Lawrence Livermore National Laboratory

Science & Technology REVIEW

April/May 2016

SECURING CRITICAL MATERIALS FOR CLEAN ENERGY

Also in this issue:

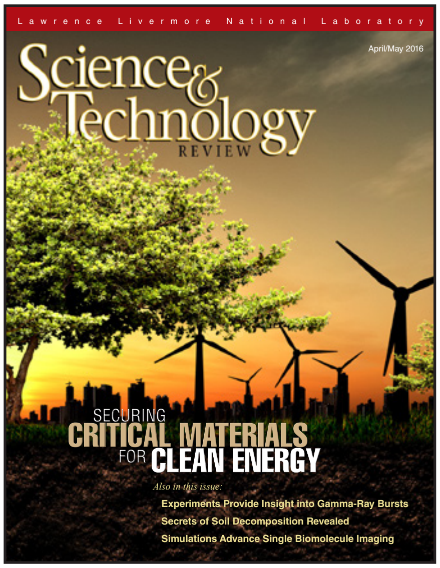
Experiments Provide Insight into Gamma-Ray Bursts

Secrets of Soil Decomposition Revealed

Simulations Advance Single Biomolecule Imaging

About the Cover

The Department of Energy's Critical Materials Institute (CMI) is working to ensure the nation has adequate supplies of certain scarce materials that are essential to the U.S. clean-energy industry. As the article beginning on p. 4 describes, Lawrence Livermore researchers have partnered with CMI to address the materials criticality issues associated with rare-earth elements. These materials are found in a wide array of products, including magnets, catalysts, metallurgical additives, phosphors, polishing powders, and ceramics. More than 95 percent of rare earths are mined outside the United States, and demand for some elements often outpaces supply. Livermore scientists are supporting CMI objectives by developing new alloys and substitute materials that reduce the need for rare-earth elements in high-efficiency motors, magnets, and fluorescent lightbulbs, as well as producing novel methods to reuse and recycle existing materials.



Cover design: Amy E. Henke

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At Lawrence Livermore National Laboratory, we focus on science and technology research to ensure our nation's security. We also apply that expertise to solve other important national problems in energy, bioscience, and the environment. *Science & Technology Review* is published eight times a year to communicate, to a broad audience, the Laboratory's scientific and technological accomplishments in fulfilling its primary missions. The publication's goal is to help readers understand these accomplishments and appreciate their value to the individual citizen, the nation, and the world.

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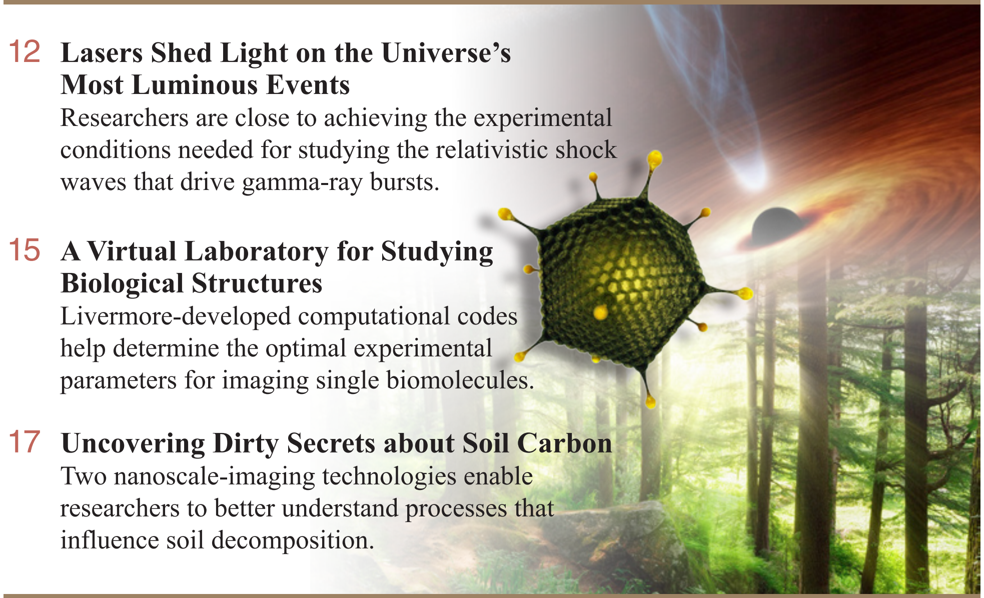

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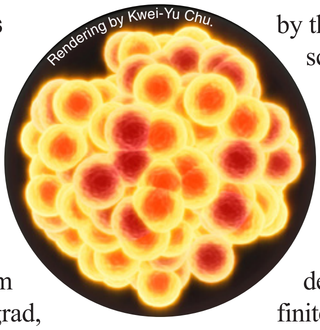
Livermore Credited with Discovery of Elements

The International Union of Pure and Applied Chemistry (IUPAC) has officially credited Lawrence Livermore scientists and international collaborators with the discovery of elements 115, 117, and 118. Livermore teamed with the Joint Institute for Nuclear Research in Dubna, Russia (JINR) in 2003, and again in 2006, to discover elements 113, 115, and 118. The Livermore–JINR team then worked with researchers from the Research Institute for Advanced Reactors (Dimitrovgrad, Russia), Oak Ridge National Laboratory, Vanderbilt University, and the University of Nevada at Las Vegas to discover element 117 (shown at right) in 2010.


Rendering by Kwei-Yu Chu.

Elements beyond atomic number 104 are referred to as superheavy elements. Not found in nature, superheavy elements have been created in a laboratory by accelerating beams of nuclei and shooting them at the heaviest possible target nuclei. The fusion of two nuclei occasionally produces a superheavy element that generally exists for only a short time. The discovery of heavier elements brings researchers closer to the "island of stability," a term that refers to the possible existence of a region beyond the current periodic table where new superheavy elements with special numbers of neutrons and protons would exhibit increased stability.

Altogether, the Livermore–JINR team has reported the discovery of 6 new elements (113, 114, 115, 116, 117, and 118—the heaviest element to date.) IUPAC officially credited a Japanese collaboration with the discovery of element 113, although the Livermore–JINR team had submitted a paper on the discovery of elements 113 and 115 at about the same time as the Japanese group. Dawn Shaughnessy, Lawrence Livermore's principal investigator for the Heavy Element Group, says, "It is a wonderful gift to the entire team that we are recognized for our efforts in accomplishing these highly difficult experiments and for the years of work it takes to successfully create a new chemical element."

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New Tools Help Analyze and Evaluate Nuclear Material

With support from the National Nuclear Security Administration's nonproliferation and counterterrorism offices, Livermore scientists have created new, powerful mathematical tools to detect, analyze, and assess unknown objects containing fissionable material for a wide range of applications, including safeguards, border security, arms control, and counterterrorism. The research appears in the November 4, 2015, edition of the journal *Nuclear Science and Engineering* and was featured on the issue's cover.

Special nuclear materials (SNM)—highly enriched uranium and plutonium-239—are unique among radioactive materials in that they create self-perpetuating fission chain reactions and in turn emit bursts of many neutrons and gamma rays. The novel Livermore-developed detection and analysis methods are designed to exploit the burst-timing pattern of neutrons and gamma rays emitted by these fission chains. Project leader and Laboratory scientist Les Nakae says, "We have been developing new detection systems that can count neutrons and gamma rays on nanosecond timescales. This counting capability can isolate individual fission events within a fission chain and requires a new theory to fully exploit and interpret the data."

Livermore nuclear engineer Jerome Verbeke helped develop a new Monte Carlo code to exactly reproduce the finite statistic realization of probabilities for specific fission chain signatures. The code can rapidly generate characteristics of SNM sources and serves as a check for theoretical solutions. Using this theory, the team accurately predicted measurements from real systems with SNM in the form of time-correlated neutrons and gamma rays. The theory also has potential applications in scientific areas beyond nuclear physics, including the study of how disease spreads.

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Results Deepen Understanding of Dark Matter

A new set of calibration techniques developed in part by Livermore scientists has improved the sensitivity of the Large Underground Xenon (LUX) experiment—the most sensitive dark matter detector in the world. LUX, located at the Sanford Underground Research Facility in Black Hills, South Dakota, is designed to detect low-mass weakly interacting massive particles (WIMPs), which are among the leading candidates for dark matter. The recent improvements have increased LUX's sensitivity to these elusive particles by more than two orders of magnitude. The research is described in a paper that was submitted to the journal *Physical Review Letters* and posted to arXiv on December 11, 2015.

The research team's recent work re-examines data collected during LUX's first experimental run in 2013, and helps rule out the possibility of dark matter detections at low-mass ranges previously reported possible with other experiments. "The first analysis of the LUX data was published in 2014," says Livermore principal investigator and physicist Adam Bernstein. "Since then we have expanded our knowledge of the detector response through a combination of low-energy nuclear recoil measurements, low-energy electron recoil measurements, and an improved understanding of our background in the low-energy recoil regime where dark matter interactions are likely to appear."

One calibration technique used neutrons as stand-ins for dark matter particles in experiments. Bouncing neutrons off xenon atoms allows scientists to quantify how the LUX detector responds to the recoil process. LUX scientists have also calibrated the detector's response to the deposition of small amounts of energy from struck atomic electrons. As a result of their work, researchers can search with higher confidence for particles that were previously thought undetectable by LUX. The LUX experiment began its latest search for dark matter in late 2014 and is expected to run until July 2016.

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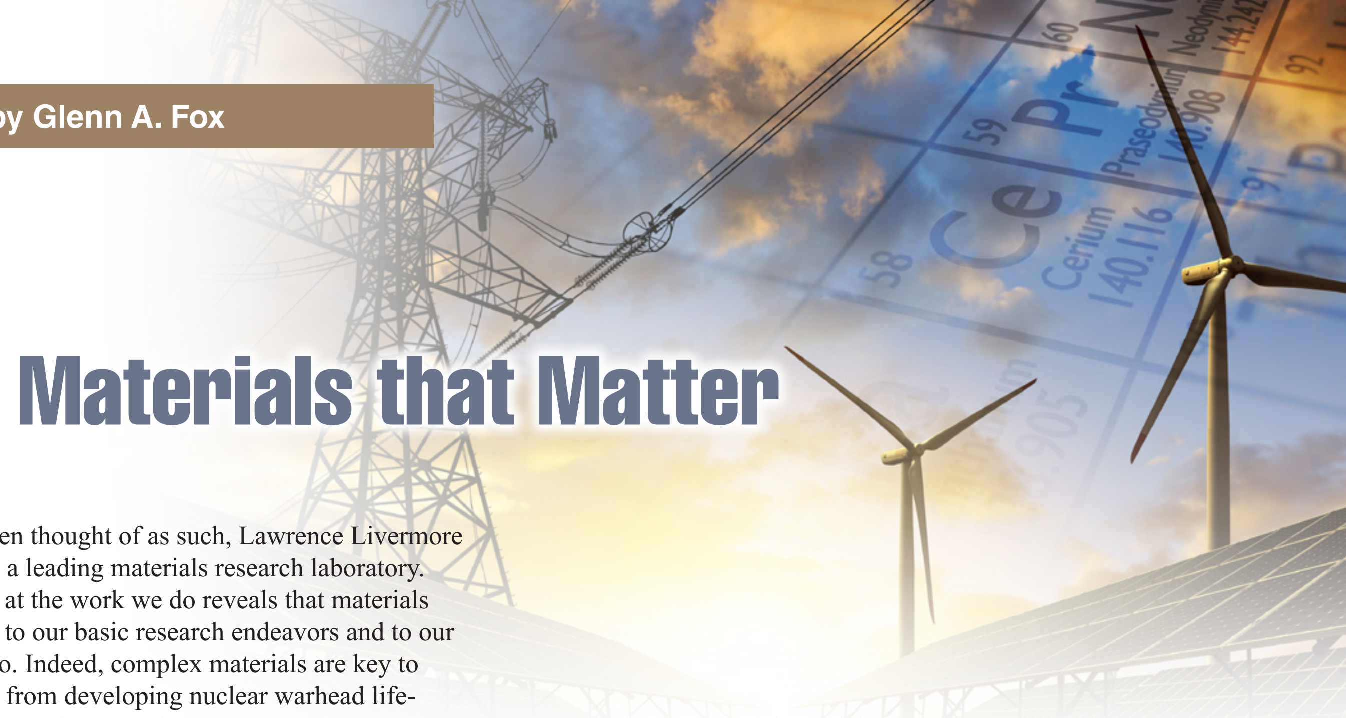
Commentary by Glenn A. Fox



Materials that Matter

ALTHOUGH not often thought of as such, Lawrence Livermore is by any measure a leading materials research laboratory. Even a cursory glance at the work we do reveals that materials science is central both to our basic research endeavors and to our programmatic portfolio. Indeed, complex materials are key to many research efforts, from developing nuclear warhead life-extension programs to creating complex targets for experiments at the Laboratory's National Ignition Facility. Such experiments rely on "tailored materials," those created with the right properties for a specific application.

