Science & Technology at the Ames Laboratory

inquiry

2014
Issue 1

Behind the Science at The Ames Laboratory

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

inquiry

Contents

A New Era in Ames Laboratory Leadership PAGE 5

6 BEAUTIFUL CHEMISTRY

8 SHAKING UP the Hydrogen Fuel Race

10 Snapshots at 1/1,000,000,000,000 of a second

12 Science of the small offers big diversity

14 Turning methane into valuable feedstock

Reading Spectral Fingerprints 16

18 EDUCATION

4 Awards

Steve Karsjen: Public Affairs Director
Kerry Gibson: Editor
Breehan Gerleman Lucchesi: Contributing Editor
Laura Millsaps: Contributing Editor
Grant Luhmann: Art Director

Copyright 2014 by the Ames Laboratory. All rights reserved. For additional information about the Ames Laboratory or topics covered in this publication, please contact:

Editor, Inquiry
Ames Laboratory
111 TASF
Ames, Iowa 50011-3020
515-294-9557
www.ameslab.gov

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.

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

From the Director

Laboratory Teamwork

Most great achievements in life aren't singular events. There's a foundation that's laid through basic work with involvement of many different and talented people. The success of a basketball team requires dedicated teamwork and countless hours spent practicing jump shots or ball-handling skills. Before a race car driver takes the checkered flag, his dedicated crew spends hours tweaking the car to eke out every last ounce of horsepower and makes sure the pit stops come off like clockwork.

Science is no different. For every discovery, big or small, there are countless hours spent in the lab developing experiments, analyzing data and then trying to replicate the results. It takes experimentalists, characterization experts, and theorists all working together.

Research at the Ames Laboratory exemplifies just this type of teamwork, as you'll see in the stories presented in this issue. While projects must have designated principal investigators, or PI's as we call them, our work is very much a team effort. Experimental work by Vitalij Pecharsky in hydrogen storage media (story on page 8) and Aaron Sadow in methane catalysis (story on page 14) relies heavily on solid-state NMR characterization work by Marek Pruski (story on page 16). Read about these and other projects and find out who and what is "Behind the Science" at Ames Lab.

We also broke ground in June for the Sensitive Instrument Facility. This state-of-the-art building will provide some much needed space for the next generation of electron microscopy equipment that's integral to our characterization capabilities. Its unique isolation features will allow an unimpeded view of materials at the atomic scale.

This Director's Message is also my last as I'm handing the Director reigns over to the very capable hands of Adam Schwartz. Adam brings to the laboratory a great deal of experience and a deep well of infectious enthusiasm for materials sciences and materials discovery, and I look forward to continued successes and growth of the Laboratory under his leadership. I've enjoyed my time as interim director and appreciate all the support I've received from the staff here and at the DOE. I'm excited about our collective future and wish Adam all the best as he prepares to lead us in the months and years to come.

For every discovery, big or small, there are countless hours spent in the lab developing experiments, analyzing data and then trying to replicate the results. It takes experimentalists, characterization experts, and theorists all working together.

Tom Lograsso, Interim Director

Awards

Soukoulis wins Born Award

Ames Laboratory senior physicist Costas Soukoulis has been named as the recipient of the 2014 Max Born Award by the Optical Society. Soukoulis is being recognized for "his creative and outstanding theoretical and experimental research in the fields of photonic crystals and left-handed metamaterials and for novel applications of these materials to manipulate electromagnetic radiation."

The award, which recognizes contributions to physical optics, is named for Max Born, a German physicist and mathematician who was instrumental in the development of quantum mechanics, solid-state physics and optics and winner of the 1954 Nobel Prize in Physics.

Costas Soukoulis

Andreas Kressig

Pat Thiel

Outstanding APS Referees

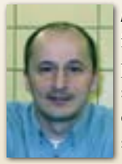
Two Ames Lab scientists, **Andreas Kressig** and **Pat Thiel**, were named 2014 American Physical Society Outstanding Referees. The award recognizes scientists for their exceptional quality, number and timeliness of their work assessing manuscripts for publication in APS scientific journals.

Three named APS Fellows

Three Ames Lab scientists have been named 2014 Fellows of the American Physical Society. The Fellow award recognizes exceptional contributions in the field of physics through research, application, service or education.

Klaus Schmidt-Rohr for "inventing and improving advanced solid-state NMR techniques that provide important new information about polymers, such as the Nafion used in fuel cells, those which occur naturally in plants and soils, and those which form nanocomposites in bone."

Makariy Tanatar for "studies of the superconducting and normal states of unconventional superconductors using directional charge and heat transport measurements."



Adam Kaminski for "angle-resolved photoemission spectroscopy studies of unconventional superconductors."

Gordon named Schrodinger Medal winner

The World Association of Theoretical and Computational Chemists has named Ames Lab scientist **Mark Gordon** the 2014 Schrodinger Medal winner. The WATCC awards the Schrodinger medal each year to one outstanding theoretical and computational chemist.

