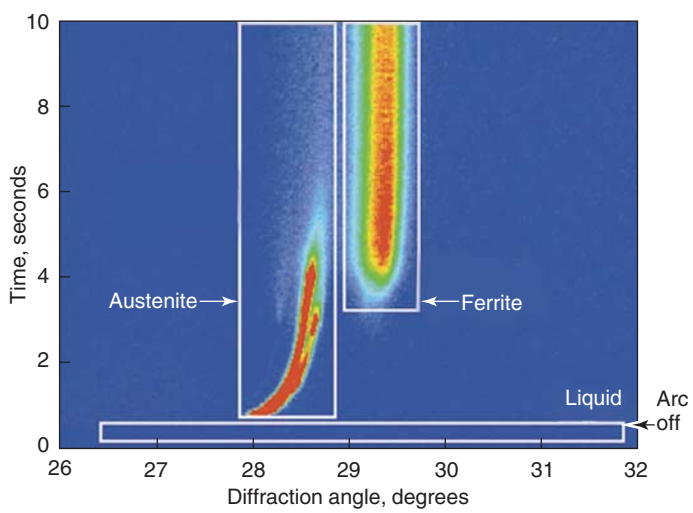
The Livermore–Penn State collaboration has continued to study phase transformations in duplex stainless steels. SRXRD observations of the phases present around the weld pool of an arc-welded 2205 duplex stainless steel have been combined with the results of a Penn State heat-transfer model to produce a thorough map of the phase transformations occurring in the heat-affected zone. An infrared image of a duplex stainless-steel weld, taken during the synchrotron experiments, is shown in the figure on the right on p. 73.

Further analysis of the data available in the diffraction patterns allowed the team to determine the amount of ferrite and austenite present at each location. The top figure below shows the variation in the ferrite volume fraction as a function of location around the weld pool. This is the first time the phenomenon was observed and quantified.

Once again demonstrating its unique capabilities, the SRXRD technique allowed the team to observe a decrease in the ferrite volume fraction at rather large distances from the weld pool (on the order of 9 millimeters). This change in the ferrite volume fraction was unexpected and had not been previously observed. Because evidence for this reaction disappears as the welding process continues, SRXRD provides the sole means available for monitoring these phase transformations.



Results of a spatially resolved x-ray diffraction experiment portray the dominant phase transformations and the regions over which they occur in the heat-affected zone during welding of duplex stainless steel.



Time-resolved x-ray diffraction results show phase transformations during weld solidification and cooling of a flux-cored arc-welding electrode.

Research Leads to Smarter Welds

This pioneering work is not going unnoticed by the welding research community. Elmer was named a Fellow of the American Welding Society in 2000. And in May 2001, the society honored a paper by Elmer, Wong, and colleagues at Penn State with the prestigious William Spraragen Memorial Award. Their article on modeling of titanium welding was selected the best paper of 2000 in the *Welding Journal Research Supplement*.

The ultimate purpose of all research on welding is to move useful information out to the welders of the world, to help them make better welds. In fact, Livermore synchrotron investigations of welds, combined with computer modeling and postweld characterization of microstructure, are beginning to do just that.

Powdered filler metal additions, which include aluminum, in flux-cored arc-welding electrodes alter the microstructure and properties of the resulting welds in unpredictable and undesirable ways. In the bottom figure at the left, TRXRD results

show phase transformations during the solidification and cooling of a weld in a mild steel consumable welding electrode. This figure comprises over 500 diffraction patterns, taken at the rate of 20 patterns per second, and indicates an unexpected nonequilibrium solidification of the weld.

Nonequilibrium solidification translates into a possible safety hazard for welded structures. To mitigate the hazard, this research, which is being done in collaboration with Oak Ridge National Laboratory, is now being used to help design new self-shielded welding electrodes with improved weld properties for safer building and bridge construction. You can't get much more useful than that.

—Katie Walter

Key Words: fusion welding, phase transformation, solidification kinetics, spatially resolved x-ray diffraction (SRXRD), stainless steel, synchrotron radiation, time-resolved x-ray diffraction (TRXRD), titanium, x-ray diffraction.

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About the Scientists

JOHN ELMER received his B.S. and M.S. in metallurgical engineering from the Colorado School of Mines in 1979 and 1981, respectively, and his Sc.D. in metallurgy from the Massachusetts Institute of Technology in 1988. After working briefly at Lawrence Livermore in the early 1980s, he rejoined the Laboratory as a postdoctoral scientist in 1988 and was named group leader for Materials Joining in 1989, a position he continues to hold. The group is responsible for electron- and laser-beam welding, vacuum brazing, and diffusion bonding.

Elmer has written or cowritten over 60 technical papers on materials joining, metallurgy, rapid solidification, the interactions of high-energy-density beams and materials, and the kinetics of phase transformations under nonisothermal conditions. He is a member of the American Welding Society (AWS) and the American Society of Metals International. In 2000, he was made a fellow of AWS; in 1991 and 2000, he received the William Spraragen Award from AWS; and in 1995, he received the Professor Masubuchi-Shinsho Corporation Award from AWS.

JOE WONG received a B.Sc. in pure and applied chemistry in 1965 and a B.Sc. in physical chemistry in 1966 from the University of Tasmania, Australia. In 1970, he received his Ph.D. in physical chemistry from Purdue University, and in 1986, he received a D.Sc. from the University of Tasmania. In 1986, he joined Lawrence Livermore as a senior chemist.

Wong's primary research interests include glass science and materials science. He has also examined the chemical dynamics and phase transformation of various materials and processes using high-resolution electron microscopy, various kinds of spectroscopy, and novel synchrotron instrumentation. He has written or cowritten over 175 journal articles, holds 7 U.S. patents, and has received numerous prizes and awards, most recently (with John Elmer) the William Spraragen Memorial Award from the American Welding Society for the best paper published in *Welding Journal Research Supplement* in 2000.

Big Glass for a Big Laser

THE National Ignition Facility (NIF), the largest, most energetic laser in the world—with 60 times more energy than any laser in existence—will be coming on line at Livermore in the next few years. In this laser, energy will be stored in special glass and later extracted as high-power optical pulses. High-energy lasers such as NIF need large pieces of optical-quality glass—and lots of them—to operate as designed. NIF will be about the size of a football stadium and will require more than 3,000 pieces of laser glass, each about 1 meter long, 0.5 meter wide, and 4 centimeters thick.

A revolutionary process developed by Lawrence Livermore and two industrial partners produces meter-size plates of laser glass at a rate 20 times faster and 5 times cheaper than is possible with the previous technology, and the glass itself has 2 to 3 times better optical quality. This work is the culmination of a 6-year research and development project between Livermore and the two leading (and competing) laser glass producers, Schott Glass Technologies of Duryea, Pennsylvania, and Hoya Corporation USA of Fremont, California. Physical chemist Jack Campbell of Livermore led this team.

