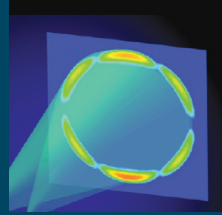
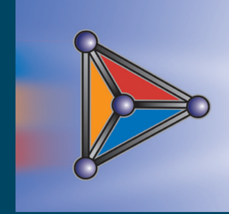




LOS ALAMOS SCIENCE AND TECHNOLOGY MAGAZINE

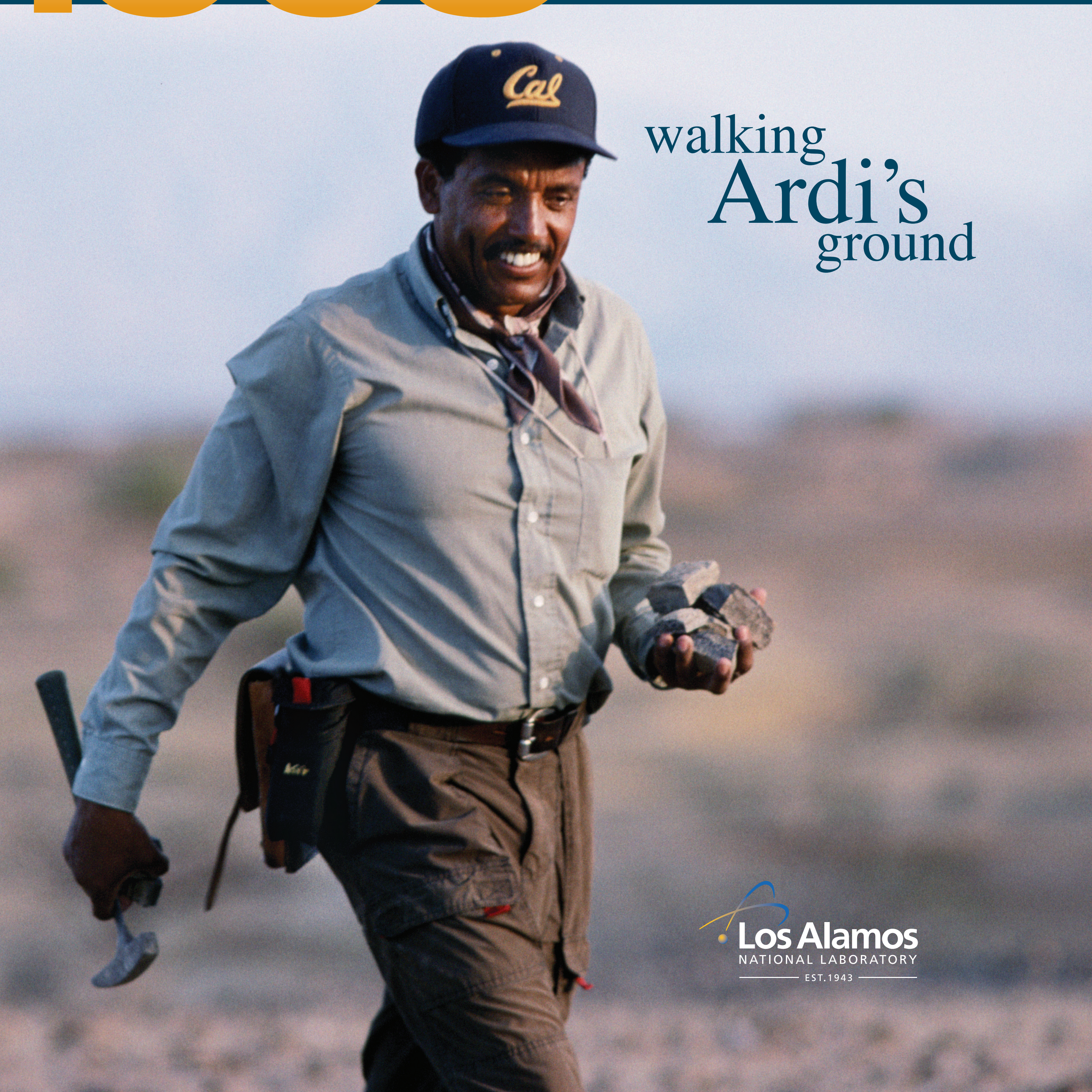
JUNE 2010

1663

Nanocrystals for Solar Energy

MaRIE—A Facility in the Making

At the Chemical Movies



walking Ardi's ground

Los Alamos
NATIONAL LABORATORY
EST. 1943

1663

About Our Name: During World War II, all that the outside world knew of Los Alamos and its top-secret laboratory was the mailing address—P. O. Box 1663, Santa Fe, New Mexico. That box number, still part of our address, symbolizes our historic role in the nation's service.

Located on the high mesas of northern New Mexico, Los Alamos National Laboratory was founded in 1943 to build the first atomic bomb. It remains a premier scientific laboratory, dedicated to national security in its broadest sense. The Laboratory is operated by Los Alamos National Security, LLC, for the Department of Energy's National Nuclear Security Administration.

About the Cover: Giday WoldeGabriel of the Laboratory's Earth and Environmental Sciences Division is an Ethiopian-educated geologist with a doctorate from Case Western Reserve University in Cleveland, Ohio. He serves as lead geologist and co-leader of the international Middle Awash research team, which searches for hominid fossils in Ethiopia.

LOS ALAMOS ARCHIVE

Future Laboratory director Harold Agnew (left) stands with future Nobel Laureate Luis Alvarez as Larry Johnston (left) and Bernard Waldman kneel next to a diagnostic canister outside a Quonset hut on Tinian in the Mariana Islands.

My View

Serving the Nation's Evolving Needs

During the Manhattan Project, Los Alamos National Laboratory's mission was not only secret but very focused—to build the first atomic bomb. In the years that followed, the focus broadened as the Laboratory took on new missions, including developing and maintaining our nation's nuclear deterrent, and expanded its capabilities to help achieve those missions. Today, Los Alamos is an open, diversified research Laboratory that contributes to a widening array of scientific disciplines related both directly and indirectly to national security.

In this issue of 1663*, you'll find clear examples of the Laboratory's wide-ranging involvement in science. The work of Giday WoldeGabriel, highlighted by* Science *and* Time *magazines for its contribution to 2009's "Science Breakthrough of the Year," benefits the whole world by revealing the origins of hominids, our earliest ancestors. WoldeGabriel's approach to geology, integrating information from the macroscopic to the microscopic, supports both the international search for hominids and the Laboratory's efforts to minimize environmental impacts.*

The new Center for Advanced Solar Photophysics, led by Victor Klimov, is exploring how quantum phenomena that appear only on the nanoscale can contribute to next-generation solar photovoltaics (solar panels) that are both cheaper and more efficient and therefore an affordable alternative to fossil fuels. Such efforts at applying fundamental physics to sustainable energy are now considered central to the Laboratory's role as the premier national security science laboratory.

This issue also provides a glimpse into the Laboratory's future with a prospective on MaRIE, the Laboratory's proposed flagship experimental facility, now in the planning stages. Standing for Matter-Radiation Interactions in Extremes, MaRIE is being designed to revolutionize how we investigate and predict material behavior under extreme temperatures, pressures, and radiation environments. The data gathered with MaRIE's unique probes, combined with computer modeling capabilities that are second to none, should enable predictive certification and lifetime extension of our nuclear stockpile as well as efficient design of materials for future nuclear fission and fusion reactors. At the same time, MaRIE will be an international user facility advancing the search for revolutionary materials to solve global problems.

John Sarrao
MaRIE project
program director

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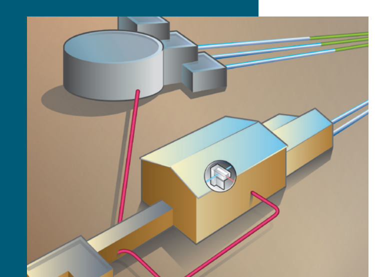


TINY CRYSTALS *in solution*

A Next Step for Solar

Could tiny quantum dots grown in solution make solar energy affordable for everyone? Researchers at the new Los Alamos Center for Advanced Solar Photophysics are exploring that tantalizing possibility.

Every day that goes by, greenhouse emissions from fossil fuels increase the pace of global warming. At the same time, the sun is dousing the planet with thousands of times more light energy than is needed to sustain modern civilization. The solution to global warming would seem to be a no-brainer. Just harness the power of the sun's rays and leave carbon emissions behind. If only it were that simple.

The most direct way to convert the sun's rays into electric power is with a solar cell—a thin wafer of semiconductor material sandwiched between two conducting terminals. When light strikes the cell and passes into the semiconductor, a voltage develops across the solar cell like that in a standard battery. A wire placed across the terminals allows the voltage to drive a current that can power a load. A detailed description is in "Photovoltaics: Converting Sunlight to Electricity," on the next page.

Crystalline silicon, the poster child of the electronics industry, was the photovoltaic material used in the first modern solar cell. That cell was invented at Bell Labs in the 1950s, an unexpected spinoff of transistor development. Today, these Generation-I cells, now made of crystalline silicon wafers, are the most popular cells on the market because of their efficiency.

A Generation-I cell converts up to 25 percent of the incident solar power to electric power (25 percent power-conversion efficiency). Installed solar panels (hundreds of Generation-I cells wired together) have a power-conversion efficiency of about 15 percent. That's very encouraging. When the sun is overhead, each square meter of a solar panel receives, on average, 1,000 watts of solar power, which means solar panels covering 30 square meters (only a portion of a typical roof) produce enough power (around 5 kilowatts) to run a small household.

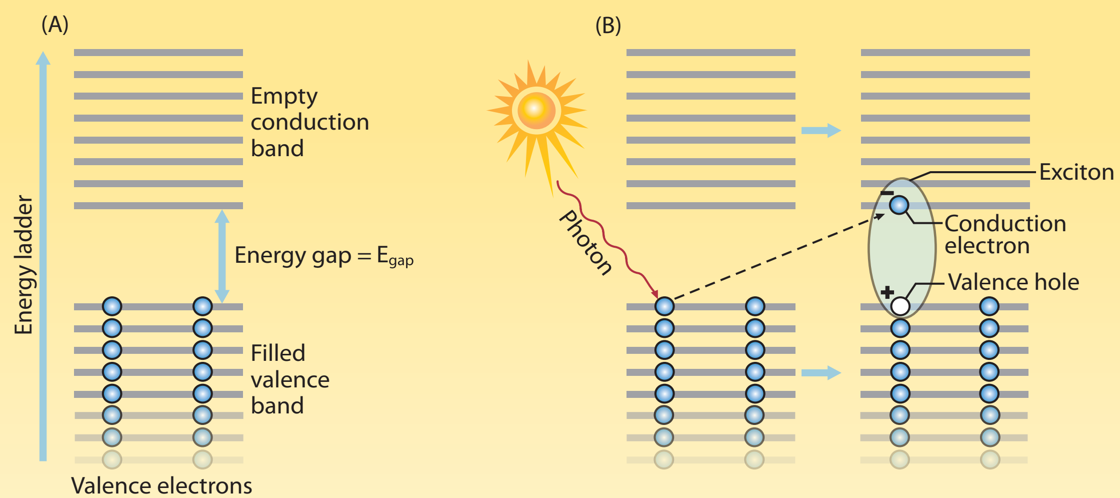
But Generation-I panels also have a problem: cost. Solar panels for that 5-kilowatt household cost around $15,000 and up, and the whole system, including storage batteries for standalone systems or power connections for the electric grid, double that cost.

Unfortunately, it's the crystalline silicon wafers in the Generation-I cells that make the solar panels so expensive. Elaborate processes and lots of energy are required to grow large, perfect single-crystal ingots of high-purity silicon, which are then sliced into paper-thin (200-micron-thick) single-crystal wafers (a micron is a millionth of a meter). In the world of electronic devices, 200 microns (500,000 atoms) is very thick and, by industry standards, very expensive to produce.

Scientists have brought costs down in Generation-II cells by abandoning the "thick" single-crystal wafer and instead going to thin films of different kinds of photovoltaic material, for example, amorphous (noncrystalline) silicon or cadmium telluride. Reducing the amount of material in each cell reduces the fabrication cost, but then the cells also become less efficient. Either they absorb less sunlight, or they are less efficient at transporting the charge carriers to the terminals. So while the public's interest in solar is growing, as long as electric power from solar photovoltaics remains many times more costly than power from fossil fuels, solar photovoltaics will likely remain a minor player in the energy sector. The challenge is to identify an approach that is both cheap and efficient.

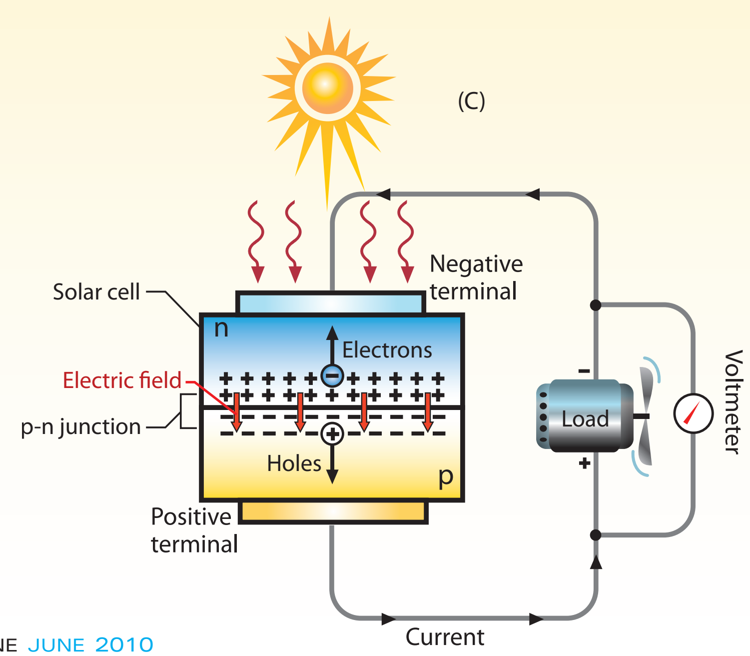
Los Alamos' Victor Klimov and other scientists worldwide are betting that intensive research in the next two decades will produce a quantum leap forward in solar technology, one that will create the higher-efficiency, lower-cost Generation-III solar cells people have been waiting for. Klimov sees the possibility of photovoltaic cells with efficiency above 20 percent and a price low enough to compete with the cost of oil and coal. To develop such things, he's turning to novel physics at the nanoscale.

Photovoltaics: Converting Sunlight to Electricity



(A) The Energy Gap—In a semiconductor, electrons (blue dots) fill up the ladder of allowed energy states to the top of the valence band. An energy region with no energy states (the energy gap) separates the highest rung of the valence band from the bottom rung of the empty conduction band. The gap has an energy value denoted by E_{gap}.

(B) Creating Excitons—An electron absorbs a photon with energy E_{gap} and jumps across the energy gap to the conduction band, where it becomes a negative-charge carrier. The electron leaves a vacancy, a hole that looks like a positive-charge carrier. The electron and hole are slightly bound together, and the pair is called an exciton.