Gschneidner receives Acta Materialia award

Karl A. Gschneidner Jr., senior metallurgist at Ames Laboratory, was presented the 2014 Acta Materialia Materials and Society Award in February. The award honors scientists who have made a major positive impact on society through materials science.

ADAM SCHWARTZ HAS BEEN NAMED THE next director of the Ames Laboratory. The announcement was made April 17 and Schwartz began his duties on June 2.

Schwartz comes to Ames from Lawrence Livermore National Laboratory where he served as division leader of the Condensed Matter and Materials Division and also coordinated LLNL's projects for the Critical Materials Institute, a $120 million DOE Energy Innovation Hub led by the Ames Laboratory.

"Ames is a world-class institution known for its work in materials science, computational chemistry and condensed matter theory, and Adam will certainly maintain the high caliber of research," said Secretary of Energy Ernest Moniz. "He will guide Ames Lab as it confronts new challenges in science and technology in service to our nation."

"Iowa State is honored to operate the Ames Lab on behalf of the Department of Energy, and the partnership between the University and Lab is important to the entire nation," said President Steven Leath. "Dr. Schwartz's outstanding scientific credentials, leadership skills, and vision will be tremendous assets in moving the Lab forward."

Schwartz is an accomplished researcher whose work has focused on plutonium aging and alloys, advanced characterization, and the dynamic properties of materials. In addition to serving as director of the Ames Laboratory, he will also hold the rank of tenured professor in Iowa State's Department of Materials Science and Engineering.

"The Ames Lab is a world leader in materials science, with an exceptional reputation, and with great momentum," Schwartz said. "I look forward to working with the Lab's scientists and operations staff to develop new materials and technologies that address America's energy challenges."

Schwartz earned bachelor's and master's degrees in metallurgical engineering, and a Ph.D. in materials science and engineering, all from the University of Pittsburgh. He joined Lawrence Livermore National Laboratory as a postdoctoral research associate in 1991.

Schwartz replaces former Ames Lab director Alex King, who stepped down in April 2013 to become director of the Critical Materials Institute. Tom Lograsso, acting deputy director and division director for materials science and engineering, served as interim director during the year-long search process.

THE AMES LAB
U.S. DEPARTMENT OF ENERGY

Beautiful Chemistry

BY LAURA MILLSAPS

One thing Andreja Bakac knows about her 37 years as a chemist — it has been beautiful.

"There is a lot of beauty to chemistry, the kind that anyone can appreciate. You don't have to be a scientist to see it," she says.

"I love the colors. Inorganic compounds cover the entire spectrum, from sky blue to emerald green, purple, yellow and everything in between. Sometimes the hues are different at different concentrations of reagents or when observed from different angles. And crystals, tiny or large, can take breath-taking shapes and colors."

Bakac, a senior scientist for Ames Laboratory and adjunct professor in the Department of Chemistry at Iowa State University, was drawn to the beauty of chemistry in middle school. Though she enjoyed studying other subjects like physics, math, and literature, chemistry had special appeal.

As she gained knowledge in the science, attending the University of Zagreb and University of Leeds, it became clear that it also suited her personality.

"By nature I am not a patient person," Bakac says. "I can't wait to see results. Organic chemistry is typically slow, so that you set up an experiment and let it run for hours. In inorganic chemistry, especially the kind we do, reactions are finished in minutes, microseconds, nanoseconds. I like that."

Bakac has turned that beauty and speed into an entire career exploring and understanding the nature of chemical reactions.

Her research group studies ways to activate normally unreactive molecular oxygen (0_2) through the use of specially designed complexes of transition metals, such as iron or cobalt. The ultimate goal is to develop catalytic oxidations with 0_2 in ways that are efficient and environmentally friendly, ideally using light as an energy source.

"Oxidation is the most prevalent type of chemical reaction, occurring in nature and useful in industry. Oxygen is free and all around us. Light is provided by the sun. Thus the ingredients are freely available. What we need to do is to find a way to make them work together toward our goal," says Bakac.

Another research area for Bakac is the reactivity of nitric oxide (NO), a free radical so vital in biology, medicine, and the environment that it was named "Molecule of the Year" by the journal Science in 1992. Bakac's group has produced and studied several metal-based precursors that use visible light to release NO slowly and in a controlled manner, properties crucial for many applications

"My research team and I work to contribute to the basic understanding of how all these reactions happen on the molecular level, how fast they are, what intermediate states are involved, and how the conditions affect the outcome," says Bakac." In-depth understanding of a particular reaction gives you the power to tailor the outcome by changing temperature, pressure, reagent concentrations and other parameters. If you understand it, you can control it."

A scientist and a writer

Bakac will be retiring at the end of the year, and is thinking about the new directions her life will take outside of the lab. While she will include leisure time and travel, Bakac is also thinking about a second calling.

"I'm sure I will miss science. It will be hard to leave the lab, my colleagues and students behind. But science takes all of your time, energy, and enthusiasm, and there comes a point when you start thinking about other things that you are interested in and want to do before it is too late."

For Bakac that means picking up another thing she finds beauty in: literature. Not only does she have a lengthy backlog of books to read, she's got a plan to write some of her own.