With 290 people, the Materials Science Division is the largest group in Livermore's Physical and Life Sciences Directorate. This organization is dedicated to creating novel materials and understanding the properties and performance of new and legacy materials often subjected to the most extreme conditions. The division uses state-of-the art experimental, theoretical, and computational tools to accelerate the discovery, qualification, and deployment of uniquely functional materials and advanced manufacturing methods.

The article beginning on p. 4 describes our work with the Department of Energy's Critical Materials Institute (CMI). The institute's goal is to find innovative solutions for avoiding a supply shortage of any material, especially rare-earth elements, that could threaten the U.S. clean-energy industry and our broader national security interests. A particular focus of CMI is to address the materials criticality issues associated with five of the rare-earth elements: dysprosium, terbium, europium, neodymium, and yttrium.

Lawrence Livermore has a very close connection to CMI. Going back to the institute's origin, Laboratory researchers helped develop the ideas and proposal that ultimately resulted in CMI's establishment in 2013. In addition, the institute is operated by the Department of Energy's Ames Laboratory, whose director is former Livermore scientist Adam Schwartz.

The article cites current CMI–Livermore research efforts that are aimed at lessening dependence on rare-earth elements in a host of products, including powerful magnets and fluorescent lightbulbs. Researchers are finding ways to substitute materials with equivalent or superior properties to those found in rare-earth elements, as well as develop new products with reduced rare-earth content. Finally, we are deepening our understanding of rare-earth properties by taking advantage of computational materials models that use Livermore's supercomputing resources. With these simulations, we are improving our knowledge of how to effectively use materials models, link them across various length and timescales, and couple them with experiments.

Our CMI-related research is both innovative and practical. For example, in our search for efficient new approaches to rare-earth extraction and recovery from ores, we have genetically engineered a common bacterium to adsorb rare earths on its exterior. The accumulated rare earths are then washed off and collected, and the bacteria can be reused. In a related effort, we are testing whether the types of x-ray machines used at airports for baggage screening can also be implemented to pinpoint the location of magnets found in discarded computer hard drives. After removal from the hard drives, these magnets could either be recycled or have their rare earths extracted for other purposes.

One of the Laboratory's enduring strengths is its ability to forge partnerships and collaborations with other institutions, including universities, other national laboratories, government agencies, and private industry. As an example, Livermore is partnering with Oak Ridge National Laboratory and General Electric to develop new formulations with reduced rare-earth content for phosphors used in fluorescent lightbulbs. Livermore researchers, responsible for reformulating the red-light emitting phosphor, have created a compound that is rare-earth free. This phosphor appears to meet requirements of long use, high efficiency, proper color rendition, low cost, strong absorption at the required wavelength, chemical stability, and environmental safety. Experiments to find the ideal replacement have been assisted by quantum simulations of prospective phosphors.

Unique to CMI is a team of economists who monitor the state of critical materials and their likely effect on U.S. global competitiveness. The team's work recognizes that today, economic and security interests are increasingly inseparable and that science and technology are at the heart of the United States' competitive advantage. Livermore researchers also acknowledge this fact as we strive to develop materials and manufacturing technologies to advance the nation's clean-energy industry.

■ Glenn A. Fox is associate director for Physical and Life Sciences.

REDUCING RELIANCE on CRITICAL MATERIALS

Livermore researchers support efforts to limit the need for rare-earth elements in U.S. clean-energy technologies.

HIGH-TECHNOLOGY products, from car motors to fluorescent lighting, often rely on small amounts of scarce raw materials that possess key properties, such as strength, thermal resistivity, and magnetism. No easy substitutes exist for these so-called critical materials, and as a result, demand for them can at times exceed available supply. Indeed, shortages of critical materials can impair entire industries and prevent the development and implementation of new products.

Critical materials include a group of related elements called rare earths, which traditionally include the lanthanide series of elements in the periodic table as well as scandium and yttrium (see the box on p. 7). Rare earths are essential to high-performance magnets and magnetic powders, catalysts, metallurgical additives, polishing powders, phosphors, glass additives, and ceramics used in a variety of industries, including health care, computer, automotive, communications, and optics to name a few. For example, at Lawrence Livermore's National Ignition Facility— the world's largest laser—optics made from ultrapure glass doped with neodymium atoms amplify laser light to the extremely high energies required for experiments.

Many rare-earth elements are also considered critical materials for the U.S

clean-energy industry. Hybrid-electric vehicles, fluorescent lights, large wind turbines, and other clean-energy products all rely on small quantities of rare earths. The Department of Energy's (DOE's) Critical Materials Institute (CMI) was established, in part, to assure supply chains for these precious commodities, thereby enabling innovation in U.S. manufacturing and enhancing the nation's energy security. Established in 2013 with help from Livermore materials scientists, CMI is one of DOE's four Energy Innovation Hubs and is headquartered at Ames Laboratory in Ames, Iowa. A particular focus of CMI is to address the materials criticality issues

Many rare-earth elements are essential to the nation's clean-energy industry. Europium, a rare earth that has the same relative hardness as lead, is used to create fluorescent lightbulbs. With no proven substitutes, europium is considered a critical material to the clean-energy economy. (Photo courtesy of Ames Laboratory.)

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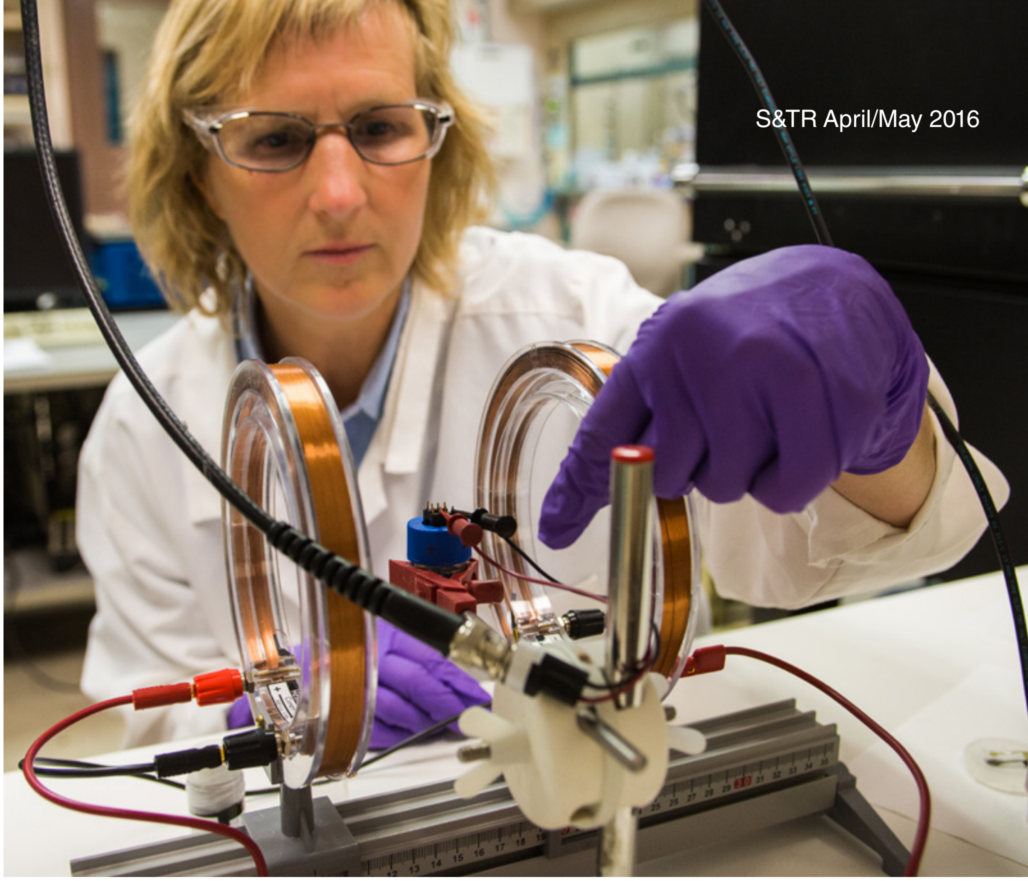
associated with five of the rare-earth elements: dysprosium, terbium, europium, neodymium, and yttrium.

CMI-sponsored research is conducted at national laboratories, universities, and U.S. companies. Lawrence Livermore physicist Eric Schwegler, who coordinates CMI-funded research at the Laboratory, notes that rare-earth research has implications for national security and economic vitality. More than 95 percent of rare earths are mined outside the United States. Occasional export restrictions by rare earth–producing nations have prompted concern about the effects a shortage could have on the U.S. clean-energy industry.

CMI is working to reduce the nation's dependence on rare earths through three research focus areas: diversifying supply, developing substitutes, and reuse and recycling. This work is further enhanced by cross-cutting research initiatives that range from establishing new additive-manufacturing technologies to conducting economic analyses of potentially new critical materials. Schwegler says, "Livermore's work for CMI has established the Laboratory's expertise in rare-earth materials synthesis, characterization, and modeling and has contributed to its mission of safeguarding energy security."



Laboratory materials scientist Christine Orme is helping develop exchange spring magnets—objects that are twice as strong, contain half the required rare-earth content, and operate more effectively at higher temperatures than existing permanent magnets. Such technology could drive design of smaller, lighter, and more efficient motors for cars and wind turbines. (Photo by Lanie L. Rivera.)

A More Varied Supply

Despite their name, rare-earth elements (with the exception of promethium) are found in relatively high concentrations across the globe. However, they seldom occur in easily exploitable deposits because of their geochemical properties. Schwegler adds that rare earths are chemically very similar and thus are generally found mixed together and are difficult to separate. In addition, the lighter rare-earth elements, such as cerium, are often present in greater concentrations than the heavier elements.

To better diversify supply, one strategy under consideration is finding novel applications for rare-earth materials that are relatively abundant but less used. Cerium, for example, is often discarded as a byproduct in the separation and extraction of the more valuable rare earths. If new, significant applications could be found for cerium, the economics of mining rare earths that occur in smaller concentrations could change considerably.

A promising research avenue takes advantage of cerium's low demand to explore the element's suitability as an alloying agent. Currently, no low-cost aluminum alloys have been developed that can operate at elevated temperatures while maintaining the mechanical properties needed for high-performance automotive and aerospace applications. "By combining 10 percent cerium with aluminum and perhaps other elements, we could make stiff, lightweight materials for creating engines that operate at higher temperatures," says Livermore physicist Scott McCall. A high-performance aluminum alloy would enable design of higher efficiency internal combustion engines and lighter drivetrains, thereby improving fuel economy.