(C) Harvesting the Charge Carriers—A crystalline silicon solar cell quickly separates the excitons' electrons and holes because the cell contains two silicon layers: a p-doped layer containing "acceptor" atoms, which tend to accept extra electrons, and an n-doped layer containing "donor" atoms, which tend to give away their electrons. When these layers are brought into contact, they form a p-n junction—electrons are exchanged, and ionized donors and acceptors create a strong electric field. It is this electric field that drives the electrons and holes apart as soon as sunlight creates them, thereby preventing recombination (in which the electron falls back into the hole, and solar energy is re-emitted as a photon). The charge carriers collect at opposite conducting terminals and flow around a circuit to power, for example, an electric motor.

Betting on Nanocrystals

Klimov has just become director of the new Center for Advanced Solar Photophysics at Los Alamos, a collaborative effort with six other institutions: the National Renewable Energy Laboratory (NREL) in Colorado, Rice University in Texas, the University of Colorado, Colorado School of Mines, the University of California at Irvine, and the University of Minnesota. The center is one of the 46 Energy Research Frontier Centers funded by the Department of Energy to do high-risk, potentially breakthrough research for making renewable, carbon-free energy available and affordable across the globe. Of those 46 centers, 13 are devoted in whole or part to harnessing solar energy.

Klimov says, "Our center is focused on semiconductor nanostructures, mainly nanocrystal quantum dots because they're cheap to make—and that's because they can be grown and processed in solution." Klimov is a world leader in the physics of quantum dots, tiny specks of matter that each contain from 100 to 10,000 atoms and extend only 2 to 20 nanometers (billionths of a meter) in each direction.

Nanocrystal quantum dots have a number of properties that fit right in with the needs of photovoltaics. First, they are easy to grow and process. Jeff Pietryga, a leading chemist on Klimov's Los Alamos team, and other chemists at the center have refined the methods for growing nanocrystals in solution, achieving excellent uniformity in their size and composition. Making a uniform film of these can be as easy as pouring drops of crystals in solution onto a spinning surface and allowing the fluid to spread and dry. Such films can be much cheaper to fabricate than ordinary semiconductor thin films, which require expensive deposition techniques.

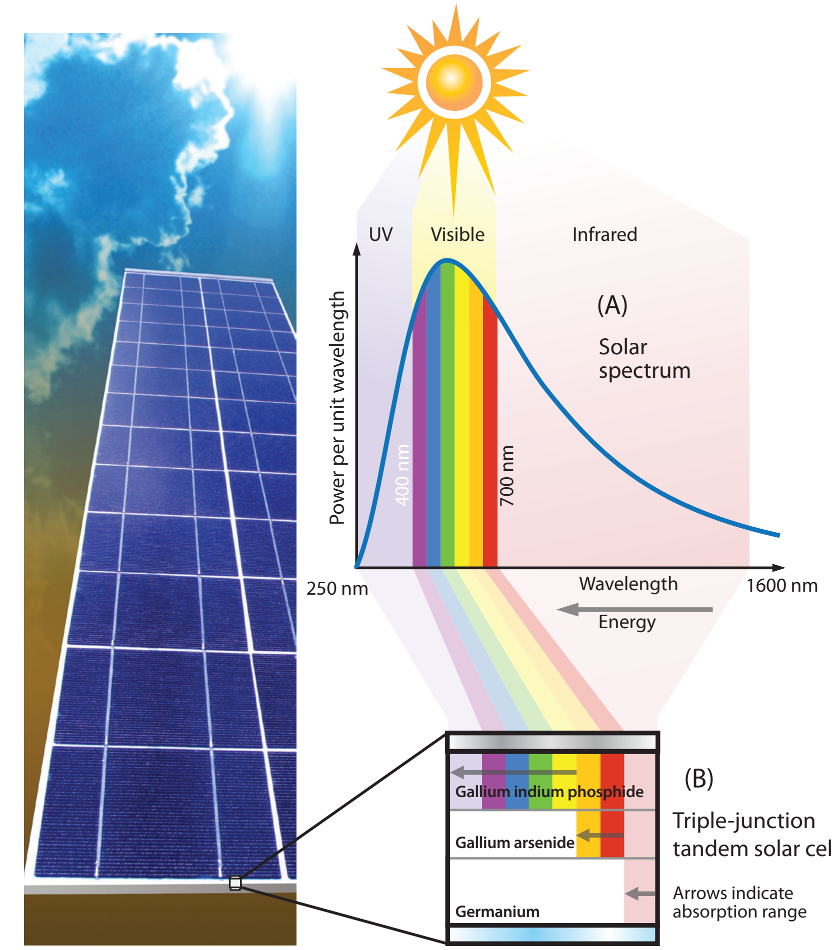
Second, a thin film of nanocrystals (50 to 100 nanocrystals thick) can absorb as much light as the standard single-crystal silicon wafer, which is 1,000 times thicker.

Third, nanocrystals can be grown to many different sizes, an advantage that requires some explanation.

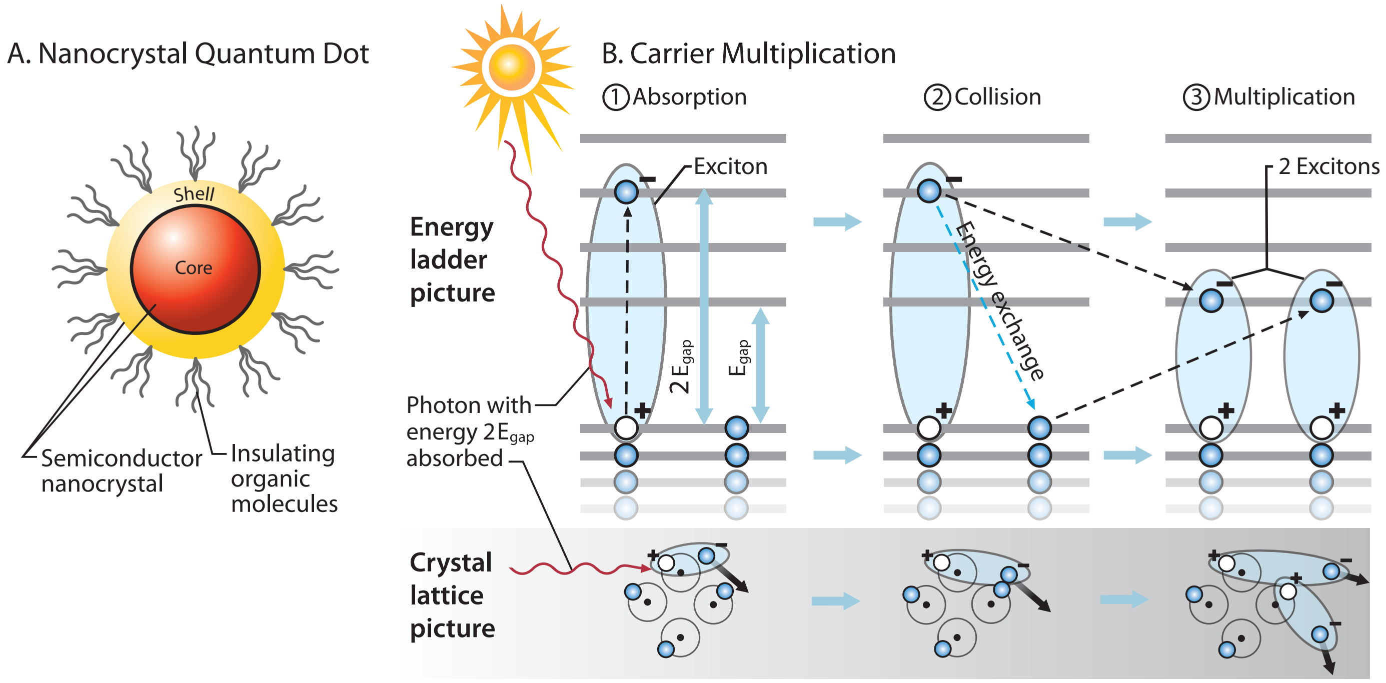
Consider first how a voltage develops when light strikes a solar cell made of bulk silicon. Individual photons (quantum particles of light) are absorbed by individual electrons that are bound to atoms in the semiconductor's crystal lattice. The solar photons have the right amount of energy to free the electrons from their bound positions and give them a certain voltage. It is those freed (conduction) electrons that collect at the negative terminal of the solar cell and flow as current when the cell is placed in a circuit.

What is the "right amount" of energy to free the electrons? As shown in "Photovoltaics: Converting Sunlight to Electricity" (facing page), a semiconductor's electrons exist on an ascending hierarchy (ladder) of energy levels (allowed energy states). The ladder is divided into the valence band, for bound electrons, and the conduction band, for conduction electrons, with an energy gap between the two bands.

The bound electrons on the highest "rung" of the valence band can move to the lowest rung of the conduction band (becoming conduction electrons) only by absorbing enough energy to jump the gap—



Above: (A) Sunlight contains photons with a spectrum of colors, or energies. (B) A high-efficiency tandem solar cell developed by NREL has three thin-film layers of different semiconductors. As shown, each starts absorbing light at a different wavelength (color). Together they operate like batteries in a series (the same current flows through each, and the total voltage equals the sum of their separate voltages). The cell operates at more than 40 percent power-conversion efficiency, but the expense of producing the thin-film layers limits use of the tandem solar cell to satellites and other niche applications.



energy equal to or greater than the amount of energy represented by the gap (E_{gap}). Solar photons have energies in that range, so a bound electron that absorbs a solar photon can take the leap, becoming a conduction electron.

But the electron does something else as well: it leaves a vacancy where it once sat in the valence band. That hole (it's in the crystal lattice) acts like a positive charge, attracting the new conduction electron's negative charge. Together, the two are called an exciton. Electricity is created when an electric field causes the conduction electrons and holes to move to opposite terminals.

In macroscopic samples of a given semiconductor, the energy gap is always the same, independent of the sample size, but in tiny nanocrystals, quantum effects cause the energy gap to vary with size: the larger the nanocrystal, the smaller its energy gap. Klimov points out that solution chemistry can be used to grow nanocrystals of a precise size, thus "tuning" the energy at which the crystals begin absorbing photons.

To take advantage of that fact, one could layer three nanocrystal thin films, each with progressively smaller nanocrystals (and therefore larger energy gaps). The smallest nanocrystals (in the top layer) would selectively convert the highest-energy photons into charge carriers at a voltage about equal to the energy gap. Lower-energy photons would pass through to the second or third layer, where they'd produce charge carriers at successively lower voltages. The total voltage would equal the sum of the voltages derived from the three layers. Thus, the layering would allow a higher voltage to be extracted from the solar spectrum and result in higher power output than is obtained from a single layer. Potentially, this three-layer device could perform as efficiently as the very costly tandem solar panels used to power satellites (see figure on p. 5).

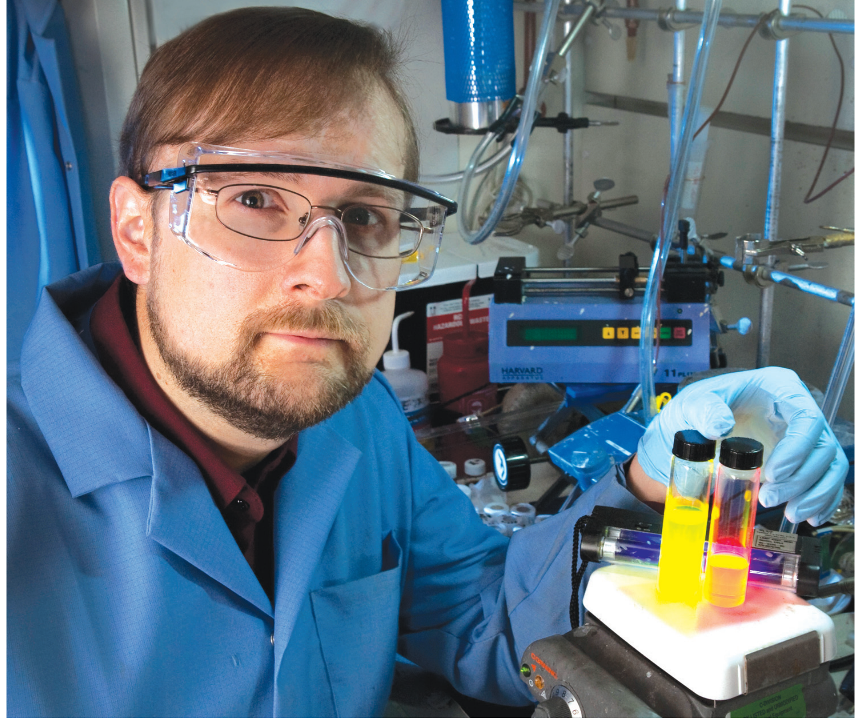
Most intriguing of all, the new center will try to exploit a number of novel nanoscale phenomena that could raise the maximum possible power-conversion efficiency of a single-layer device, dramatically increase its light-absorption properties, and circumvent present difficulties of transporting the charge carriers to the terminals.

Step One—Getting Two for One

First, the question of maximum efficiency for a single-layer device. Typically, in a macroscopic semiconductor, each photon with energy of E_{gap} or greater gets absorbed, freeing one electron. If the photon energy equals E_{gap}, it boosts an electron to the bottom rung of the conduction band, where it becomes a negative-charge carrier with a voltage equal to E_{gap}.

Surprisingly, a photon with still more energy that boosts an electron to a higher conduction rung does not result in a higher-voltage electron and potentially higher power-conversion efficiency (electric power is equal to current times voltage). Instead, that electron immediately begins to lose energy to heat through collisions with the atoms of the crystal lattice. Like the operation of a pinball machine, but in energy space not real space, each collision sets off a lattice vibration (phonon), causing the electron to lose energy and descend another rung of the energy ladder until its energy (voltage) is E_{gap}, that is, until it's sitting on the bottom rung of the conduction band. The descent takes a few picoseconds (trillionths of a second) at most. Thus, irrespective of the photon energy absorbed, the generated photovoltage (and electric power) in a semiconductor photocell is the same, and a single semiconductor layer can never have 100 percent power-conversion efficiency. In fact, the maximum power-conversion efficiency is 31 percent.

Above: (A) Nanocrystal quantum dots are surrounded by a layer of organic molecules (surfactants) that allows precise size control, prevent conduction electrons from getting trapped at the surface, and make nanocrystals soluble. (B) The process of carrier multiplication—the freeing of two electrons (or creation of two excitons) with one high-energy photon—is depicted two ways: on the energy ladder and within the crystal lattice. In the latter, the valence electons orbit the atomic nuclei, and the conduction electrons move freely.



Jeff Pietryga shows two vials of different-size nanocrystals, each emitting light of a different color (energy) that corresponds to the nanocrystal's size (and energy gap).

"Nanocrystals can beat that limit," explains Klimov excitedly, "because when you confine the electrons to small nanocrystals, all of sudden, for each high-energy photon absorbed, you can free not just one but two or more negative-charge carriers with voltage E_{gap}. If you can transport those carriers to the terminals, you can get a higher electric current, and that's the kind of effect we're looking for."

Called carrier multiplication, this phenomenon of creating two free electrons with one high-energy photon was first measured in nanocrystals in 2004 at Los Alamos by Klimov and Richard Schaller. The original motivation for searching for this effect in nanocrystals traces back to the concept of a "phonon bottleneck." As shown in the figure on the facing page (part B) the energy ladder of a nanocrystal is different from one in a macroscopic sample; namely, the rungs are so widely spaced that the energy difference between rungs is much larger than the energy it takes to create a single phonon. An electron boosted to a high-energy rung in a nanocrystal (step 1, B), must create several phonons at once to descend to the next rung down, but that process is much slower (has lower probability) than creating a single phonon. Therefore, the "hung-up" electron with its extra energy courses back and forth through the nanocrystal and is more likely to strike a bound electron (step 2, B), boosting the latter up to the conduction band and bumping itself down to a lower rung (step 3, B). Now absorption of a single high-energy photon has created two electrons in the conduction band instead of one.