"I have a diploma in children's literature, and I'm planning to write for children. I don't have a specific topic or story just yet, but whatever I write will have a strong science component to it."

Andreja Bakac

Shaking up the Hydrogen Fuel Race

BY KERRY GIBSON

THE CONCEPT SEEMS SIMPLE. YOU PUT TWO compounds into a steel container, add some stainless steel ball bearings, tighten down the lid, then shake the heck out of it. When you open the container, the two compounds have undergone a transformation, creating new compounds that normally require the use of a solvent.

Ames Laboratory scientist Vitalij Pecharsky has been studying "mechanochemistry" for more than a decade to unlock the secret of how ball-milling is able to facilitate important solid state reactions at room temperature without the use of solvents.

"Because of the process – stainless steel balls smashing together inside a sealed stainless steel container – you can't probe the materials while you process them," Pecharsky says. "The best you can do is take samples periodically and hope to develop a map for what's taking place."

While solvent-free mechanochemical processing could revolutionize industries across the spectrum, Pecharsky and his Ames Lab colleagues have focused most of their attention on aluminum trihydride (AlH_3, also known as alane) because of its potential as a hydrogen fuel source. Alane shows promise because it can safely store and distribute large amounts of hydrogen confined in a solid material and it releases its hydrogen at a relatively low temperature so it doesn't require much input energy. It can also be used as a solid propellant, such as rocket fuel, with both the hydrogen and aluminum consumed as fuel.

As a fuel, hydrogen has about three times more energy than gasoline by weight. However, for a car to carry an equivalent amount of hydrogen fuel as a typical tank of gasoline, it would have to be stored at extremely high pressure or liquified at -253 degrees Celsius, neither of which is economically or commercially feasible. Storing hydrogen as a solid material offers the auto industry a more practical alternative.

To produce AlH_3, Shalabh Gupta and Ihor Hlova – members of the team – place an alkali metal hydride, such as lithium hydride, sodium hydride or potassium hydride in a ball mill with an aluminum halogenide, such as aluminum chloride, aluminum bromide or aluminum iodide.

"If you start with lithium hydride (LiH) and aluminum chloride ($AlCl_3$) and mill them together, you wind up with LiCl and AlH_3," Pecharsky says. "You don't lose anything and it doesn't require a solvent. We can get the same results using sodium hydride, which is much more readily available. So it can be relatively inexpensive to produce; you don't have waste other than LiCl or NaCl (common kitchen salt) or used solvent to dispose of."

Importantly, it doesn't require a lot of energy to break AlH_3 into its individual components. According to Pecharsky, it degrades into aluminum and hydrogen at about 100 degrees C – the boiling point of water.

"The Department of Energy has set targets for hydrogen production systems at six percent by weight by the year 2015," he says. "Our technique is capable of producing a total hydrogen capacity of 10 percent so we're optimistic about its potential."

Besides Pecharsky's group's experimental work, other Ames Lab scientists are involved in the project. Characterization by solid-state NMR (nuclear magnetic resonance) expert Marek Pruski and his group members – Takeshi Kobayashi and Jennifer Goldston, and microscopist Scott Chumbley and his student Tim Prost are helping to unlock what is taking place inside the ball mill. And theorist Duane Johnson and members of his team – LinLin Wang and Nikolai Zarkevich – are working to understanding the how. The work is being funded by DOE's Office of Basic Energy Sciences.

One Scientist, Several Hats

"My basic training, going all the way back to the 70s was in chemistry," says Pecharsky, who received his B.S. and M.S. degrees in chemistry and his Ph.D in inorganic chemistry all from L'viv State University in L'viv, Ukraine. "But later on, I switched to materials science and then physics, so I don't really know who or what I am anymore."

He came to Ames Laboratory and Iowa State University in 1993 as a visiting scientist, working with Karl Gschneidner Jr. on magnetic refrigeration and stayed on full time in 1995. His involvement in the hydrogen research came about as a result of scientific curiosity.

"How did I get involved in this? That's probably the million dollar question," Pecharsky chuckles. "There are two things that we look at; one is the science and the second is potential practical application – do we have a useful product at the end."

"The science here is very interesting because there's little you can do to characterize the materials during the process," he adds. "You monitor them at various points and then try do deduce what's taking place. But it's that difficulty that makes it interesting. Advanced characterization and strong theoretical support help a lot."

"Together with my former colleague – Dr. Viktor Balema, who is now with Sigma Aldrich – we initiated an exploratory effort related to mechanochemistry of complex hydrides more than 15 years ago," says Pecharsky. "And today we have a useful process that leads to alane, as described in our recent provisional patent application filed with the U.S. Patent and Trademark Office."

Shalabh Gupta holds a ball mill canister where the solvent-free reaction takes place. The sealed canister presents challenges to understanding just how the reaction is carried out.

Snapshots at 1/1,000,000,000,000 of a second

BY BREEHAN GERLEMAN LUCCHESI

Ames Laboratory physicist Jigang Wang is revealing the mysteries of new materials using ultra-fast laser spectroscopy. Wang likens the technique to high-speed photography where many quick images reveal subtle movements and changes inside the materials. Seeing these dynamics is one emerging strategy to better understanding how new materials work, so that we can use them to enable new energy technologies.

