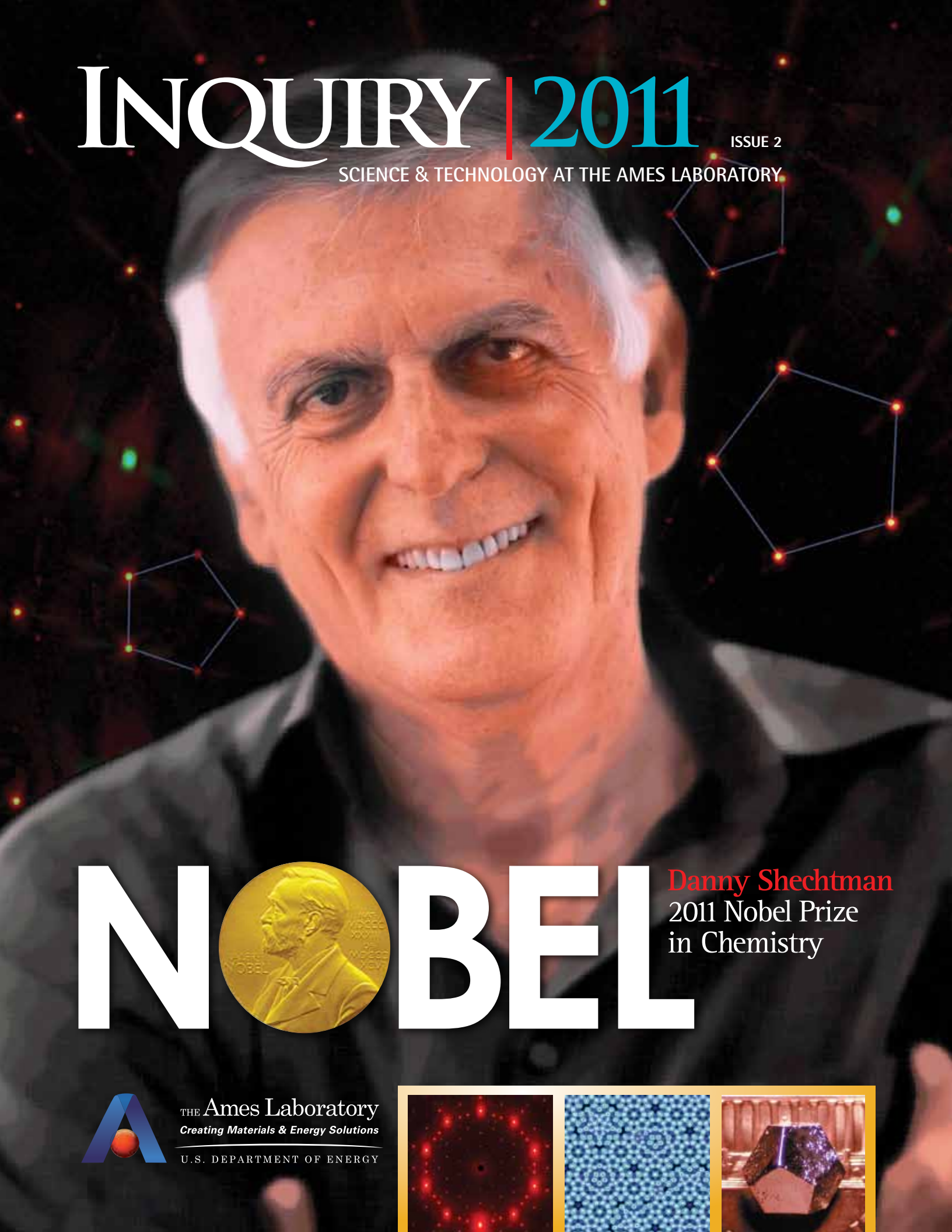
# INQUIRY | 2011

ISSUE 2

SCIENCE & TECHNOLOGY AT THE AMES LABORATORY



# NOBEL

## Danny Shechtman
## 2011 Nobel Prize in Chemistry

THE Ames Laboratory
*Creating Materials & Energy Solutions*
U.S. DEPARTMENT OF ENERGY

# INQUIRY

The Ames Laboratory is a U.S. Department of Energy national laboratory seeking solutions to energy-related problems through the exploration of chemical, engineering, materials and mathematical sciences, and physics. Established in the 1940s with the successful development of the most efficient process to produce high-purity uranium metal for atomic energy, Ames Lab now pursues much broader priorities than the materials research that has given the Lab international credibility. Responding to issues of national concern, Ames Laboratory scientists are actively involved in innovative research, science education programs, the development of applied technologies and the quick transfer of such technologies to industry. Uniquely integrated within a university environment, the Lab stimulates creative thought and encourages scientific discovery, providing solutions to complex problems and educating and training tomorrow's scientific talent.

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Inquiry is published biannually by the Ames Laboratory Office of Public Affairs. Iowa State University operates the Laboratory for the U.S. Department of Energy under contract DE AC02 07CH11358.

U.S. DEPARTMENT OF ENERGY | Office of Science

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***Cover:*** *Danny Shechtman's Nobel Prize in Chemistry for the discovery of quasicrystals was also the impetus behind discoveries by other Ames Laboratory scientists. Pat Thiel's work on surface structure resulted in the development of the blue, five-fold symmetry pattern shown in the small inset. Paul Canfield helped prove the existence of quasicrystals by growing a large, single crystal of holmium-magnesium-zinc (Ho-Mg-Zn) that clearly shows five-fold symmetry. Alan Goldman captured the X-ray diffraction image of a scandium-zinc quasicrystal that shows the same 10-dot pattern that Shechtman first witnessed. A larger version of Goldman's image appears on the* ***back cover****.*

# From the Director

AS THIS ISSUE OF INQUIRY WAS BEING PUT TOGETHER, we learned that our colleague Danny Shechtman had been awarded the 2011 Nobel Prize in Chemistry for the discovery of quasicrystals. This stunning discovery was based entirely on a single observation made using a transmission electron microscope - one of the workhorse tools of materials characterization. Much controversy followed the initial discovery, and the Ames Lab played a large role in settling the arguments in favor of the assertion that materials had been discovered with five-fold symmetry. Some of the iconic images from this work are shown as insets on our cover. The story of the discovery, and eventual acceptance of quasicrystals, rests very much upon sophisticated, advanced materials characterization, sometimes using techniques invented or modified "on the fly" to cope with the challenges of the unexpected discovery.

The Ames Laboratory has a unique ability to create materials. Theory, computation and not a little scientific instinct all come together here and allow us to invent new materials for energy applications. The Ames Lab also has world-leading capabilities for making the materials that it designs, to prove that the designs work. (We try very hard not to contribute to the ever-growing list of theoretically wonderful materials that cannot actually be made.)

But once you have designed a new material and made some of it, what do you do next?

Materials characterization is used to determine the properties of a material, from its chemical composition to its structure, its thermodynamic, mechanical, electrical, optical, magnetic and other properties, its chemical properties, and even the details of how electrons interact with each other inside it or on its surfaces.

Because we make materials that sometimes have novel or exotic properties, we also have a high investment in world-leading materials characterization to probe and explore those properties. When the Ames Lab first started, its job was to purify uranium metal, and it quickly developed chemical-analysis tools to characterize the purity of the product, resulting in some of the most sensitive chemical analysis techniques used in the world today. As we focus on ever more complex materials, we still work on a parallel path to develop the capability to characterize them. The result is that we have world-leading research on tools like solid-state nuclear magnetic resonance (see Inquiry, 2009 issue 2) and angle-resolved photo-electron spectrometry.

*The race to create new materials produces a corresponding race to develop better ways to characterize them, and one of the directions that this race leads is toward ever-increasing sensitivity.*

In this issue of Inquiry, we are providing an update on some of the materials characterization tools and techniques under development at the Ames Lab. These provide exciting new capabilities, such as studying the behavior of single layers of atoms on crystal surfaces, seeing the internal workings of materials as they deform, or seeing how materials behave inside living cells, among many others.

The race to create new materials produces a corresponding race to develop better ways to characterize them, and one of the directions that this race leads is toward ever-increasing sensitivity. If you design materials atom-by-atom, you need to characterize them at a corresponding level, but it is very hard to see a single atom if your specimen is shaking, even by just a tiny amount. In pursuit of ever-greater sensitivity, we are beginning the design of a new building that will house ultrasensitive characterization equipment in an environment that will have ultralow vibration, electrical interference and magnetic interference, allowing the most sensitive kind of analysis anywhere on earth. Funding for the planning phase for this sensitive instrument facility has been received from DOE, and we are hard at work identifying a suitable site, developing plans and learning from our sister labs, Argonne National Laboratory and Oak Ridge National Laboratory, which have both built similar facilities in the last few years.

*Alex King, Director*

*Tanya Prozorov*

## Prozorov receives DOE Early Career Award

Tanya Prozorov, an Ames Laboratory scientist, will take an unprecedented look at how magnetic nanocrystals grow thanks to a DOE Office of Science Early Career Research award. Prozorov was one of just 65 researchers (21 from the national laboratories) selected from about 1,150 applications to the program, which is designed to bolster the nation's scientific workforce by supporting "exceptional researchers during the crucial early years of their scientific careers when many scientists do their most formative work."