Victor Klimov, director of the Center for Advanced Solar Photophysics.

Klimov notes, however, that "while energy loss through phonon emission is likely suppressed in nanocrystals relative to bulk solids, experiments indicate that other energy-loss processes compete with carrier multiplication. Understanding those is one area of the center's research.

Klimov estimates that if carrier multiplication worked perfectly, the extra current created would raise the power output, thereby increasing the maximum possible power-conversion efficiency for a single-layer device to about 41 percent. "Right now, we seem to need two and one-half to three energy gaps of photon energy to create two excitons. We would like to learn enough of the fundamental physics to reduce that threshold to the theoretical limit given by energy conservation, which is two energy gaps for two excitons," says Klimov.

Another approach to exceeding the 31-percent limit is to increase the voltage by harvesting the "hot" (high-energy) electrons directly, before they either lose their energy to phonons or create multiple carriers. In particular, a phonon bottleneck could be used to maintain the photogenerated electrons in the hot state for times sufficient to collect those electrons at the negative terminal and send them down a wire. The hot electrons would drive a voltage that is greater than the energy gap, resulting in increased power output. Researchers for the Center for Advanced Solar Photophysics hope to develop novel nanoscale materials that exhibit a pronounced phonon bottleneck and, in addition, to develop efficient schemes for harvesting hot electrons.

Step Two—Getting Them Out There

Whether solar photons create a single conduction electron, multiple electrons, or hot electrons, the real bugaboo for nanocrystal devices is transporting, or conducting, the charge carriers to the terminals.

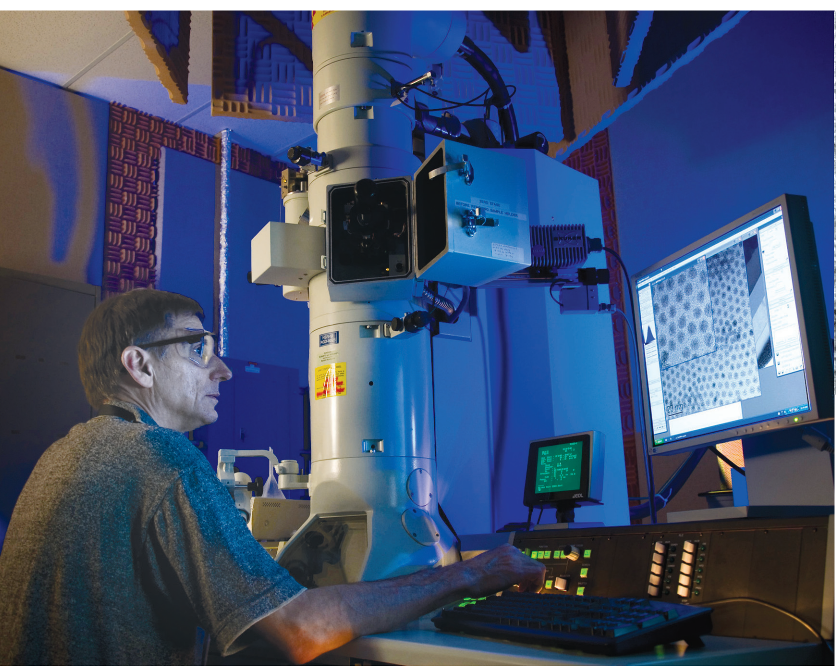
It's been mentioned that each electron is not completely free but instead slightly bound to a hole, forming an exciton. What's not been said is that these two charge carriers must be separated and transported very quickly; otherwise, the exciton will decay in less than a microsecond through recombination, the electron falling back into the hole and emitting the absorbed solar energy as a photon.

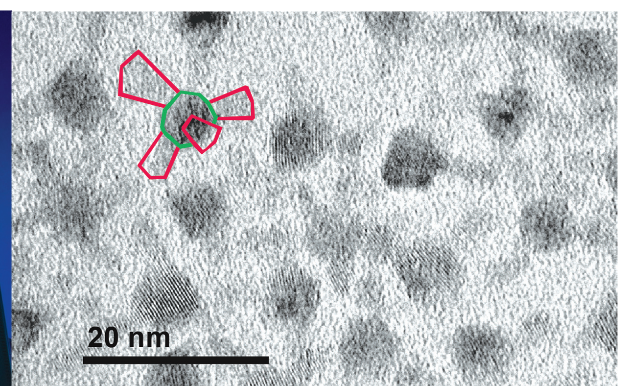
In Generation-I cells, charge separation and transport happen readily. First, the silicon wafer is doped with impurities that provide ready-made charge carriers (conduction electrons and holes) and therefore a high conductivity. Second, as shown in "Photovoltaics" (part C), the doping creates an interface with electron-donating impurities on one side (the "n" layer) and hole-donating impurities on the other (the "p" layer). Electrons migrate across this interface, or "p-n junction," setting up a permanent electric field that separates electron-hole pairs as soon as they are created, and helps transport the electrons with their negative charges to the negative terminal and the holes with their positive charges to the positive terminal.

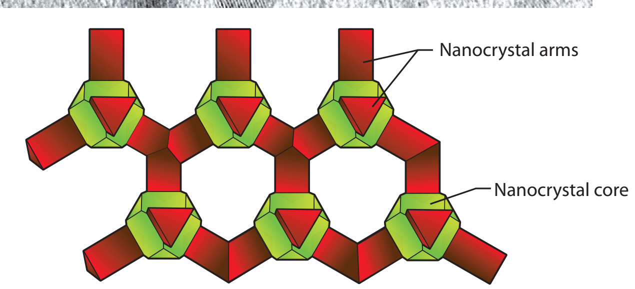
This method of charge separation and transport doesn't work in nanocrystal thin films. Nanocrystals tend to expel impurities during crystal growth, making it difficult to create well-defined p-n junctions. Furthermore, nanocrystals are surrounded by insulating organic molecules (see figure on p. 6), and the charge carriers, once created, must tunnel through that layer and then hop from nanocrystal to nanocrystal to reach the terminals. All of this is inefficient. Charge carriers can be trapped in the insulating layers or lost through recombination with an oppositely charged carrier as they hop to the terminals.

Recombination becomes a very serious and immediate problem when carrier multiplication creates two excitons. Those two can interact and share energy so that one electron gets boosted back up to a higher energy, and the other electron recombines with its hole. This process, called Auger recombination, happens in tens of picoseconds (trillionths of a second). To take advantage of the carrier-multiplication effect, the carriers have to be extracted from the nanocrystal more quickly than Auger recombination can occur. Finding ways to do that is another research objective within the center.

One approach is to give the electrons someplace to go to get away from the holes. Pietryga and center postdoctoral fellow Doh Lee have done this by growing projections (arms) on the nanocrystals. These arms are bits of semiconductor that can act as electron acceptors (see figure below). Each time a photon generates an electron-hole pair, the electron rapidly separates from the hole (it stays in the central core) by traveling to the arms. That separation buys time because it reduces the chance that the electron will recombine with a hole before being extracted from the nanostructure.





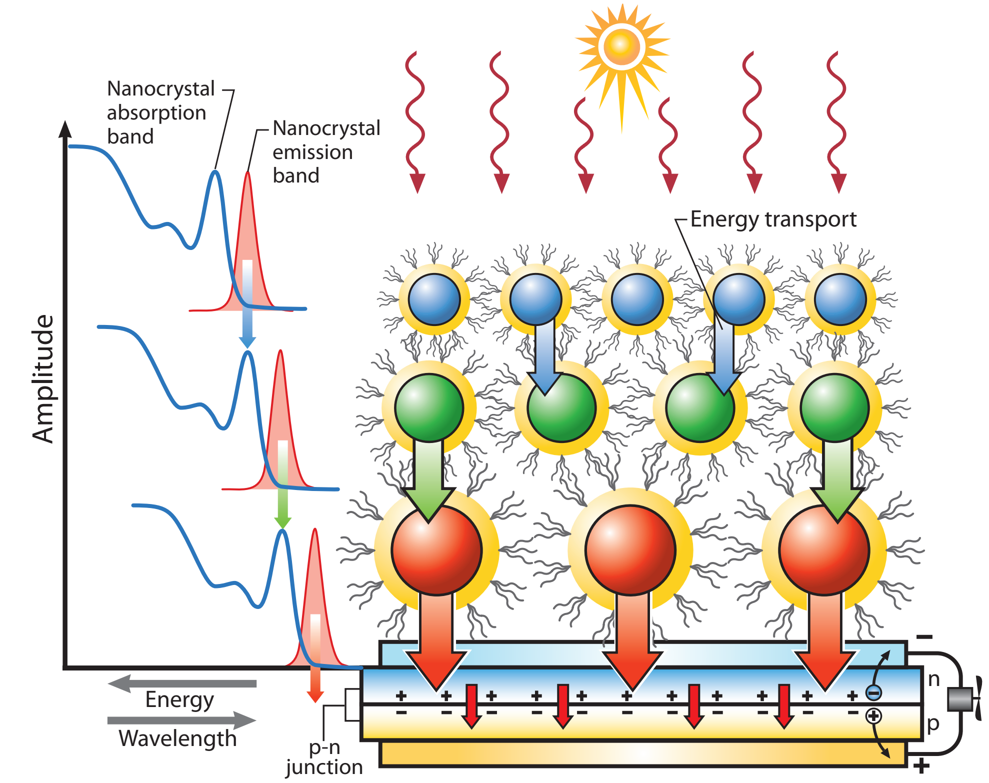


Don Werder (left) works at a transmission electron microscope to image nanocrystals. Those with electron-accepting "arms" (shown in the electron micrograph, upper right), could be grown into a continuous network (lower right) that would dramatically enhance electron transport in nanocrystal thin films.

"If we can assemble a nanocrystal thin film with the arms forming a continuous network and the nanocrystals and arms are embedded in a material that conducts holes, charge transport and charge collection might happen pretty easily, a key to efficient photovoltaics," explains Pietryga (see figure on p. 8).

Energy Transport—Beyond Charge Hopping

An interesting solution to harvesting current avoids the need for having charge carriers hop between nanocrystals. Instead, the exciton in one nanocrystal decays (electron and hole recombine), and the energy emitted goes not into a photon, but into an electric field that *acts like* a photon, exciting an exciton in a neighboring nanocrystal. That transport of energy between nanocrystals repeats until the exciton reaches a p-n junction, where it is split into an electron and a hole by an electric field (see figure, this page).



To understand this energy-transport process, consider that at a distance the exciton's electron-hole pair looks like a positive charge and a negative charge separated by a very small distance, what physicists call an electric dipole. The dipole produces a characteristic electric field that extends well beyond the nanocrystal. That dipole field puts one nanocrystal in contact with another and allows nanocrystals to transport energy from one to the other.

Because the energy emitted when an exciton decays is lower than the energy absorbed to create it, the energy-transport process is especially favored from a small nanocrystal with a large energy gap to a larger nanocrystal with a smaller gap. In that case, each energy exchange produces an exciton with slightly less energy than its predecessor.

Researchers with the center are actively exploring these different mechanisms of charge and energy transport in the hope that one or more will actually pan out, dramatically increasing the efficiency of harvesting usable electricity from nanocrystal thin-film solar cells.

Where the Rubber Meets the Road

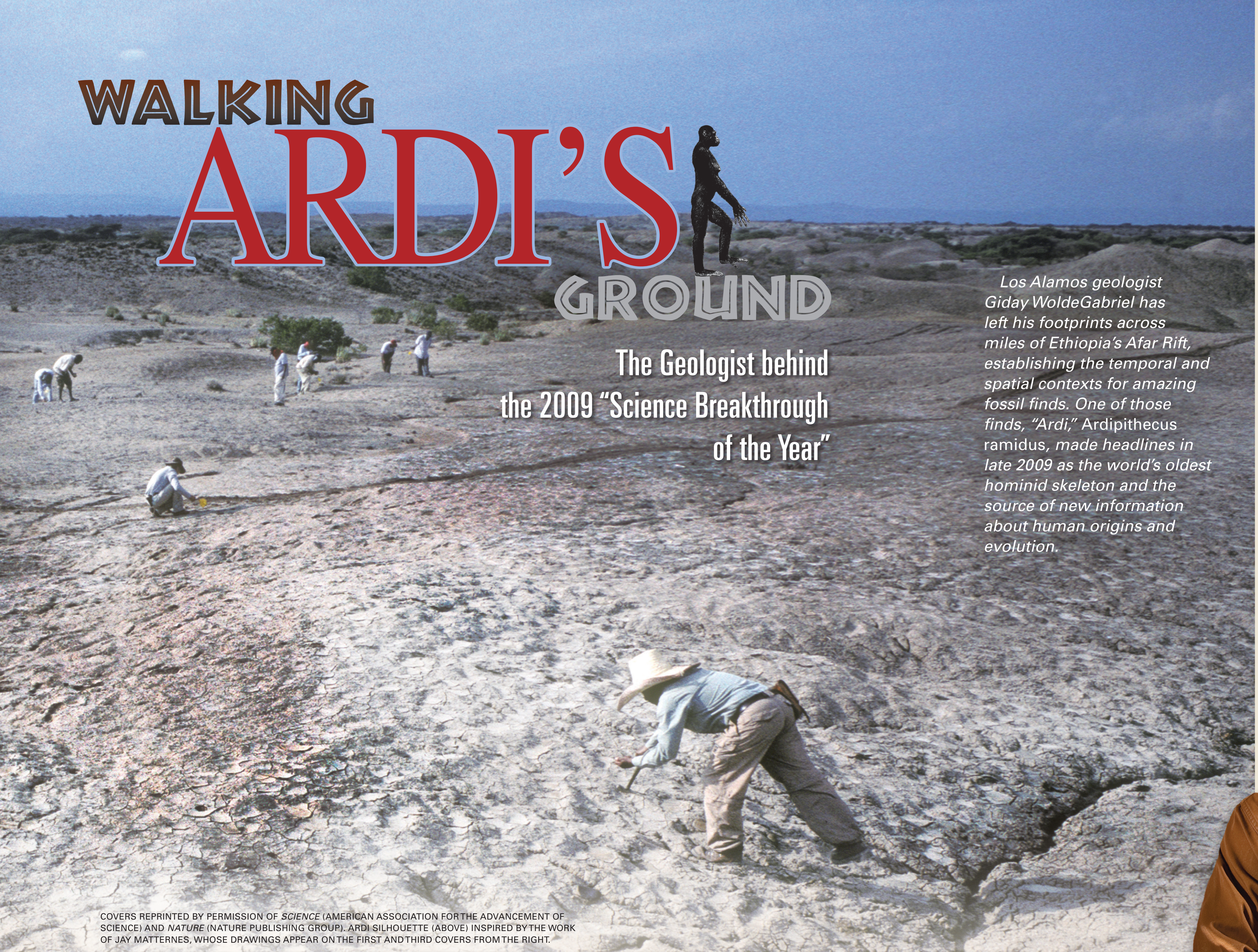
The real test comes when these processes are integrated into a working device. The Los Alamos team has built a clean room and other facilities specifically designed to fabricate and test nanocrystal thin-film devices. It's now positioned to benefit from the unique expertise of its center partners from NREL, who have been dealing with issues of practical photovoltaics for two decades. Says Klimov, "I am very excited by the productive relationships we're already developing with our collaborators outside Los Alamos. Clearly, our biggest chance for success is for all of us to work closely together."

