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MPA Materials Matter

INSIDE

Nathan Mara designs materials with specific properties by manipulating and controlling atoms one by one at the nanoscale—and using novel nanomanufacturing processes.
Photo by Richard Robinson, NIE-CS

Nathan Mara

Bulking up lightweight nanomaterials

By Diana Del Mauro, ADEPS Communications

Mara's research has revealed that manufacturing methods can change a material's behavior just as much—and sometimes more than—its combination of elements.

When Nathan Mara, who works toward making damage-tolerant materials Los Alamos National Laboratory, tells his four children he is inventing an Iron Man suit, they beg to see it. Yet designing a finished good like a superhero's outfit is a considerable feat due to the complexity of nanomaterials, which create its unique attributes.

Mara is known in his field for bulking up nanolayered composites. Through the Lightweight Materials Consortium, sponsored by DOE's Vehicle Technologies Office, American industries can tap into Mara's expertise, including his techniques for damage-tolerant layered nanocomposite bulk fabrication.

Increasing materials in size from the nanoscale to the bulk scale is the hardest part, Mara explained. In his office, he removed from a plastic vacuum chamber a thin foil made of 1,000 layers of copper. The material exhibited "indestructible Iron Man suit kind of properties," Mara said, "as strong as the strongest tool steels and healing itself under ion irradia-

continued on page 4

From Rick's desk . . .

It has been a great start to an incredibly busy summer. Thank you to everyone for your attendance, support, and contributions with this year's Materials Capability Review and CINT Triennial Review. Both reviews went extremely well; our presentations and posters were well received and once again, it reminds me of how proud I am to be part of MPA.

This year's Materials Capability Review focused on the Material Strategy Refresh, our leadership in Materials Dynamics and MaRIE. Talks for the Materials Strategy Refresh focused on the goals of the Refresh and further integration of our Materials Strategy. Recall, among the goals for the Refresh, we want to include a stronger connection to our broader national security mission and better position LANL to be a world-changing organization by providing transformational material science with applied technologies. I hope you will attend the additional town halls, deep dives, and focused meetings throughout the summer to ensure that our new strategy is even better.

The Materials Dynamics session focused on processing-microstructure-properties-performance, new constitutive models, and the use of advanced light sources. It is amazing to see the wealth of new data from light sources around the world. MaRIE continues to move forward with a number of high-level reviews in DC this spring. The MaRIE material presented at this year's capability review focused on current capabilities with bright and coherent light sources, and data, theoretical modeling, and simulations across multiple length scales.

Look for opportunities to participate in MaRIE-related workshops and town hall meetings this summer, as there will be a total of 13, with 3 of them focused on M4 (Making, Modeling, and Measuring Materials). Other interesting internal meetings and workshops that are still to come include the BES review later this fall, the NSF site visit, and the user committee meeting for the magnet laboratory.

This year continues to be a great year for capability investments in MPA and throughout ADEPS. Hopefully you have heard that we have reopened the cleanroom at SM-40 to establish a flexible fabrication capability to support the fabrication of nano-to-meso- scale device assemblies. Capabilities planned for the cleanroom include systems for photolithography, e-beam and sputtering deposition, x-ray diffractometry, reacting ion etching, three dimensional profilometry, as well as ventilated benches for performing chemical processes. As you can tell, this will be an outstanding open-access capability for the Laboratory.

"This year continues to be a great year for capability investments in MPA and throughout ADEPS."

Summer is a great season to be in New Mexico and an exciting time at the Laboratory. I enjoy the enthusiasm and energy of the students, postdocs, new hires, and old friends alike. Please take time to enjoy New Mexico and participate in the workshops at Los Alamos and use this as an opportunity to make the Lab even better.

MPA Deputy Division Leader Rick Martineau

From George's desk

It seems hard to believe that is has been nearly two years since I joined MPA Division. We have seen tremendous change and growth over this time, and I wanted to take the opportunity to use this "From the desk" to highlight one of our experimental actinide science facilities and some of the exciting new capabilities we have added over the last few years.

I have had the privilege to serve as the point of contact and facilitator for the Actinide Research Facility (ARF) for the last seven years. The ARF is a multi-user laboratory located in building RC-1 at TA-48, and is the largest of the synthetic and characterization laboratories for transuranic science at TA-48. From the mid-1950s to the late 1990s the ARF was called the "Dissolving Wing" and was built to chemically process and analyze shot core samples from underground nuclear testing. Today, the ARF hosts a wide range of R&D projects supporting both fundamental and programmatic work from sponsors such as the Office of Science, DOE-Nuclear Energy, DOE-Nuclear Physics, NNSA, DSW, DHS, and DTRA. Research topics range from discovery science synthesizing novel actinide compounds to understand *f*-element bonding and electronic structure, to developing novel separations processes for nuclear fuel reprocessing or special nuclear material production, to nuclear forensics and diagnostics development. In recent years the ARF has supported active collaborations with simultaneous users from as many as seven different divisions and three different directorates. The ~3,000 square-foot lab is outfitted with 12 fume hoods and 3 different gloveboxes (including inert atmosphere capability) and can accommodate plutonium-239 samples up to the 10-gram scale. In addition to a number of ovens and tube furnaces, the ARF houses a wide number of analytical spectroscopic characterization instruments (UV-vis-NIR, FT-IR, Raman, and fluorescence).