Prozorov's project, "Real-Time Studies of Nucleation, Growth and Development of Ferromagnetism in Individual Protein-Templated Magnetic Nanocrystals," will focus on isolating individual bio-templated magnetic nanocrystals in an attempt to identify mechanisms that control how these crystals form and develop their magnetic properties. The award will provide a total of $2.5 million over a five-year period. (To read more about Prozorov's research, turn to page 14.)

"I am excited about Tanya's project because it promises to answer some really intriguing questions about materials at the nanoscale," says Ames Laboratory Director Alex King. "Winning the funding against steep odds reflects DOE's sense of the importance of the work, and confidence that she can overcome its challenges to get the job done."

## Soukoulis receives honorary degree

Ames Laboratory associate scientist and Iowa State University Distinguished Professor Costas Soukoulis received an honorary doctorate from Vrije Universiteit in Brussels, Belguim. Soukoulis was one of five scientists honored for accomplishments in their respective fields. He received the award during a ceremony held May 25 in Brussels.

## Withers awarded Silvius-Wolansky Graduate Fellowship

Ames Laboratory industrial hygiene manager Jim Withers has been selected for the Silvius-Wolanksy Graduate Fellowship in the Iowa State University Department of Agricultural and Biosystems Engineering. Withers was selected for the fellowship based on his professional involvement in industrial hygiene/safety and his excellent dissertation research.

This fellowship was established to honor the work of G. Harold Silvius and William Wolansky, a long-time professor in industrial education and technology at Iowa State. Silvius and Wolansky were nationally recognized leaders committed to vocational education and training and international programs.

*Jim Withers*

## Thiel serves on ISU Presidential search committee

Ames Laboratory scientist and John Corbett Distinguished Professor of Chemistry Pat Thiel served as a member of the search committee tasked with finding the next president of Iowa State University. The 18-member committee met through much of the summer and narrowed the field to two finalists, with Steven Leath being named the 15th president of ISU on Sept. 27 by the Iowa Board of Regents.

*Pat Thiel*

## Karsjen appointed to National Science Bowl Planning Committee

Ames Lab Public Affairs manager and education programs director Steve Karsjen has been invited to join the National Science Bowl Planning Committee. He will be involved in planning the event's media/public awareness activities.

*Steve Karsjen*

## Ames Lab plays prominent role in superconductor workshop

Ames Laboratory played a prominent role in the 13th International Workshop on Vortex Matter in Superconductors, held in August in Chicago. Ames Lab was one of the sponsors, along with Argonne National Laboratory, the Materials Theory Institute of Argonne, the Institute for Theoretical Sciences of the University of Notre Dame, and the EFRC-Center for Emergent Superconductivity.

In addition, Ruslan Prozorov, Ames Lab senior physicist, served as a co-organizer for the workshop, and Ames Lab physicists Vladimir Kogan and John Clem were part of a special distinguished lecturers symposia and received special citations for their work. Clem also serves as a member of the workshop's international advisory committee.

Kogan was recognized "for pioneering contributions to the vortex behavior of type II superconductors, especially the roles of anisotropy, non-locality, and multiple bands." Clem was cited for his "seminal contributions to the phenomenological theory of vortices in superconductors including the concept of 'pancake' vortices in layered superconductors."

*John Clem*

*Vladimir Kogan*

*Ruslan Prozorov*

## Ames Lab projects receive ARPA-E funding

The Ames Laboratory was selected for funding for two cutting-edge research projects by the Advanced Research Projects Agency-Energy (ARPA-E) program.

The first of the two projects is for research to develop a new class of high-energy permanent magnets using the rare-earth element cerium. Cerium is four times more abundant than the rare-earth element neodymium, which is critical for today's permanent magnets. The research will look at combining other metals with cerium to create a new, powerful magnet with high-temperature stability for electric vehicle motors. Partners in the project will also include General Motors, NovaTorque and Molycorp Minerals.

The $2.2 million research project is for three years and will be led by Ames Laboratory senior metallurgist Bill McCallum, who says General Motors and NovaTorque will evaluate the material for traction motors in vehicles while Molycorp will provide the important materials supply chain and development path for commercialization of these materials.

In the second project, Ames Laboratory scientists will team with Pacific Northwest National Laboratory on research to reduce dependence on critical materials like rare earths by developing a new alternative to rare-earth permanent magnets that use manganese. These manganese composite magnets hold the potential to double the magnetic strength of current rare-earth magnets while using raw materials that are inexpensive and abundant.

## Chumbley elected Fellow of ASM International

Ames Laboratory scientist Scott Chumbley has been elected a 2011 Fellow of the American Society for Metals International. Chumbley was recognized at the ASM awards dinner during the ASM annual meeting on Oct. 18 in Columbus, Ohio.

ASM Fellowship is awarded for distinguished contributions in the field of materials science and engineering and provides a broad-based forum for technical and professional leaders to serve as advisors to the Society. Specifically, Chumbley was cited for "outstanding achievements in recruiting and mentoring of materials science and engineering students, and in the development of web-based SEM technology used by K-12 students worldwide."

*Scott Chumbley*

## Ness honored for 50 years of service

Paul Ness, senior research technician, was honored for 50 years of service to the Ames Laboratory. Ness was one of nearly 30 Ames Lab employees recognized for their years of service completed in 2010 at an awards luncheon held Sept. 22.

Ness joins John Corbett and Karl Gschneidner as the only employees to reach their golden anniversary at the Lab. Ness received a gold watch bearing the Ames Lab logo and a certificate in recognition of his half century of service.

*L-R: Alex King, Paul Ness*

## Yeung Selected as ACS Fellow

Ames Laboratory senior chemist Ed Yeung has been selected to the 2011 class of Fellows of the American Chemical Society. Yeung and the rest of 2011 ACS Fellows were honored at a special ceremony during the ACS National Meeting in Denver on Aug. 29, 2011. The ACS Fellows Program recognizes members of ACS for "outstanding achievements in and contributions to Science, the Profession, and the Society."

*Ed Yeung*

# Battin' a Thousand in SULI Success

BY STEVE KARSJEN

IT WOULD BE HARD TO RIVAL AMES LABORATORY SENIOR scientist Mark Gordon's success rate in attracting Science Undergraduate Laboratory Internship students to graduate school. Since the SULI program's inception at Ames Lab, Gordon has been a program mentor four times. To his great credit, all three of the students he mentored those four years (one of his students participated in SULI twice) are now pursuing PhDs at Iowa State University and are working for him in the Applied Math and Computational Sciences program at Ames Lab. Anyone aware of Mark Gordon's love of the New York Yankees would say team Gordon is batting a thousand.

"Mark Gordon is a shining star when it comes to getting students to see the importance of going on to graduate school," says Steve Karsjen, education programs director for the Ames Laboratory. "I think you'd be hard pressed to find many scientists throughout the entire DOE system who could equal Mark's success rate in this area."

Ames Laboratory's SULI program started in 2005. That first year, the Lab hosted 10 undergraduates from colleges and universities around the country. Now just six years later, a total of 101 undergraduates have participated in the Lab's SULI program, thanks in part to the great scientist/mentors they come in contact with at the Ames Lab and Iowa State. Sponsored by the Department of Energy's Office of Science, the SULI program works to immerse undergraduate students in research settings at DOE's national laboratories in an effort to encourage the students to pursue science, technology, engineering and mathematics, or STEM, careers. SULI students produce research reports, PowerPoint presentations and posters. Students conduct their research with an eye toward writing scientific papers worthy of being published in peer-reviewed journals. To date, Ames Laboratory SULI students have published 14 papers.

Team Gordon's perfect batting average began in 2008 with the arrival of Caleb Carlin, then a junior majoring in physics with a minor in computational chemistry at Michigan Technological University. Upon graduation, Carlin enrolled in graduate school at ISU and began working in Gordon's group. Carlin expects to graduate with his PhD in fall 2014. Ultimately, he says it was Gordon's style and the overall style of the Gordon group that led him back to the Ames Laboratory and ISU following his SULI experience and college graduation.

"The Gordon group is very open and welcoming, always happily answering any question no matter how mundane," says Carlin. "In this Mark leads by example, personally making sure students stay on track. In short, he not only has a mastery of theoretical chemistry but also a mastery of guiding graduate students."

The SULI program itself, but to a larger extent his experience as a SULI student with Gordon and his group in 2010, provided the impetus for the "hard right turn" Justin Conrad made in his post-graduation plans from the College of the Ozarks in Missouri. Prior to completing his first SULI internship, Conrad's intention was to finish his undergraduate degree and pursue an entry-level job as a research chemist, possibly with the military. But that changed when in 2011 the SULI program provided him the option to participate a second year in an internship with Gordon and his group.

"Prior to SULI, graduate school was just a word," says Conrad. "Without Mark's guidance, I would not be here."

Getting students to Ames Laboratory and Iowa State for graduate school takes a coordinated approach that goes beyond simply analyzing a student's background, according to Gordon. First, he says, students must be motivated, "wanting to learn, do cool stuff."

Second, mentors must be nurturing. "If mentors don't nurture, then it's a total turnoff for students," Gordon says.

Finally, comes the student's "background." Gordon contends all of his students are bright, which helps level the playing field in that area, so he says of the three, a student's background comes in last.