The center is also developing novel materials that can find almost immediate use in photovoltaics. One example is inexpensive germanium nanocrystals that can be made in different sizes and applied in inexpensive multilayered devices that absorb energy from the infrared to the ultraviolet.

Klimov emphasizes that new physics being developed at the center will eventually lead to real-life devices capable of replacing bulky and expensive silicon solar panels. The researchers are studying fundamental physics on the nanoscale, but the goal of making solar truly affordable has their attention riveted on the practical. ❖

—*Necia Grant Cooper*

Above: Energy transport in a layering of nanocrystal thin films that have progressively larger quantum dots. The top layer, the smallest quantum dots, will absorb, say, a blue photon and create an exciton. The exciton moves from smaller to larger quantum dots through a two-step sequence of decay and excitation (arrows) and then to the p-n junction, where the electric field splits the exciton into an electron and a hole that travel to different terminals. This process eliminates charge hopping.



WALKING ARDI'S GROUND

The Geologist behind the 2009 "Science Breakthrough of the Year"

Los Alamos geologist Giday WoldeGabriel has left his footprints across miles of Ethiopia's Afar Rift, establishing the temporal and spatial contexts for amazing fossil finds. One of those finds, "Ardi," Ardipithecus ramidus, *made headlines in late 2009 as the world's oldest hominid skeleton and the source of new information about human origins and evolution.*

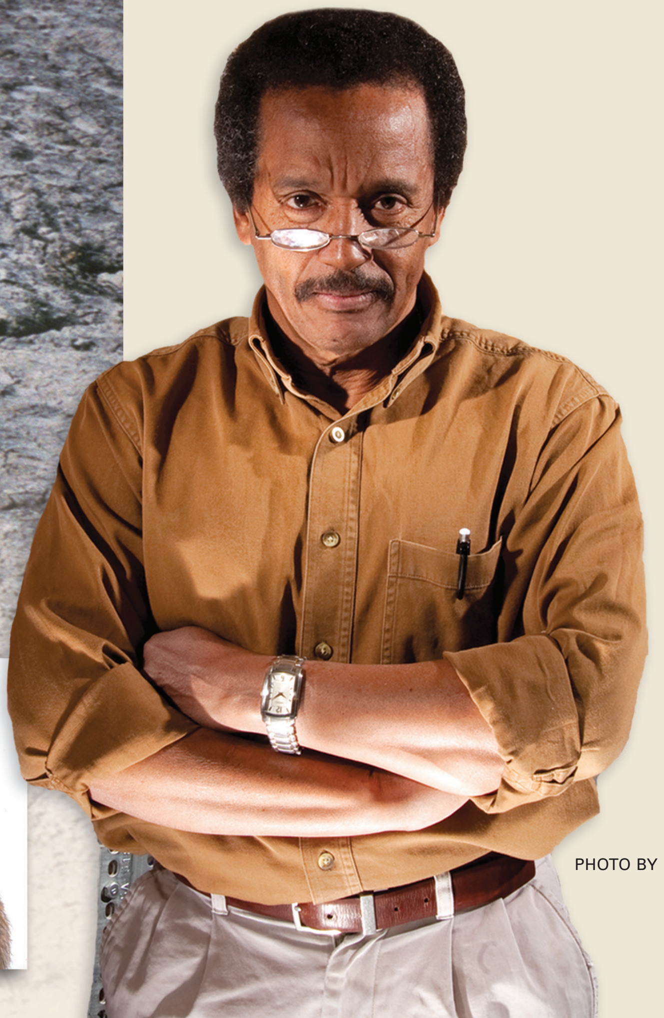
COVERS REPRINTED BY PERMISSION OF *SCIENCE* (AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE) AND *NATURE* (NATURE PUBLISHING GROUP). ARDI SILHOUETTE (ABOVE) INSPIRED BY THE WORK OF JAY MATTERNES, WHOSE DRAWINGS APPEAR ON THE FIRST AND THIRD COVERS FROM THE RIGHT.

Ethiopian-born geologist Giday WoldeGabriel, a staff member at Los Alamos National Laboratory, leads a double professional life.

As a member of the Earth and Environmental Sciences Division, WoldeGabriel is the Laboratory's resident expert in the geology of rifts—places where Earth's shell is being stretched and thinned, as it is in the Rio Grande Rift, where Los Alamos makes its home in northern New Mexico. He uses geochronology and geochemistry to help the Laboratory build a three-dimensional geological model of the formations that underlie Los Alamos, its immediate surroundings on the Pajarito Plateau and the entire Española Basin.

Simultaneously, as co-leader and lead geologist of the world-renowned international Middle Awash paleoanthropological research team, he annually takes his skills to Ethiopia's Afar Rift. There WoldeGabriel's geological field surveys have led the team to some of the world's most exciting hominid finds, including the nearly complete skeleton of an ancient lady named "Ardi," *Ardipithecus ramidus*.

The Middle Awash team discovered Ardi in 1994 in its study area, a 35-by-45-mile tract around Ethiopia's Awash River. She became a worldwide sensation on October 2, 2009, when team members published the results of their 15-year study of her in a special issue of *Science*. On December 18, 2009, *Science* declared her to be "Science Breakthrough of the Year." *Time* magazine



Giday WoldeGabriel (left) is co-leader of the Middle Awash research team, whose hominid discoveries in Ethiopia's Afar Rift have been featured on the covers of *Science* and *Nature*. WoldeGabriel's detailed geological knowledge of the team's study area is crucial to the authentication of each find. His work in Ethiopia is supported by a minigrant from the Institute of Geophysics and Planetary Physics in Los Alamos.

PHOTO BY LEROY SANCHEZ

The distant tents under acacia trees are home for the Middle Awash team during its field sessions in the Afar Rift. The rift is the year-round home of the seminomadic Afar people (foreground), who herd goats and cattle.

followed suit, naming her 2009's top scientific discovery.

What's so special about Ardi? A nearly complete hominid skeleton is an extreme rarity, and Ardi is the oldest one yet found, 4.4 million years old. She's also the most significant skeleton since 1974's 3.2-million-year-old Lucy, *Australopithecus afarensis*. Her significance stems from more than her age. Her skeleton reveals surprising information about how she looked and moved, changing our view of human evolution.

Scientists long assumed that the ancestor we share with chimpanzees (thought to have existed around 8 million years ago) would be like a chimpanzee, right down to knuckle walking: the body's weight resting forward on the knuckles of the hands. Ardi has ended that notion. The bones of her feet and pelvis show she was bipedal, an upright walker, and her hands were not adapted for knuckle walking. No one expected these characteristics in a hominid so close in time to the common ancestor. Project members now believe that knuckle walking evolved separately in apes after hominids branched off. It's a radically new theory.

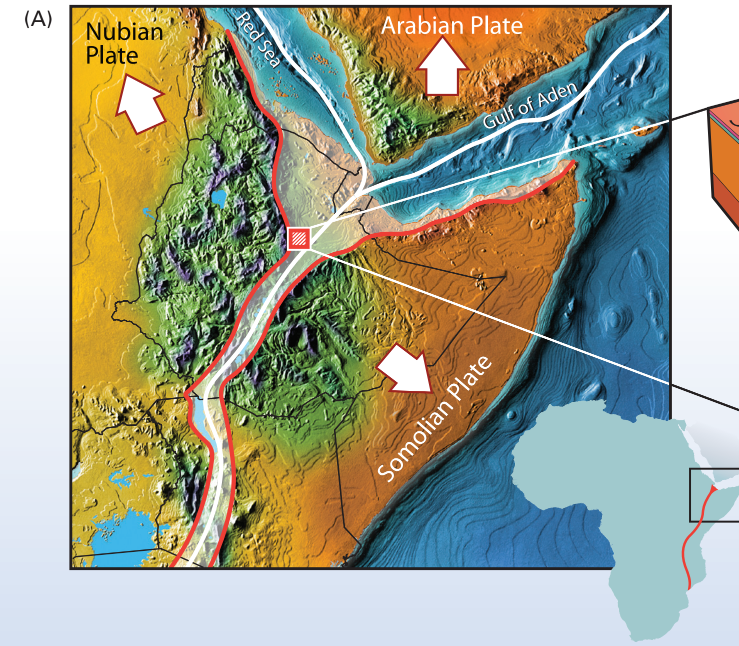
Ardi's skeleton reveals her stature (about 4 feet tall, 100 pounds), her brain size (small), and her form of locomotion (bipedal). Her big toe was angled to one side like a modern thumb, so she could grasp and clamber up low tree branches. Such a foot has never been seen in other hominids.

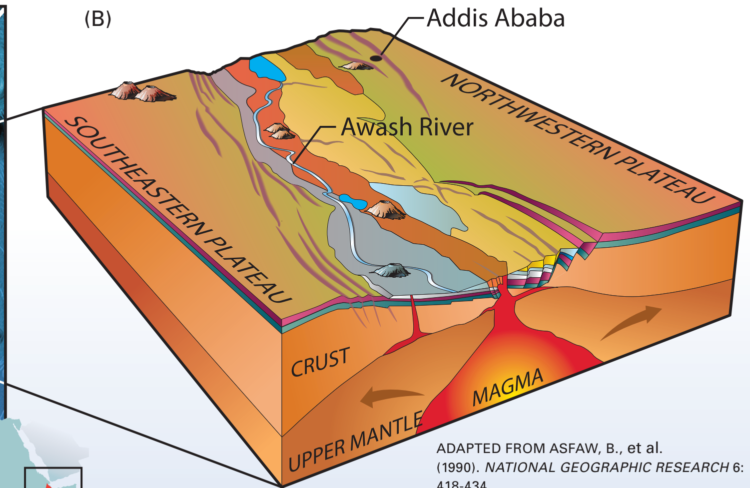
Bedrock

Ardi is one of an unparalleled number of prestigious finds for the Middle Awash team. Members have found seven of the world's known hominid species in their study area. Three of those, *Australopithecus garhi*, *Ardipithecus ramidus*, and *Ardipithecus kadabba* were first-time discoveries, yet to be found anywhere else. The team's hominid discoveries have been featured often on the covers of *Science* and *Nature*.

Such acclaim is born of the team's meticulous care at retrieving each fossil and piecing together its story—a story told not just by bones, but also by the ground that held them. For 18 years, WoldeGabriel has made accurate storytelling possible through a unique geological study of the Middle Awash that incorporates satellite and aerial photos, on-the-ground field work, and high-tech laboratory analysis of collected rock samples.

He has deciphered the land's complex code to produce a detailed geologic picture that another of the team's leaders, Tim White (University of California, Berkeley) calls "the project's bedrock." It enables the team to keep finding promising sites time after time. Integrated with paleontology, archaeology, and studies of the paleoenvironment, it becomes a critical part of a superior, multidisciplinary approach that makes all the difference in the team's ability to place fossils accurately in time. Other explorers made the area's first hominid find in the 1970s, an "archaic" *Homo sapiens* cranium, but they lacked the best geologic data and so misdated the find. WoldeGabriel's studies redated that hominid to 600,000 years, almost twice the initial perception of its age.





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The Tectonics of a Fossil Repository

(A) The continents sit on tectonic plates that slide over Earth's upper mantle. But the African tectonic plate is gridlocked, so Africa cooks in the rising heat from Earth's core. On the continent's east side, magma wells up, fracturing the African plate into the Nubian and Somalian subplates. The result is the East African Rift (red lines), which extends through Eritrea, Ethiopia, Kenya, Tanzania, Malawi, and Mozambique. The Red Sea and the Gulf of Aden are also rifts, caused by the movements (arrows) of the Arabian plate and Africa's two subplates. The boundaries of the three plates (white lines) meet where the rifts all intersect, in what geologists call a triple junction.

(B) At the triple junction, the Afar Rift, the north end of the East African Rift, began forming more than 25 million years ago and grows wider and deeper every year. Magma rises there, pushing Earth's crust up and back to form plateaus with a valley subsiding between them. In the past, sediments from the plateaus buried the remains of animals (including hominids) that were attracted to the valley. The result is a treasure trove of fossils that now attracts scientists. But it's a disappearing treasure trove, eroding away and destined for a watery end. Part of the rift is already 512 feet below sea level. Water will eventually flood the area, then spill down the entire East African Rift, cutting off the Somalian plate.

WoldeGabriel joined the Middle Awash team in 1992, becoming one of the team's more than 70 scientists from 19 different countries. He shares team leadership with White, a paleontologist; Berhane Asfaw, also a paleontologist, from Ethiopia's Rift Valley Research Service; and Yonas Beyene, archeologist, from Ethiopia's Authority for Research and Conservation of the Cultural Heritage. The team operates under a permit from the Ethiopian government.