McCall is working with colleagues at Oak Ridge National Laboratory and CMI's strategic partner Eck Industries, Inc. of Manitowoc, Wisconsin. They are developing alloys containing cerium, along with appropriate techniques to efficiently manufacture them. Livermore researchers are testing the most promising alloys. "If the tests prove successful, the alloys could trigger a huge demand for cerium," says McCall. Early tests of aluminum alloys with cerium concentrations of 6 to 16 percent have proven that the material is castable and remains strong at room temperature.

Bring in the Replacements

Livermore researchers are also searching for rare-earth substitutes in magnets used in automobiles, especially hybrid-electric cars. Developed in the 1970s and 1980s, rare earth–based magnets are the strongest type of permanent magnets available. They are found in the more than 40 electric motors and actuators that control various vehicle devices from windshield wipers to speakers. In hybrid-electric cars, rare-earth magnets are part of the vehicles' regenerative braking system. These magnets are also found in lightweight motors for compact computer hard drives and even powerful hand tools. Large, megawatt-scale wind turbines contain approximately 1,000 kilograms of magnets, of which 25 percent by weight are made from rare earths.

Many of these magnets contain neodymium and the expensive rare earth dysprosium. "We want to make these motors cheaper and smaller while using fewer rare-earth elements," says McCall. He is working on a new class of magnet that offers high magnetic coercivity (ability to withstand an opposing external magnetic field without demagnetizing) and high magnetic remanence (the magnetization remaining when the magnetizing field is removed). Other team members include Jonathan Lee, Sarah Baker, Christine Orme, Joshua Kuntz, and Tony Van Buuren.

Rare-earth magnets, such as those made from neodymium–iron–boron or samarium–cobalt alloys, are hard magnetic materials that have high coercivity but only modest remanence. In theory, if these hard

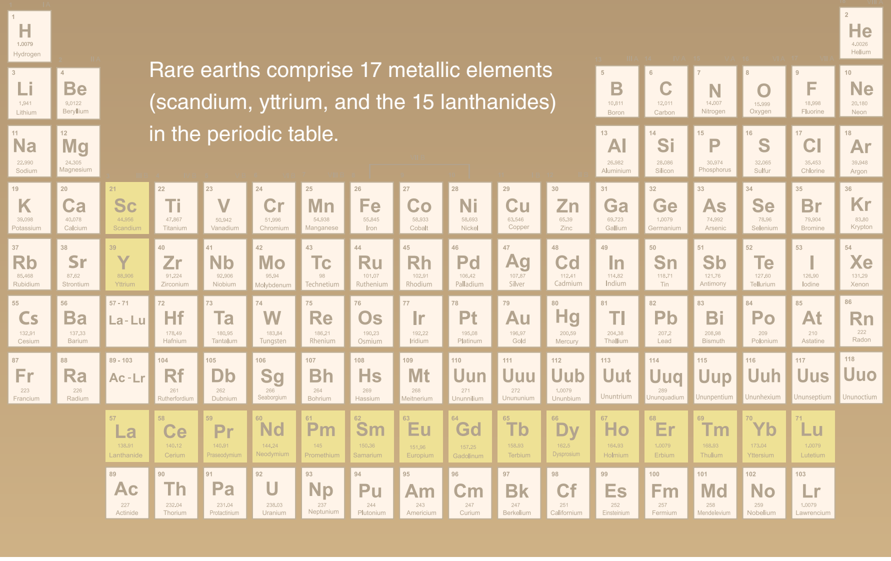
Rare Earths Have Special Properties

The rare earths comprise 17 metallic elements in the periodic table: scandium, yttrium, and the 15 lanthanides (lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium). Scandium and yttrium are considered rare-earth elements because they tend to occur in the same ore deposits as the lanthanides and exhibit similar properties. Used in various technologies from computer hard drives to speakers, rare earths are also essential for U.S. competitiveness in the global clean-energy industry.

Despite their name, rare-earth elements (with the exception of promethium) are found throughout the world. Cerium is particularly plentiful, about as abundant as copper. However, most rare-earth production is concentrated in China. A growing concern exists among scientists and high-technology industries regarding the future supply of five rare-earth elements—dysprosium, terbium, europium, neodymium, and yttrium. Shortages of these materials could affect clean-energy development in the coming years. For example, the largest wind turbines require very powerful neodymium–iron–boron magnets.

The atomic number of each rare earth is exactly one more or one less than its neighboring element along the periodic table. The nominal increase is the result of the successive addition of an electron to a material's 4f electron shell. Understanding the behaviors of these electrons is therefore central to determining how rare-earth elements produce the properties they confer to products. Better theoretical models for f-shell electrons, validated by experiment, are needed to accelerate the discovery and design of new products containing rare earths. In addition, studies of rare earths can provide insight into the properties of actinide elements, which have similar properties and are important for stockpile stewardship research.

When alloyed with other metals, rare earths provide enhanced magnetism, strength, thermal resistance, and other properties. Several rare-earth elements confer material properties that cannot be provided by anything else. For example, neodymium and dysprosium are used in high-strength magnets found in hard drives, speakers, and cars, all of which benefit from higher efficiency and smaller-size magnets.



Rare earths comprise 17 metallic elements (scandium, yttrium, and the 15 lanthanides) in the periodic table.

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materials could be interspersed with a soft magnetic material that has high magnetic remanence, the resulting magnet could be twice as strong, contain half the required rare-earth content, and operate more effectively at higher temperatures. Called exchange spring magnets, these objects could drive design of smaller, lighter, and more efficient motors for cars and wind turbines.

"The exchange spring magnet idea has been around since the early 1990s," says McCall. However, their manufacture has posed significant challenges because the hard material must be distributed at the nanoscale within the soft material matrix. Additive-manufacturing techniques have made fabricating the magnets more feasible. In collaboration with Brown University and General Electric (GE), Livermore scientists are showing how hard and soft magnetic materials can be put down in a checkerboard array using electrophoretic deposition and nanomanufacturing technology. McCall says, "It's a very promising technique."

Exchange spring magnets could be commercially available within three to four years after laboratory demonstration. The development team is aiming to produce a prototype for testing by late 2016. Economists see a potential $10 billion market for these magnets. According to McCall, the market for high-strength permanent magnets is so large that even small improvements in magnet strength or reductions in the quantity of rare-earth elements required could save hundreds of millions of dollars annually.

Modeling Material Alternatives

In a separate project, physicist Patrice Turchi is combining quantum-mechanical simulations and thermodynamic modeling to estimate the phase stability, magnetism, and other properties of potential rare-earth alloys for hard magnet and structural applications. The effort takes advantage of progress in computational materials modeling and Lawrence Livermore's vast supercomputing resources to optimize design and development of new materials.

Turchi and his team are developing a materials design simulator to accelerate the search for replacements to rare earths or rare-earth alloys that provide the same or enhanced materials stability and performance. Turchi says, "We want to find the optimum proportion of elements that will produce alloys with the best magnetic properties in the case of hard magnet applications, or mechanical properties in the case of structural materials applications."

By combining the team's modeling efforts with available experimental data, Turchi and his colleagues Per Söderlind, Alexander Landa, Aurélien Perron, and Vincenzo Lordi can validate quantum-mechanical simulations of rare earths and build a series of validated databases that include the thermodynamic and magnetic properties of rare earth–based materials. Toward this end, they are studying the permanent magnet that combines samarium with cobalt. These strong permanent magnets are similar in strength to neodymium magnets, but they can withstand higher temperatures and have higher coercivity. However, they are brittle and prone to cracking and chipping. The Livermore quantum-mechanical model computationally reproduces the properties of this magnet and gives researchers confidence as they search for solutes that could further improve the technology.

One goal of this effort is to partially substitute cobalt, a material sensitive to market price swings, with iron. The

Livermore researchers Patrice Turchi (foreground) and Scott McCall review the phase diagrams of aluminum–cerium–silicon and cobalt–iron–samarium alloys. Quantum-mechanical simulations and thermodynamic modeling are used to estimate the phase stability, magnetism, and other properties of potential rare-earth alloys. (Photo by Lanie L. Rivera.)

Livermore model has predicted the ideal mixture of iron and cobalt for maintaining the desirable properties of high-temperature and magnetic stability. "If stable, the material created from combining the rare earth samarium and iron could have fantastic properties," says Turchi. "We may want to add other rare earths as well as transition metals to fully stabilize the materials." For structural applications, thermodynamic modeling has been successfully used to optimize alloy composition in materials combining aluminum and cerium with other solutes. These models are helping guide the experimental efforts being conducted at Oak Ridge and Livermore.

Lighting the Way

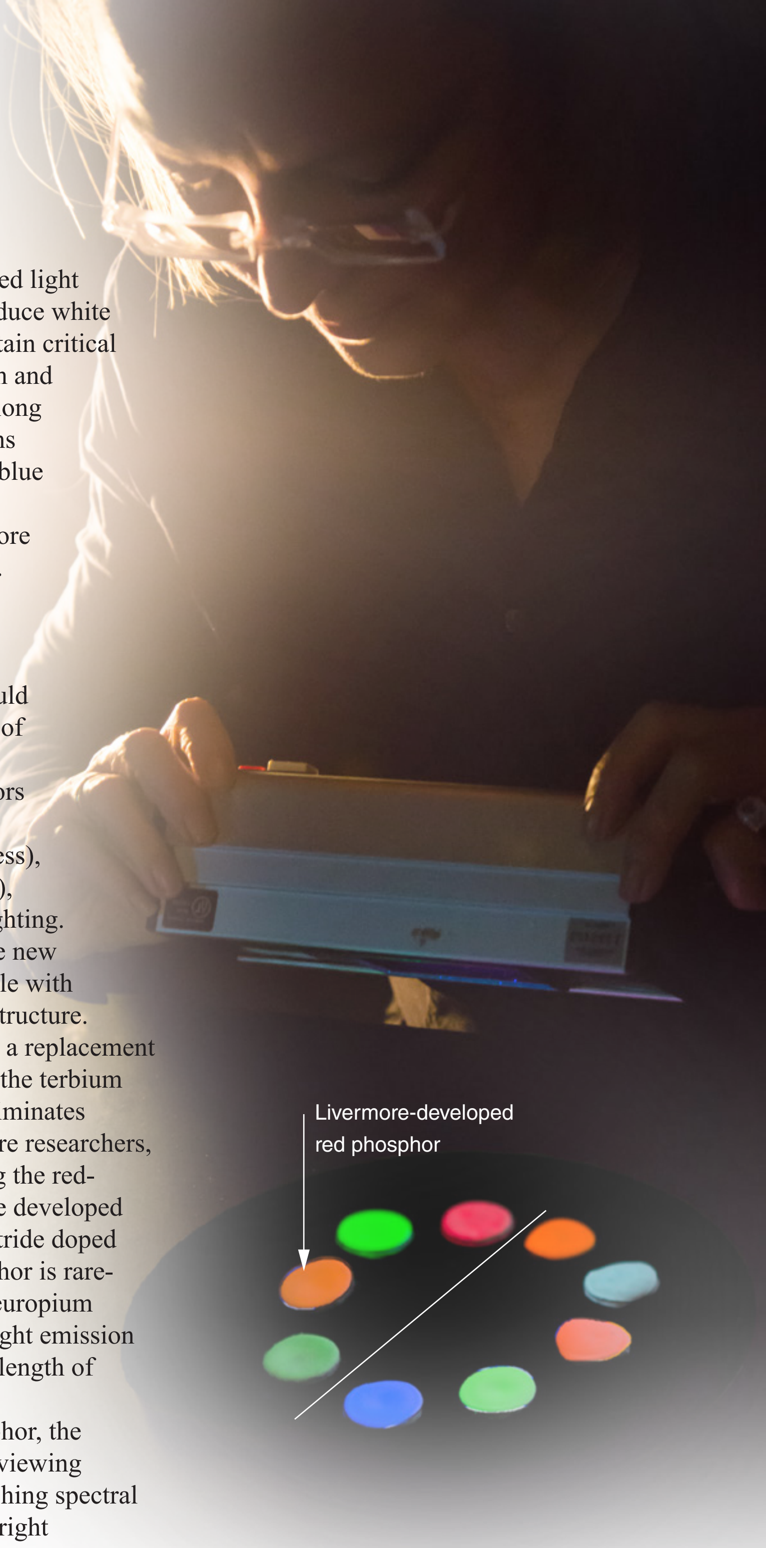
Advanced lighting systems are another technology that could benefit from rare-earth substitutes. Livermore researchers Steve Payne, Nerine Cherepy, Daniel Aberg, and Fei Zhou are working with colleagues from GE, Ames, and Oak Ridge to sharply reduce the rare-earth content of the three phosphors used in fluorescent lighting. Other Livermore team members include Zach Seeley, Kiel Holliday, Nick Harvey, Paul Martinez, Ich Tran, Alex Drobshoff, and several college summer students.