Wang and his colleagues recently used ultra-fast laser spectroscopy to examine and explain the mysterious electronic properties of iron-based superconductors.

Superconductors are materials that, when cooled below a certain temperature, display zero electrical resistance, a property that could someday make possible lossless electrical distribution. Superconductors start in a "normal," often magnetic, state and then transition to a superconducting state when they are cooled to a certain temperature.

What is still a mystery is what goes on in materials as they transform from normal to superconducting. And this "messy middle" area of superconducting materials' behavior holds richer information about the why and how of superconductivity than do the stable areas.

"The stable states of materials aren't quite as interesting as the crossover region when it comes to understanding materials' mechanisms because everything is settled and there's not a lot of action. But, in this crossover region to superconductivity, we can study the dynamics, see what goes where and when, and this information will tell us a lot about the interplay between superconductivity and magnetism," says Wang, who is also an associate professor of physics and astronomy at Iowa State University.

But the challenge is that in the crossover region, all the different sets of a material's properties that scientists examine, like its magnetic order and electronic order, are all coupled. In other words, when there's a change to one set of properties, it affects all the others. So, tracing what individual changes and properties are dominant is difficult.

Wang and the team use ultra-fast laser spectroscopy to "see" the tiny actions in materials. In ultra-fast laser spectroscopy, scientists apply a pulsed laser to a material sample to excite particles within the sample. Some of the laser light is absorbed by the material. Other time-delayed light pulses subsequently hit the material and can be used to take super-fast "snapshots" of what is going on in the material following the laser pulse. The snapshots are replayed afterward like a stop-action movie. One decisive advantage of this approach is the capability to shoot the first frame in less than one trillionth of a second.

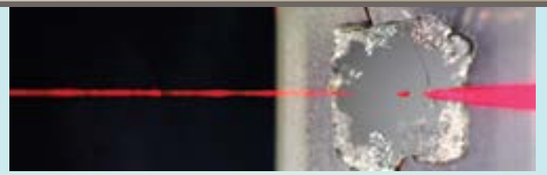
"Ultra-fast laser spectroscopy is still a relatively new characterization technique. "My goal is to help merge the field with the traditional materials research community, which may orchestrate a new paradigm for quantum materials discovery, understanding and control."

The technique is especially well suited to understanding the crossover region of iron-arsenide based superconductors materials because the laser excitation alters the material so that different properties of the material are distinguishable from each other in time. With the help of successive "snapshots and replays," even the most subtle evolutions in the materials' properties can show their secrets.

"Ultra-fast laser spectroscopy is a new experimental tool to study dynamic, emergent behavior in complex materials such as these iron-based superconductors," says Wang. "Specifically, we answered the pressing question of whether an electronically-driven nematic order exists as an independent phase in iron-based superconductors, as these materials go from a magnetic normal state to superconducting state. The answer is yes. This is important to our overall understanding of how superconductors emerge in this type of materials."

Wang and his colleagues have also used ultra-fast laser spectroscopy to demonstrate broadband terahertz wave generation using deep-sub-wavelength metamaterials emitters, quantum ultrafast magnetic switching, and stimulated emission of Dirac fermions in graphene monolayers.

"Ultra-fast laser spectroscopy is still a relatively new characterization technique," says Wang. "My goal is to help merge the field with the traditional materials research community, which may orchestrate a new paradigm for quantum materials discovery, understanding and control."



Ames Laboratory scientists use ultra-fast laser spectroscopy to "see" tiny actions in real time in materials. Scientists apply a pulse laser to a sample to excite the material. Some of the laser light is absorbed by the material, but the light that passes through or reflected from the material can be used to take super-fast "snapshots" of what is going on in the material following the laser pulse.

More is Different

"If there's a theme to my research, it's small things and complex things," says Jigang Wang.

His fascination with the small started as an undergraduate physics student.

"I was interested in the scientific philosophy of reductionism: that to understand phenomena, we have to go to the small, smaller and smallest until we find and understand the most fundamental particles. That by understanding one small piece, we can better understand the whole," says Wang.

The interest led him to study very small semiconductor nanostructures in graduate school and carbon nanotubes as a postdoctoral researcher. But, along the way, Wang turned to physicist Philip Warren Anderson's concept of "more is different," which emphasizes the importance of complexity – how small particles organize themselves and how the organization creates different levels of principles that help explain the whole.

"We see that this concept cuts across different subdisciplines of physics, biology, chemistry, and applied science, and, of course, also in materials science, like superconductivity or magnetism," says Wang. "You have these fascinating functions from these many particles bound by simple interactions. I study these complex systems: their dynamics, or how they change; how certain changes in the systems correlate to other changes to drive cooperative behaviors; and their nonlinearity, or how the output from a system is different from the input, to build functionalities."

"More is indeed different," he adds. "And my goal using femto-second laser spectroscopy is to build our understanding how these complex quantum materials work by revealing their organization principles from nanoscale to mesoscale and how we can harness their properties for energy applications."