Gordon's own background, however, did play a key role in guiding Colleen Bertoni, who participated in the SULI program in 2009 as a graduating senior, back to Ames Laboratory and ISU. Following graduation from the University of Texas at Austin with a degree in chemistry, she decided to stay a fifth year in order to take additional coursework in computer science. All that time, she kept in contact with Gordon, who helped her see how the two degrees could mesh with one another, which, ultimately, helped her make the decision to come back to the Gordon group and ISU this fall.

"Mark has been in the field a long time so he has a really good feel for what's important in quantum chemistry and computational chemistry," says Bertoni. "His knowledge of the field makes it very exciting. He helps you see all the connections."

As for the future of these students, well, it's as different as you might expect. Carlin wants to become an analyst for the government. Bertoni likes the appeal of doing research at a DOE national lab. Conrad wants to first find a job in industry and then return to academia as a teacher.

Whatever their ultimate decisions, Gordon feels he will have accomplished one of his main goals, which is to help maintain the flow of American students into science.

"More and more of our international students are educated here and then go home to their home countries, so it's important to educate young domestic students that science is a really exciting and viable career."

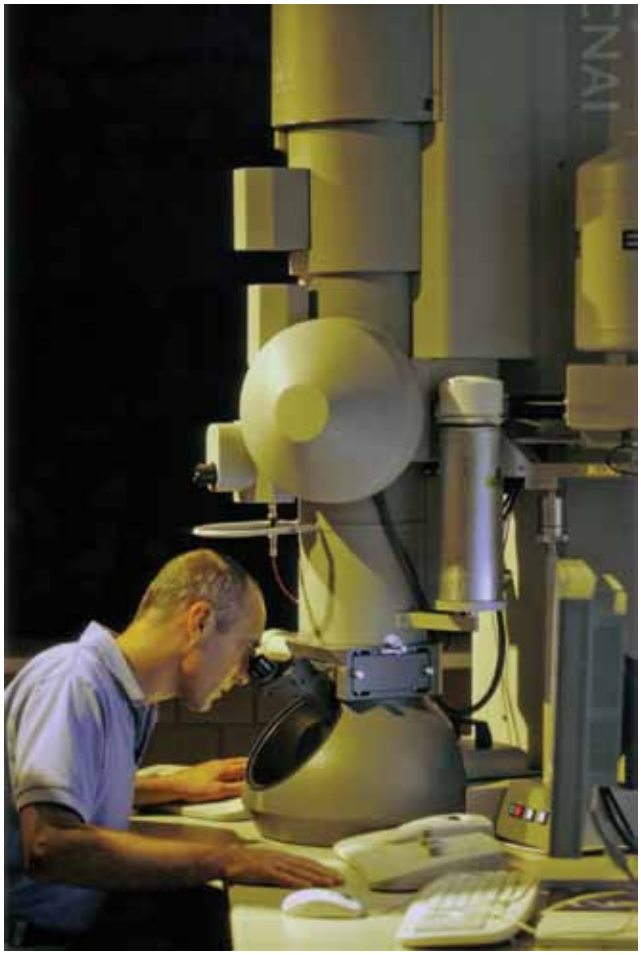
"This is what the SULI program allows," he adds. "To have students come here and get their PhDs and get excited about science is really important to the future of our country."

*Up to bat (left to right) are Justin Conrad (SULI '10 and '11), Mark Gordon (SULI mentor), Caleb Carlin (SULI '08) and Colleen Bertoni (SULI '09).*

# Finding Out What Makes Materials "Tick"

BY KERRY GIBSON

TO FIGURE OUT WHY A MATERIAL HAS PARTICULAR properties, scientists need to know far more than just the elemental chemical composition of that material. To really understand what makes a material "tick," scientists need to probe the internal structure of the material to decipher just how the atoms and molecules within the material fit together, how they interact in various states and phases and how conditions such as temperature and magnetic field affect those interactions.

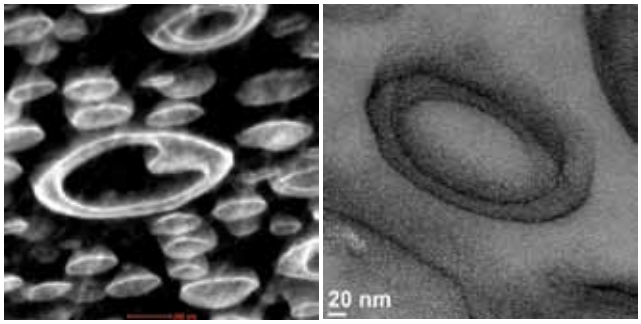


*Ames Lab scientist Matt Kramer operates the Lab's transmission electron microscope. Various equipment options allow scientists to probe different aspects of a material. In scanning mode, or scanning transmission electron microscopy (STEM), the electron beam is scanned back and forth across the sample.*

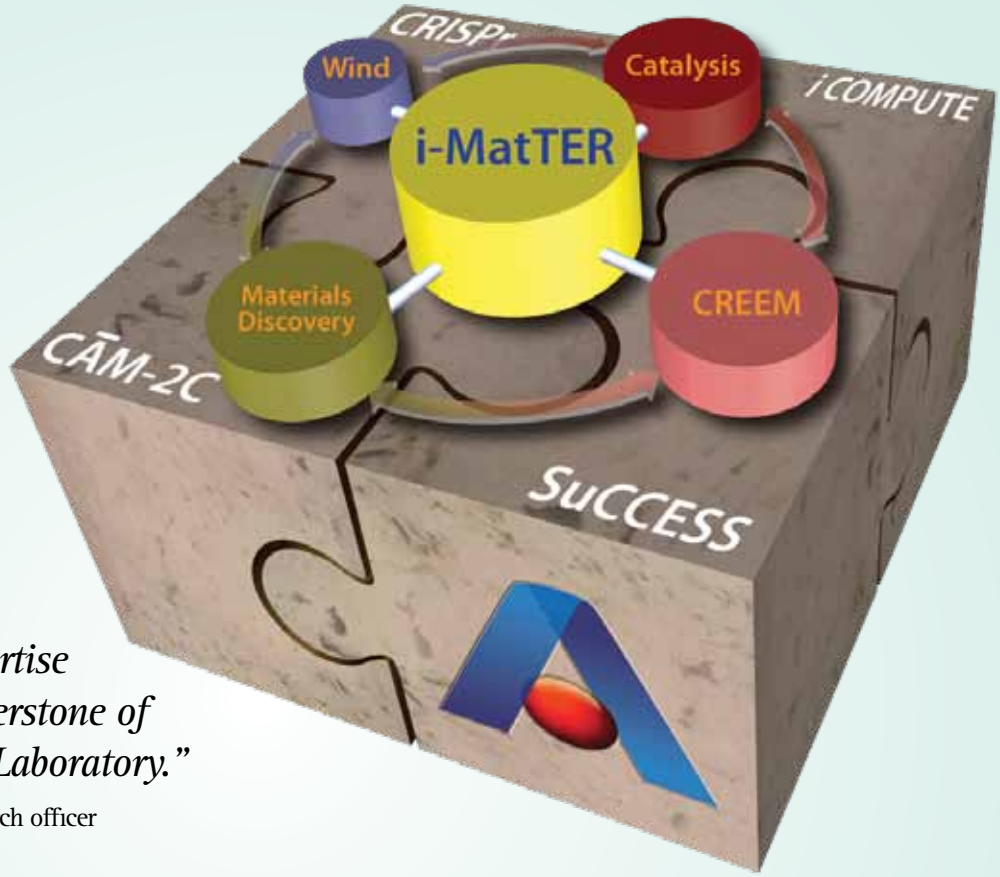
To characterize a material, scientists rely on a wide variety of analytical techniques. While individual characterization techniques are specialized to highlight different aspects of a material, they do share some things in common. Many techniques rely on the principle that atoms and molecules have a unique signature on the spectrum when subjected to electromagnetic radiation. The signature can manifest itself in different ways, but a simple example of this principle can be seen in a TV screen where a europium phosphor shows only the vivid red portion of the light spectrum when subjected to the broadcast signal.

Spectroscopy allows scientists to "see" what's inside a material by viewing what happens to the electromagnetic radiation directed at the sample. Depending on the type of radiation used – running the gamut from radio waves, microwaves and light to X-rays and gamma rays – and its strength, scientists can measure how the energy is absorbed by the material, emitted by the material or scattered by the material.

In nuclear magnetic resonance (NMR) spectroscopy, for example, researchers use radio-frequency magnetic energy on a sample to measure the local magnetic fields generated by the nuclear spins. This provides detailed spectral information about the physical and chemical properties of the material, such as the distance between nuclei and their specific positions at a particular point in time.




*A technique known as high angle annular dark field (HAADF) STEM can be used to create a high contrast image, such as the one of a co-block polymer on the left, to give a better view of the crystal structure of materials. At right is a TEM bright field image of the same co-block polymer, which provides a better view of the sample's surface.*




*"Our characterization expertise and capabilities is a cornerstone of who we are at the Ames Laboratory."*

**Duane Johnson,** Ames Lab's chief research officer

Similarly, X-ray diffraction spectroscopy uses X-rays to probe the sample, and the interaction of the X-rays with the electrons in the materials results in the transference of energy from the X-rays. These "scattered" or defracted X-rays will have a different wavelength than the original beam. In highly ordered materials, these scattered rays will form a pattern that corresponds with the distribution of atoms within the material, providing keys to its crystal structure.