Current phosphors in fluorescent lighting consume more than 1,000 metric tons of rare-earth oxides yearly. GE, a major manufacturer of fluorescent lamps, has set a goal of reducing the quantity of rare earths in lighting by at least 50 percent without compromising the quality of the light or increasing the cost.

Cherepy and Payne explain that inside fluorescent bulbs electrons collide with atoms of mercury vapor. The excited mercury atoms emit energy in the form of ultraviolet photons (invisible to human eyes), which interact with three fluorescent phosphors coating the inside of the bulb. The current tri-phosphor blend uses a mixture of blue, green, and red light emitters that combine to produce white light. Fluorescent lamps contain critical rare-earth elements europium and terbium in their phosphors along with the lower cost rare earths yttrium and lanthanum. The blue phosphor has inherently low rare-earth content and therefore does not need to be replaced. However, europium and terbium are in high demand and eliminating them in the green and red phosphors would help stabilize the future cost of fluorescent lighting.

Any replacement phosphors must also sustain the color temperature (desired whiteness), lifetime (about 15,000 hours), and brightness of existing lighting. Further, the processing of the new phosphors must be compatible with current manufacturing infrastructure. GE scientists have identified a replacement green phosphor that reduces the terbium content by 90 percent and eliminates lanthanum entirely. Livermore researchers, responsible for reformulating the red-light emitting phosphor, have developed a compound of aluminum nitride doped with manganese. This phosphor is rare-earth free, eliminating both europium and yttrium oxides, and its light emission is close to the required wavelength of 610 nanometers.

In creating the new phosphor, the Livermore team began by reviewing scientific literature and searching spectral databases for emitters at the right wavelength. They then produced a small amount of candidate phosphors and tested them to determine their performance. In addition, physicists Aberg and Zhou performed quantum simulations of the prospective phosphors to calculate the substances' emission energies and various oxidation states. Much of their



Scientist Nerine Cherepy illuminates phosphor samples under ultraviolet light. Standard phosphors used in fluorescent lightbulbs (bottom right) could soon be replaced with those being developed by Livermore and collaborators that contain little or no rare-earth elements (top left). The Livermore-developed red phosphor is rare-earth free (Photo by Lanie L. Rivera.)

focus was on compounds containing manganese dopants.

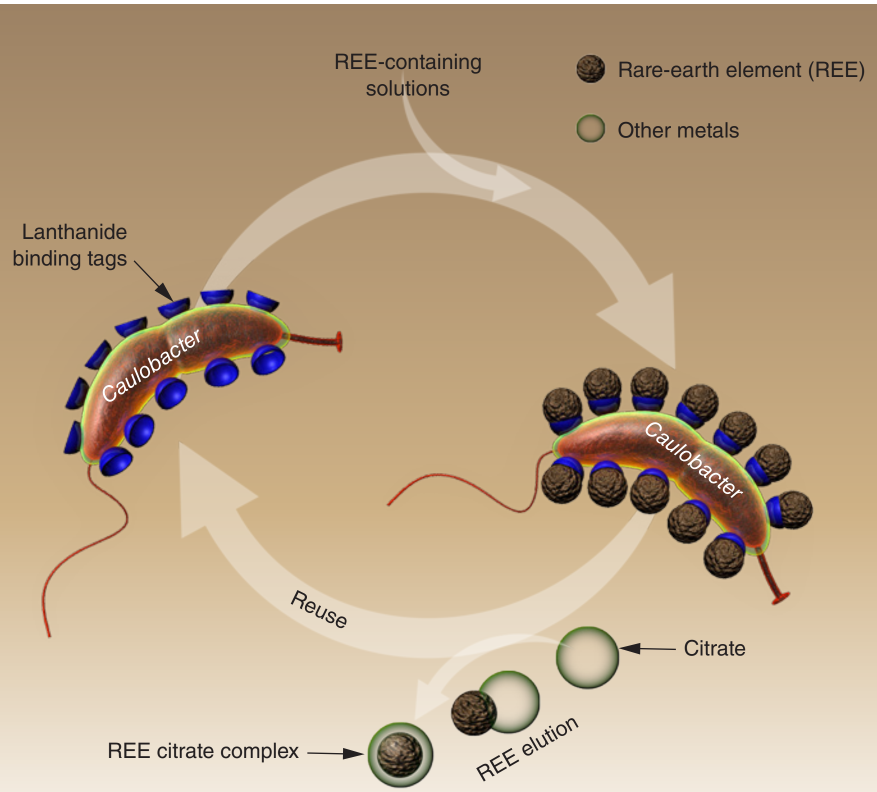
Cherepy points out that the original phosphor used in fluorescent bulbs was a mined mineral, willemite, which is naturally doped with manganese. Several decades later, in the 1970s, rare earth–containing phosphors became the standard. Aberg explains that depending on their oxidation state, manganese ions exhibit different colors and are often used as pigments. “Manganese is a versatile dopant,” he says. “We focused on finding a host for manganese that allows the element to emit red in a phosphor.”

Work is still underway to ensure the commercial feasibility of producing fluorescent lighting using these phosphors, but the future prospects look good. “The fundamental physics of the green phosphor being developed by GE as well as Livermore’s red aluminum nitride–manganese phosphor is compelling,” adds Payne. “We are taking the next steps in advancing this research by evaluating chemical issues such as slurry compatibility, improving procedures to synthesize the elements, and refining cost estimates.”

Bacteria Create a Sticky Situation

The increasing demand for rare earths in emerging clean-energy technologies has triggered an urgent need for new approaches to efficiently extract these materials from ores and recyclable products. Livermore staff scientist Yongqin Jiao and colleagues are leading a project to develop a bioadsorption strategy for rare-earth recovery using genetically engineered bacterium.

Caulobacter crecentus is a common bacterium found in soil and lakes. (See *S&TR* April/May 2014, pp. 13–16.) The research team’s genetically engineered *C. crecentus* has lanthanide binding tags attached to its outer cell wall. The tags have molecules called ligands that bind to metal atoms with 1,000 times greater affinity for rare earths than other metals. They also have an adsorption preference for heavy rare-earth elements relative to light elements.



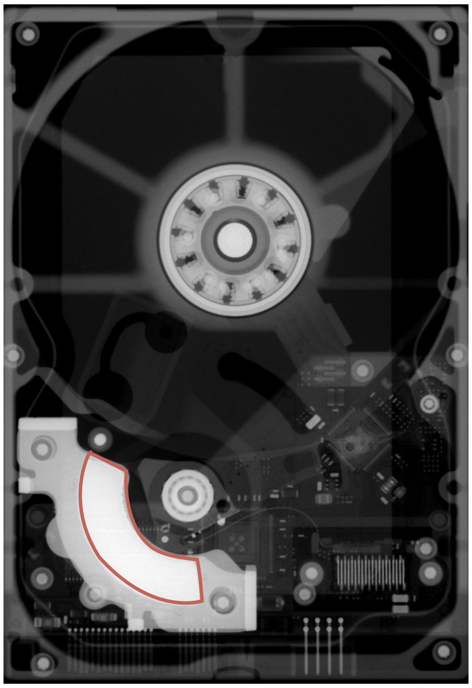
An urgent need exists for new approaches to efficiently extract and recover rare-earth elements from ore and recyclable products. Toward this goal, Livermore scientists have genetically engineered the bacterium *Caulobacter crescentus* to adsorb rare earths onto its cell surface. The adsorbed elements can be recovered using citrate solution and the bacteria can be reused. (Rendering by Adam Connell.)

The rare earths adsorbed by the bacteria can be washed off with a solution of citrate (a derivative of citric acid). In addition, citrate is harmless to the bacteria so it can be reused many times. “Our results have demonstrated a rapid, efficient, and reversible process for rare-earth adsorption with potential industrial applications,” says Jiao, who adds that the novel technique would be applied mainly to low-grade waste material left over from mining. The rare earths would be leached from mine tailings, and the engineered bacteria would be added to the slurry to extract all the rare earths.

Extraction and Retrieval

If discarded materials can be mined for their rare-earth content, these materials can also find new purpose. For example, magnets in computer hard drives are made with neodymium. Data centers for companies like Google and Amazon.com use millions of hard drives per center. Industry practice suggests one-third of hard drives be retired and recycled yearly to ensure data integrity, making them an ideal source for rare-earth retrieval.

Researchers Karina Bond, Jeffrey Kallman, William Brown, and Harry Martz are developing a method to automate the recovery and recycling of neodymium–iron–boron magnets from discarded computer hard drives. Bond’s prototype test bed for the method subjects hard drives to 160-kiloelectronvolt x rays, similar to those used in airport x-ray scanners. The magnets can be easily seen on the recorded x-ray images. Unfortunately, the magnets are located in different places depending on the hard drive. In addition, their size and shape can vary from one manufacturer to another. To facilitate an automated “punch” mechanism for extracting the magnets, machine-vision techniques are applied to locate their position and shape from the x-ray images. Bond says, “We need to demonstrate we can achieve a processing throughput of greater than 100 hard drives per hour to make this method economically feasible.”



An x-ray radiograph of a hard drive shows the rare earth–containing motor magnet outlined in red. X-ray images such as the one shown here are part of a Livermore-developed method to automate the recovery and recycling of magnets from discarded computer hard drives.

Once extracted, a magnet could be reused in its entirety or chemically processed to recover just the neodymium. Oak Ridge is responsible for developing methods to extract magnets given their location in the drives. Scientists at the Colorado School of Mines and Ames Laboratory are researching chemical processing methods to recover the rare-earth elements from the extracted magnets. Co-locating this type of magnet-extraction machine with data centers would eliminate logistics and supply chain challenges for rare-earth recycling. One idea is to design and install such a machine in the back of a truck for processing discarded hard drives at various server farms.

Promoting Research Success

In addition to coordinating CMI-funded research at the Laboratory, Schwegler also leads CMI’s cross-cutting initiatives. This work, which involves researchers at eight different institutions, focuses on developing tools and techniques that are useful in three areas: enabling science, environmental sustainability, and supply chain and economic analysis. By creating validated predictive simulation tools and materials databanks, conducting environmental impact assessments of new technologies and strategies for mitigating deleterious effects, and evaluating supply chain and future materials criticality issues, cross-cutting research enables CMI’s overarching goal to diversify supply, develop substitutes, and reuse and recycle rare earths.

As demand for rare earths continues to grow commensurate with growth in clean-energy technologies, Livermore’s support of CMI and its critical materials research is ever more important. For the U.S. clean-energy industry, the payoff is reduced negative effects from a supply disruption and strengthened assurance of new products and technologies.

—Arnie Heller

Key Words: Ames Laboratory, *Caulobacter crecentus*, cerium, clean energy, cobalt, Critical Materials Institute (CMI), exchange spring magnet, fluorescent lighbulb, neodymium, phosphor, quantum mechanics, rare-earth element, samarium.