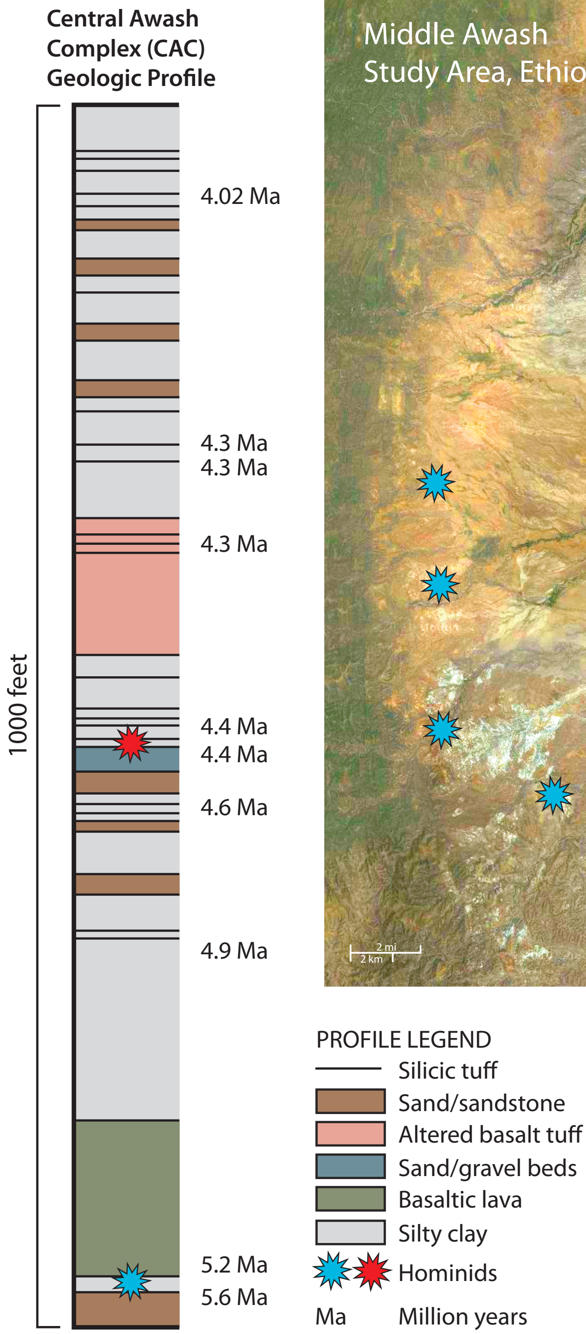
A Rip in the Earth's Crust

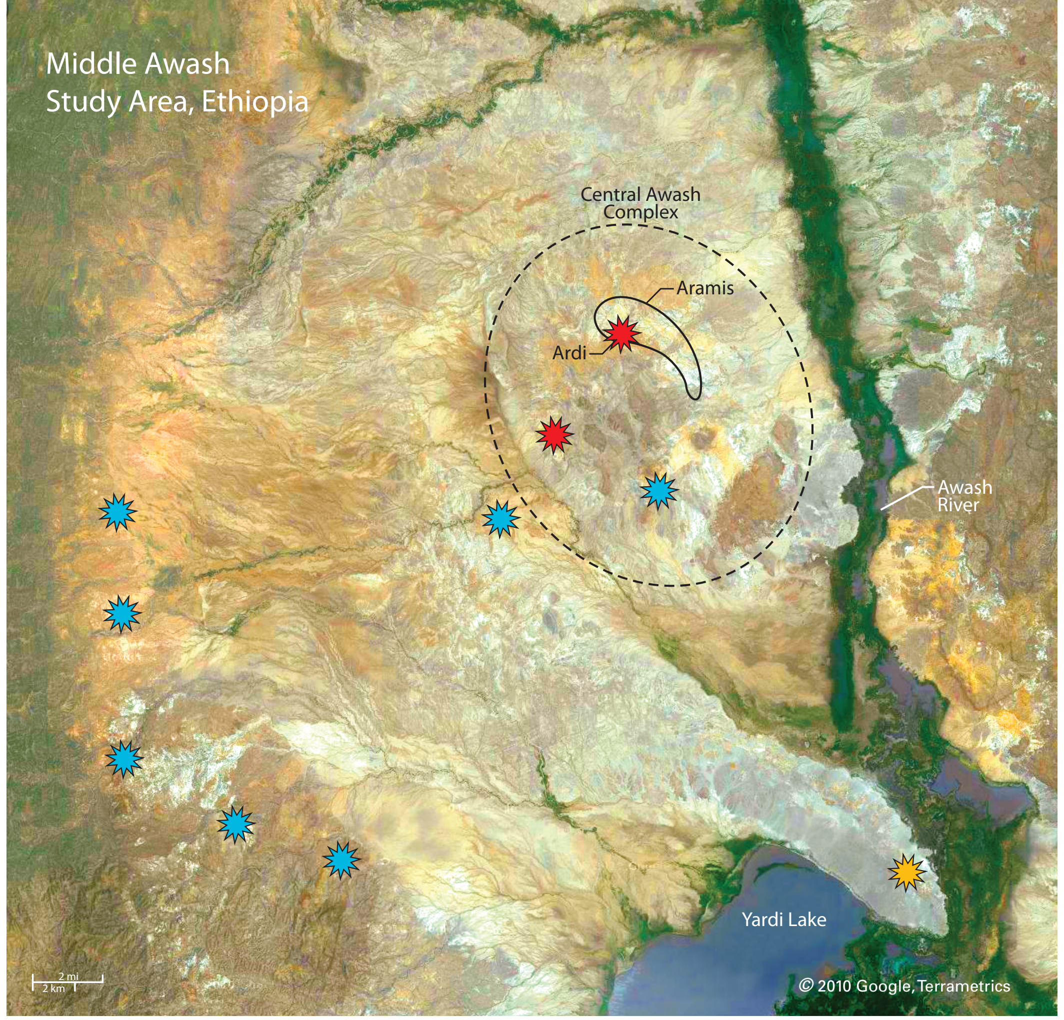
The Middle Awash study area sits in the southwestern portion of the Afar Depression, a sunken area in the Horn of Africa. A sizzling desert, the Afar Depression is at the northern end of the fossil-famous East African Rift (the Great Rift Valley) and so is known to geologists as the Afar Rift. Intermittently active volcanoes mark the horizon, and cracks and fissures split the ground, annually widening the rift an eighth of an inch—sometimes more. In September 2005 a volcanic eruption pushed magma close to the surface in a huge, ground-splitting wedge that, in one week, opened a new fissure 38 miles long and 26 feet wide.

WoldeGabriel explains that the volcanoes are a sign of gargantuan movements deep underground: magma rising and shouldering aside tectonic plates. The magma's inexorable push created the East African Rift and is particularly pronounced in the Afar Depression, where the Afar Rift meets rifts at the bottom of the Red Sea and the Gulf of Aden (see "The Tectonics of a Fossil Repository," above). Water from one or both of these will eventually spill down the East African Rift, separating the bulk of Africa from its eastern side.

Meanwhile, the Afar Rift and, within it, the Middle Awash study area are rich fossil-hunting ground, and not coincidentally. "If it weren't for the tectonics and the resulting rifts," says WoldeGabriel, "we wouldn't be there."

As the rift opened, the land within it subsided and the bordering highlands regulated its climate, making it an ideal place for life to proliferate. At the same time, sediments washed in and covered the bodies of dead animals; then vast layers of ash from periodic volcanic eruptions locked down the sediments and the bones they contained. Subsidence, sedimentation, and volcanic eruption—the pattern repeated itself over and over, creating a multitude of deeply buried,





In its study area, the Middle Awash team has found hominid fossils spanning the past 6 million years. Three have been found nowhere else: Ardipithecus ramidus *(red stars),* Ardipithecus kadabba *(blue stars), and* Australopithecus garhi *(orange star), a new 2.5-million-year-old species of Lucy's genus.*

The Central Awash Complex (CAC), dotted line, yielded Ardi (at Aramis) and other Ar. ramidus *samples and* Ardipithecus kadabba. *At left, the stratigraphic profile shows CAC rock strata and CAC finds:* Ar. ramidus (red star) *and* Ar. kadabba (blue star). *Remains of* Ar. kadabba *on the study area's western margin are as much as 5.8 million years old.* Australopithecus garhi *was found on the study area's southwest margin.*

alternating sedimentary and volcanic layers. (See "The Tectonics of a Fossil Repository," p. 13.)

As the land sank lower—more than 2,000 feet lower today than in Ardi's time—the surrounding high ground held in more and more heat until what had been cool, wet forest became today's hot, dry desert. At the same time, tectonics pushed blocks of the buried layers upward. These now exist as discontinuous ridges, weathered into undulating hills, their layers revealed only where a fault has made a vertical break or where seasonal streams have sliced into a hillside.

Ground Truth

Fossilization is a chance occurrence, so only one-quarter of the sedimentary layers now exposed in the Middle Awash contain fossils, but those that do are a treasure trove. "It's the most prolific paleoanthropological area ever discovered," says WoldeGabriel, "with the longest hominid record yet available."

The Middle Awash team has recovered about 20,000 vertebrate fossils, including hominids, from more than 200 different sites. The hominids, 160,000 years to 5.8 million years old, were found in 13 different layers.

Excavating Ardi's fragile bones required infinite patience and the utmost delicacy. Here her lower jaw is revealed with the use of a dental tool. Many bones had to be treated with a stabilizing solution.

Leading the search for fossil-bearing sediments is part of WoldeGabriel's job. The search begins from a distance—and from a great height. Satellite photos, Google Earth images, and aerial shots from airplanes reveal locations the team may want to visit.

"It's important to discriminate," says WoldeGabriel, "before you climb the next ridge into the next valley." Because, in the end, the hard work is done on foot. "You have to physically walk the site to be sure the things are what you think they are."

Geologists call data gathered on the spot "ground truth," and the truth the team needs is the difference between sediments, something that has to be learned up close. Lacustrine sediments, laid down in standing water, yield aquatic fossils—crocodiles, hippos, and fish—but contain no hominids. For those, you need the fluvial sediments of streams and rivers, deposited in floodplains along deltas and lake margins.

The difference reveals itself in grain size. Fluvial sediments are generally coarser than lacustrine, and grain size diminishes with slope gradient. The largest materials, rocks and gravel, are moved by high-energy water on steep ground and are deposited where the ground levels out. There they solidify into conglomerate, a rock composed of tumbled stone fragments. Conglomerate is a signal to WoldeGabriel.

"It means you've found the ideal fossil environment," he says, "not in the conglomerate itself—the big rocks break up animal remains—but in the layers farther downstream on a flatter plane." The stones in conglomerate show the way because their tips often overlap and point in the direction of flow. On a mild slope, like a lake's edge or a floodplain, water's sedimentary load is reduced in both volume and grain size and becomes a gentle covering for animal remains. It's there that fossils may be found.

Ardi was found in an ancient floodplain at Aramis (named for a nearby village) in the Central Awash Complex (CAC), west of the Awash River.

A broad 8-by-10-mile dome, the CAC is the hardened heart of a group of extinct volcanoes, now weathering 100 to 400 feet above its surroundings and wearing slabs of the rocks it displaced. Those slabs contain millions of years of rock layers, still mostly buried but, as WoldeGabriel suspected, exposed where erosion and faulting have cut into the uplifted ground. When

The pieces of Ardi's skeleton were found where she died, at a single site. Each flag marks a fragment's position. The local Afar people (background) enjoy watching and are sometimes paid to help with general labor. Team leaders' careful diplomacy with these independent people wins the team access to fossil sites.

the team explored the CAC in 1992, a Japanese team member, Gen Suwa, found the first piece of Ardi's species, a tooth, in a layer of salmon-colored sediment.

WoldeGabriel identified exposures of that layer at many separate spots in a 5-mile arc of the CAC. The sites contained fragile fossil pieces, most appearing at Aramis, the western end of the arc. The fossils were examples of an entirely new hominid. Team members mined that layer for two years and in November of 1994 found what they hadn't dared hope for: the skeleton of a single individual, Ardi.

Ethiopian paleoanthropologist Yohannes Haile-Selassie, then White's graduate student but now a member of the Cleveland Museum of Natural History in Ohio, found the first piece of Ardi, a finger bone. The team then spent three years in a single 3-foot by 4-foot spot, uncovering more than 125 pieces of Ardi's skeleton, including most of the skull, pelvis, lower arms, leg bones, hands, and feet. Twelve more years of study followed, at a laboratory for antiquities research and stewardship in Ethiopia's capital, Addis Abba.

Marking Time

A layer of rock is a point in geologic time, so to learn the age of Ardi and the pieces of 35 more of her kind found in the same layer, WoldeGabriel needed to date the sediments that held them. But sedimentary rocks are secondary materials, made of particles of older rocks formed elsewhere, then eroded and transported to a new location. Dating sedimentary layers requires looking to the adjacent volcanic layers, which are primary, still sitting where they cooled. Volcanic layers are time markers for the sediments they touch.

WoldeGabriel identified two layers of volcanic tuff (consolidated volcanic ash and fragments) bracketing the Ardi sediments and took samples back to the United States for radiometric dating, a laboratory technique that relies on the known decay rate (half-life) of radioactive isotopes to determine when magma erupted, cooled, and solidified. The amount of an unstable (radioactive) isotope is compared with the amount of the stable one it becomes through decay.

For Middle Awash samples, the method used is argon-argon dating, led by Paul Renne at the Berkeley Geochronology Center in California. Renne and his graduate students use a laser to melt a crystal of feldspar from a collected sample, extract and purify argon (a gas), and then determine the ratio of argon-40 to argon-39 (^{40}Ar/^{39}Ar dating).

The tuffs both above and below Ardi's sediments proved to be about 4.4 million years old, the difference between them—and the time it took for the intervening sediments and fossils to accumulate—being only a few thousand years. Geologically, that's a very short time, so the sediments, and Ardi too, are the same approximate age.

Two independent techniques were used to verify the date. One was biochronology, in which the ages of rock layers are checked against a known sequence of fossil life forms. WoldeGabriel led the team to many sites containing fossils of plants and animals that lived alongside Ardi. Ancient pigs that existed in a narrow space of time confirmed Ardi's age. The totality of the fossil plants and animals revealed Ardi's world: a life-crowded forest, grading into wooded grasslands. That Ardi was a forest dweller surprised the team. Bipedalism was assumed to have developed on Africa's savannahs.

The other technique involved paleomagnetism: the north-south orientation of iron grains in volcanic and sedimentary rocks reveals the North Pole's position when the rocks formed. Earth's poles periodically reverse, and scientists have calculated their position back through time.

Above: The tuff layers bracketing the *Ardipithecus ramidus* sediments are marked here with dotted lines. The tuff layers are almost contemporaneous, the top one being 4.416 million years old, plus or minus 0.031 million years, and the bottom one 4.419 million years old, plus or minus 0.068 million years. The sediments between them were deposited over only a few thousand years and are 18 to 20 feet thick in places but nearly nonexistent in others, where erosion washed them away before deposition of the top tuff layer. PHOTO COURTESY OF TIM WHITE.

Chemical Fingerprints

If stacked in a continuous column, the Aramis layers would be about 1,000 feet high, but not all the layers show at every site; despite some overlap, each site is a slightly different slice. In such a complex landscape, WoldeGabriel couldn't chance a mistake in pinpointing the exact tuffs marking Ardi's sediments.

So he identified and collected samples pristine enough to be chemically fingerprinted for their unique percentage of common elements: silicon, titanium, iron, aluminum, magnesium, manganese, calcium, potassium, sodium, and phosphorus. The specific percentage mix allows him to correlate all of a single tuff's exposures, wherever they appear.

WoldeGabriel labeled each sample with an exact GPS reading and, back in Los Alamos, had the samples sliced thin enough for light to pass through. Discrete fragments of volcanic glass in the slices were then examined with an electron microprobe to reveal the constituent elements. In addition, collaborator William Hart of Miami University in Oxford, Ohio, and his team of graduate students and postdoctoral fellows, joined WoldeGabriel in identifying the less-common trace and rare-earth elements.

No End in Sight

The team was back in Ethiopia early in 2010, searching for potential new sites and scouring Aramis again for more pieces of Ardi's species. Returning to the same ground is necessary because each rainy season reveals more fossils but just as easily washes them away. "It's a fragile erosional system," says White. "You get one chance to do this right." This year the team turned up a new *Ardipithecus ramidus* bone that confirms bipedality.

WoldeGabriel returned briefly to the area's oldest rocks, west of Aramis on the border of the rift, and will walk that ground again and again in the future. Years ago in this portion of the rift, he led then-graduate-student Haile-Selassie in search of a new fossil site and followed a promising sedimentary layer until Haile-Selassie made the find that eventually earned him his doctorate. He found fragments of a more-primitive example of Ardi's genus, *Ardipithecus kadabba*, also bipedal and as much as 5.8 million years old.

How much this earlier specimen has to tell is still unknown. So far, the fragments are sparse, but the hunt will continue. And WoldeGabriel's practiced eye and deep knowledge of the land will remain at the center of the work. ❖

—Eileen Patterson

Fossilized seeds (shown here), wood, and silica parts of plants are evidence of a long-departed forest. Ardi's world was filled with insects, gastropods, diverse birds, and mammals, both small (shrews, mice, and bats) and large (for example, bears, rhinos, elephants, monkeys, and antelopes).

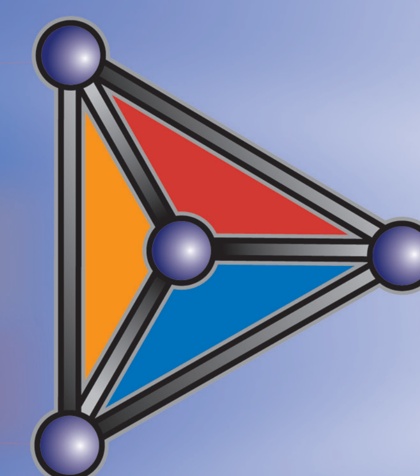
The Middle Awash team visits its study area yearly, driving from Ethiopia's capital, Addis Ababa. Visits are timed for October through January.