The Continuous Laser Glass Melting Process developed by the collaboration replaces the only other way to manufacture large pieces of laser glass—the batch method, a one-at-a-time process that produces at most three pieces of glass per week. Not only is this method too slow to meet the demands of NIF, but it is also more expensive, and the optical quality of the glass is not consistent. Practically speaking, continuous glass melting is the only method that can be used to produce the large quantity and high quality of laser glass necessary for NIF. Without this technology, it would be extremely difficult to build a huge solid-state laser such as NIF.

"Developing this process was extremely difficult technically," says Campbell. "In fact, we had a saying, 'laser glass knows no friends,' to describe our frustrations. Now that the process has worked out successfully, frustration has given way to pride. But believe me, there were many anxious moments."

A River of Glass

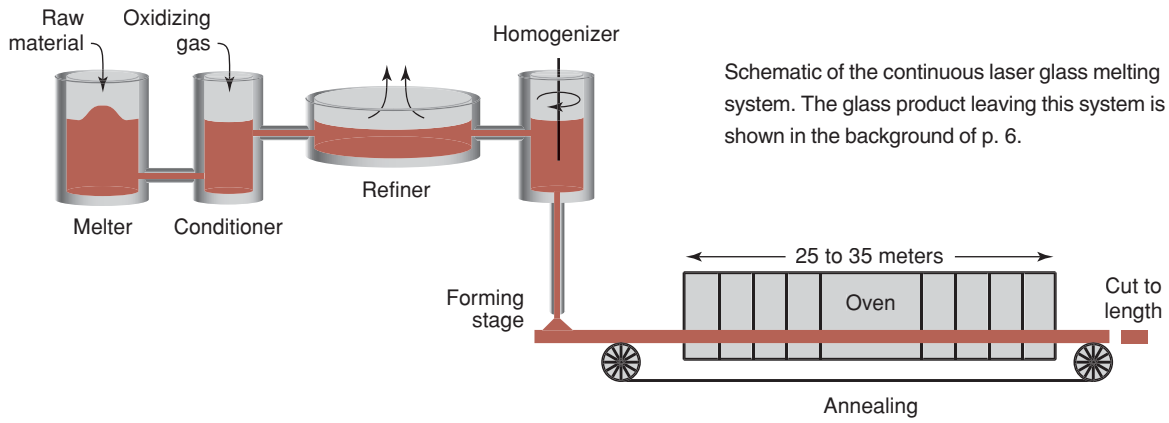
The Continuous Laser Glass Melting Process, shown schematically on the next page, converts high-purity, powdered raw materials into one continuously moving strip of high-optical-quality laser glass. Plates of laser glass are then cut from the end of the strip as it leaves the production system.

The laser glass melting process requires seven operations carried out in separate vessels. The vessels are interconnected to make the process continuous. The first process unit is designed to mix and dry the high-purity raw materials with minimal contamination.

The second unit is the melter system, which dissolves the powdered raw materials into a pool of molten glass and mixes these ingredients using convection currents.The melter consists of custom-designed, high-purity refractory materials and uses a proprietary electrical heating system.

All units beyond the melter are lined with high-purity platinum, as are the interconnecting pipes. Platinum is required to achieve the fine-scale (parts-per-million) optical homogeneity necessary for laser applications. However, the

Livermore developers of the Continuous Laser Glass Melting Process are (left to right) Paul Ehrmann, William Steele, Charles Thorsness, Michael Riley, Tayyab Suratwala, and Jack Campbell. The system was developed in partnership with Koji Suzuki, Kohei Yamamoto, Ryo Konta, Kunio Takeuchi, and Julie Storms of Hoya Corporation USA and Steve Krenitsky, Joe Cimino, Hardy Pankratz, Michael Timms, Dave Sapak, Ed Vozenilek, Joseph Hayden, and Alfred Thorne of Schott Glass Technologies.



Schematic of the continuous laser glass melting system. The glass product leaving this system is shown in the background of p. 6.

platinum can contaminate the glass with microscopic metallic inclusions. When a high-power laser beam hits an inclusion, the beam causes it to vaporize, generating small fractures within the glass. To overcome this problem, the team developed a unique conditioner unit that uses oxygen and chlorine to remove platinum inclusions as well as any residual water. The conditioner unit is perhaps the most complex part in the whole system.

The glass from the conditioner next moves to a refiner section, where bubbles are removed using a combination of high temperature and proprietary additives. From here, the glass enters the homogenizing unit, where it is thoroughly mixed to achieve the one-part-per-million chemical uniformity required to meet optical homogeneity specifications. Finally, molten glass flows through a platinum tube to a mold, where it is formed into one continuously moving strip about 5 to 8 centimeters thick, 0.5 meter wide, and nearly 30 meters long. The glass strip passes through a custom-designed annealing oven where it is gradually cooled from more than 600°C to room temperature. Annealing the laser glass strip is difficult because of the size of the strip and the unusually high thermal expansion and low inherent strength of the glass. Laser glass is five times more sensitive to fracture by thermal shock than most other optical glasses.

Older Process Not Adequate

Neodymium-doped phosphate laser glass can be manufactured by either the batch method, a one-at-a-time melting process, or this new continuous melting method. Schott and Hoya are the only companies in the world making meter-size plates of phosphate laser glass, either by a continuous or discontinuous process. Thus, the only competitor for the new process is the old, discontinuous technology for producing laser glass.

The former technology, which has been used for over 25 years, involves first melting raw materials in a refractory vessel and then manually transferring the melt to a second platinum-lined vessel. Finally, the pieces of glass are individually cast in a large mold. The entire operation is repeated for every piece of glass. Product quality can vary from one melt to the next simply because of small, run-to-run variations in processing conditions. The cost—more than $5,000 per liter of glass—is also high.

Continuous glass melting, however, has a much greater production rate of 70 to 300 pieces per week, and little, if any, measurable variation in glass properties from one glass plate to the next. Plus, the cost is less than $1,000 per liter.

NIF and Beyond

Hoya and Schott will also be manufacturing large pieces of glass using the continuous melting method for the Laser Megajoule (LMJ) in France. The LMJ's requirements are similar to those of NIF.

Both Hoya and Schott are applying several new technologies developed for the Continuous Laser Glass Melting Process to the manufacture of other optical glasses. Most notably, some of this technology is being used to manufacture the most common optical glass, BK-7, in large sizes. BK-7 is commonly used to manufacture optics for cameras, binoculars, and precision optical instruments. Other aspects of the process are being used to improve the manufacture of glass used in digital cameras, hard-disk-drive substrates, liquid crystal displays, projector lenses, and telecommunication devices.