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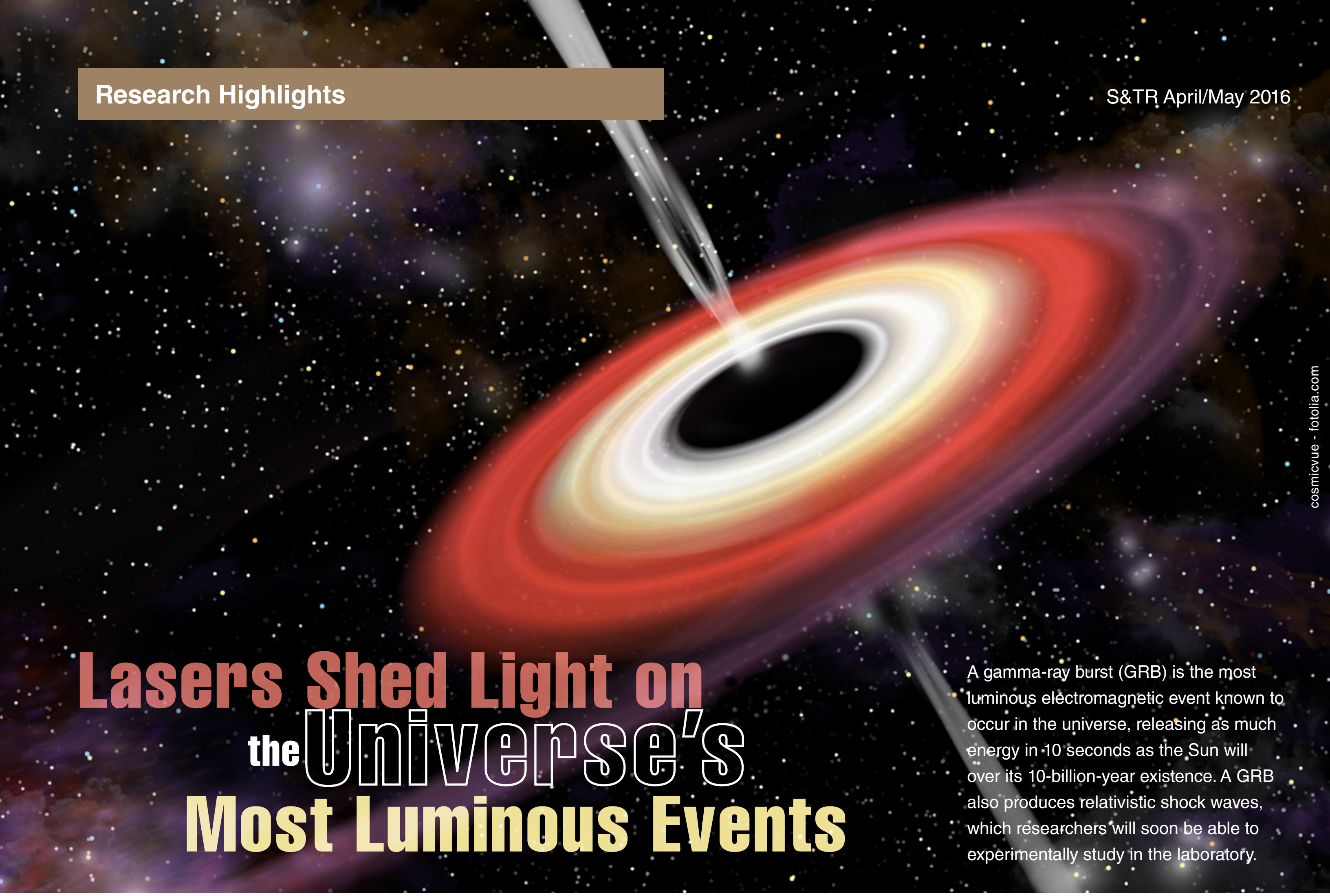

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Lasers Shed Light on the Universe's Most Luminous Events

A gamma-ray burst (GRB) is the most luminous electromagnetic event known to occur in the universe, releasing as much energy in 10 seconds as the Sun will over its 10-billion-year existence. A GRB also produces relativistic shock waves, which researchers will soon be able to experimentally study in the laboratory.

IN the 1960s, while hunting for illicit nuclear explosions with gamma-ray-detecting satellites, scientists first spotted flashes of high-energy gamma rays originating deep in space. These flashes are produced by gamma-ray bursts (GRBs), which are known to be the universe's most luminous electromagnetic events. A typical GRB releases as much energy in 10 seconds as the Sun will over its 10-billion-year existence. Scientists theorize that GRBs are initiated during cosmic explosions, such as those that occur when a massive star collapses into a black hole or two neutron stars merge. However, the process by which the bursts are produced remains something of a mystery.

Scientists suspect the GRB phenomenon begins when high-energy jets of electron–positron pairs collide. (Positrons are the antiparticles of electrons. They have the same properties as electrons except that their charge is positive.) This interaction may then initiate electromagnetic instabilities that create a relativistic (moving at a velocity near the speed of light) shock wave. The wave generates twin beams—jets—of focused energy that travel through space at a similar speed, and if "pointed" toward Earth, produce the signature gamma-ray flash previously recorded by satellites. Establishing whether relativistic shocks are indeed the source of a GRB's gamma radiation is of great interest to scientists. Indeed, validating this theory would answer one of five outstanding fundamental questions in high-energy-density physics posed by the National Research Council.

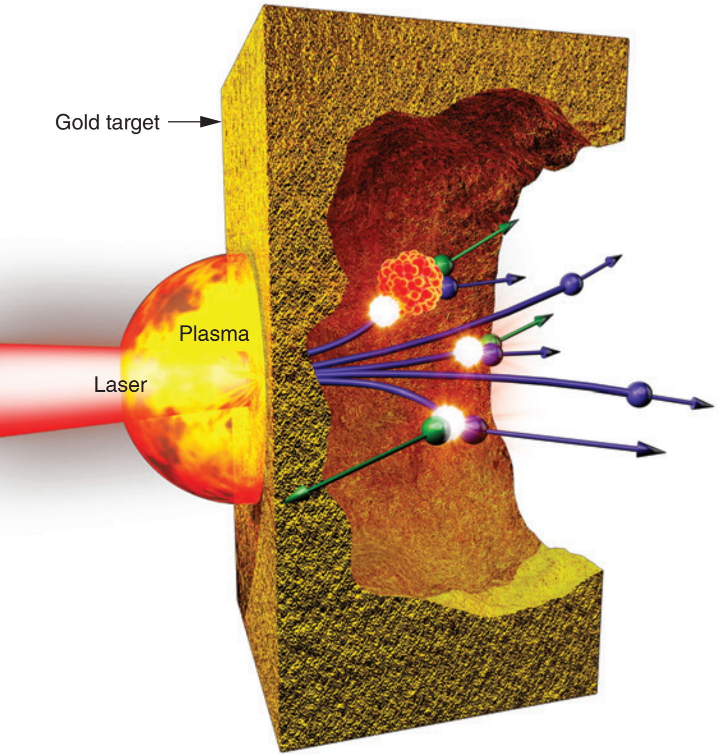
Over the last 13 years, Livermore physicist Hui Chen has been leading an effort to develop and refine experimental methods for generating jets of electron–positron pairs using high-intensity, short-pulse lasers. (See *S&TR*, July/August 2009, pp. 18–20; and January/February 2012, pp. 4–11.) Although the total energy and volume of laser-produced jets are a tiny fraction of those in a true GRB, the energy of each electron–positron pair is similar in both. However, the pair density in laboratory-created jets has been insufficient for initiating and studying electromagnetic instabilities relevant to astrophysics.

With funding from the Laboratory Directed Research and Development Program and the Lawrence Postdoctoral Fellowship Program, Chen and her colleagues at Livermore, the University of Rochester, the University of Nevada at Reno, the University of Alberta, and the U.K.'s Atomic Weapons Establishment have been exploring how pair production scales with laser parameters and how to best increase pair density. Their work is bolstering confidence that laser-based relativistic shock wave experiments will soon be achievable.

Higher Yields, New Insights

By directing short, intense laser pulses onto a millimeter-scale gold disk, Chen's team has generated billions of electron–positron pairs in the laboratory through a pair production method called the Bethe–Heitler process. In these experiments, the laser pulse delivers energy to electrons in a plasma that forms at the front of the target. These high-energy electrons interact with the nuclei of the gold atoms, which causes electrons to lose energy and emit high-energy photons. The photons in turn interact with the gold nuclei, and some split into electron–positron pairs. The higher the electrons' energy, the higher the energy of the photons and the greater the likelihood they will produce electron–positron pairs. Electrons escaping from the back of the target produce an electric field that accelerates the accompanying positrons to relativistic velocities. Gold's high nuclear charge makes for a strong electromagnetic field and substantial acceleration, while the short laser pulse and small targets used in these experiments produce comparatively dense jets.

In experiments to produce electron–positron pairs, a short-pulse laser fires a tightly focused pulse at a tiny gold disk. The laser transfers energy to electrons in the plasma in front of the target. As these high-energy electrons interact with the gold nuclei, some of them transfer their energy to high-energy photons, which then interact with the gold nuclei and transform into a lower energy electron (green) and its mirror, a positron (purple). (Rendering by Kwei-Yu Chu.)



During the last five years, Chen's team has performed experiments with the Titan laser at Lawrence Livermore; the Omega Extended Performance (EP) laser at the Laboratory for Laser Energetics in Rochester, New York; and the Orion laser at the Atomic Weapons Establishment in the United Kingdom. Each laser has different capabilities—for instance, Orion can produce the shortest pulses, while Omega EP produces the highest energies—but Chen has closely controlled experimental conditions to facilitate data comparison. Although laser availability has dictated which facilities can be used and when, the variety has had benefits, explains Chen. "Using multiple facilities helps confirm that the results we're seeing are due to common physics at work."

The experiments have produced large numbers of pairs—between 1 billion and 600 billion positrons from 10-picosecond (trillionth of a second) laser pulses at Titan and Omega EP and between 10 billion and 550 billion positrons from 1-picosecond pulses at Titan and Orion. The Omega EP experiments in particular set a new record for positron production, yielding 30 times more than any previous experiments. While these results still fall short of what is required for studying GRB phenomena, they have helped the researchers to assess the feasibility of experiments. Comparing the yield data from 54 different experiments conducted at the three facilities using two laser pulse lengths, the researchers calculated the scaling of positron yield as a function of laser energy. They concluded that an increase in laser energy by a factor of 10 should increase the positron yield by a factor of 100.

Pairing Model and Experiment

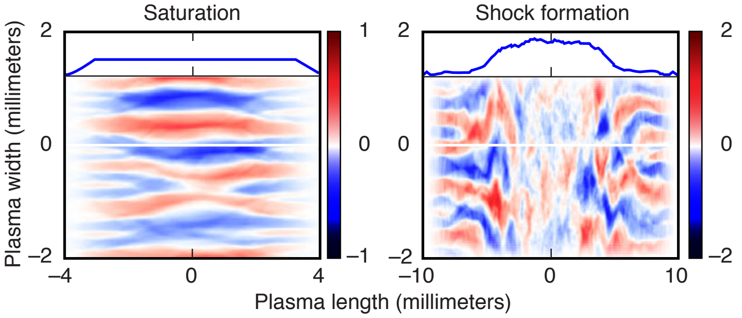
Team member and former Lawrence Fellow Frederico Fiuza—now at SLAC National Accelerator Laboratory—has modeled the interaction of laser-generated pair jets from first principles, that is, directly from physics equations. "These simulations allowed us to understand how many positrons we need to produce to study these fundamental processes in the laboratory," he explains. First-principles simulations, which track the individual motion of charged particles, electrons, and positrons, and the electric fields they create, tend to require significant computational resources. Fiuza's simulations were performed on Lawrence Livermore's Vulcan and Argonne National Laboratory's Mira machines, which currently rank as the world's 12th and 5th most powerful supercomputers, respectively.