Some types of electron microscopy also rely on the material's spectroscopic properties. In transmission electron microscopy, very thin samples are probed with an electron beam that passes through the material. As the beam passes through, some of the beam's electrons are reflected. Different particles have a particular angle of reflection, so by using sensors to measure the angle of the reflected beam, scientists learn about the structure of the material.

The Ames Laboratory's strength in creating materials relies in large part on the expertise of its researchers in these various techniques to quantify particular aspects of a material. And the Lab's highly collaborative atmosphere allows the snapshots gathered by these various characterization techniques to be drawn together to form a more complete picture.

"Our characterization expertise and capabilities are a cornerstone of who we are at the Ames Laboratory," says Duane Johnson, Ames Lab's chief research officer. "The Chemical and Advanced Materials Characterization Center, or CĀM-2C (came to see), encompasses a broad range of techniques that directly benefit the DOE's energy-sciences portfolio."

**CĀM-2C'S CAPABILITIES INCLUDE:**

- **Scattering Sciences:** X-ray, electron, and neutron
- **Microscopies:** chemical imaging, gene expression imaging, differential interference contrast, field ion, scanning tunneling, atomic force and ultrafast stimulated emission depletion microscopies
- **Spectroscopies and Elemental Analysis:** Auger, Raman, energy-dispersive X-ray spectroscopy, mass spectroscopy, angle-resolved photoemission spectroscopy, X-ray photoelectron microscopy, and solid-state NMR
- **Property Measurements:** magnetization; susceptibility; transport; and thermodynamic quantities (e.g., heat capacities, enthalpies, magnetocalorics, thermopower, DTA, DSC and TGA) measured across a wide range of temperatures and applied magnetic fields (up to 14 Tesla)

"What sets Ames Laboratory apart from most materials research labs is the broad, yet integrated nature of the research, synthesis and characterization within our material discovery efforts," Johnson says. "It involves numerous researchers, which are mirrored within the Lab's four science cornerstones, and founded on our unique synthesis and processing of high-purity, bulk single crystals that may involve volatile elements."

"With our `theoretical characterization' capabilities (computational materials science and chemistry)," he adds, "we have an integrated feedback loop between theory and experiment that works very well, helping to speed up development and understanding."

# Characterization Anomaly Leads to Nobel Prize

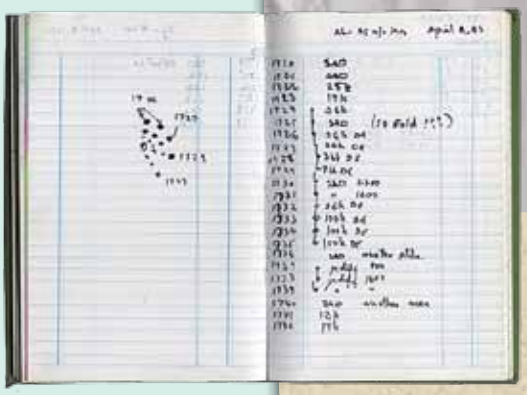
BY KERRY GIBSON

Danny Shechtman

WHEN DANNNY SHECHTMAN FIRST SAW the diffraction pattern with 10 points in 1982, he had no idea the ridicule he would face because of it, or that it would eventually lead to complete vindication in the form of the 2011 Nobel Prize in chemistry. As a scientist characterizing a new aluminum-manganese alloy, he simply knew he was seeing something unique that didn't fit with the accepted rules for crystalline structure. And he believed what his eyes were seeing.

"I was working alone in the electron microscope lab (as a guest researcher at what was then the National Bureau of Standards) studying this new material and right away, it looked very strange to me," Shechtman says. "So I took an electron diffraction and I counted 10 spots and said, 'No, it cannot be!'"

"I counted again another way and it was still 10 spots," he continues. "I thought, '10-fold symmetry … this is an amazing thing! I must share it with somebody.' So I went out in the corridor, but there was no one else around, so I went back and spent the rest of the day performing experiments."



Shechtman's original lab notes

His initial thought was that the pattern he was seeing was the result of a phenomenon known as twinning, where two rows of atoms form a mirror image with a boundary in between them. But as he looked, he could find no evidence of twins. In rotating the crystal, he also discovered the material actually had an equally impossible five-fold rotational symmetry, not 10-fold as he first suspected, and he knew he was seeing something new and unexplained.

Shechtman's discovery, which contradicted conventional wisdom, was discounted as "outrageous" and he was ridiculed by even his colleagues, including being dismissed from his research group. But he continued to study the material and in November 1984, with support from physicist John Cahn, materials scientist

> "… I counted 10 spots and said, 'No, it cannot be!'"

Ian Blech, and crystallographer Denis Gratias, published his data in an article, "Metallic Phase with Long-Range Orientational Order and No Translational Symmetry," in Physical Review Letters.

The article took Shechtman's discovery, and criticism of it, to a whole new level. One of the harshest opponents was two-time Nobel Prize winner Linus Pauling.

"He was a highly respected scientist and the idol of the American Chemical Society and to his last day, he would stand on those platforms and declare, 'Danny Shechtman is talking nonsense," Shechtman recalls. "Pauling would often say, 'There is no such thing as quasicrystals, only quasi-scientists.'"

However, Shechtman's article also began to win over supporters who were able to replicate his results. Theoretical support for quasicrystals soon came about from an aperiodic mosaic developed by British mathematician Roger Penrose. By 1992, the International Union of Crystallography altered its definition of a crystal to "any solid having an essentially discrete diffraction diagram," where it had previously suggested crystals had to be periodic in nature.

Shechtman's selection for the 2011 Nobel Prize in chemistry is the ultimate vindication for the years spent defending his discovery. His unwavering belief in his original findings holds an important lesson for anyone in the field of science or the broader scope of human endeavor.

"If you're a scientist and believe in your results, then fight for it … fight for the truth," he says. "Listen to others, but fight for what you believe in."

Ames Laboratory senior scientist **Pat Thiel**, who was instrumental in bringing Shechtman to Ames Lab and Iowa State University, marvels at Shechtman's tenacity and his ability to stay cordial and respectful with even his most vocal critics.

"The stories of his life and career have been inspirational to me, especially the controversy with Linus Pauling and the fact that they remained on cordial terms even as they battled professionally," says Thiel. "In fact they met several times for dinner at conferences, and Danny once made a special visit to Linus to try to convince him about quasicrystals."

"Most people would have become bitter and incensed," Thiel continues, "but Danny didn't and in fact, he did not even take the controversy as a personal affront. To remain on civil and respectful terms with people, even in the face of strong disagreements, is one of my professional aspirations and also one of the most remarkable aspects of Danny's achievement."

For **Paul Canfield**, Ames Lab senior physicist, Shechtman's discovery has been an ongoing subject of study throughout Canfield's career.

"Danny's discovery was profound," Canfield says. "Quasicrystals offered a mysterious waystation between crystalline and amorphous. Just how this new form of order affects the physical properties of quasicrystals is something I keep coming back to over the decades."

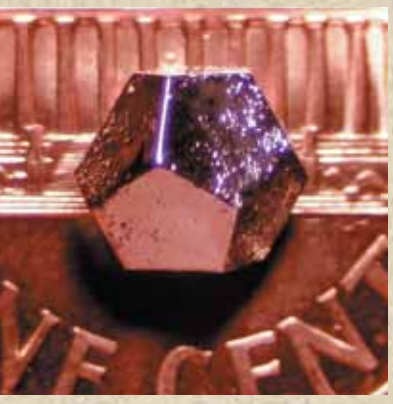
Canfield's first publication as a graduate student at UCLA was the measurement of meltspun quasicrystalline ribbons. At Ames Lab, he was able to grow some of the first faceted single-grain, rare-earth-magnesium-zinc quasicrystals, a perfect blend of Ames Lab's expertise in rare earths and quasicrystals.

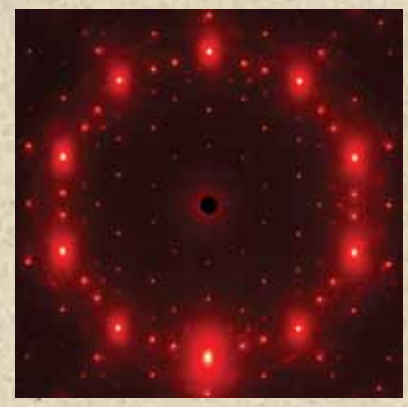
"With (Ames Lab senior physicist) Alan Goldman we were able to determine that rare earths, ordered in a quasicrystal, act in a manner similar to a glass, but a highly ordered one," he says. "With our discovery that solution growth was an excellent way to grow these complex materials, we expanded the number of systems we studied and actually taught the world how to grow these compounds."

"It is my firm belief that if we look carefully enough and grow carefully enough, there will be many examples of quasicrystals lurking in binary and ternary phase diagrams," Canfield concludes. "The real big remaining question is to understand why a material forms a quasicrystal rather than a crystalline phase."

**Alan Goldman** agrees that Shechtman's findings have ultimately changed the way researchers think about the composition of matter.