"The success of this venture is illustrated by the fact that neither company is willing to openly discuss the details of the other applications for the new technology," says Campbell. "The bottom line here is that everyone is a winner from this partnership. NIF gets the laser glass it needs, and our industrial partners get a technology that is a springboard to new glass products."

—Katie Walter

Key Words: Continuous Laser Glass Melting Process, National Ignition Facility (NIF), neodymium-doped phosphate laser glass, platinum inclusions, R&D 100 Award.

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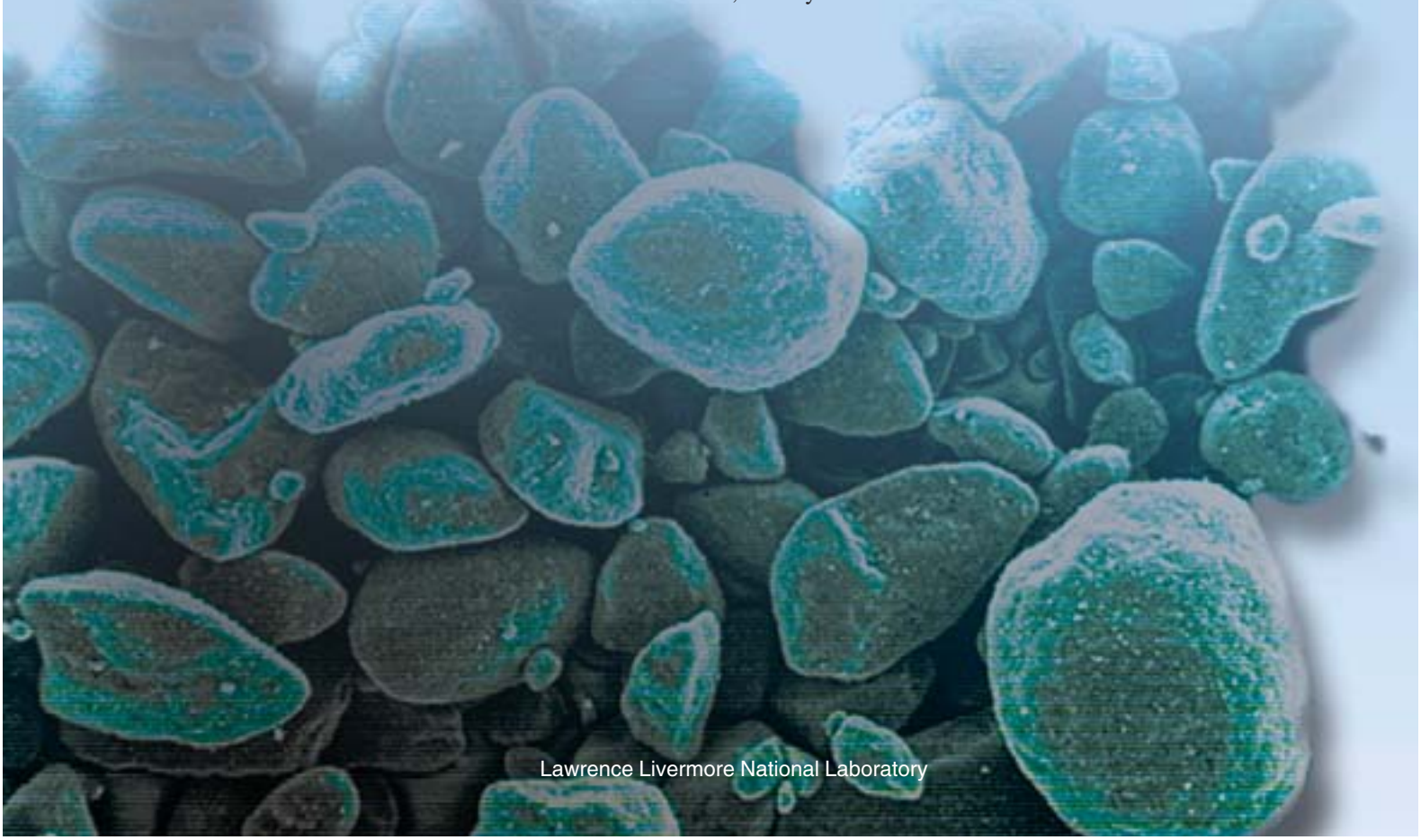
Turning Carbon Directly Into Electricity

The carbon conversion fuel cell pushes the efficiency of using fossil fuels to generate electricity closer to theoretical limits.

THE long-term energy—and environmental—future of the United States is much in the headlines these days. Helping to make the prospects brighter is a team of Lawrence Livermore scientists working to develop a method for producing electricity that is safe, relatively simple, remarkably efficient, and kind to the environment.

Called direct carbon conversion, the process has been demonstrated convincingly in the laboratory over the past year. The electrochemical process converts carbon particles, obtained from different fossil fuels, directly into electricity without the need for such traditional equipment as steam-reforming reactors, boilers, and turbines.

The breakthrough Lawrence Livermore method, the result of a two-year study funded by the Laboratory Directed Research and Development Program, pushes the efficiency of using fossil fuels for generating electricity far closer to theoretical limits than ever before. If adopted on a large scale, direct carbon conversion would help to conserve precious fossil resources by allowing more power to be harnessed from the same amount of fuel. It would



also improve the environment by substantially decreasing the amount of pollutants emitted into the atmosphere per kilowatt-hour of electrical energy that is generated. Perhaps most important, it would decrease emissions of carbon dioxide, which are largely responsible for global warming.

"What if we could nearly double the energy conversion efficiency of fossil fuels in electric power generation over the conversion efficiency of today's coal-fired power plants—which is about 40 percent—and thereby cut the carbon dioxide emissions per kilowatt almost in half?" asks lead researcher John Cooper, scientific capability leader for electrochemistry and corrosion in Lawrence Livermore's Chemistry and Materials Science Directorate. "And what if we could produce a pure carbon dioxide byproduct for sequestration or industrial use at no additional cost of separation while avoiding the air pollution problems associated with combustion?"

Cooper explains that direct carbon conversion requires a unique kind of fuel cell. A fuel cell is an electrochemical device that efficiently converts a fuel's chemical energy directly to electrical energy without burning the fuel. However, instead of using gaseous fuels, as is typically done, the new technology uses aggregates of extremely fine (10- to 1,000-nanometer-diameter) carbon particles distributed in a mixture of molten lithium, sodium, or potassium carbonate at a temperature of 750 to 850°C. The overall cell reaction is carbon and oxygen (from ambient air) forming carbon dioxide and electricity.

The reaction yields 80 percent of the carbon–oxygen combustion energy as electricity. It provides up to 1 kilowatt of power per square meter of cell surface area—a rate sufficiently high for practical applications. Yet no burning of the carbon takes place.