Using the number of positrons calculated by Fiuza's modeling and the experimentally obtained results, the team predicted the laser parameters needed for future studies of relativistic shocks. "I had thought we would have to wait many years, probably more than ten, to study the physics of these relativistic shocks in the laboratory," notes Fiuza. "However, our results show that with the favorable scaling of positron number to laser energy, we may be able to start studying these processes with newly available lasers, such as the Advanced Radiographic Capability (ARC) at Livermore."

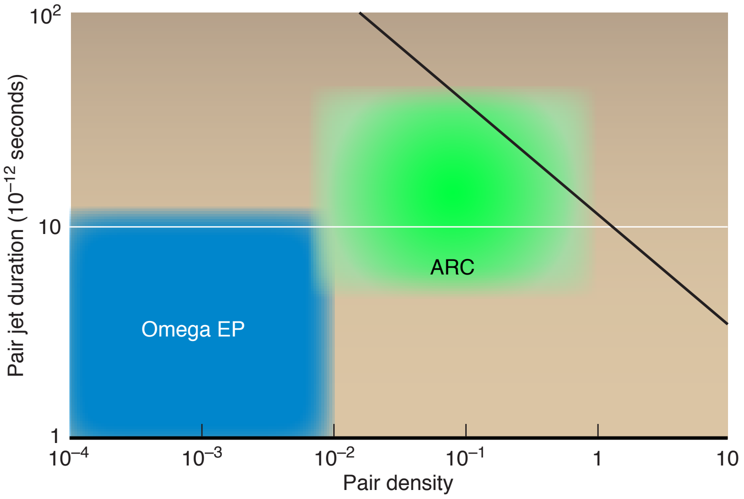
The researchers expect that 10-kilojoule-class short-pulse lasers, including ARC, will boost the number of particles produced sufficiently to enable experiments within the desired shock-physics regime. This prediction will be tested relatively soon. The team obtained approval in December to perform experiments on ARC (see *S&TR*, December 2011, pp. 12–15; and January/February 2014, pp. 4–11) in either 2017 or 2018. Chen has been involved in ARC's commissioning, which was completed last fall, and the capabilities of the powerful and flexible multi-kilojoule short-pulse laser. However, more work lies ahead before the laser will be ready for GRB-related experiments. Notes Chen, "To get from current ARC commissioned levels to what we need for our experiments, we must shrink the pulse both in diameter and in time to create a more compact beam." Chen is confident that ARC will meet the required levels by the time they conduct the experiments.

Under the Lens

Chen's team is also exploring how to control jet properties and optimize experimental parameters for future studies. For example, the researchers have recently begun experiments to collimate the positrons using an externally applied magnetic field. In these tests, a small circular coil, designed by the University of Rochester, creates a cylindrically symmetric field that acts as a lens to focus the particles. As demonstrated by experiments at Omega EP, this magnetic collimation produces a much narrower beam with a divergence angle of 4 degrees instead of 20, thereby increasing the electron–positron pair density of the jets. Collimation also has other benefits, such as improving the electron-to-positron ratio by 40 fold. To reach the conditions needed for GRB research, the jets need roughly equal numbers of each particle. The team's next steps will include using stronger magnetic fields for greater jet collimation.



Particle-in-cell simulations of colliding high-speed jets of electron–positron pairs indicate that (left) creating an electromagnetic instability and (right) forming a shock should be achievable with near-future laser systems. (Color gradients represent the sign and strength of the magnetic field.)



Data from experiments and simulations indicate that Livermore's 10-kilojoule-class Advanced Radiographic Capability (ARC) laser—as compared with the Omega Extended Performance (EP) laser—may reach the physics regime necessary for studying the electron–positron pair jets thought to be central to GRB physics. (Pair density is the number of pairs per cubic centimeter divided by their relativistic Lorentz factor.) Shocks are expected to form at or above the black line.

Unraveling how GRBs work is taking ingenuity and time, which is fitting given the millions or billions of light years most GRBs must travel before making an appearance in our skies. Livermore researchers have made important progress by contributing new evidence that the phenomenon can be probed in the laboratory. With the help of a new generation of lasers such as ARC, researchers may gain insight into the evolution and destruction of certain types of stars. This work could also help reveal why more matter than antimatter—antiprotons, antineutrons, and positrons—survived the Big Bang at the start of the universe, when the two were thought to be in balance initially. Observes Chen, "Both the energy and the distance involved in GRBs are so extreme they seem almost beyond science fiction, and yet we are starting to better understand this phenomenon through our experiments in the laboratory, which is very exciting."

—Rose Hansen

Key Words: Advanced Radiographic Capability (ARC), antimatter, Bethe–Heitler process, electron–positron pair jet, gamma-ray burst (GRB), Mira supercomputer, Omega Extended Performance (EP) laser, Orion laser, positron, relativistic shock, short-pulse laser, Titan laser, Vulcan supercomputer.

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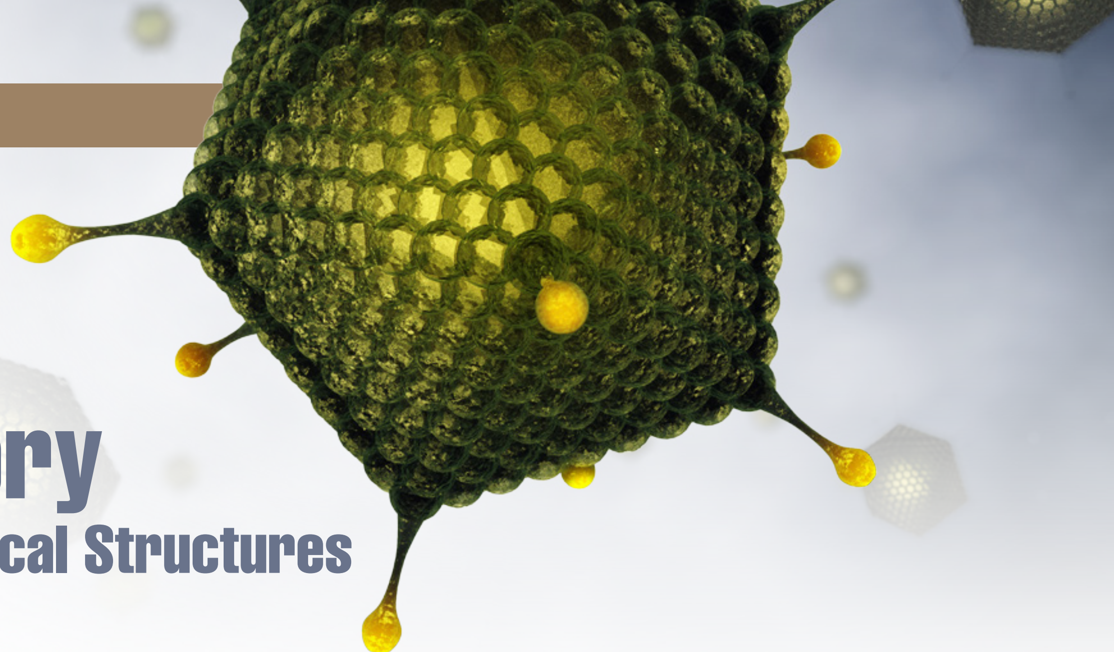


A Virtual Laboratory for Studying Biological Structures

THE structure of complex biological macromolecules, such as proteins and DNA—the building blocks of life—can provide essential clues about their biological function. Since the early 20th century, x rays have been used to study the underlying crystalline structure of materials. More recently, researchers have turned to powerful x-ray free-electron lasers (XFELs) for probing the internal structure of proteins. Using XFELs, scientists can obtain diffraction patterns from small (submicrometer) protein crystals at room temperatures to build high-resolution three-dimensional (3D) images of their structures, even capturing the dynamic changes of the material on short timescales in response to external stimuli. (See *S&TR*, December 2015, pp. 21–24.)

The SLAC National Accelerator Laboratory's Linac Coherent Light Source (LCLS)—the world's most powerful XFEL—has become a key tool for studying complex biomolecules. The facility has already been used to image structural changes in light-absorbing proteins and to characterize dense materials, including graphite. Researchers will take a major step forward in structural biology research when they start using XFELs to image single biomolecules that comprise viruses and bacteria. This capability is not yet possible with conventional experimental methods, either because the biomolecules are too small, noncrystalline, or cannot be expressed in a large enough quantity.

As part of SLAC's Single-Particle Initiative, Lawrence Livermore researchers and LCLS collaborators are working to determine, over the next decade, if atomic-scale imaging of individual biomolecules is possible, and if so, how to design and optimize future experiments. As part of this effort, Laboratory scientists and computational experts are using Livermore's high-performance computers to develop, adapt, and run advanced computer codes that can accurately model the experimental parameters needed for this research.

Peering into Damage Effects

XFELs use bunches of individual electrons moving through a vacuum chamber at nearly the speed of light to create x-ray beams that bombard a target material. During an experiment, the beam's photons excite the electrons in the target, and some photons scatter in a distinctive pattern, called a diffraction pattern, that relates to the material's structure. The diffraction pattern is recorded using x-ray detectors, and computer software pieces the individual snapshots of the material's internal movement during its exposure to the high-intensity radiation into a 3D image. This image helps determine the material's molecular structure.

In the early 2000s, Livermore physicists Stefan Hau-Riege, Richard London, and Abraham Szöke began modeling the x-ray imaging process with a focus on understanding and alleviating the effects of radiation damage sustained by the molecule. According to Hau-Riege, although Livermore's simulation expertise is supported by a host of novel codes, none of them had all the capabilities needed to accurately simulate the processes in radiation-exposed single biomolecules. To help remedy this issue, they adapted existing hydrodynamics and molecular dynamics (MD) codes to account for the relevant physics considerations necessary for atomic-scale imaging.

Using these codes to simulate future LCLS experiments on single biomolecules, Hau-Riege and collaborators have established a virtual laboratory that uses Livermore's high-performance computers to mimic extreme states of matter and address mission-relevant science questions. Simulations lessen experimental costs by allowing researchers to more quickly optimize parameters, such as beam duration and wavelength, which also helps researchers to best use their allocated laser time and increase the likelihood of an experiment's success.

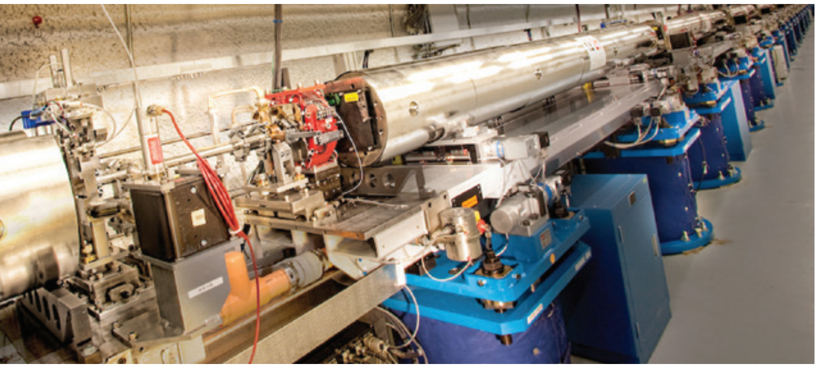
Building a Better Fit

The foundation for the Laboratory's simulation work on single biomolecules was Livermore's domain decomposition molecular dynamics (ddcMD) code. (See *S&TR*, July/August 2006, pp. 17–19.) The code uses the fundamental properties of particle interactions to identify a material's macroscopic properties such as equations of state, conductivity, and diffusivity. "We use what we know about a material's fundamental properties to improve our understanding and simulations of its macroscopic properties," says Livermore physicist Frank Graziani, who has led the decade-long effort—called the Cimarron project—to improve ddcMD for plasma modeling.