Science of the small offers big diversity

BY LAURA MILLSAPS

TO THE CASUAL OBSERVER, THE SCIENCE OF DEVELOPING mesoporous nanoparticles would seem to be a narrowly focused, even esoteric area of chemistry.

But to Igor Slowing, a scientist for Ames Laboratory since 2009, the research is a jumping off place for a wide range of scientific disciplines, and that's the attraction.

"These particles are really a means of accomplishing many different things—they are a platform we can modify or adapt to do anything, from making fuels to delivering medicines to cleaning the environment to things like creating specialized lenses. These structures give me many opportunities to learn more about other areas of science, and that is really exciting to me."

Pursuing a wide range of interests has always been important to Slowing, who taught organic chemistry at three different universities, published books of short stories, and operated a theater company in his native Guatemala before coming to Iowa State University to pursue his Ph.D. studies.

He completed his Ph.D. in 2008 and post-doctoral work with the late Victor Shang-Yi Lin, researching the use of nanoparticles for intracellular drug delivery.

Now, Slowing and fellow Ames lab researchers have successfully developed a biofuel refining technique using mesostructured nanoparticles that combine two processes—sequestering free fatty acids and catalyzing the conversion to green diesel.

Pursuing the use of nanoparticles as catalysts for renewable fuels presents big challenges, says Slowing, as well as big advantages.

"There's such a big diversity of renewable resources. For each resource, whether it's grass or microalgae or orange peels, the technology must be adapted to best process it. This can be a difficult thing," Slowing explains. "But the advantage is this: if we can develop smart, clean, economical processes that are specific to each material, these biorenewable resources can then be used not only for fuel, but also as sources for other things like pharmaceutical components. In that way, we can exploit the benefits of each of these resources fully."

In another project, Slowing is also working to develop nanoparticles that can be used as a substitute catalyst in place of chromium, used in the processing of hydrocarbons but is also an environmental contaminant and carcinogen.

And in a different application, Slowing will be partnering with a researcher from Mississippi State University in a project to develop nanomaterials that can absorb nuclear waste contamination in the environment.

It is a far cry from the technology's origins. With the increasing complexity and capabilities of these particles, they have gotten larger, Slowing says, and are more properly categorized in the mesoscale, or structures larger than 100 nanometers. Because the chemical and physical properties of nanoscale materials differ from the bulk properties of the same material and are the key to their amazing potential, these mid-range or mesodomain materials may hold even more surprises.

"These can act as a bridge between the macro- and nano-world, and we don't know a lot right now about what other properties may emerge. It's one of the great questions I have for future research, and that I look forward to tackling," says Slowing. "Throughout history, it has been the understanding of these properties and how to control them that has been missing," Slowing adds. "As we gain better understanding, the possibilities for their application will continue to expand."

Academic Family Tree:

Slowing also conducts research in an area unrelated to nanoparticles: he keeps an academic genealogy tree on the wall of his office—with names, dates, and pictures.

With pages hanging in a line reaching to the ceiling, Slowing can trace his academic heritage starting with his own doctoral research at Iowa State. From there, his academic heritage goes back on this office wall a few hundred years. It includes scientists who were history books unto themselves, like Benjamin Rush, a signer of the Declaration of Independence and a physician; or Justus von Liebig, a 19th century German chemist and inventor.

"I've always loved history in general and the history of science in particular," says Slowing. "When I began to study chemistry, I was curious to know how I was related to these people that I was reading about."

And Slowing's historical research enabled him to trace his academic genealogy over 600 years, to the flowering of scientific thought that occurred in Western Europe.

Slowing says he'd like to learn more about the scientists in his family tree that are still alive and actively researching. Among them is Harry Gray, a pioneering bioinorganic chemist at the California Institute of Technology whose work Slowing finds fascinating.

"These are scientists actively working in areas very different from mine, and yet their accomplishments keep inspiring my work. The influence of ideas across the years and across scientific disciplines is a great history lesson."

Turning methane into valuable feedstock

BY KERRY GIBSON

PLENTIFUL NATURAL GAS HAS BEEN A BOON TO the U.S. energy sector. While it is fueling electrical power plants and providing heat for industry and homes, natural gas still can't hold a candle to petroleum as a feedstock when it comes to making other products, such as plastics, chemicals and other types of fuels.

The problem with natural gas is that it's primarily methane, along with some ethane and propane. Methane, comprised of one carbon atom and four hydrogen atoms, is tough to process because those hydrogen-carbon bonds are quite strong, and stronger than carbon-hydrogen and carbon-carbon bonds in valuable fuels and chemicals. But Ames Laboratory scientist Aaron Sadow hopes to develop catalysts that will break those bonds, yet control the outcome.

"The chemical industry can't use methane," Sadow says. "It can't go into high-value applications because it's difficult to efficiently and selectively convert. Ethane, by comparison, can easily be converted into ethylene, which is a precursor for a lot of chemicals and polymers."