"Danny's discovery really opened a new frontier in materials research and certainly had a very strong impact on my own career," Goldman says. "Very soon after his discovery, I began to study the structure and properties of quasicrystals at Brookhaven National Laboratory. When I came to Ames in 1988, I continued that work with other Ames Lab scientists such as Pat Thiel, Paul Canfield, Matt Kramer, Bill McCallum and Tom Lograsso," he continues, "and I can only say that it has been a 'fantastic journey' that epitomizes the Ames Lab's interdisciplinary approach to science."





*far left: A holmium-magnesium-zinc (Ho-Mg-Zn) quasicrystal, grown by Ames Laboratory senior physicist Paul Canfield, that clearly shows five-fold (pentagonal) symmetry.*

*left: An X-ray diffraction image captured by Alan Goldman that shows the "10-spots" that Shechtman first noticed through his transmission electron microscope.*

# Laser-guided Discovery

## *Raman spectroscopy shines a light on biofuels processing*

BY KERRY GIBSON

DEVELOPMENT OF BIOFUELS HINGES ON THE ABILITY to convert lignocellulose, the "woody" cell membrane that comprises most plant material, into something that's useable as fuel. One method is to use enzymes to break down the cellulose into sugars, which can then be converted into ethanol through fermentation and distillation.

Because different plants have different cell-wall structures and compositions, scientists need to understand those differences and how efficiently enzymes are able to break the lignocellulose into simple sugars. To do this, Ames Laboratory scientist Emily Smith uses a characterization tool called Raman spectroscopy, which is ideally suited to working with such materials.

"This method has several advantages over alternative analytical techniques," Smith explains. "First, analysis requires very little material so you can take small samples from a growing plant over time with little damage to the plant." The technique is also high-throughput. Because only very small samples are needed and little time is required to prepare samples, multiple samples can be analyzed quickly.

The basic Raman technique used by Smith, who is also an Iowa State University assistant professor of chemistry, employs an optical microscope, and specimens are illuminated with a laser beam. As the laser light hits the sample, some of the light is scattered. By analyzing the scattered light with a spectrometer, Smith can easily and quickly determine the chemical makeup of the plant material.

"Raman spectroscopy provides chemical signatures of what's in your sample," Smith says. "We can focus on the signature of the particular species we're interested in, for example lignin or cellulose."

Because lignin binds the cellulosic polymers together, the higher the lignin content of the cell wall, the harder it is to access the cellulose. For some biofuel applications, plants with a higher cellulose-to-lignin content are more ideal.

Smith's group is also using Raman spectroscopy to measure the enzymatic reactions used to break down the cellulosic polymers into sugars.

"Because the enzymes used can be expensive, it's important to determine what conditions are optimum to produce the highest yield," Smith says.

Besides the type of plant material used, variables include the maturity of the plant material, the size of the pieces being processed, pretreatment of the material, and the type and amount of enzyme used.

Also being studied is a hydrolysis process that uses enzymes attached to silica nanoparticles. This allows the nanoparticles and their attached enzymes to be recycled. It also increases the yield of ethanol when saccharification and fermentation reactions are performed simultaneously.

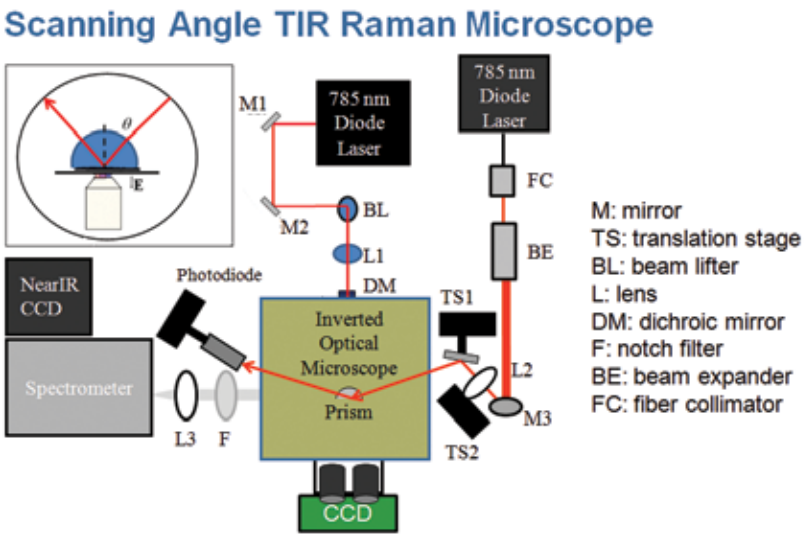
Smith's work has also focused on developing new instrumentation and uses for it. She is currently developing a different type of Raman technique known as scanning angle, total internal reflection Raman microscopy.

"Basically, it allows us to control the angle that the laser is directed on the sample," Smith says. "By changing the incident angle, we hope to be able to develop a 3D image of the sample's chemical content."

Motorized controls allow the incident angle of the laser to range from 25.5 degrees to 75.5 degrees with a .05 degree angle resolution, giving researchers the capability to study the materials with 5 nanometer spatial resolution.

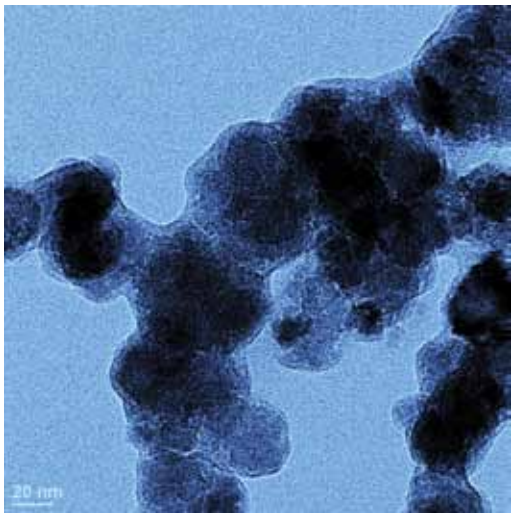
At an even more fundamental level, Smith's group is looking at how the spectral signal is generated and how to enhance the signal strength.

"When I first arrived, I wasn't expecting to do anything related to biofuels, but there is such an interest in them and a wealth of expertise here and at Iowa State that it's really taken off," Smith said. "As we've worked on that, our understanding of these techniques has grown and it's brought up all kinds of new research projects for us to work on."




*Above: A schematic for the scanning angle total internal reflection microscope that Emily Smith displays on the opposite page.*

*"This method has several advantages over other analytical techniques," Smith explains. "First, analysis requires very little material so you can take small samples from a growing plant over time without damaging the plant."*




*Tanya Prozorov demonstrates working with biological samples using existing equipment. Prozorov is awaiting arrival of a new continuous flow liquid cell holder for the Lab's transmission electron microscope that will allow her to study how magnetic nanocrystals, similar to those shown in the micrograph at the right, form.*

# Uncharted Territory:
## Watching Nanocrystals Grow

*"With the majority of current characterization techniques, what you see is a static picture – a snapshot – of multiple nanocrystals,"* **Prozorov says.** *"These particles interact with each other, and it masks what's really taking place."*

BY KERRY GIBSON

AMES LABORATORY SCIENTIST TANYA PROZOROV is clearly enthusiastic when she talks about her research. She has trouble suppressing a smile as she excitedly details the project that will take her into uncharted territory.

This "expedition," however, won't take her and her yet-to-be-named research team to some exotic location. The new territory will be trying to watch biomagnetic crystals as they form using a custom-built sample holder for the Lab's Technai transmission electron microscope. The work is being funded through a five-year, $2.5 million Department of Energy Early Career Award which Prozorov was awarded earlier this year.

Prozorov's project, "Real-Time Studies of Nucleation, Growth and Development of Ferromagnetism in Individual Protein-Templated Magnetic Nanocrystals," will focus on isolating individual biotemplated magnetic nanocrystals in an attempt to identify the mechanisms that control how these crystals form and develop their magnetic properties.

"With the majority of current characterization techniques, what you see is a static picture – a snapshot – of multiple nanocrystals," Prozorov says. "These particles interact with each other, and it masks what's really taking place."

"Also, we normally observe them after they've formed," she continues. "I want to try to isolate and view individual particles as they grow, in situ, to see what's taking place. There's nothing like actually seeing it to help you understand how they form. And understanding this will ultimately allow controlling the emergent magnetism."

Building her expertise in specialized electron microscopy techniques is the first step, according to Prozorov, who describes herself as "just a materials chemist with a passion for electron microscopy." For example, to study growing, bio-inspired samples requires that they be suspended in liquid, which presents a particular set of problems.

"It takes a specialized piece of equipment – a continuous flow liquid cell TEM (transmission electron microscope) holder – to be able to view the nanocrystal formation in liquid," she says. Additionally, a "molecular printer" called a Nano Enabler is necessary to dispense the requisite nano-scale quantities of the biological templating material. Cryo-electron microscopy techniques will be used to literally freeze the particles in various stages of development so their images can be captured.

Prozorov will collaborate with Ames Lab scientist and electron microscopy expert Matt Kramer and his group. She'll also continue to work closely with faculty scientist Surya Mallapragada, whose research group focuses on the bio-inspired magnetic nanocrystals that led to Prozorov's proposal for the Early Career Award program.