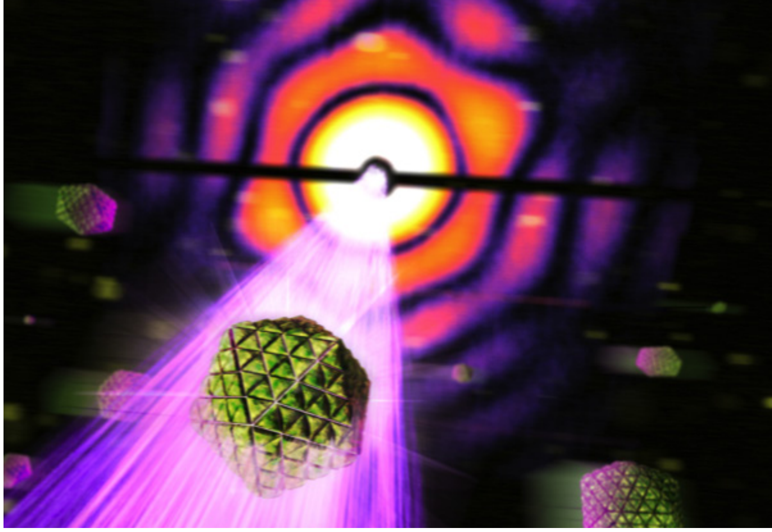
Traditional Laboratory hydrodynamics codes, such as HYDRA or CRETIN, were designed to model the evolution of systems whose electrons are at equilibrium, meaning that their statistical properties do not change over time. When an x-ray laser radiates a target, the electrons in the material are knocked far out of equilibrium—some electrons are very fast, others are slow, and some electrons leave the molecule and thus increase its charge. Material in such an excited state transforms into a plasma. "Livermore has many simulations that are suitable for modeling plasma experiments," says Hau-Riege, "but with these established simulations, we found a discontinuity between studying native molecules (those in their original functional state) and molecules that have become part of a plasma by the intense XFEL radiation. Understanding plasma dynamics for this application requires us to study time-dependent physics during the transition."

To address this issue and better match simulated processes with those that happen in an XFEL experiment, the team, in collaboration with Jon Weisheit from the University of Pittsburgh, adapted the ddcMD code to incorporate atomic physics phenomena. (This work was performed as part of the Cimarron collaboration.) The new code tracks every atom and electron to characterize the microphysics of the plasma. Of particular interest is the interaction of radiation with atoms and electrons—one of the least understood aspects of XFEL experimental data.

The team has exploited other microphysics codes and proof-of-principle experiments to verify the empirical models used in their adapted MD code. Similarly, because this code was co-developed by several groups at Lawrence Livermore, it can be used to validate models for other Laboratory programs, such as those in the Weapons and Complex Integration Principal Directorate, in addition to being useful for simulating diverse LCLS experiments. Hau-Riege says, "It's quite impressive that the plasma codes we use for programmatic applications can be applied to a variety of research areas."



The SLAC National Accelerator Laboratory's Linac Coherent Light Source (LCLS)—the world's most powerful x-ray free-electron laser (XFEL)—is the first machine of its type to probe matter with hard x rays. In the LCLS Undulator Hall (shown here), short pulses of electrons travel back and forth through a 100-meter-long stretch of alternating magnets. The process produces the extremely bright x rays that are used to image structural changes in complex biomolecules, such as proteins.



As part of SLAC's Single-Particle Initiative, Livermore scientists are helping develop an advanced capability for imaging individual biomolecules, which comprise viruses and bacteria, using the LCLS XFEL. In this artist's rendering, a 20-sided structure from a bacterial cell, called a carboxysome, is struck by an LCLS x-ray pulse (purple). (Image courtesy of SLAC's LCLS.)

Diffraction—Not Without Nuances

Single biomolecule imaging would enable a system's evolution to be tracked at the smallest relevant time and length scales. However, obtaining high-resolution diffraction patterns for such materials is part of the challenge of making this capability a reality. "Since the diffraction pattern is never a direct image, it can still be skewed," explains Hau-Riege. "With too much intensity, the material experiences more damage, and the resulting diffraction pattern becomes distorted. On the other hand, with too little intensity, we cannot record a clear pattern." Adding more photons to the beam improves the clarity of the diffraction image, but it also increases the temperature of the material, which causes image distortion.

Furthermore, materials typically destruct when radiated by intense XFEL beams, thus sometimes destroying the material before the diffraction pattern can be captured. The short, intense LCLS XFEL pulses should help researchers acquire diffraction data faster and more efficiently prior to the material's destruction. Hau-Riege and his team will conduct simulations of matter–radiation interactions to tailor future experimental parameters to ensure high-quality diffraction patterns can be recorded.

Harnessing state-of-the-art resources and expertise, collaborations between national laboratories and academic institutions often lead to breakthrough scientific research. As part of SLAC's Single-Particle Initiative, Livermore researchers and LCLS colleagues will use advanced high-performance computer codes and modeling to bring single biomolecule imaging closer to fruition. Such a capability will help advance research in many disciplines including biodefense, medicine, and energy.

—Lanie L. Rivera

Key Words: biomolecule, diffraction, domain decomposition molecular dynamics (ddcMD) code, Linac Coherent Light Source (LCLS), molecular dynamics (MD) code, Single-Particle Initiative, SLAC National Accelerator Laboratory, x-ray free-electron laser (XFEL).

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Uncovering Dirty Secrets about Soil Carbon

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TWO-THIRDS of the carbon in the terrestrial biosphere (land inhabited by living organisms) is stored underground as soil organic matter (SOM), a complex mixture of molecules that results from decaying plant and microbial cell material. During decomposition, carbon within SOM is either retained in the soil or released into the atmosphere as carbon dioxide (CO_2). This carbon reservoir is so huge that even small increases in decomposition rates could accelerate climate change. Yet scientists still question the fundamental mechanisms that regulate decomposition rates at the level of individual microbial cells and mineral particles.

Bringing together the capabilities of two advanced, high-resolution imaging technologies, the nanometer-scale secondary ion mass spectrometer (NanoSIMS) at Livermore and the scanning transmission electron microscopy (STXM) instrument at Lawrence Berkeley National Laboratory, a Livermore-led team has uncovered some of SOM's secrets at the microscopic level. The researchers' discoveries provide crucial information for improving climate models and managing soil resources. Project leader and Livermore biologist Jennifer Pett-Ridge says, "By investigating the mechanisms of soil decomposition, we can more accurately predict the effects of shifting climate conditions on soil carbon sequestration and then incorporate these data into climate models."

Funded through Livermore's Laboratory Directed Research and Development Program, the Department of Energy's Office of Biological and Environmental Research (OBER), and the Livermore Scholar Program, the work was conducted by Pett-Ridge, NanoSIMS laboratory lead Peter Weber, former graduate student Marco Keiluweit (now a faculty member at the University of Massachusetts at Amherst), and their collaborators at Oregon State University and Lawrence Berkeley. They carried out three projects that provide new information about the processes that influence soil decomposition. In one project, the team tracked the fate of nitrogen-rich organic compounds that are decomposed by microorganisms dwelling within forest-floor litter. A second examined the critical role of the element manganese in decomposing leaf litter. The last illustrated how organic compounds exuded from roots into the soil affect organic matter–mineral complexes and can lead to net soil carbon loss.

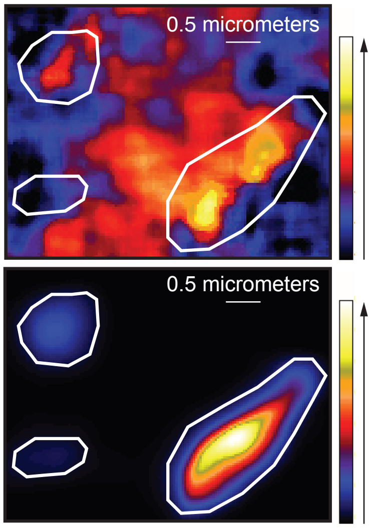
The Nitrogen Mystery

Nitrogen-rich amino sugars, such as chitin, are a major component of the cell walls of soil fungi, whose thread-like structures, called hyphae, provide an important source of organic carbon and nitrogen in many forest soil ecosystems. Despite its abundance, little is known about how microbes decompose chitin and how its breakdown products become stabilized in soil.

To follow the decomposition of soil fungal cell walls, the research team tagged chitin with a rare isotope of nitrogen (^{15}N), which allowed them to trace what happens as chitin undergoes microbial decomposition. They mixed the ^{15}N-labeled chitin with soil rich in organic matter from the U.S. Forest Service's H.J. Andrews Experimental Forest in Oregon and let the mixture incubate. After three weeks, the team used two complementary nanometer-scale imaging instruments to determine how the ^{15}N-labeled chitin had become incorporated into the soil. The synchrotron-based STXM instrument at Lawrence Berkeley's Advanced Light Source helped measure the molecular composition of the soil microstructures. The researchers then used NanoSIMS to assess where the ^{15}N isotope had migrated.

The Laboratory's NanoSIMS is one of only a few such instruments in the world dedicated to isotope imaging in microbial biology and soils research. The machine uses a finely focused primary ion beam to erode ions from a sample's surface. These secondary ions are then analyzed to reveal the elemental and isotopic composition of the sample's uppermost atomic layers. Combined results from NanoSIMS and STXM show that soil bacteria assimilate the nitrogen from the chitin, then resynthesize and incorporate it into their own bodies. When the bacteria die, their cellular materials (particularly proteins and lipids) adsorb onto iron-oxide mineral surfaces.

Livermore researchers Jennifer Pett-Ridge and Peter Weber prepare a sample for testing in the nanometer-scale secondary ion mass spectrometer (NanoSIMS), one of only a few such instruments in the world dedicated to isotope imaging in microbial biology and soils research. (Photo by Lanie L. Rivera.)



Fungal biomass—enriched with the ^{15}N nitrogen isotope—was allowed to decompose in situ in soil. NanoSIMS revealed patterns of (top) nitrogen enrichment and (bottom) iron distribution, suggesting that nitrogen derived from fungal cell walls was digested by microbes and preferentially deposited on iron-oxide surfaces. (Color gradient represents intensity.)

An incubation period longer than three weeks is needed to understand what happens to these nitrogen-rich organic coverings over long timescales. Questions exist as to whether the cellular materials remain tightly bound to the iron oxide for months or years, making them chemically unavailable to microbes, or whether they can easily re-enter the nitrogen cycle. Answers to these questions have implications for understanding the available sources of nitrogen in ecosystems and how organic matter becomes stabilized in soil. Pett-Ridge says, "If this mechanism causes nitrogen-rich organic matter to be tightly held in the soil, then the system has a means of holding onto its organic matter in a way we didn't understand before."

Underground Attraction

The decomposition of forest-floor litter is a critical process that regulates the release of nutrients needed for plant growth and is the first step in SOM formation. Observations in a variety of forest ecosystems show that manganese content in this material is an important predictor of its decomposition rate, but the reason for this correlation is unknown.

To investigate why manganese is such a good predictor of decomposition, Pett-Ridge's team used chemical imaging to analyze samples collected from the H.J. Andrews Experimental Forest during a seven-year-long project. At the end of each year, a fine-mesh screen was placed on top of the leaf debris. The result was a six-layer "litter cake" where the bottom layers were far more decomposed than those nearer the top. Analysis of samples from multiple points along the decomposition sequence revealed that in the more highly decomposed samples, the microorganisms living in the litter recruited more external manganese.