"Before shale gas, companies were looking for alternative sources of ethylene, because the price of petroleum was going up and it wasn't economically feasible to use it for ethylene production," he continues. "Thanks to abundant natural gas, that's no longer the case. But if you look at other types of chemical feedstock that you can't get from shale gas, those prices have continued to climb."

But if methane could be unlocked as a source for those compounds, the value of natural gas would be increased and reliance on petroleum would be diminished.

Methane conversion has been tried for quite some time. However, methane reactions are hard to control and some of the intermediate products are unstable. In other words, once a reaction starts, it's hard to stop methane from breaking down all the way to carbon dioxide and water.

"The chemical industry can't use methane." Sadow says. "It can't go into high-value applications because it's difficult to efficiently and selectively convert. Ethane, by comparison, can easily be converted into ethylene, which is a precursor for a lot of chemicals and polymers."

A group of Ames Lab researchers, with collaboration from other national labs and private industry, has been looking for ways to control those reactions via catalysis. Within Ames Lab, Sadow's group has looked to Igor Slowing for help with high-surface-area metal oxides and to Marek Pruski's group to help characterize those materials via solid-state NMR. Theoretical groups led by Mark Gordon, Teresa Windus and Jim Evans are working to develop models for what's taking place.

"We (Sadow's group) had found some reactions where we were able to break what we thought were strong bonds with reducing reagents and that suggested a strategy for activating surfaces for bond activation chemistry," Sadow says. "Since these are dynamic systems, understanding how conversions happen will be really important. We had some recent results where we'd seen some molecular chemistry which suggested strategies for activating surfaces and high surface area materials towards bond activation."

"A lot of the general ideas are out in the literature, but what we bring is explicit insight into what goes on at single sites. We hope to then extrapolate that to high surface areas," he says. "We're well set up to try figure out what's taking place and how we might control it."

Sadow believes in teamwork

The current work relates somewhat to research Sadow did as a graduate student at the University of California-Berkeley.

"I was in Don Tilley's group where we were using organometallic molecules to activate methane," Sadow says. "Unfortunately the organometallic systems are delicate – they're very sensitive to air, moisture and temperature. In our current work, we're hopeful that a metal oxide surface with lots of sites will overcome that problem."

For Sadow, cracking the methane problem is both a chemical challenge and an economic imperative.

"Methane activation has been a challenge for 100 years," he says. "We know how to burn it and we can turn it into syngas under gasification conditions, but that's an inefficient pathway. At the same time, we also can't continue to rely on oil for all these chemical precursors."

"The group we have here at Ames Lab is in a unique position," he continues. "To be industrially useful, you need systems that are thermally stable. Fortunately, there have been tremendous advances in spectroscopic techniques for heterogeneous catalysis. The nano revolution has really given us new insight into what's on surfaces and how to think about surfaces and surface reactivity."

"Ames Lab has experts in materials, characterization, and expertise in trying to understand reactivity and develop single-site catalysts, so you bring it all together and we hope to affect some exciting changes."

Reading Spectral Fingerprints

BY BREEHAN GERLEMAN LUCCHESI

"WHY IS SOLID-STATE NUCLEAR MAGNETIC resonance is so powerful? Because it can tell us how individual atoms are arranged within a material," says Ames Laboratory scientist Marek Pruski. "And, it can tell us how molecules or molecular fragments move in very short time frames."

To obtain this detailed information about materials' structure and dynamics, solid-state NMR monitors the response of atomic nuclei to excitation with radio frequency waves.

"The frequency at which nuclei respond creates a unique spectral 'fingerprint' of their local environment within a material," says Pruski.

These "fingerprints" are especially useful in understanding the structure of non-crystalline materials — that is, materials that do not display regular crystalline structure amenable to diffraction studies. But, solid-state NMR is a challenging business. Because it operates at the low-energy end of the electromagnetic spectrum, the population difference between energy levels involved in NMR transitions is exceedingly small—only a few spins per million effectively generate the NMR signal.

To remedy the sensitivity woes, solid-state NMR experts, like Pruski, are constantly looking for new strategies, which include innovative radio frequency pulse sequences and advanced instrumentation: stronger magnets, state-of-the-art probes, and novel computational tools.

In the last few years, several approaches involving 'hyperpolarization' of nuclear spins have emerged that are poised to revolutionize NMR spectroscopy. Chief among these is dynamic nuclear polarization (DNP). In short, DNP NMR relies upon excitation of the unpaired electrons by microwave irradiation and subsequent transfer of the resulting spin polarization to the material's nuclei, resulting in a much stronger response from these nuclei than is possible in conventional solid-state NMR.

"The frequency at which nuclei respond creates a unique spectral 'fingerprint' of their local environment within a material," **says Pruski.** "These 'fingerprints' are especially useful in understanding the structure of non-crystalline materials—that is, materials that do not display regular crystalline structure amenable to diffraction studies."

In June, Ames Laboratory became home to the first DNP NMR used for materials science in the United States.

"This instrument will allow us to improve the sensitivity by 100 times, and thus take data up to 10,000 times faster," says Pruski.