ALL PHOTOS BY DAVID L. BRILL, BRILL@MINDSPRING.COM, UNLESS OTHERWISE NOTED

Many of today's materials will fail if used for tomorrow's technology. MaRIE is the result of integrating some of Los Alamos' core resources into unique capabilities that will help speed the development of new materials.

MaRIE
A Facility in the Making

There's a critical need for new materials that can function under extreme temperature, pressure, or radiation environments. Scientists are hoping MaRIE will fill that need by forever changing the way materials are developed.



It's a material world, all right. Materials are the backbone of modern civilization, which wouldn't exist without the metals, plastics, ceramics, semiconductors, and other marvelous solids we've fashioned from the elements. We've made everything from aluminum alloys to Zytel thermoplastics, but truth be told, we don't exactly know what we're doing.

Materials-savvy scientists cannot modify the composition of, say, a steel alloy and be certain of the results, nor can they predict which modifications will produce a desired product. Rather, their approach to material development is largely Edisonian—tinkering with an existing material's recipe until, through trial-and-error and perseverance, something novel is produced. It's a slow process that's always been stunningly successful.

However, at a 2007 Department of Energy workshop,[†] some of the country's best scientists made it clear that a different approach was needed. They stressed that solving many of our most challenging technical problems will require revolutionary new materials, and the nation can't afford to wait for serendipity to supply them.

Enter MaRIE, a proposed national user complex for materials research that will be Los Alamos National Laboratory's signature science center in the 21st century. Intended to hasten the development of materials that must function within extreme temperature, pressure, radiation, or other environments, MaRIE (for Matter-Radiation Interactions in Extremes) will also be part of a general effort to transform materials development from a "try it and see what happens" discipline into a "predict it and *control* what happens" science.

A Complex Overview

The MaRIE approach to materials research and development will be a science-based methodology. Specific steps will include fabricating a sample, exposing it to an extreme environment, and making measurements in situ that reveal how the sample changes over time. Experimentalists will coordinate their efforts with theorists and modelers to identify parameters or indicators that lend predictability to materials development. Their collective insights will then guide new experiments and new discoveries. The ultimate goal is to create materials that are

[†] Basic Research Needs for Materials under Extreme Environments, http://www.er.doe.gov/bes/reports/list.html

perfectly suited to any given extreme environment.

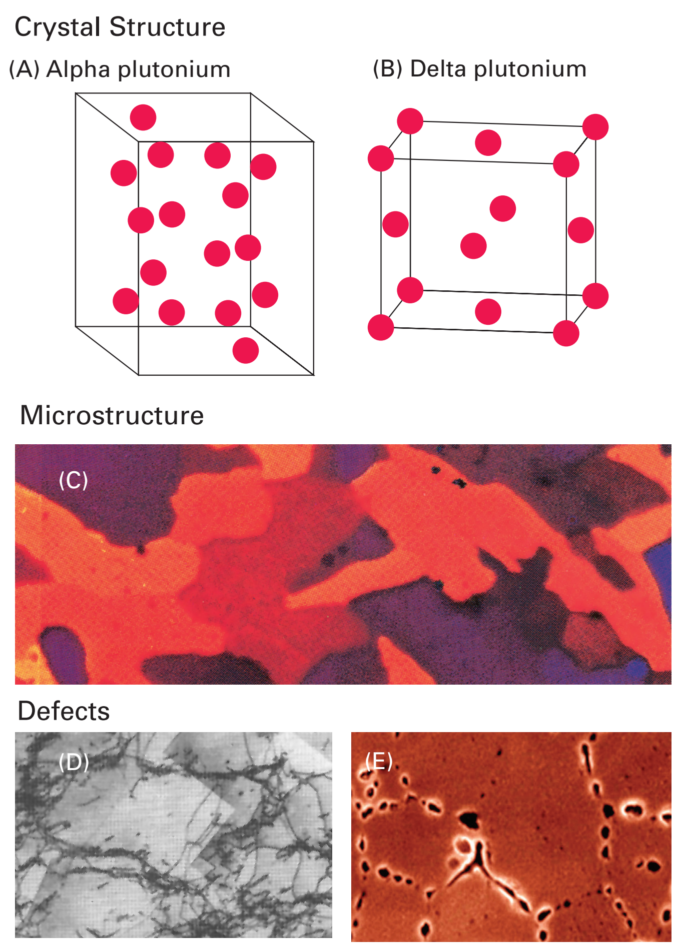
"We're looking at a very different approach to materials research," says John Sarrao, project lead of the MaRIE effort, "a much more complete integration of experiment, theory, simulation, and fabrication than has ever been done before."

Plans for MaRIE call for a complex of three facilities and two particle accelerators, with the accelerators—the beating hearts of the complex—providing high-energy beams of protons, electrons, or x-rays for experiments. The beams will serve as common links between the facilities, create some of the extreme environments, and most important, provide scientists with state-of-the-art tools, such as proton microscopy and an x-ray free-electron laser (XFEL), for interrogating samples. Initially, MaRIE will focus on materials and environments relevant to national security, with an emphasis on energy security. Each facility will play a role in achieving that focus.

The Making, Measuring, and Modeling Materials Facility (M4) is where new samples will be fabricated as well as characterized before and after they're tested in extreme environments. The facility will also house a cadre of theory, modeling, and computation (TMC) experts who will use MaRIE data to validate computer simulations and inform the next generation of materials models.

The Fission and Fusion Materials Facility (F^3) (pronounced "eff cubed") will specialize in creating neutron environments to mimic what's expected in advanced reactors. The Laboratory has already been a pioneer in nuclear-reactor design and safety and has a strong interest in using MaRIE to develop materials for nuclear power. Researchers will be able to interrogate a sample in situ, using the XFEL or other photon sources.

The third facility, the Multi-Probe Diagnostic Hall (MPDH), will be well suited to the study of materials for national security. There, samples will be hit by shock waves or subjected to other dynamic extremes and probed by the XFEL for analysis of the sample's interior with atom-scale resolution (better than one-billionth of a meter). Simultaneously, researchers will be able to use proton microscopy to make images (similar to an x-ray image) of larger features inside the sample and/or do spectroscopy on the sample's surface.



The bulk properties of a material, say, plutonium (Pu), are determined by a combination of its crystal structure (atom-scale), microstructure (micron-scale), and defects (atom-to-bulk scale). (A) Plutonium has six distinct solid-state crystal structures, or phases. The complex, room-temperature alpha phase makes the metal brittle. (B) The high-temperature delta phase makes the metal ductile. (C) This micrograph shows several Pu grains. The different colors indicate different orientations. (D) The threadlike lines are dislocation defects that run through the Pu grains. (E) Plutonium decays naturally by emitting helium nuclei (alpha particles), and helium gas slowly accumulates within the metal. The dark bubbles are voids filled with helium gas. Such voids can affect the thermal conductivity of the metal.

Extreme Matters

Why is MaRIE focused on extreme environments? Because operating at the extremes opens the door to new solutions, especially in energy security.

It is estimated that the already-enormous global need for electric power—approximately 15 billion-billion watts (15 terawatts)—may *double* within the next 40 years because 2.5 billion people will be added to the planet and because China, India, and other countries will continue their steady industrialization. The immense deficit between the energy we'll need versus the energy we currently produce requires full development of every known energy source, from fossil fuels to renewables to nuclear fission and fusion (although commercial fusion power is still several decades away).

One way to ease the situation is to increase the efficiency with which electricity is generated. The standard coal-fired power plant, for example, uses the heat from burning coal to convert water into high-pressure steam, which spins a steam turbine that turns an electric generator. The plant's efficiency would nearly double if the temperature of the steam were increased to around 750 degrees Celsius and its pressure doubled to about 380 atmospheres, but pressure vessels inside the boiler (where the water-to-steam conversion takes place) would fatigue and burst. Developing stronger high-temperature steel would remove one barrier to making more than 50,000 of the world's coal power plants burn less coal.

Similarly, next-generation nuclear reactors will be designed to achieve higher fuel efficiency and produce far less long-term nuclear waste because they'll run nearly 3 times hotter than today's reactors and produce 10 times the neutron flux. Existing structural materials or nuclear fuel claddings could not survive such extreme conditions but instead would become brittle, swollen, and structurally unsound. Next-generation reactors will require next-generation materials.

Renewable energy resources such as solar and wind power also present some formidable material challenges, with needs for lower-cost, higher-efficiency photovoltaic materials and stronger wind turbine blades. And what's generally not appreciated is that using renewable energy sources is often tied to extreme chemical and electric-field environments.

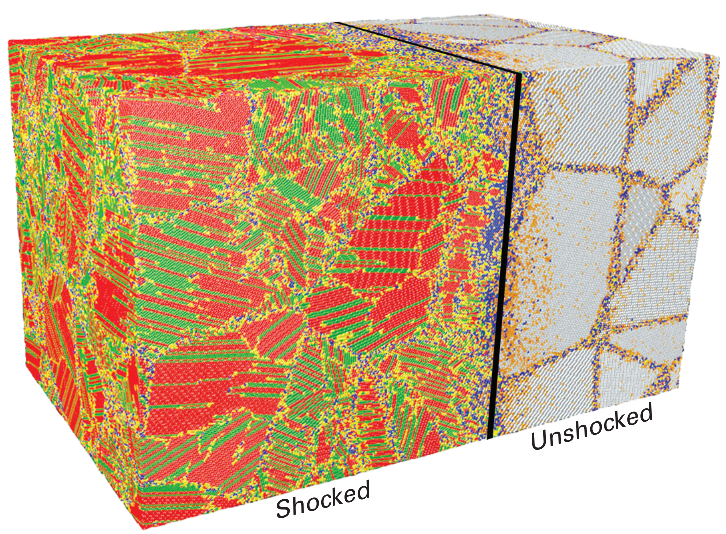
For example, energy storage is crucial if solar or wind power is to be a reliable source of electricity. For small-scale systems, batteries are often the storage medium of choice. A battery stores energy by changing the oxidation state of a metal electrode through processes that are intrinsically extreme—chemical bonds get ripped apart. Indeed, the electric field near the electrode's surface is more than 10,000 times greater than the field in a lightening bolt. Unfortunately, charging a battery also changes the metal's surface structure, and a battery loses the ability to be recharged because of repeated structural changes.

"Maybe there's a way to build a better battery," says Mark McCleskey, one of MaRIE's technical leads. "With the ability to image the surface structure, scientists at MaRIE could examine the electrochemical interfaces to see microscopically why breakdown occurs, information that can help us build more-durable high-capacity energy-storage devices."

Maintaining the Nuclear Arsenal

MaRIE will also help scientists fulfill the Laboratory's mission of maintaining the nation's nuclear deterrent. Furthermore, on April 6, 2010, the Obama administration released its Nuclear Posture Review, which establishes U.S. nuclear policy for the next 5 to 10 years. In a follow-up commentary, Vice President Joe Biden wrote that "although we will not develop new warheads or add military capabilities as we manage our arsenal for the future, we will pursue needed life-extension programs so the weapons we retain can be sustained."

Los Alamos plays a large role in the life-extension programs, including evaluating the safety and reliability of the weapons. Radiation emitted by plutonium and uranium components in the weapons causes many parts to age at an accelerated pace, so one aspect of life extension involves replacing various weapon parts. Some of the original parts were manufactured more than 30 years ago, so new ones will likely be manufactured differently and be made from different materials. In the extreme environment of an exploding weapon, what guarantee is there that those new parts will function as intended?



"In the absence of nuclear testing, such guarantees can come about only through advanced computer simulations that, closely coupled with experiment, can predict the outcome of detonating a weapon," says Deputy Associate Director of Weapons Mary Hockaday. "Those simulations must account for any changes that might happen to a part when it sits for years in a radiation environment. Data from MaRIE could tell us how the microstructure evolves in that environment; if we know that, we know a lot."

Microstructure

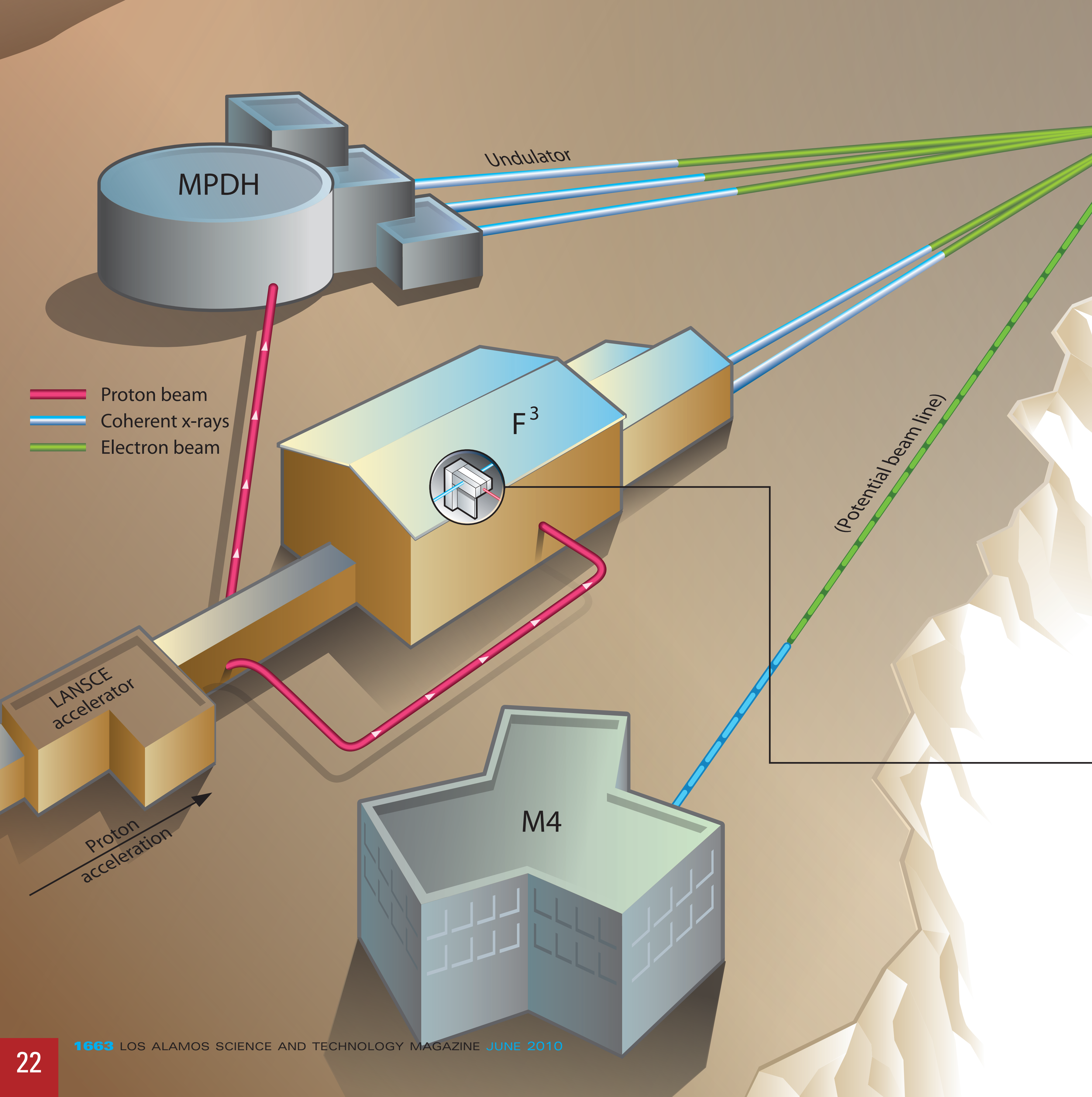
A material's microstructure refers to structural features—crystal grains, grain boundaries, defects—that are usually on the order of a millionth of a meter in size (micron scale). Explicitly, a metal forms crystals and, under the right conditions, can be a single crystal, its atoms all sitting at precise positions in an imaginary lattice. Normally, however, it will be polycrystalline, its

Continued on page 24

Above: Los Alamos' Tim Germann and co-workers recently conducted a simulation of phase transitions in a polycrystalline iron sample. Initially, in a body-centered-cubic crystal phase (gray with yellow boundary), the sample was shocked, resulting in primarily a low-symmetry, hexagonal-close-packed phase (red) with some twinning (green). The challenge is to understand what controls the evolution of these phases.