"We've known that decomposition rate and manganese concentration are positively correlated, but until our analyses, we didn't know why," says Pett-Ridge. "By imaging the activity of the microorganisms at the micrometer scale, our research showed manganese activates enzymes in the fungi that decompose carbon-rich lignin. This substance forms the rigid cell walls found in plant tissues and takes a long time to decay. Manganese makes the enzymes work, enabling the fungi to do their job breaking down the lignin.” The next step, she says, “is to better understand what mechanisms regulate the proportion of stored carbon versus carbon released to the atmosphere.”

Roots Rule

Living plant roots provide the primary input to soil carbon, releasing organic compounds, called root exudates, into the rhizosphere—the region of soil immediately nearby. Within the rhizosphere, roots create their own microbiome by exerting control over both the surrounding chemistry and microorganisms. Scientists have long thought that root exudates provide easy energy for soil microbes, allowing them to break down SOM. Recent research suggests that increased atmospheric CO_2 created through the SOM-decomposition processes stimulates plant growth, which leads to greater exudate production and a net loss of soil carbon. Scientists need a better understanding of how root exudates affect the balance of soil carbon to create more accurate climate models.

Using NanoSIMS and STXM, the team studied the mechanisms of rhizosphere carbon loss resulting from three exudate compounds: oxalic acid, glucose, and acetic acid. The study revealed, for the first time, that exudates can act directly on “old” carbon bound to soil minerals, breaking these bonds and exposing previously protected carbon to microbial decomposition. This previously unknown mechanism suggests a new way that roots and their microbiome could accelerate the release rate of atmospheric CO_2.

Collectively, the work being done by Pett-Ridge and her colleagues informs a new OBER biofuels research project and several other projects on plant–microbial interactions in the rhizosphere. These efforts seek to define and understand the biological mechanisms underlying soil carbon sequestration that are critical for predicting climate change. “What we know about the future effects of climate change comes from computer models,” says Pett-Ridge. “A better mechanistic understanding leads to greater predictive power and more accurate climate models. Studying soil mechanisms at the microscale helps us connect the dots.”

—Karen Kline

Key Words: carbon cycle, chitin, climate change, decomposition, forest-floor litter, H.J. Andrews Experimental Forest, manganese, microbial organisms, nanometer-scale secondary ion mass spectrometer (NanoSIMS), nitrogen cycle, root exudates, scanning transmission x-ray microscopy (STXM), soil carbon sequestration, soil organic matter.

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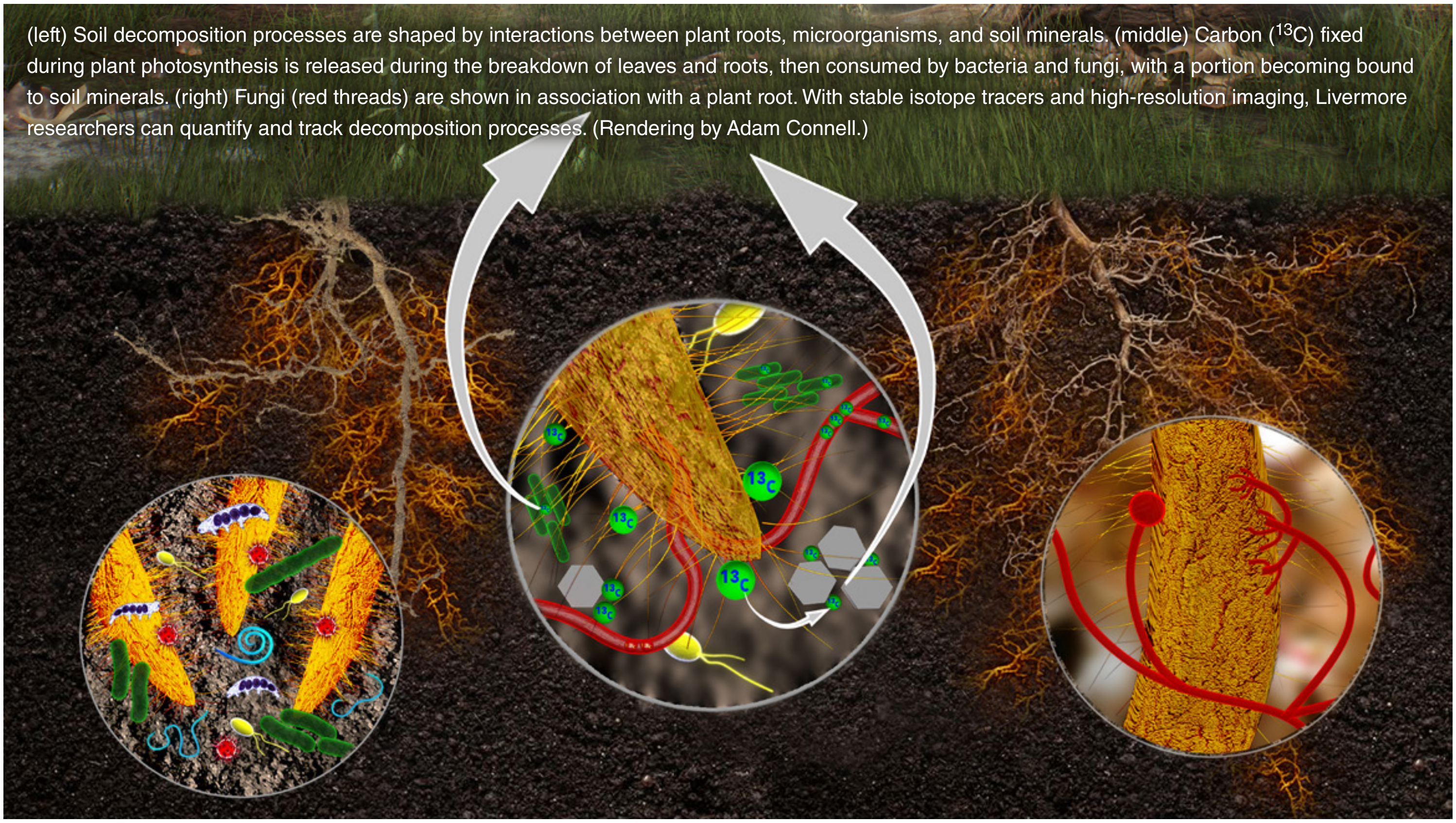

(left) Soil decomposition processes are shaped by interactions between plant roots, microorganisms, and soil minerals. (middle) Carbon (^{13}C) fixed during plant photosynthesis is released during the breakdown of leaves and roots, then consumed by bacteria and fungi, with a portion becoming bound to soil minerals. (right) Fungi (red threads) are shown in association with a plant root. With stable isotope tracers and high-resolution imaging, Livermore researchers can quantify and track decomposition processes. (Rendering by Adam Connell.)

Patents and Awards

In this section, we list recent patents issued to and awards received by Laboratory employees. Our goal is to showcase the distinguished scientific and technical achievements of our employees as well as to indicate the scale and scope of the work done at the Laboratory. For the full text of a patent, enter the seven-digit number in the search box at the U.S. Patent and Trademark Office's website (http://www.uspto.gov).

Patents

Fiber Optic Coupled Multipass Gas Minicell, Design Assembly Thereof
Tiziana C. Bond, Mihail Bora, Michael A. Engel, James F. McCarrick, Bryan D. Moran
U.S. Patent 9,234,794 B2
January 12, 2016

Nuclear Radiation Cleanup and Uranium Prospecting
Raymond P. Mariella, Jr., Yves M. Dardenne
U.S. Patent 9,250,353 B2
February 2, 2016

Awards

Ten teams of Laboratory researchers and engineers and one individual were honored with **Defense Programs Awards of Excellence** from the **National Nuclear Security Administration** (NNSA). The **S-1 Long-Term Deterrence Study of Emerging Threats Team** contributed to the tri-lab study of emerging threats and possible implications for U.S. nuclear deterrence in the 21st century. The **High-*Z* Diffraction Team** helped demonstrate the technical and facility readiness needed to execute the first high-pressure high-*Z* diffraction experiment at the National Ignition Facility. The **E-MSAD Team** made significant contributions to the Weapons Program and improved legacy mechanical-safety-and-arming device (MSAD) design, safety, and producibility for future generations. The **Additive Manufacturing Focused Experiment Team** designed, manufactured, and executed the first physics hydrotest using additive-manufacturing techniques and materials. The **Intermediate Range KEP Arena Test Team** designed, manufactured, and executed an arena test of a new intermediate-range kinetic energy projectile (KEP) warhead concept for the Navy's Strategic Systems Program. The **Reuse Hydrotest Team** designed, manufactured, and executed a hydrotest series to validate an innovative pit-reuse concept in support of the IW-1. The **Direct Ink Write Cushion Team** developed an exceptionally creative additive-manufacturing process for producing cushions and pads. The **Deterministic Particle Transport Team** developed highly scalable, next-generation transport capabilities. The **Advancement in the Understanding of Boost Team** improved understanding of boost by developing advanced analytical models. The Laboratory **Bluebook Team** conducted work in support of the Bluebook Update Program, requested by the Air Force Nuclear Weapons Center, the Department of Energy, and NNSA. **Thomas McAbee**, leader of the Primary Metrics Project at Livermore, helped enhance the primary metrics suite as a tool for design assessment, which contributes significantly to the Laboratory's stockpile stewardship mission.

Brigadier General Stephen L. Davis, acting deputy administrator for Defense Programs, presented the awards. Approximately 10 percent of the awards given complex-wide were elevated to "**Exceptional Achievements**." The two groups to receive this recognition were the **Direct Ink Write Cushion Team** and the **Advancement in the Understanding of Boost Team**.

The team responsible for executing the **Observations for Model Intercomparisons** (obs4MIPs) project, a joint effort between NASA and the Department of Energy to make NASA and other satellite data sets more accessible for global climate model evaluation, has been awarded a **NASA Group Achievement Award**. The team, which includes Livermore's Peter Gleckler, Karl Taylor, and Denis Nadeau of the Laboratory's Program for Climate Model Diagnosis and Intercomparison, was recognized for "…innovative leadership and implementation of the NASA Observations for Model Intercomparisons project and its contribution to the international climate research community." The results of obs4MIPs dramatically reduce the data preparation workload for climate scientists and significantly increase the impact of NASA observations on international climate modeling and assessment research and development.

Lawrence Livermore's **Roger Rocha** and **Mark Zagar** were recently honored with **Patriot Awards** from **Employer Support of the Guard and Reserve** (ESGR), an office of the Department of Defense. ESGR was established in 1972 to promote cooperation and understanding between Reserve Component Service members and their civilian employers. The Patriot Award recognizes supervisors for contributing to national security and protecting liberty and freedom by supporting employees who participate in America's Reserve and National Guard. Rocha, deputy principal associate director for operations, and Zagar, nuclear and hazardous operations manager, are part of Livermore's Weapons and Complex Integration Principal Directorate. Brian Cracchiola, the facility manager of the Laboratory's High Explosives Applications Facility and a 26-year Army reservist, nominated his supervisors.

Abstract

Reducing Reliance on Critical Materials

The Department of Energy's (DOE's) Critical Materials Institute (CMI) is working to ensure the nation has adequate supplies of certain scarce materials that are essential to developing high-technology products and advancing U.S. manufacturing. One of DOE's four Energy Innovation Hubs, CMI is headquartered at Ames Laboratory in Ames, Iowa. Lawrence Livermore researchers have partnered with CMI to address the materials criticality issues associated with rare-earth elements. More than 95 percent of rare earths are mined outside the United States, and demand for some elements often outpaces supply. Occasional export restrictions by rare earth–producing nations have prompted concern about the impact a shortage could have on the U.S. clean-energy industry, as hybrid-electric vehicles, fluorescent lighting, large wind turbines, and other clean-energy products all rely on small quantities of rare earths. Livermore efforts center on finding substitutes for rare earths used in magnets and fluorescent light bulbs, as well as on developing novel methods to recycle rare earths. The research combines experiments with advanced computational materials modeling using the Laboratory's supercomputing resources.

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