Commercial DNP NMR systems only became available in the last few years. Pruski and his Ames Laboratory colleague, Takeshi Kobayashi, collaborated with research groups in Europe to demonstrate how useful the DNP NMR will be for materials research at Ames Laboratory.

"We have solid evidence that the DNP NMR is a game-changing technique," says Pruski. "Remarkably, DNP NMR is still emerging. There's great potential for its further development, and we are looking forward to making these advances. Most importantly, however, we want to utilize this new capability within several Ames Lab's research programs to study complex metal hydrides, novel heterogeneous catalysts, biological nanocomposites, thermoelectrics and other energy-related materials."

Serendipity sets Pruski's career path

Ask Marek Pruski what keeps him interested in his work and he doesn't pause for even a second: "Nuclear magnetic resonance is a superbly exciting discipline that continues to develop. And the rate at which it develops just doesn't slow down."

"And, it's just the right mix, for me, of physics and chemistry and experiment and theory. The variety keeps it exciting," he adds.

Pruski's path to joining the solid-state NMR research community was quite serendipitous. He was attending an NMR conference in Poland when he literally bumped into Bernie Gerstein, a former leader of Ames Lab's solid-state NMR program.

"I was coming in a hotel lobby through a revolving door, and Bernie was going out and we ran right into each other. I recognized him as one of the plenary lecturers at the conference, and we got to talking and decided to go to dinner. A three-hour dinner conversation turned into an offer to become a post-doctoral researcher in Bernie's group at Ames Lab."

Pruski joined Ames Laboratory in 1985 as a post-doc and became a staff scientist in 1988. Since then, he's enjoyed being at the leading edge of the field and watching the community of solid-state NMR grow.

"The development of NMR is an absolutely phenomenal thing to watch and be a part of. It's just fascinating. I love it."

From Science Bowler to Scientist

BY STEVE KARSJEN

For the hundreds of students who travel to Washington, D.C. each year, the Department of Energy's National Science Bowl provides an incredible opportunity for teams to participate in intense competition, sightsee at the National Mall, and make new friends.

But for some students, the benefits don't end with just the obvious. The event also includes Saturday Science Day talks, given by the DOE's leading scientists, that provide the perfect forum for students to bombard scientists with questions on leading-edge topics. The answers they get can also hold importance down the road.

At least that's the way it's worked out for student William Meier. Meier was a member of the Oak Park High School team from Kansas City that competed in the 2008 National Science Bowl. Meier remembers his team having a great time during Science Bowl, as well as the Saturday Science Day talk that made a lasting impression on him, both because of the topic and the scientist who delivered it.

William Meier

The scientist was Paul Canfield, senior physicist at the Ames Laboratory and Distinguished Professor of physics and astronomy at Iowa State University, who spoke on the design, discovery, growth, characterization and use of novel materials. The lively session included an informative back-and-forth exchange between the veteran scientist and the student participants.

"I have always enjoyed hearing from scientists very knowledgeable on a topic," says Meier. "I had a background in earth science and mineralogy at the time of the talk so I found Dr. Canfield's lecture incredibly interesting. Crystal growth seemed to be a great example of how I could combine several topics I loved."

"That was a really neat event," Canfield adds. "I specifically remember William coming up after the talk and discussing details of new materials growth and characterization. I was impressed with the depth of his knowledge, even at that time. He clearly had an interest in geology as well as basic crystallization."

As enjoyable as he found the exchange with Canfield, Meier's desire to learn more about crystal growth took a back seat to the National Science Bowl competition matches that weekend. After Science Bowl were his junior and senior years of high school and preparing for college and selecting a college major. Ultimately, Meier chose to pursue ceramic engineering at Missouri University of Science and Technology.

"I took a temporary detour from physics to materials," says Meier, "but I still took many courses in physics and chemistry at MS&T, which allowed me to indulge my interest in these topics."

"I even thought about changing my major to physics, but I enjoyed the engineering faculty in my department so I decided to finish my undergraduate degree first, then switch to physics for graduate school."

And that's when the interaction with Canfield he'd enjoyed some five years earlier resurfaced.

"I remembered Dr. Canfield's talk from 2008," said Meier. "So I called him up and he encouraged me to apply to the physics program at Iowa State."

Now a first-year graduate student in physics at ISU, Meier says his next step is to join Canfield's crystal-growth group. "I'm attending his group meetings, and it sounds like I will be learning some of the growth techniques this semester and summer."

"I was so pleased when William called me," Canfield says. "He really made an impression during that Saturday talk, and I was delighted at the idea of having him perform his Ph.D. research here. I think his background in geology and material science compliments the condensed matter physics work we emphasize. Ultimately new materials research draws from all of these sources and William has a good start at a very interdisciplinary foundation. The interdisciplinary nature of research is something that the Science Bowl, as well as the Science Saturday event, tries to emphasize."