No Water to Boil

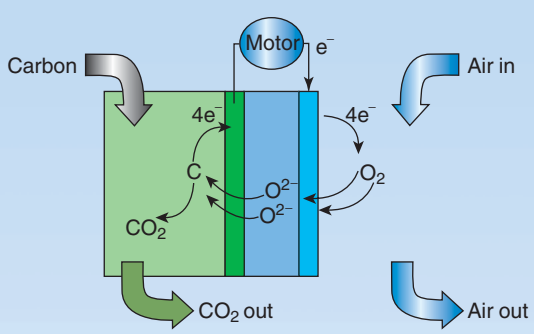
"We're not burning fossil fuels to boil water to drive turbines and dynamos to generate electricity," says Lawrence Livermore electrochemist Nerine Cherepy, who has been researching the breakthrough concept. "This is a simpler, more efficient, and more environmentally friendly process that obtains the greatest possible fraction of energy from the starting fossil fuel with little waste heat."

The thermodynamic efficiency of the direct carbon conversion cell exceeds the 70-percent requirement of the next-generation fuel cell envisioned by the Department of Energy. In contrast, conventional coal- and natural-gas-fired power plants are typically between 35- and 40-percent efficient. Combined-cycle pilot plants that burn natural gas in multistage turbines now operate at 57-percent efficiency, based on the higher heating value of the fuel. (Higher heating value, or HHV, is the total amount of heat released when a fuel is burned completely and the products are returned to their natural, room-temperature states.) High-temperature fuel cell hybrid systems (fuel cells combined with turbines), such as a technology developed by Westinghouse, are expected to operate on natural gas at 60-percent HHV.

Direct carbon conversion can use fuel derived from many different sources, including coal, lignite, petroleum, natural gas, and even biomass (peat, rice hulls, corn husks). Cooper notes that 90 percent of Earth's electric energy comes from the burning of fossil fuels. Half of our fossil-fuel resources is coal, and 80 percent of the coal belongs to the United States and Canada, the former Soviet Union, and China. Coal-fired plants produce 55 percent of U.S. electricity—as well as large amounts of pollutants. As a result, the vast energy reserves of coal remain underused. Direct carbon conversion has the potential to be the long-sought "clean coal" technology.

The carbon–air fuel cell gives off a pure stream of carbon dioxide that can be captured without incurring additional costs of collection and separation from smokestack exhausts. The stream of carbon dioxide, already only a fraction of current processes, can be sequestered or used for oil and gas recovery through existing pipelines. (Lawrence Livermore environmental scientists are studying the sequestering of carbon dioxide in geologic formations as part of a Department of Energy effort. See *S&TR*, December 2000, pp. 21–23.)

Pyrolysis—the thermal decomposition method used to turn hydrocarbons into hydrogen and tiny pure carbon particles



Carbon (C) and oxygen (O_2) can react in a high-temperature fuel cell with the carbon, delivering electrons (e) to an external circuit that can power a motor. The net electrochemical reaction—carbon and oxygen forming carbon dioxide—is the same as the chemical reaction for carbon combustion, but it allows greater efficiency for electricity production. The pure carbon dioxide (CO_2) product can be sequestered in an underground reservoir or used to displace underground deposits of oil and gas.

used in direct carbon conversion—consumes less energy and requires less capital than the electrolysis or steam-reforming processes required to produce hydrogen-rich fuels. Pyrolysis produces billions of kilograms of carbon blacks annually in the U.S. Carbon black is a disordered form of carbon produced by thermal or oxidative decomposition of hydrocarbons and is used to manufacture many different products, including tires, inks, and plastic fillers.

Old Dream

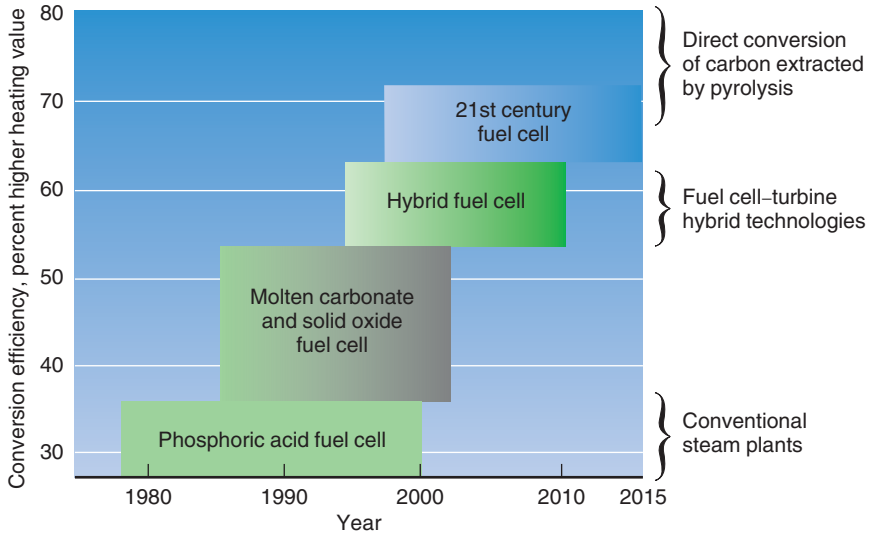
Electricity direct from coal is one of the earliest dreams of electrochemical science. The first attempts date from the late 19th century, when Boston entrepreneur William Jacques fashioned a coal fuel battery that used coke electrodes in a molten sodium hydroxide electrolyte. Because the molten electrolyte became exhausted, Jacques's invention operated as an exhaustible battery, not as a fuel cell, despite impressive demonstrations on the kilowatt scale. Other problems included a buildup of ash entrained with the fuel, the cost of making the carbon anodes, and the difficulty of distributing carbon fuel electrodes to the many cells. Efforts to develop practical carbon-based fuel cells during the 20th century, such as those tested at the Stanford Research Institute in the 1980s, were also hindered by the buildup of ash and by the costs and difficulties of carbon electrode manufacture.

The Lawrence Livermore approach circumvents the historic barriers to a coal fuel cell by using extremely fine, virtually ash-free, "turbostratic" carbon particles that contain small amounts of ash and have a high degree of structural disorder on the nanometer scale. The team found that turbostratic carbon particles, when mixed with molten carbonate to form a slurry, operate like rigid electrodes when the melt is brought into contact with an inert metallic screen. Exactly how the carbon particle delivers energy to the screen is under investigation, but reactive chemicals in the melt produced by the carbon are likely intermediates.

Also, the team found that carbon particles can be distributed pneumatically to individual cells by a small amount of carbon dioxide fed back to the cell from the continuously produced carbon dioxide stream. (The pneumatic transport of carbon particles through complex equipment is a widespread industrial practice.)