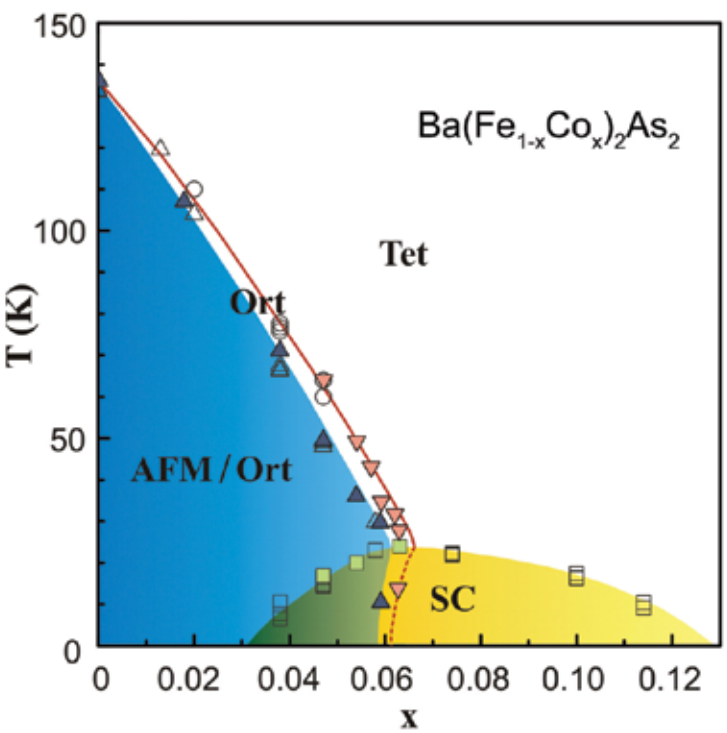
# Scattering at the Ames Laboratory

BY BREEHAN GERLEMAN LUCCHESI

A NEW MATERIAL'S JOURNEY FROM DISCOVERY TO ultimately improving everyday products often starts with scientists studying the material's microscopic properties through neutron and X-ray scattering.

"The first thing that we need to know about a new material is its structure and how it behaves under external stimuli," says Alan Goldman, Ames Laboratory physicist and member of the Lab's scattering research group. "Minor changes in material composition, made to either reduce costs or weight or to enhance efficiency, can represent significant savings over current materials. So, the structure and behavior of materials is critical for understanding how to create the next generation of materials and products."

Take, for instance, the new type of iron-arsenic superconductor discovered several years ago. Scientists hope iron-arsenides may prove useful in applications, such as in high-strength superconducting magnets, but first the materials' properties must be mapped out. In particular, Ames Laboratory's scattering group — which includes Goldman, Rob McQueeney, David Vaknin and Andreas Kreyssig, all Ames Laboratory physicists, along with several post-doctoral researchers and graduate students — was interested in the magnetic structure of a type of iron-arsenide where a small percentage of the iron was replaced with cobalt in a process called "doping."




*The scattering research group at Ames Laboratory uses X-ray resonant magnetic scattering, along with other types of scattering, to map out the phase diagrams for new materials. Shown here is the phase diagram for a cobalt-doped iron arsenide. The scattering team's research indicates that in this material, magnetic order (blue area) and superconductivity (yellow area) can coexist (green area), which is unusual.*

The team studied the material using neutron scattering, which is best suited for studying magnetic structure as neutrons are sensitive to the magnetism in materials. In neutron scattering, a beam of neutrons is generated in a nuclear reactor or an accelerator-based spallation source and, using specialized instrumentation, is aimed at a sample of material. The neutrons in the beam encounter nuclei and atomic magnetic moments in the sample and bounce off. The way the neutrons "scatter" from a material gives scientists information about where the nuclei and magnetic moments are located and how they are moving.

In studying cobalt-doped iron-arsenides, the Ames Laboratory scattering group used finely-tuned samples synthesized at Ames Lab by fellow physicist Paul Canfield. The scattering research group was able to gather enough information about the magnetic order and superconducting phase to map out a phase diagram of the material.

"Turns out this cobalt-doped iron-arsenide is an interesting case where the magnetic order and superconductivity can coexist in a finite doping range," says Rob McQueeney. "Our group was the first to discover that."

For other scientific questions, like studies of rare-earth materials, one of Ames Laboratory's specialties, X-ray resonant magnetic scattering is better suited. In X-ray resonant magnetic scattering, a material sample is exposed to a beam of finely tuned X-ray energy that is specific to the probed element. The X-rays scatter from electrons in the material, revealing information about materials' magnetic structure.

"This technique is only possible at high-brilliance X-ray sources like the Advanced Photon Source at Argonne National Laboratory," says Goldman. "In fact, we spend a lot of time traveling because our research requires 'beam time' at the major scientific facilities in the United States and around the world."

The scattering group also uses various scattering techniques in research on bio-inspired materials. It tries to understand the mechanisms by which organisms build functioning minerals such as bones, teeth and shells, and magnetic nanocrystals. The objective of the group is to employ similar biomineralization processes to design novel materials for various applications.

"In all these projects, we use the scattering technique that is appropriate to the scientific question, and often we use both neutron scattering and X-ray resonant magnetic scattering because the data gathered from each is complementary," says Andreas Kreyssig. "I think that is a strength of our team here at Ames Laboratory."

"From sample growth and the variety of very detailed kinds of scattering techniques we use, to theoretical interpretation, we have it all here at the Ames Laboratory," adds McQueeney. "That's what makes it possible for us to make such an impact in this field."

# Unlocking the Power of Nanomachines

BY BREEHAN GERLEMAN LUCCHESI

THE ANSWERS TO BIG QUESTIONS – HOW TO CREATE green fuels or how to cure deadly diseases – may have their answers in tiny motions in living cells. To understand these small movements, Ning Fang, associate scientist, is using optical microscopy to see how nanoparticles are manipulated by "nanomachines" in cells.

In living cells, numerous biological nanomachines perform various functions. But according to Fang, scientists have only a limited understanding of how these nanomachines work, especially in cellular environments. And because the malfunction of any of these nanomachines can lead to diseases, there is a great need for new techniques to help investigate the composition, dynamics and working mechanisms of these nanomachines. Nanomachines are also very efficient at converting chemical or other energy into motion, so understanding them may give scientists ideas for how to build efficient green-energy technology at the micro- or macroscale.

To understand how these nanomachines work, scientists examine how nanoparticles move with various types of motion induced by nanomachines that are essential to their function.

Translational motion, or movement in which the position of an object is changed, can be tracked through a variety of current techniques. However, rotational motion, which is as important and fundamental as translational motion, was largely unknown due to technical limitations.

Previous techniques, such as particle-tracking or single-molecule fluorescence polarization, only allowed rotational movement to be resolved in simplified, controlled in vitro systems. In its research, Fang's group has gone beyond studying motions in the in vitro environment to imaging rotational movement in the in vivo, or live cell, environment.

To do this, the group relies upon the use of gold nanorods, which are only 25 by 73 nanometers in size (a well-packed bundle of 1000 nanorods has the same diameter as a human hair). In live cells, these nontoxic nanorods scatter light differently depending upon their orientation. Using a technique called differential interference contrast microscopy, or DIC, Fang's team can capture both the orientation and the position of the gold nanorods in addition to the optical image of the cell and, thus, reveal a particle's 6D (three spatial coordinates, two orientation angles and time) movement within living cells.

"This new technique opens doors to understanding the working mechanism of living nanomachines by revealing their complex internal motions," says Fang. "Studying rotational motions at the nanometer scale inside a living cell is just something that has never been done before."

He added that understanding this rotational motion is important in the fight against diseases, such as Alzheimer's, because it can help scientists better understand how neurons are impacted by the environment.

Fang's research group is also developing another type of DIC microscopy that generates a high-contrast, high-resolution view of materials that would be invisible under conventional light microscopes, so Fang and his colleagues can visualize the composition of block copolymers.

"DIC uses a special principle based on interference so we can see inside these polymers down to about a domain of a few tens of nanometers or even smaller," Fang says. "The polymers appear to have different patterns of nanostructures, and we are now hoping that this understanding will lead to applications in clean energy."

In addition, Fang's team is working in the area of super-resolution fluorescence imaging, with the goal of visualizing ever finer details of materials.

"The overall goal is to break the diffraction limit of light," says Fang. "For example, we want to be able to distinguish between two fluorescent molecules that are so close to each other that they previously would have appeared as one."

His team's technique, called 3D super-resolution fluorescence microscopy, has the added benefit of automation.

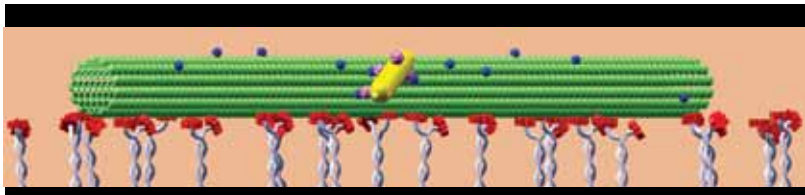
"Compared to others' systems, we can control most parts of the microscope by computer, so the computer automatically calibrates and carries out the scan," says Fang. "This means the system is very convenient for end users, and, more importantly, we can better reproduce the results of our imaging process."

In all these types of imaging, Fang's group is working to improve the ability to manipulate samples during imaging.

"We need better control of the sample so that we can pinpoint when and how we introduce external triggers to samples," explains Fang. "For instance, we are studying the enzymatic reaction for breaking down cell walls to examine how to best make biofuel. That type of experiment requires introducing a reagent to the sample to start the reaction."