A Look at MaRIE

MaRIE will be the first materials research center to have high-energy, high-repetition-rate, coherent x-ray capability along with charged-particle imaging. It will create any number of extreme environments and allow in situ measurements of a sample.



MaRIE will have two accelerators.

The LANSCE proton accelerator *(existing) will provide a high-current beam of 800-megaelectronvolt protons for irradiating samples and generating neutrons. The protons can also be used for proton microscopy, which can map density variations within a sample. Proton microscopy is uniquely suited to imaging micron-scale voids within dense metal and to following void formation and evolution.*

The electron linear accelerator *(proposed—only the beam line is shown here) will create a pulsed beam of relativistic electrons that, when sent through a long line of magnets known as an undulator, will emit coherent x-rays that can image the microstructure in the sample's interior. The accelerator/undulator combination is commonly called a free-electron laser. MaRIE's would be a high-energy x-ray free-electron laser (XFEL).*

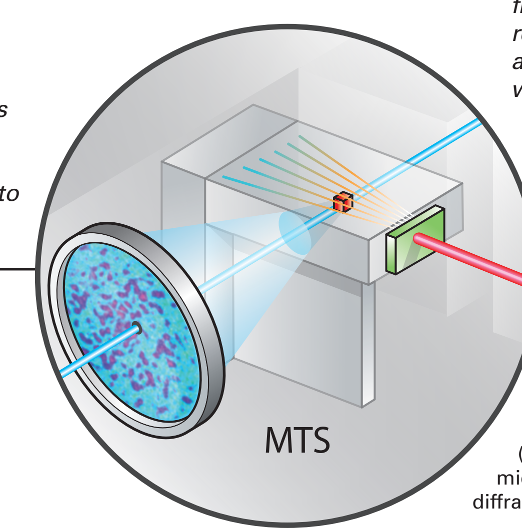
MaRIE will have three experimental halls.

In the Multi-Probe Diagnostic Hall (MPDH) *(proposed), samples will be exposed primarily to high-stress environments. The XFEL and proton beams will be directed to any of several user stations and trained simultaneously on a single sample to correlate what's happening to the sample's atoms and to its microstructure. Standard laser or electron diffraction and scattering techniques will measure surface and bulk-scale properties.*

Making in situ measurements with different size (or time) resolutions simultaneously will make the MPDH unique among materials facilities and will be extremely valuable. For example, nanometer-size dislocations within a material can coalesce into cracks 100 nanometers long, which over time (seconds to years) grow into visible fault lines.

The Fission and Fusion Materials Facility (F^3) *(proposed) will be unique in that it will be able to create a variety of high-flux, high-energy neutron environments that will mimic the extreme neutron environment in next-generation fission and/or fusion reactors. Protons from the LANSCE accelerator will be directed to a tungsten target in the Materials Test Station (MTS) (currently under construction) to generate the neutrons. Scientists at F^3 will use photons to study samples in place.*

The Making, Measuring, and Modeling Materials Facility (M4) *(proposed) will enable controlled synthesis of complex materials (including chemical synthesis, thin film and crystal growth, and microstructural processing) and nondestructive, multiscale characterization of a sample's thermal, mechanical, and electrical properties. Characterization during synthesis will permit control of the nucleation and growth of material defects and interfaces. Materials can also be characterized during exposure to extreme environments (scaled down from those at F^3 and MPDH), and researchers will be able to watch defects and interfaces evolve in extremes. M4 will also have a theory, modeling, and computation (TMC) centerpiece and will serve as a gateway to other Laboratory capabilities.*



Schematic representation of an experiment being conducted at F^3. The high-energy proton beam (pink) will enter the building and strike a tungsten target (green), producing copious neutrons with energies similar to what's produced in an advanced nuclear reactor. The neutrons will strike the target (red cube), and their effect on the sample's microstructure will be found by analyzing the diffracted x-rays (blue circle).

Continued from page 21

interior composed of millions of micron-scale crystals (or grains) of different sizes and shapes, each randomly oriented. The grains are typically riddled with defects, ranging from point defects—an atom sitting where it shouldn't be (an interstitial) or not sitting where it should be (a vacancy)—to larger defects.

The microstructure is important because, in combination with the crystal grains and defects, it determines the material's macroscopic engineering properties, such as its strength, its stability under heat and pressure, or its elastic properties.

"Much of today's materials research is focused on nanoscience because new phenomena arise when quantum mechanical effects dominate observed behavior," says Sarrao. "So people are trying to understand things on the scale of nanometers. But that understanding isn't enough to translate into actual utility. What matters for doing the materials revolution is a material's microstructure and the micron frontier."

The micron frontier is the evocative name given to the gap that exists between understanding how changes to the microstructure occur and knowing how they result in changes to the bulk material. Conquering the frontier will take more than just making micron-scale measurements—materials scientists have been doing that for a long time. Rather, it means knowing where atoms are and are not inside a three-dimensional (3-D), macroscopic solid (as a function of time) and how the atoms move from place to place.

The tool that can perform that minor miracle is the XFEL, a technology that is just now becoming available. The two current XFELs, the Linac Coherent Light Source in California and the European XFEL in Germany, will begin to revolutionize materials sciences because they allow users to watch chemical bonds break and form, but only in highly prepared samples that are often so thin as to be essentially two dimensional (2-D). Such samples are once-only affairs; they vaporize from the heat that's generated when they absorb or scatter too many high-energy x-rays.

Los Alamos scientists are working hard to develop a next-generation XFEL that will produce x-rays with 5 to 20 times higher energy than either the Californian or European machine. Higher-energy x-rays (known as very-hard x-rays) can penetrate dense, multigranular metal samples that are thick enough to exhibit real-world properties.

Through a technique known as coherent x-ray diffractive imaging, already demonstrated on thin samples, researchers may be able to make 3-D images of the atoms making up the thick sample's microstructure.

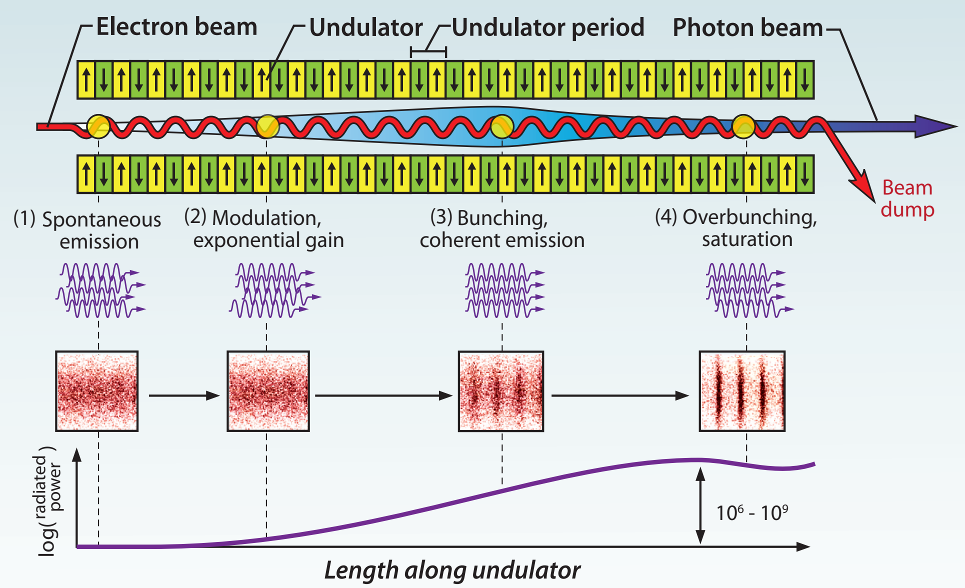
"Fewer very-hard x-rays will be absorbed by the sample, and any heat that does get deposited from x-ray interactions will be distributed among more atoms," says Cris Barnes, the MPDH technical lead. "The result is that even thick samples will survive long enough to be probed several times."

Furthermore, because XFELs can take a series of rapid "snapshots" (a couple every billionth of a second), scientists will be in a position to follow transient yet critically important processes such as the introduction and early development of environment-induced damage.

A Free-Electron Laser

A free-electron laser (FEL) generates intense, highly monochromatic (single-color) light. Electrons are accelerated to nearly the speed of light, then sent through a structure of alternating magnets called an undulator. The electrons wiggle back and forth as they pass over the magnets, emitting light at a frequency that depends on the undulator period, the magnets' strength, and the electron's energy. The frequency increases when the electron energy increases.

A pulse of coherent x-rays can be produced if a pulse of highly energetic electrons is sent through a very long undulator (80–100 meters or longer). Remarkably, the light from each pulse is a million to a billion times brighter than a pulse from a conventional x-ray storage ring. The reason is a nonlinear process called self-amplified spontaneous emission (SASE). With reference to the figure: (1) the electrons (red dots) spontaneously emit x-rays, (2) interactions with those x-rays cause the electrons to start bunching, increasing the pulse brightness, (3) electrons bunch at a spacing equal to the x-ray wavelength, so all x-rays are emitted in lock-step with each other, and (4) the bunching gets so tight that an instability develops, and the electrons begin to debunch. A single pulse emits enough photons to image a microscopic volume inside a dense solid.



"SASE was first demonstrated in the infrared at Los Alamos in 1997," says Los Alamos XFEL designer Dinh Nguyen. "Today's XFELs use the same SASE principle." Nguyen and colleagues are developing a preliminary design for the first XFEL that can produce very high energy, 50–100-keV x-ray pulses needed for penetrating dense, thick samples. With x-ray pulses coming less than a nanosecond apart, one can create a movie of fast, dynamic processes.

Unfailing Materials

As an example of MaRIE science, consider a metal support structure inside a nuclear reactor and the general sequence of events that occurs after neutron bombardment causes atomic-scale defects in the material.

A neutron penetrates the metal, strikes an atom, and like a cue ball hitting a rack of billiard balls, initiates a cascade of atom displacements. The displacements take place within a volume much smaller than a crystal grain. In nearly no time (about 10 picoseconds) the cascade ends, and most of the displaced atoms find new homes within the grain's crystal structure. But some don't, and the grain harbors a nanoscale cluster of interstitial atoms and vacancies.

The high temperature inside the reactor allows the interstitials to migrate and coalesce into larger defects, while the vacancies merge to become voids. The defect structures continue to merge with others until the damage has grown into micron-scale cracks and voids.

Surprisingly, recent theoretical research at Los Alamos suggests a way to design a material that can "heal" itself before the damage reaches the micron scale. Simulations show that if the initial impact occurs inside a crystal grain close to a grain boundary, the boundary will trap and hold onto some of the homeless atoms. Later it will "unload" these excess atoms into the body of the grain, where they will annihilate vacancies. Thus, nanocrystalline materials with very small crystal grains (and a high grain-boundary to grain-body ratio) may be highly resistant to neutron damage.

Without MaRIE, it would be very difficult to confirm that result experimentally. But once the F^3 facility is built, a nanocrystalline alloy can be placed in it and bombarded with fast neutrons. Training the XFEL on the sample while it's being irradiated, researchers could image the atom displacements and then record the exact distribution of defects that remain after localized melting and recrystallization have occurred. A series of images would show how the defects diffuse and coalesce into nanoscale and micron-scale clusters and to what extent the atoms are "loaded" onto the grain boundary. More images would reveal the extent of unloading and self-healing.

The integrated MaRIE facility would then provide the tools to purposely manipulate the sample's microstructure and accelerate materials development. Before long, high-performance computing simulations of the data could be compared in real time with the real thing, and the cycle would repeat until the birth of a new, neutron-resistant material.

The Beginning

Sometime in the rapidly approaching future, a switch will close and coherent x-rays and a high-power proton beam will simultaneously strike a thick sample in the MPDH: MaRIE will be fully operational. Thanks to breakthroughs in experimental characterization, theoretical modeling, and multiscale simulation on ultrafast supercomputers, scientists will then have an unprecedented opportunity to address what were once considered to be impossible materials problems. And although large facilities like MaRIE can take 10 or more years to build, plans for it can be driven by ideas scientists are having now about the future. Currently, the MaRIE design and program remain flexible and will continue to incorporate new research ideas. ❖

—Jay Schecker
(contributions from Anthony Mancino)

Above: The leaders of the MaRIE project (left to right): Mark Bourke (F^3), Mark McCleskey (M4), Turab Lookman (TMC), Cris Barnes (MPDH), and John Sarrao (project lead).

ON THE FOREFRONT

At the Chemical Movies

During a chemical reaction, a molecule can go through some changes; for example, its atoms can change position or the molecule can break up or become part of other molecules. To see exactly what happens, one must precisely track the positions of all the atoms in a molecule as the reaction unfolds.

Such a technique does not yet exist, but Los Alamos theorists Suxing Hu (now at the Laboratory for Laser Energetics, University of Rochester) and Lee Collins, along with Barry Schneider of the National Science Foundation, recently used supercomputer simulations to explore a technique that could one day do the trick.

The technique's potential was proved experimentally in 2005 by researchers at the University of Arizona. The main result of that experiment was a plot of the distance, as a function of time, between two iodine atoms drifting apart after a laser pulse split an iodine molecule in two. This plot is now referred to in the scientific literature as a "movie."

To make the movie, the Arizona researchers first hit an iodine molecule sporting an extra electron with a 100-femtosecond pulse of infrared laser light. (A femtosecond is a million-billionth of a second.) The pulse broke the molecule into an ordinary atom and an atom with an extra electron (an ion). Then the researchers hit the atom/ion pair with another 100-femtosecond pulse, this time of ultraviolet laser light, to eject the extra electron.

The movie was possible because a subatomic particle such as an electron can behave like a wave and because any wave can be diffracted (scattered) by two closely spaced objects to produce multiple waves. When these waves contact (interfere with) each other, they create a distinctive interference pattern of regularly spaced bright spots that can be analyzed to reveal the distance between the two objects that caused the scattering.

In the Arizona iodine experiment, the electron wave was diffracted by the nuclei of the two iodine atoms produced when each iodine molecule was split apart. The experiment involved huge numbers of split iodine molecules, resulting in huge numbers of ejected electrons that, after being diffracted, impinged on a flat-plate detector some distance from the scene of the molecular crime to form an interference pattern. Analysis of the pattern revealed the distance between the two iodine nuclei.