The carbon particles and oxygen (ambient air) are introduced as fuel and oxidizer, respectively. The slurry formed by mixing carbon particles with molten carbonate constitutes the anode. The anode reaction is carbon and carbonate ions forming carbon dioxide and electrons. At the cathode, which is similar to that used in other high-temperature fuel cells, oxygen, carbon dioxide, and electrons from the anode form carbonate ions. A porous ceramic separator holds the melt in place and allows the carbonate ions to migrate between the two compartments.

The technology has been demonstrated in a number of small, experimental cells with reaction areas of about 3 to 60 square centimeters. The cells feature different designs and different materials, including stainless steel, ceramic, and sometimes graphite. Each cell type features tubes for gases to enter and exit the cell, thermocouples (for measuring temperature), and a reference electrode. Temperature is maintained by a



Various kinds of fuel cells using phosphoric acid, molten carbonate, and solid oxide yield electricity from methane fuel at efficiencies in the range of 35 to 55 percent of higher heating value. Using waste heat from the fuel cell in turbines (hybrids) can increase the total efficiency even further. The thermodynamic efficiency of the direct carbon conversion cell already exceeds the 70-percent efficiency goal of the 21st century fuel cell envisioned by the Department of Energy.

computer-controlled furnace. The computer also acquires continuous data on current and voltage.

In repeated tests, the cells deliver up to 0.1 watt continuously per square centimeter and are 80-percent efficient at 80 milliwatts per centimeter. Recently, using a new cell design that automatically regulates the amount of molten salt, the team has operated cells for days, simply by adding more carbon fuel.

Doubly Attractive

The carbon–oxygen reaction is attractive in two unique ways, says Cooper. First, almost no entropy change occurs in the overall cell reaction. (Entropy is a measure of the disorder in a system. A significant entropy decrease would mean that the cell produces a great deal of waste heat.) Because the entropy change is close to zero for the carbon–oxygen reaction, 100 percent of the heat energy of combustion of the carbon can instead be converted by the cell into electrical energy under ideal conditions.

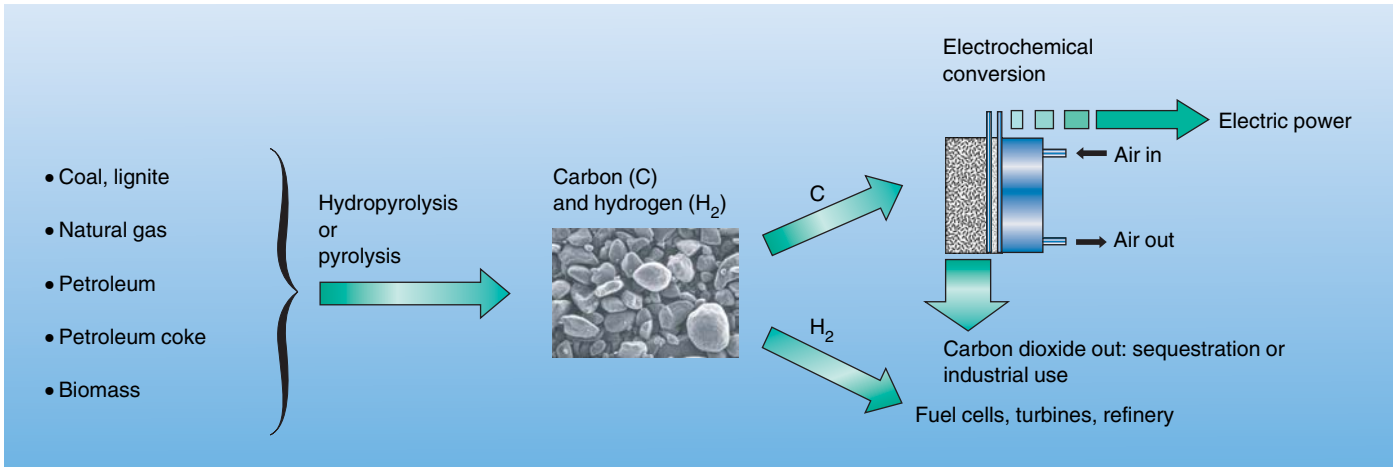
Second, the driving force for energy production, called electromotive force or maximum voltage, does not degrade as the carbon is progressively consumed to make power and carbon dioxide, so the voltage remains constant.That means that in making a single pass through the cell, all the carbon is consumed at a maximum yet constant voltage.

"Realistically, we can get out a maximum of about 80- to 85-percent efficiency, based on the heating value of the carbon, when the cell is operated at a practical rate, which is about 100 milliamperes per square centimeter," says Cooper. "The losses are primarily those associated with the sluggishness of electrode reactions and the electrical resistance of the cell. It was the two thermodynamic properties—zero entropy change and constant electromotive force—that first drew our attention to carbon as an attractive electrochemical fuel." In contrast, the entropy decrease for the hydrogen–oxygen reaction in high-temperature fuel cells limits conversion efficiency to 70 percent of the fuel's HHV, while electrical efficiencies (about 80 percent) and practical fuel use (about 80 percent) further reduce the total efficiency to below 50 percent. (See the box on p. 84.)

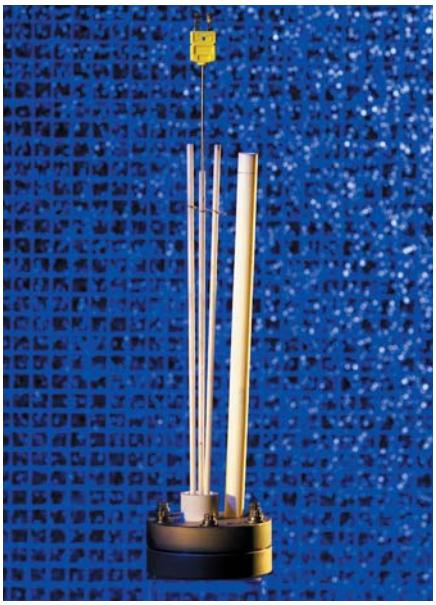
The part of a fuel's combustion energy that is not converted to electric power appears as heat. Some of this heat could be used to generate steam and drive a turbine generator, as in hybrid systems. But the additional cost and complexity must be weighed against the comparatively small additional savings in fuel.

Nanostructure Is Important

Cherepy and senior scientific associate Roger Krueger have tested a number of pure carbons that differ principally in the degree and nature of disorder on the nanoscale. They have correlated significant differences in the carbon fuels' three-dimensional atomic structures with their electrochemical reactivities. The more disordered the carbon atoms, the more easily they yield electrons. Cherepy and Krueger are paying particular attention to turbostratic carbons, which feature planes of atoms arranged at different angles and with lots of defects at the edges that make the atoms more accessible for chemical reactions. (Graphite, in contrast, has a more ordered structure and is less reactive by a factor of about 1,000.)