The controls are provided by a cleverly designed microchannel network, and Fang and his colleagues have introduced the first type that can work with high-fidelity optical imaging.

Overall, Fang's goal is to improve on the complete platform of optical imaging.

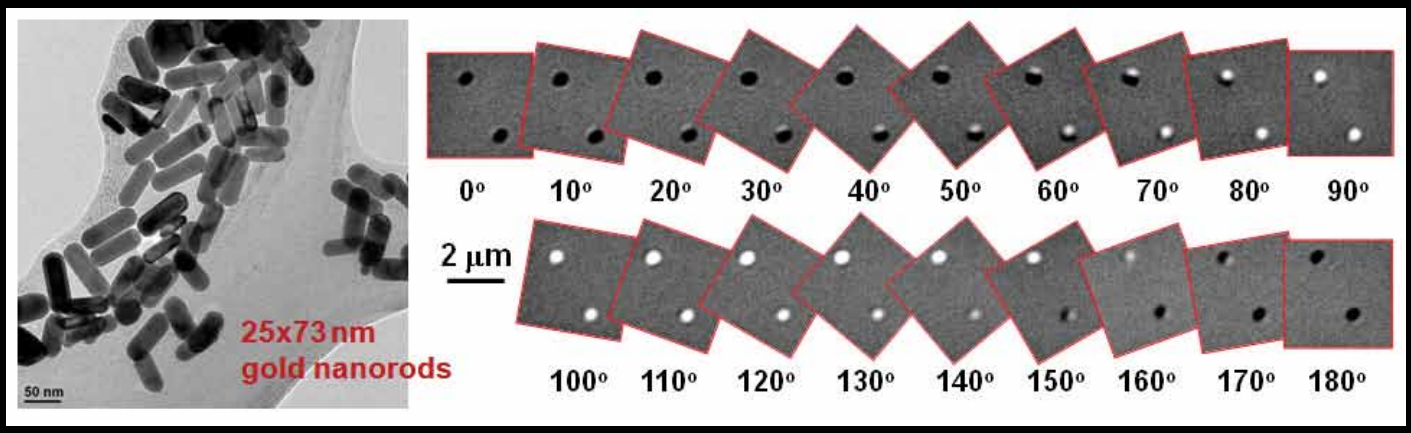


*Ning Fang is using optical microscopy to study the mechanisms of biological nanomachines. Here, a gold nanorod is attached to a microtubule. Tracking the movement of the nanorod reveals the rotation of the microtubule.*

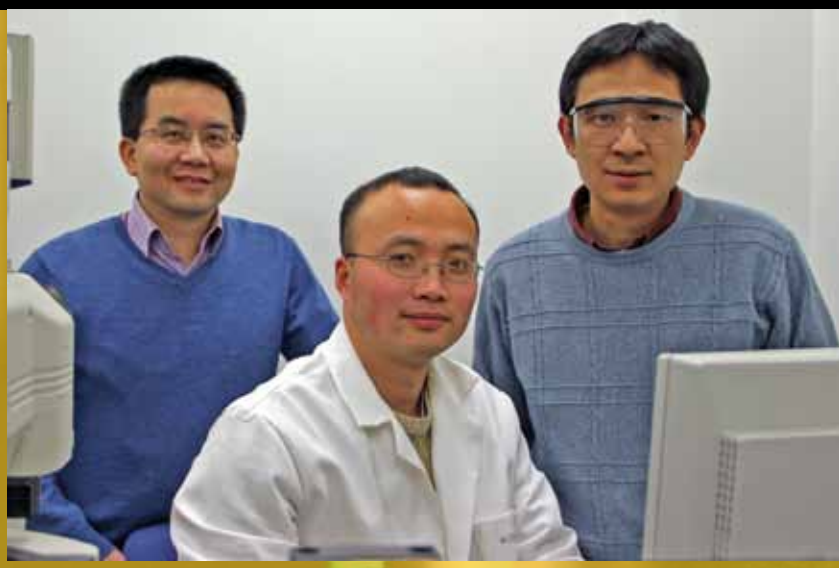
"We seek to improve localization, that is, we want to see a particle's location with nanometer precision, and we want to improve resolution, so we can identify two close particles as individuals," says Fang. "We also want to be able to track particles' movements, and we want to be able to manipulate the samples."

"The complete platform of imaging, combined with collaborating with others at Ames Laboratory with different techniques, is one advantage we have here at Ames Lab," adds Fang. "We can use all of our techniques to examine one material. We gain more basic understanding of the material that may someday lead to important applications."

*"This new technique opens doors to understanding the working mechanism of living nanomachines by revealing their complex internal motions ..."*




*left: Transmission electron microscopy image of gold nanoparticles. Right: Differential interference contrast images of two 25 by 73 nanometer gold nanorods positioned at different orientations. The periodic changes of bright and dark intensities allows the nanorods' orientation to be determined with high precision. Bottom: (from left) Ning Fang, Wei Sun and Gufeng Wang.*



# A Nanosized Look at the Bonds Between Rare-earth Metals and Graphene

BY BREEHAN GERLEMAN LUCCHESI

TRANSISTORS AND INFORMATION STORAGE DEVICES are getting smaller and smaller. But, to go as small as the nanoscale, scientists must understand how just a few atoms of metals behave when deposited on a surface. Physicists at the Ames Laboratory are studying the interaction of materials that are promising for use in nanoscale electronics: graphene and different types of metals. The team has discovered that the rare-earth metals dysprosium and gadolinium react strongly with graphene, while lead does not.

Michael Tringides, an Ames Laboratory senior physicist, and colleagues Myron Hupalo, an Ames Laboratory scientist, and Steven Binz, a graduate student in physics, deposited a few atoms of lead or rare-earth metals on the surface of graphene, a one-atom thick layer of carbon. In a process called self assembly, the atoms move on their own and form "islands" or smooth films on graphene. Tringides and the team then used scanning tunneling microscopy to study the islands' geometry.

STM creates realistic images of nanoscale surfaces in fine detail. In the STM, scientists mount a sample and deposit atoms to make nano-islands. Then they use a tiny needle to approach the sample surface. The needle gets close to the sample, as close as one atom-width away, but doesn't touch the surface, leaving a small gap.

To make measurements, the STM relies on two concepts in quantum mechanics: electrons are both a particle and a wave; and the electrons, acting as waves, "tunnel" through the gap between the sample and the needle tip.

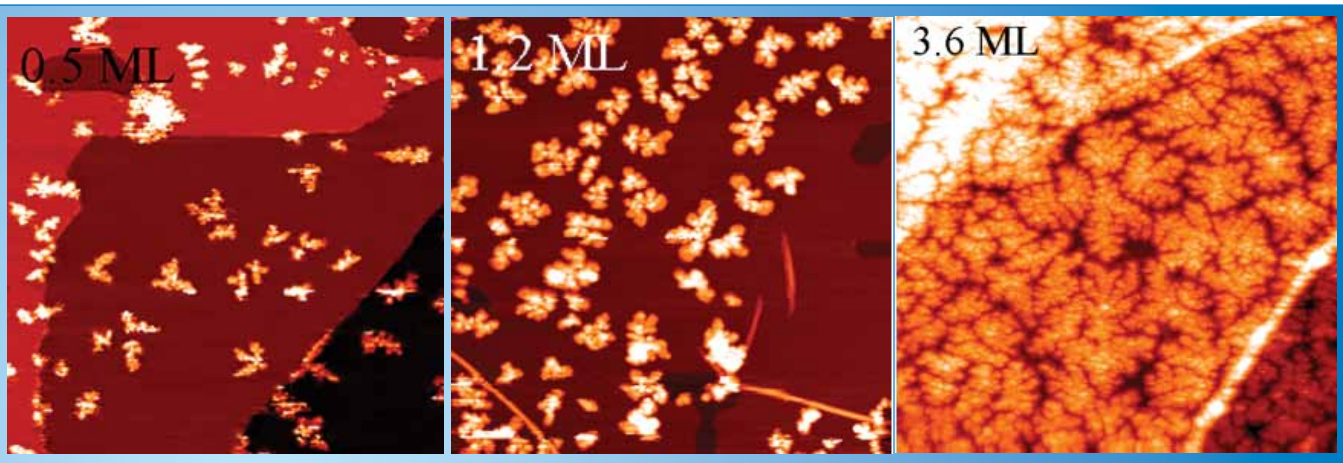
"Tunneling allows current created by the electrons to move from the sample to the STM needle," says Tringides. "The amount of current is dependent on how far the needle is from the sample, so the STM measures this current and uses it to keep the needle the same distance away from the sample."

As the needle scans the surface, it encounters dips and peaks -- where the atoms are -- but maintains an equal gap above the sample. The STM then traces the path of the needle up and down to create an image of what the sample surface looks like, representing the size and height of any structures on the surface.