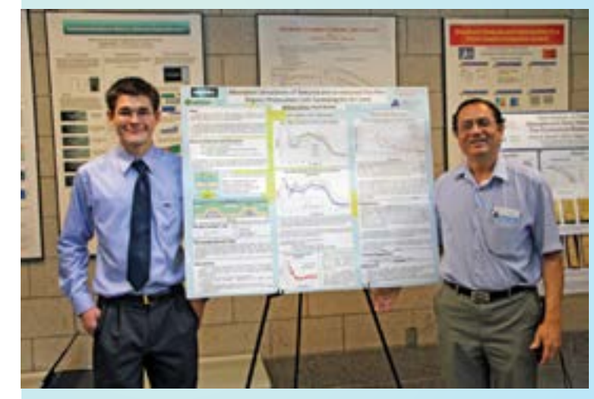
Canfield and Meier met recently in Canfield's office, which prompted another lively discussion on new materials growth and characterization.

Early opportunities for interactions with scientists can "definitely influence career choices" says Meier, who hopes that after doing research as a post-doc at a university or national laboratory he can ultimately find a faculty position in physics or materials science and teach further generations. And who knows? Perhaps one day he'll be giving an invited Saturday Science Day talk at the National Science Bowl and another inquisitive student just like him will be in attendance.

Paul Canfield answers questions from William Meier (center left) and his teammates after the conclusion of his formal Saturday Science Day talk at the 2008 National Science Bowl.

Science Undergraduate Laboratory Internship

Besides the National Science Bowl, Meier also participated in the DOE's Science Undergraduate Laboratory Internship program, first at the Ames Laboratory, where in the summer of 2011 he worked with Rana Biswas, Ames Lab physicist, doing computer modeling of textured solar cells and then the following summer with scientists at Sandia National Lab.

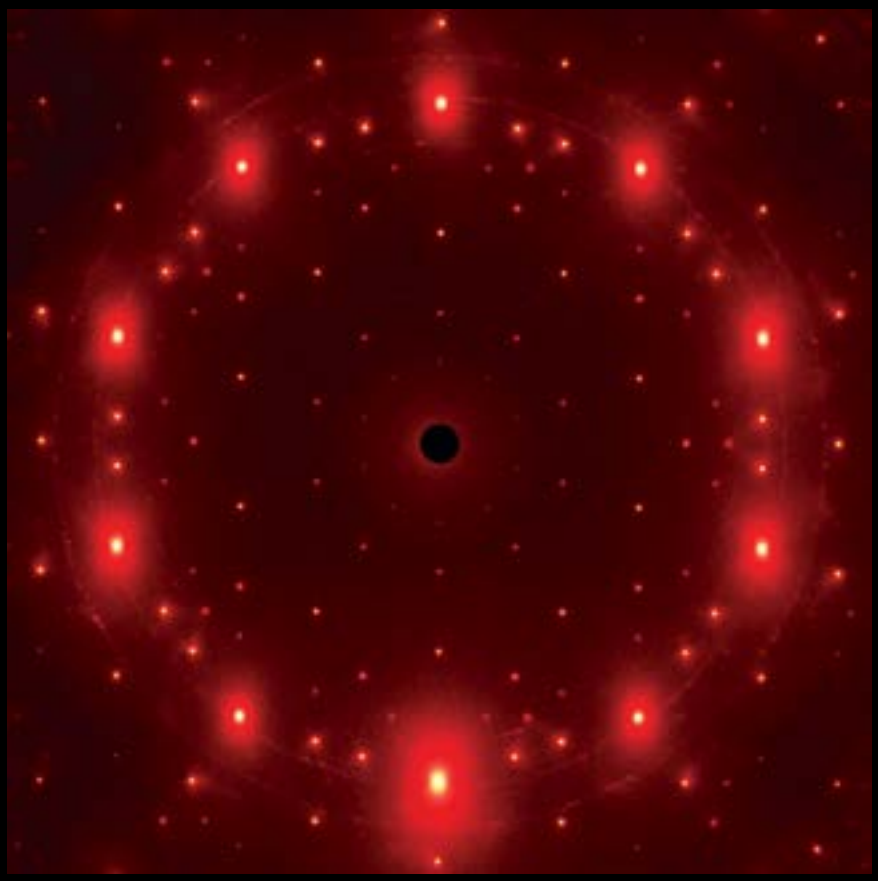


William Meier and his Ames Lab mentor, Rana Biswas, at the 2011 SULI poster session.

inquiry 2014
Issue 1

Ames Laboratory
111 Technical and Administrative Services Facility
Ames, Iowa 50011-3020
515-294-9557
www.ameslab.gov

100 YEARS OF CRYSTALLOGRAPHY



Ames Laboratory physicist Alan Goldman's x-ray diffraction work helped prove the existence of quasicrystals, materials with five-fold geometry first described by 2011 Nobel Prize winner (and Ames Lab scientist) Danny Shechtman.

Crystallography, the study of the crystalline structure of materials, was born in 1914 when German scientist and Nobel Prize winner Max vonLaue discovered that x-rays focused on crystals diffract, revealing the crystalline structure within. In the century, since von Laue's discovery, x-ray diffraction has become a powerful tool, in the field and particularly at **the Ames Laboratory**, in understanding the make-up of materials and how those structures affect a material's properties and characteristics.

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

IOWA STATE UNIVERSITY

U.S. DEPARTMENT OF ENERGY