In principle, any fossil fuel or biomass can be converted to electric power using direct carbon conversion. For natural gas and oil, pyrolysis (thermal decomposition) yields hydrogen and carbon. For dirtier resources (coals, biomass), the carbon may have to be extracted by reaction with hydrogen, followed by pyrolysis.



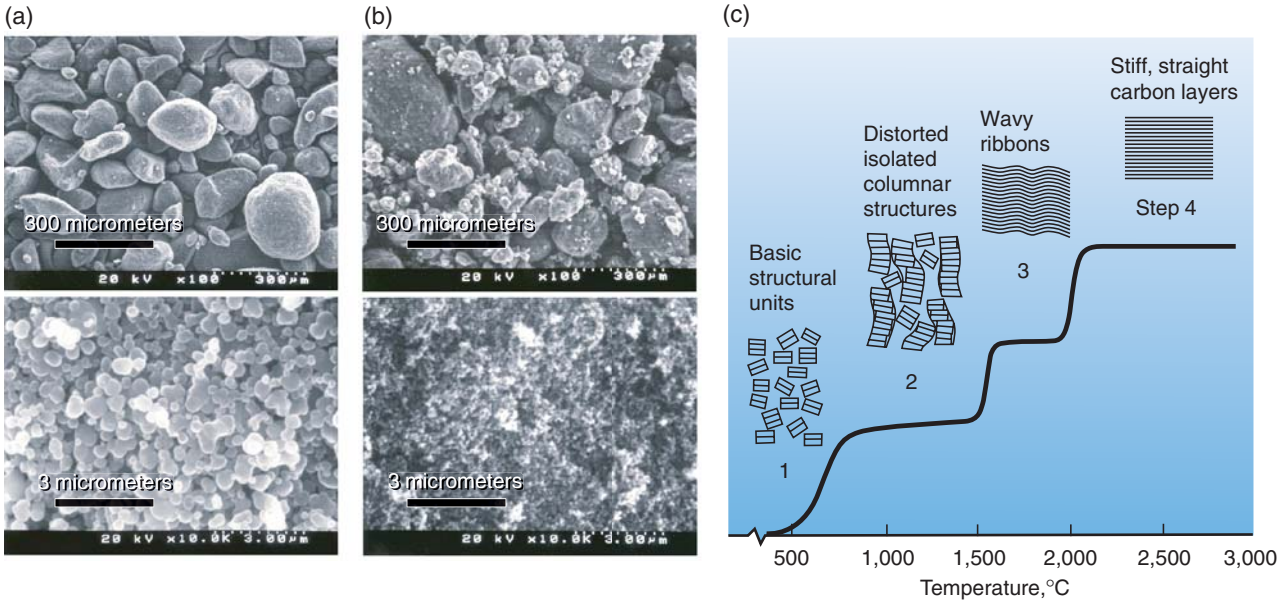
Simple cells in the laboratory are used to react carbon and atmospheric oxygen. These cells consist of a metal anode current collector, a ceramic matrix for holding the melt, and a metal screen for reacting the oxygen from the air.

Those candidate turbostratic carbons exhibiting discharge rates of more than 20 milliamperes per square centimeter at 0.8 volts have been analyzed in greater detail with transmission electron microscopy and x-ray diffraction. Researchers in Livermore's Chemistry and Materials Science Directorate conducted some of these characterization tests, and other characterizations have been done by Kim Kinoshita and coworkers at Lawrence Berkeley National Laboratory.

Cherepy's investigation has focused largely on carbon blacks because they have the highest electrochemical reactivity of any carbon fuel yet tested. Made from a variety of sources, carbon blacks are the basis of a large commercial industry. Four and a half billion kilograms per year of carbon black (all turbostratic to various degrees) are produced annually for automobile tires, pigments, plastics fillers, wire insulation, and other products. Although most carbon blacks contain about 0.02 to 0.05 percent residual ash, it should have no effect on system performance, cost, or cell lifespan because the rate of ash accumulation would be slow. (Carbon with 0.02-percent ash would clog the cell after about 50 years, five times the life expectancy of cell hardware.)

Among carbon blacks, a range of reactivities has been measured. For example, one carbon material had a peak power density of about 8 milliwatts per square centimeter while a second material measured almost 50 milliwatts per square centimeter. A third, the best material tested, yields energy at about 100 milliwatts per square centimeter and 100 milliamperes at 0.8 volts, sufficient for many fuel cell or battery applications.

Significant differences in microstructure and nanostructure were found in electron micrographs of the three samples, although all are nearly



The structure of the carbon material is the key to widely different electrochemical reactivities. The two carbon blacks in (a) and (b), revealed in photomicrographs at two magnifications, were produced by pyrolysis at different temperatures and started out as different fossil fuels. In (c), the degree of disorder of the carbon increases as the temperature of formation decreases from 2,000°C down to about 700 to 1,000°C.

pure carbon and look like black dusts. X-ray diffraction measurements showed that all had much greater spacing between layers of carbon atoms than does graphite. The x-ray data also revealed only small areas of crystallinity compared to graphite. Finally, the more reactive carbons have higher surface area and were found to oxidize more rapidly when exposed to high temperatures in air.

Cooper notes that the team is working to achieve a better understanding of the relationship between the nanostructure of carbons and their electrochemical reactivity in molten salts. A related goal is being able to predict carbon nanostructure from the conditions of pyrolysis and the nature of the starting materials undergoing pyrolysis. "Success here is critical to the economic attractiveness of the process and its ability to draw upon any fossil fuel resource," he says.