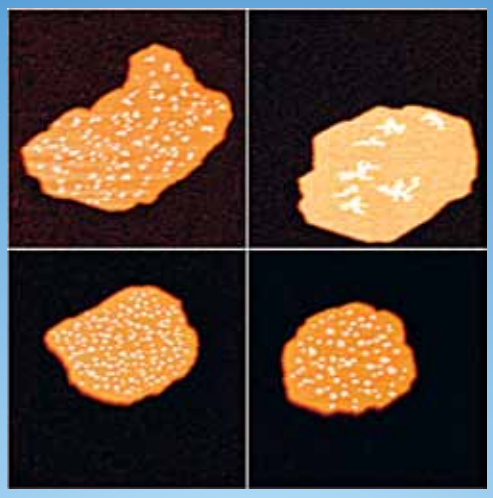
STM images are complemented with data gathered with a different instrument, using scattering of low-energy electrons. In this technique, a beam of electrons is focused on a sample that has islands on a smooth surface. Electrons bounce off the tops of the islands and the substrate. Because the electrons travel different distances, they form interference bands, giving scientists information about the nano-islands' height and size.

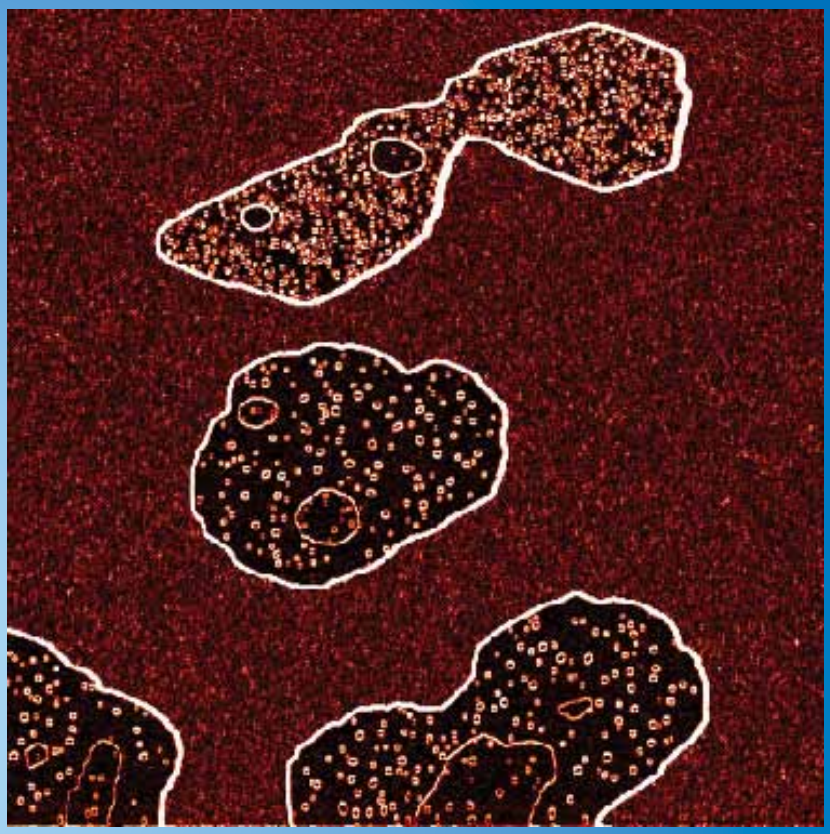
Tringides and his team also collaborate with other research groups that use additional types of characterization techniques, such as X-ray surface scattering, which is able to examine the deeper structures of the islands close to the substrate, and low-energy electron microscopy, which is able to capture real-time movies of how atoms move on surfaces.

In its research into rare-earth islands on graphene, the team used STM to help understand how the atoms diffuse, particularly how quickly.




*These micrographs show dendritic "island" growth of gadolinium on graphene at room temperature. This type of growth indicates a strong bond between gadolinium and graphene.*





*Three different types of materials yield three different types of island growth: (above, top row) lead on a lead surface; (above, bottom row) indium on lead surface; and (right) magnesium on lead surface.*

"In this case, the lead atoms moved quickly when we cooled them down, while the dysprosium moved slowly, even after we heated them up," says Tringides.

How fast or slow the atoms move and form islands offers insight into how each material interacts, or shares electrons, with the graphene.

"If the atoms move fast, it means you do not have strong interaction," Tringides says. "It's like hockey pucks skimming along on an ice rink. There's little interaction."

In the case of dysprosium, the slow-moving atoms suggest that the metal reacts strongly with graphene. Gadolinium has an even stronger interaction. The interaction is significant because harnessing the potential of graphene in electronics will require attaching metals to graphene to conduct electricity.

"The hope is that graphene can be used for super-fast transistors," says Tringides. "Our work is relevant to this because when you put metal on graphene, you want to have very good contact, so the electrical resistance is low."

Tringides also says that the rare-earth islands on graphene are tiny magnets.

"It turned out that these islands were good nanomagnets on graphene," Tringides explains. "You have a very high density of nanomagnets. Iron also has a similar high island density. This may be useful in the future for using metals on graphene in computer memory."

Ames Laboratory theoretical physicists C.Z. Wang and Kai-Ming Ho collaborated on the research, using calculations to confirm the experimental results about the bonds between graphene and the metals studied.

"These findings are interesting for both the fundamental physics and the potential usefulness," says Tringides. "Whenever you say 'nano,' you can make a lot of something in a small size. And that might be very beneficial for something like magnetic computer memory."

Tringides and his team are also working to understand several other questions about nanosized structures. They are examining the fast and correlated movement of lead atoms when they are placed on silicon at temperatures well below room temperature. At such low temperature the motion should be slow and random, but for a still mysterious reason the motion is extremely fast and the atoms "slide" together like a liquid. The team is also studying how magnesium nano-islands and films can adsorb hydrogen at the nanoscale, which may have implications for macroscale hydrogen storage technologies.

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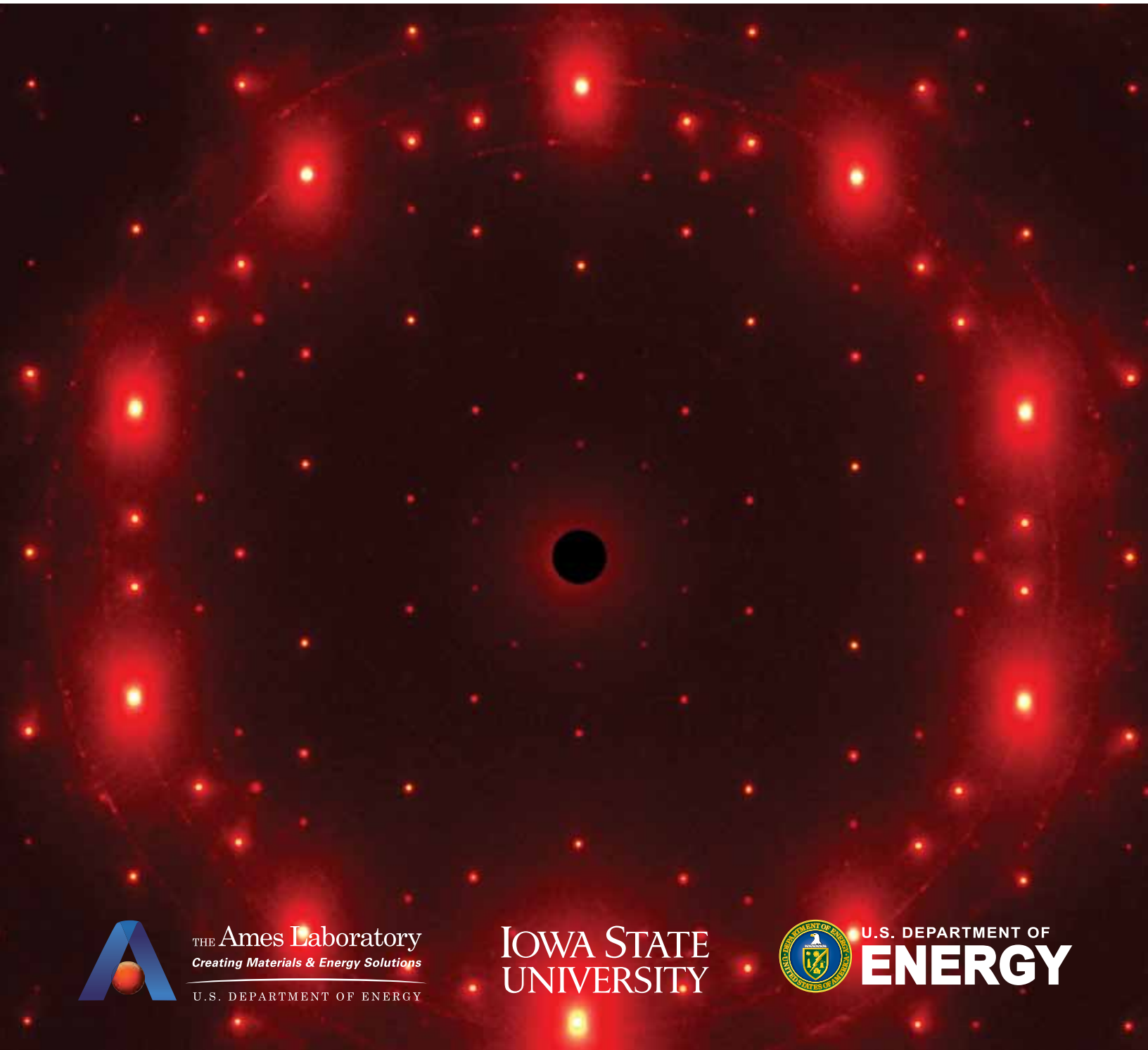

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