By running the experiment many times, while systematically increasing the time between the infrared and ultraviolet pulses, the researchers ended up with a series of interference patterns that showed—one pattern (one "movie" frame) at a time—the increasing distance between the two atoms as they drifted apart.

This arcane cinematic adventure probably wouldn't win an Academy Award, but the experiment proved the technique's very-real potential for precisely capturing the motion of individual atoms. However, some features of the experiment could be altered to make it more suitable for making movies of chemical reactions of more general interest. The theorists took that fact into account when designing their supercomputer simulations.

For one thing, the spatial resolution of the experiment, the smallest distance (between the two iodine atoms) that could be captured in one frame, was about 1 nanometer (one-billionth of a meter), acceptable for the iodine experiments but too big for chemical movies involving molecules that contain hydrogen, such as hydrocarbon molecules or biomolecules. The distance between adjacent hydrogen atoms is about 0.1 nanometer.

The spatial resolution can be sharpened by increasing the energy of the ejected electron, whose maximum energy is the energy of the light particle (photon) in the pulse that ejects it, at least for the most common case, in which a molecule absorbs only one photon.

To make the spatial resolution about 0.1 nanometer, the photon energy would need to be a few hundred electronvolts (eV).

Moreover, although the 100-femtosecond ultraviolet pulse in the Arizona experiment was short enough to stop (as a camera "stops") the motion of the relatively ponderous iodine atoms, hydrogen atoms are distinctly "nonponderous." As the lightest atoms, hydrogen atoms move much more quickly than iodine atoms do. To stop their motion, the pulse would need to be a minimum of a few femtoseconds.

Taking all these considerations into account, the theorists decided to simulate the response of a positively charged hydrogen molecule to an intense, ultrashort pulse of x-ray laser light. A positively charged hydrogen molecule is the simplest molecule imaginable: one electron and two protons, the protons being the molecule's two atomic nuclei. Even so, each simulation required 15 hours and 480 processors on Los Alamos' Coyote supercomputer. The theorists have since run simulations on 1,000 processors on Los Alamos' Lobo supercomputer and 5,000 processors on the National Science Foundation's TeraGrid computer at Oak Ridge National Laboratory. The method seems to scale well with increasing numbers of processors.

In the simulations, the x-ray pulse ejected the electron from the molecule, and the molecule's two protons diffracted the electron's wave function.

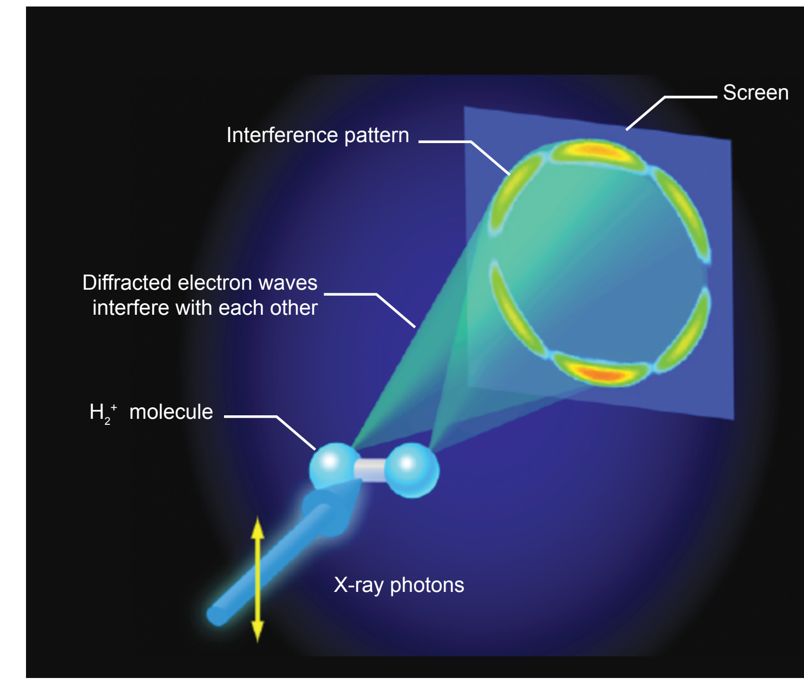
The theorists found that when the photon energy of the x-ray pulse was set high enough (greater than 350 eV), a clear interference pattern was produced that resolved the distance between the molecule's two protons—0.133 nanometer. This is about the shortest distance between two atoms in any molecule.

Such exquisite resolution is possible because the ejected electron (with an energy of 350 eV) behaves like a wave with a wavelength about equal to the distance between the two protons.

Moreover, the duration of the simulated x-ray pulse was so short (one-quarter or one-half a femtosecond) that it could easily freeze the relative positions of the protons in time, producing a very clear interference pattern.

In addition, the x-ray pulses in the simulations were of very high intensity. That fact made it easier to image the protons' positions because the electric field of each pulse was so high that it quickly pulled the electron from its molecular orbit and, as the field reversed direction several times during the pulse's duration, drove the electron back and forth through the molecular interior before it was ejected. During its intramolecular trip, the electron passed near the protons many times, so in effect, the protons diffracted the electron's wave many times, producing a highly intense interference pattern especially easy to measure.

A few years from now, it's likely that several pulsed x-ray sources now being developed will have the photon energy, pulse duration, and beam intensity required to perform experiments like the simulated ones.



The electron ejected from a positively charged hydrogen molecule (H_2^+) by an x-ray photon is diffracted by the molecule's two protons to form an interference pattern. The ejected electron's angular distribution gives the distance between the two protons. The blue arrow shows the direction of x-ray-photon propagation. The yellow arrow shows how the photon's plane of polarization is oriented.

However, making useful chemical movies will require an important addition. In the simulations, only one laser pulse was used—to produce a single interference pattern. To make a multiframe movie, two pulses will be required. Similar to the iodine experiment, researchers will use the first pulse to initiate the chemical reaction and the second to liberate an electron to form a diffraction pattern. They'll also need to increase the time delay between the two pulses in successive repetitions of the experiment, as in the iodine experiment. ❖

—*Brian Fishbine*

SPOTLIGHT

Picturing Greenhouse Gases

Most climate scientists think global warming is real and that a lid should be put on greenhouse-gas emissions. Manvendra Dubey, who heads a Los Alamos team at the forefront of monitoring such emissions, certainly thinks so.

"The world must get serious about global warming and develop international treaties to limit greenhouse-gas emissions," says Dubey. "And we need an international body to verify that all signatories are in compliance with treaties and to warn countries that are out of compliance to change their ways."

A key element of implementing such an agenda is the ability to sensitively and accurately measure the atmospheric concentrations of greenhouse gases over any spot of interest and to attribute excess concentrations to specific sources. Such a capability does not yet exist, but the Greenhouse Gases Observing Satellite (GOSAT) is a first step to acquiring it.

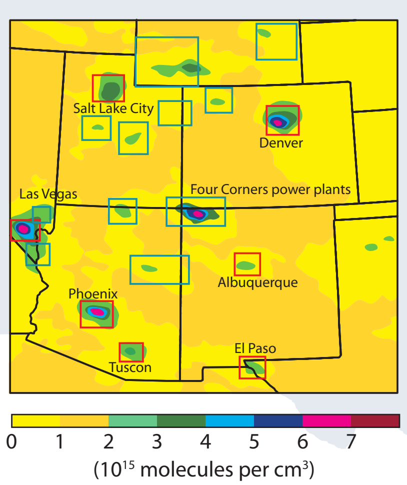
Launched in January 2009, GOSAT is the first satellite to measure, beneath its orbit, atmospheric concentrations of carbon dioxide (CO_2) and methane, two major greenhouse gases. Dubey's team will ensure that GOSAT's measurements can be trusted.

Accordingly, Los Alamos National Laboratory and the Japanese Exploration Space Agency, which launched GOSAT, have signed an agreement: Dubey's team will have access to the satellite's raw data, and the Japanese agency will aim the satellite's gas-measuring spectrometer at the Four Corners area, where Arizona, Colorado, New Mexico, and Utah meet. The Four Corners area is home to two large coal-fired power plants. GOSAT will pass over the area every few days, measuring CO_2 and methane concentrations from space. (In addition to the CO_2 emitted by the power plants, the area's oil and gas wells could emit measurable amounts of methane.) Simultaneously, Dubey and his team will use an ultrahigh-resolution, sun-tracking spectrometer on the ground to measure atmospheric gas concentrations every 5 minutes throughout the day. Their ground-based measurements will validate GOSAT's space-based ones.

The ground-based spectrometer will also be able to measure concentrations of NO and NO_2, pollutants that make ozone, another greenhouse gas. The Four Corners plants jointly emit more of those nitrogen compounds and CO_2 than any other point source in North America. In addition to validating GOSAT measurements, the ground-based measurements will help clarify how greenhouse gases disperse from major point sources. The results will help the United Nations' Greenhouse Gas Information System (GHGIS) develop ways to verify the accuracy of nations' reports of their emissions, reports that will be used to determine baselines for international climate treaties.

Los Alamos conceived the GHGIS initiative. Other national laboratories and government agencies are also participating.

—Brian Fishbine



Major cities (red boxes) and major power plants (blue boxes) emit high NO_2 concentrations 2 to 10 times the background concentration, as shown here in satellite-measured data from the Four Corners area.

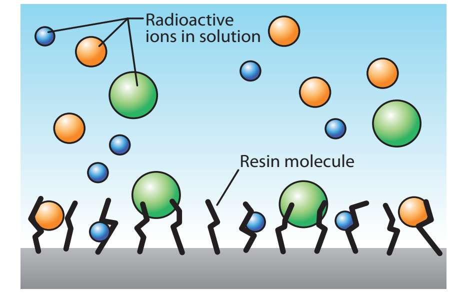
Rapid Screening for Radiation

In a major radiation emergency, medical workers would need to quickly screen thousands of people to determine if they have inhaled or ingested significant amounts of radioactive material. Such screening would indicate if treatment is needed or, more likely, help allay peoples' fears that they have received a damaging dose of radiation.

However, existing screening methods are too slow and costly to be used in such an emergency. A person's internal radiation dose is often estimated by measuring the amounts of radioactive uranium, plutonium, and americium in that person's urine, which traditionally takes from 8 hours to 5 days and costs about $1,000.

A simple method developed at Los Alamos by Dom Peterson and co-workers could yield results in as little as 5 minutes for about $10. For this reason, the Centers for Disease Control and Prevention (the CDC)—a key responder in a radiation emergency—is seriously interested in the technique.

The radioactivity of a urine specimen is often determined by measuring the rate(s) at which the radioactive isotopes (existing as ions in the urine specimen) emit alpha particles. Many radioactive isotopes are alpha emitters, including those that could be used to make dirty bombs or that could be widely dispersed in other sorts of radiation emergencies—such as an accident at a nuclear power plant or the explosion of an improvised nuclear device or stolen nuclear weapon. Measuring alpha-particle emission rates normally takes only a few hours, but preparing the specimen for that measurement takes time.



First, a chemical is added to the specimen to precipitate all the ions present—including those of the alpha emitters. Then the precipitate is dissolved in acid. The resulting solution is then divided into several portions, and each portion is put through a separate "ion-exchange" column, each packed with small resin beads that absorb alpha-emitting ions on their surfaces. (Ion-exchange columns are also used to soften water by selectively absorbing the ions that harden it.)

The ions collected in a column are flushed from it in solution and deposited on a surface that is then dried and placed in an instrument that counts the emission rate for the particular ion absorbed in that column. Different solutions are used on different columns to flush out specific ions. To assay for different alpha-emitters, the flushing/counting procedure is repeated for each column.

The new Los Alamos technique is much simpler. First, a "planchette" (French for "little plank")—a thin stainless-steel disk about an inch and a half in diameter, coated on one side with a thin mixture of ion-exchange resin and plastic—is stirred in a solution of urine and nitric acid or sodium nitrate. During stirring, some of the radioactive ions in solution form chemical bonds with resin molecules deposited in the planchette's thin film. After a rinse in deionized water and air drying, the planchette is placed in an alpha-spectrometer, which measures the energy distribution of the alpha particles emitted by the radioactive ions in the thin film.

Above: Radioactive ions are first trapped by small resin molecules deposited on a thin planchette and then assayed by alpha spectroscopy.

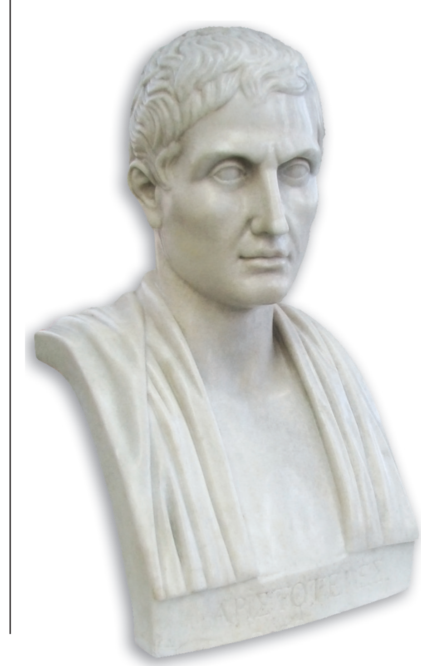
The energy distribution for a particular alpha-emitter has a narrow peak at a unique energy. The position of the peak identifies the alpha-emitter, and the height of the peak measures the amount of the alpha-emitter present. Thus, alpha spectroscopy of a planchette allows one to quickly and simultaneously assay all of the alpha-emitters present in a specimen. Moreover, alpha spectroscopy is relatively inexpensive to do, so hundreds of spectrometers could be operated in parallel to analyze the thousands of planchettes resulting from a radiation emergency.

—Brian Fishbine

Computing Happiness

Forget just wanting to be happy. According to Aristotle, it's your ethical responsibility. Marko Rodriguez, formerly of the Laboratory's Center for Nonlinear Studies, thinks computers should help you fulfill that responsibility.

Aristotle's idea, called eudaemonia, Greek for "good spirit," was that society benefits when everyone successfully pursues his or her talents and rational desires (Aristotle was big on being rational).



Aristotle (384–322 BC)

Rodriguez is designing eudaemonic algorithms for computer systems to use in directing us to whatever fulfills us.

"Eudaemonic systems are the evolutionary goal of today's recommender systems," he says. "The most ambitious ones would satisfy a need before the need is even felt."

Anticipating needs is already what recommender systems do. Select a book from Amazon or a movie from NetFlix and you get a list of other things you might like. What limits today's recommender systems is the cache of resources they can access.

"They rely on a single 'silo' of data," Rodriguez explains, "a particular niche of information, such as movies and books." And they can't cross niche boundaries; they can't, for example, recommend a place to live based on a book or movie you chose. A eudaemonic system would connect its user to resources related to all aspects of life, and for that, it would reach beyond the silo.

It's already happening. More and more datasets on the Web are open, freely available and not tied to a particular application. Open datasets can be linked in what Rodriguez calls a cloud, with accessible links ranging across a multirelational network: a network in which datasets are linked according to something they have in common.

The basis of such a network is the resource description framework, or RDF, a computer language that identifies relationships between resources rather than just pinpointing a resource's location (address) on the Web. RDF has already been used to create a "linked data cloud" of 89 datasets supplied by providers who have collaboratively integrated their data. Rodriguez, who now works for AT&T Interactive, a creator of search products and services, predicts that the linked data cloud will grow. For future seekers of a happy life, that cloud will have a silver lining.

—Eileen Patterson

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