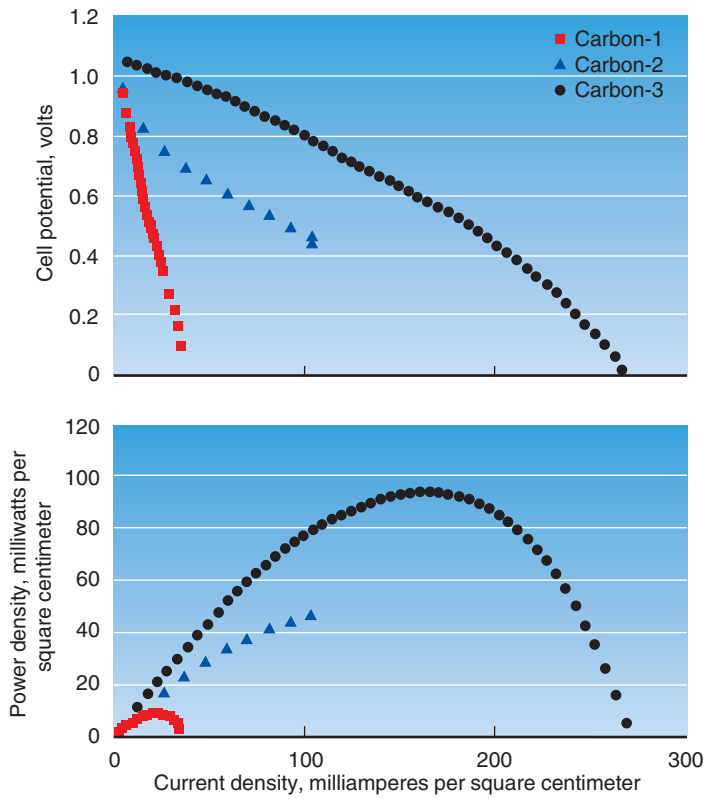
One Class of Fuels, Many Sources

A significant advantage of direct carbon conversion is that practically any fossil fuel, including coal, lignite, biomass, natural gas, and petroleum, can produce turbostratic carbons. One method, pyrolysis, uses moderate temperatures (800 to 1,200°C) to produce a stream of elemental carbon particles and a stream of hydrogen gas from a pure hydrocarbon. The byproduct hydrogen gas can be sold for a number of uses, including chemical synthesis, combustion, and powering fuel cells. The pyrolysis step consumes 5 to 10 percent of the starting fuel value (1 to 2 percent is lost because of process inefficiencies). Some fossil fuels, such as coal and biomass, first require treatment with hydrogen under high pressure to produce a hydrocarbon that can then be pyrolyzed into carbon fuel and recyclable hydrogen. This treatment is called hydropyrolysis and has many variants.

One of the most intriguing options is using coal as a carbon source because of the nation's (and the world's) vast resources of coal and the difficulty in using coal as a clean energy source. Because of most coal's high sulfur and ash content, it must undergo hydropyrolysis or some other means of purification.

Turbostratic carbon from petroleum coke could be highly advantageous for the carbon conversion cell, says Cooper, because it would likely be the least expensive source of carbon fuel. Some 2 to 8 percent of all petroleum refining ends up as petroleum coke, an inexpensive waste product that is naturally turbostratic and could be modified and used for direct carbon conversion. The amount of coke produced will increase as lighter crude resources become exhausted. Because coke commonly contains 0.25- to 5-percent sulfur, direct carbon conversion cells would require either coke refining or the use of graphite conductors in the carbon–air cell to prevent sulfur corrosion.

For natural gas, Cooper envisions small (100-kilowatt), transportable



Three carbon blacks are equally pure, are made by pyrolysis, and cost about the same, but they differ significantly in structure on the nanometer scale. As a result, their electrochemical reactivities are quite different. The two graphs depict the three carbons' voltage and power—two different functions of electrical current—as tested in a direct carbon conversion cell. Power densities (bottom) show carbon-3 reacting at a rate 10 times greater than carbon-1, providing about 100 milliwatts per square centimeter at 850°C. (Graphite, by comparison, is about 1,000 times less reactive than carbon-3.)

power stations that could be run from any natural gas pipeline. Such small power stations would be ideal in natural gas production fields; when a field becomes exhausted, the cell would be moved to a new location. Natural gas would be filtered and pyrolyzed at the wellhead. The resulting turbostratic carbon would go immediately to a direct carbon conversion cell, the hydrogen to a fuel cell, and hot carbon dioxide from the carbon cell used to displace more natural gas.

Direct carbon conversion might also make use of a significantly underused family of fuels that includes biomass, lignite, peat, and others. Some of this material, such as rice hulls, straw, and corn stalks, is simply burned in the field after harvest. Antipollution regulations are increasingly making such burning unlawful. Instead, such material could be charred, and the carbon component extracted with hydropyrolysis.

In analyzing the various fuel options, the team, together with Meyer Steinberg from Brookhaven National Laboratory, has calculated the total HHV efficiencies for electric power generation through five different routes to the production of turbostratic carbons, including petroleum coke, refinery products, natural gas, and lignite coal. The findings were 80 percent for direct petroleum coke, 67 to 75 percent for natural gas (methane), 72 percent for heavy oil, and 68 percent for lignite.

Costs Keep Things Interesting

An important aspect of the research effort is estimating costs for electrical production and for cell components. Petroleum coke is by far the least expensive source of fuel (costing as little as 5 cent per kilogram) because it is the byproduct of the oil refining industry. In the carbon black industry, the pyrolysis step costs about 20 cents per kilogram of carbon produced and thus would contribute about 3 cents to the cost per kilowatt-hour of electricity generated using carbon-black fuel.

At this time, cost estimates are difficult to make. A final design for the

Comparing Fuel Cells

Fuel cells use hydrogen, simple hydrocarbons such as methane, or carbon to produce electricity electrochemically rather than by burning them as fuels. Electrochemical means of providing electricity are generally much more efficient than burning fossil fuels in power plants to drive boilers and dynamos. The theoretical efficiencies of hydrogen or methane fuel cells top out at 69 percent and 90 percent, respectively, compared to 40-percent efficiency for typical power plants. The carbon–oxygen reaction that drives a direct carbon conversion fuel cell is unique: theoretically, all the potential combustion heat can be converted to electric power.

Methane and hydrogen fuel cells have other disadvantages. For one, the fuels are continuously diluted by their own reaction products as they are consumed. The voltage drops to ever-lower values, and as a result, not all of the fuel can be consumed. For carbon, no such dilution occurs, and all of the incoming fuel can be used to make electricity at about the same rate and voltage. Hydrogen, methane, and carbon fuel cells have practical voltage efficiency, that is, they operate at 80 percent of the maximum cell voltage.

The total electrical efficiency of a fuel cell is the product of three factors: theoretical efficiency, the fraction of fuel used, and the voltage efficiency. Carbon has a high total efficiency because of the favorable thermodynamics of the carbon–oxygen reaction. The actual efficiencies of the hydrogen and methane cells achieved in pilot plants are listed in the table below.

Of course, different kinds and amounts of energy are used in making these fuels. Methane needs only to be extracted from natural gas—a low-cost technology. Hydrogen can be produced from nuclear and renewable energies without any production of carbon dioxide. Carbon can be derived at a low energy cost from nearly any fossil fuel.

Comparison of efficiencies of fuel cells

Fuel	Theoretical limit	Fraction of fuel used in practical operation	Fraction of voltage available at practical rate	Total efficiency (higher heating value)
Carbon	1.01	1.0	0.8	0.80
Hydrogen	0.69	0.75 to 0.85	0.8	0.41 to 0.47
Methane	0.90	0.75 to 0.85	0.8	0.54 to 0.61

(Operating temperature of 750°C. Energy cost of fuel synthesis is excluded.)

hardware has not been settled on, and increases in power density are expected that inversely affect hardware size and cost. Nevertheless, the cost of the most expensive part of the cell—the commercial ceramic matrix holding the electrolyte and electrodes—is about $200 per square meter (that is, about $200 per kilowatt at 1 kilowatt per square meter). By comparison, modern gas turbine plants generate power at about $350 per kilowatt. Currently, the cost of cell hardware is low enough to be interesting.

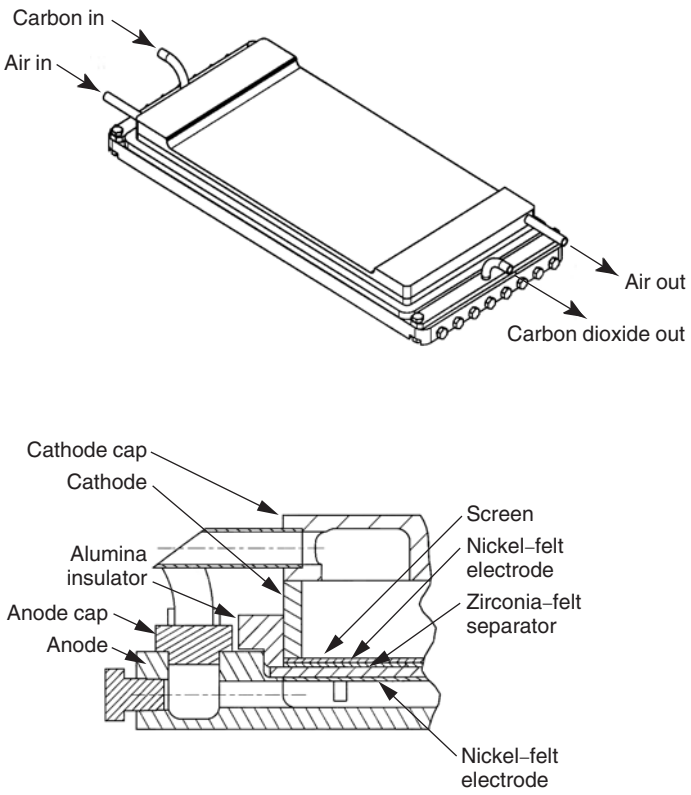
The sheer simplicity of the cell contributes to keeping costs down. The cell's fundamental thermodynamic properties mean almost no waste heat and full fuel consumption. Also, because the carbon conversion process produces pure carbon dioxide ready for sequestration or industrial use, cell design does not need costly components to collect and scrub the carbon dioxide before storage or use.

Finally, cell components and fuel are nontoxic and relatively hazard-free. In particular, because the carbon–molten salt slurry does not explode if inadvertently brought into contact with air, no explosion-prevention safeguards need to be engineered into the cells.

Destined for the Grid

Cooper is thinking ahead to the day when direct carbon conversion units could be used to generate electric power for the grid. Such a power plant would be "large, but not gigantic." A 3-gigawatt direct-carbon-conversion power plant, big enough to continuously supply some 3 million homes with about 1 kilowatt each, would only be the size of a large, two-story office building.

To achieve commercial adoption, however, requires greater understanding of the underlying science, especially the three-way relationship between conditions of pyrolysis, the resulting carbon nanostructure, and the electrochemical reactivity. While pyrolysis of natural gas and oil products to make turbostratic carbons is well known and widely practiced, the extraction of carbon from coal is less developed. "The extraction of carbon from coal, for example, by



An advanced cell design scales up the dimensions of tested cells to the 1,000-square-centimeter level. A maximum of 100 watts is expected from this design.

Nerine Cherepy and John Cooper assemble an experimental carbon conversion fuel cell.

Key Points to Understanding Carbon Conversion and Its Potential

- No single solution exists to meet 21st century energy and environmental needs. Electrification of highway vehicles, conservation, advanced turbines, electrochemical conversion of fuels (as with direct carbon conversion), nuclear power, and renewable energy are all likely to be important.
- It is critically important to develop technologies that generate electric power much closer to theoretical limits—the best large-scale commercial technologies are only halfway there.
- Direct carbon conversion generates electricity from reacting carbon and oxygen in a fuel cell and makes a pure carbon dioxide product available for industrial use or sequestration.
- Using fossil energy as carbon in a carbon fuel cell produces little waste heat and consumes all the fuel in a single pass, thereby bringing total efficiencies of 70 to 80 percent into reach.

hydropyrolysis, needs to be developed if this approach is to aid the conversion of 50 percent of Earth's fossil fuels," says Cooper.

The team is planning to scale up a demonstration unit from the 3-watt experimental cell to a stackable, 100-watt engineering module with 1,000 square centimeters of active area. The large-scale experiments should reveal any materials and operational problems on a practical scale, especially during extended tests.

Meanwhile, the team is testing more carbon blacks from commercial suppliers and turbostratic carbon fuels from new sources, such as petroleum cokes and coals. The tests with coal will be particularly important because of its large-scale reserves.

Cooper points to the complex task of providing energy while controlling greenhouse gases, particularly carbon dioxide. "The solution is beyond the scope of power production technology alone," he says, noting that electrical energy production currently accounts for just one-sixth of the total output of carbon dioxide. "Advanced combustion, fuel cells, nuclear and renewable energy, and conservation may all combine to help the situation in a way that cannot presently be predicted."

The Livermore team considers it vitally important to develop a simple fuel cell technology that greatly increases the yield of electric energy from each unit of fossil fuel, uses fuels derived efficiently from almost any fossil fuel, significantly decreases the carbon dioxide released into the atmosphere, and makes it easy to capture the carbon dioxide for sequestration or other use.

Clearly, we're just beginning to hear about direct carbon conversion.

—Arnie Heller

Key Words: biomass, carbon black, carbon dioxide, coal, direct carbon conversion, fuel cell, global warming, hydrogen fuel cell, hydropyrolysis, natural gas, petroleum coke, pyrolysis, turbostratic carbon.

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About the Scientist

JOHN COOPER received his B.A. in chemistry from Pomona College in 1968 and his Ph.D. in chemistry from the University of California at Berkeley in 1975. For 25 years, he has specialized in electrochemical science and engineering, with particular emphasis on fuel cells, fuel batteries, and power generation using reactive metals, zinc, aluminum, or elemental carbon with air-depolarized cathodes. He led the DOE National Program to develop novel metal–air fuel batteries for electric vehicle propulsion. He assembled and led a team to develop advanced processes for the growth and production of optical crystals for lasers. In addition, he has led projects to develop advanced processes, such as molten-salt oxidation, for treating mixed waste and military waste.

Currently, Cooper is scientific capability leader for electrochemistry and corrosion in the Chemistry and Materials Science Directorate. He is also the technical director of a private-sector collaboration to develop zinc–air fuel cells and batteries and is the inventor–director of projects to develop practical high-efficiency carbon–oxygen cells for mitigating the greenhouse gas emissions associated with electric power generation.