"I wanted to take the opportunity to use this "From the desk" to highlight one of our experimental actinide science facilities and some of the exciting new capabilities we have added over the last few years."

In recent years, we have made a concerted effort to expand our capabilities for both x-ray analysis and surface characterization. The x-ray capability at TA-48 includes two single crystal x-ray diffractometers (both authorized for transuranics), a thin film diffractometer and a powder diffractometer, the latter of which is located in the ARF. Our Bruker D8 Advance Powder X-ray Diffractometer is equipped with a robotic 90-sample auto-changer, a high-temperature heating stage (up to 1400°C), a variable temperature-humidity chamber, and environmental chambers for air and water sensitive compound analysis. This summer we are adding two high pressure chambers which are UL listed for up to 100 bars H_2 and 900°C, one of which will be dedicated to transuranic experiments. These high-pressure chambers are the first sold in North America and will provide a unique capability for studying materials and chemistries under high temperatures and pressures for both actinide science as well as non-radioactive applications such as hydrogen storage materials. Two years ago we added a Thermo DXR™ Smart Raman Imaging Microscope, which is capable of 3D imaging of samples with a resolution of 1 μm and is capable of analyzing non-radioactive as well as actinide (including plutonium) samples. This summer we are also adding a PhenomPro Benchtop SEM/EDS for transuranic samples with greater magnification for elemental analysis from B through Am. This will be the first SEM authorized for transuranic analysis outside of the CMR or TA-55, and will provide a valuable capability for plutonium science.

While the ARF is primarily used for actinide science, our analytical capabilities can accommodate non-radiological samples. Some of our newer capabilities are opening new avenues for scientific exploration that we are excited to explore, and we look forward to sharing some of the results from these capabilities in the near future!

MPA-11 Deputy Group Leader George Goff

Mara cont.

tion conditions." He was unable, however, to fabricate quantities bigger than a button with those desirable attributes.

Since that experiment, his research has revealed that manufacturing methods can change a material's behavior just as much—and sometimes more than—its combination of elements. He chose materials science and engineering for his doctorate at the University of California, Davis, after a double bachelors in mechanical engineering and materials science and engineering because he likes "seeing everything from materials design to engineering design come together into an impactful story," he said, and that requires a grasp of both disciplines.

Mara and his colleagues are determined to show that magnesium, one of the lowest density structural materials on earth, can be made robust enough to replace some components in cars—with the weight savings boosting gas mileage from 30 to 76 miles per gallon.

The challenge is to transform magnesium from coarse-grained to nano-grained, which results in a far stronger material. Through the Laboratory's internal research and development program, Mara and colleagues have set a target of producing nano-magnesium composites in bulk sheet form in three years. Such a breakthrough in "microstructural processing by design," he said, would transform magnesium research and manufacturing. He's banking on interface-driven properties, his area of study into the material qualities created by the interplay of atoms between constituents of composite materials, to guide the way.

When Mara and Los Alamos theorist Irene Beyerlein began their research in 2008, few teams were synthesizing multi-layered nanocomposites in bulk sizes.

With an ancient steel-making technique for forging samurai swords as their inspiration, they slashed and smashed two soft, ductile metals–copper and niobium–into extremely thin layers–down to 40 atoms across to dramatically enhance the properties of such materials. The result was a sample as big as a snow ski and as ultrahigh strength, thermally stable, and radiation resistant as an Iron Man suit. Through subsequent experiment and modeling, they saw how the manufacturing process caused the atoms where the two metals met—the interface of copper and niobium—to fall into an unusual arrangement, and thus create the material's properties, rather than the constituent metals themselves.

As Mara spoke, he picked up a copper-niobium sample about the size of a chocolate bar, but thicker and heavier, with "65,536 layers" written across it.

How do a material's interfaces form this way? Mara said if he could watch the process unfold in picosecond time scales and at nanometer length scales, such as will be possible at Los Alamos's proposed MaRIE (Matter-Radiation Interactions in Extremes) experimental facility, he could find out.

He looks forward to the day when he can drive up in a lightweight nanocomposite sports car and step out to show his children his impenetrable armor suit. Until then, he will just drive his kids around town in his '89 Chevy Van.

Nathan Mara's favorite experiment

What: Synthesizing ultrastrong, thermally stable, radiation-damage-tolerant bulk nanolayered metals with preferred atomic interfacial structure via severe plastic deformation (SPD).

Why: New materials could improve the efficiency and safety of nuclear reactors and provide strong, lightweight materials for transportation applications.

When: 2011

Where: Los Alamos National Laboratory's Sigma Facility, Center for Integrated Nanotechnologies, the Lujan Center, and Electron Microscopy Laboratory

Who: Irene Beyerlein, Curt Bronkhorst, Jason Mayeur, Keonwook Kang, Ruifeng Zhang (T-3); John Carpenter, Rodney McCabe, Jeffrey Scott, Duncan Hammon (Metallurgy, MST-6); Jon LeDonne (Carnegie Mellon University); Nate Mara, Amit Misra, Shijian Zheng (Center for Integrated Nanotechnologies, MPA-CINT); Tom Nizolek (University of California, Santa Barbara); Sven Vogel (Materials Science in Radiation & Dynamics Extremes, MST-8)

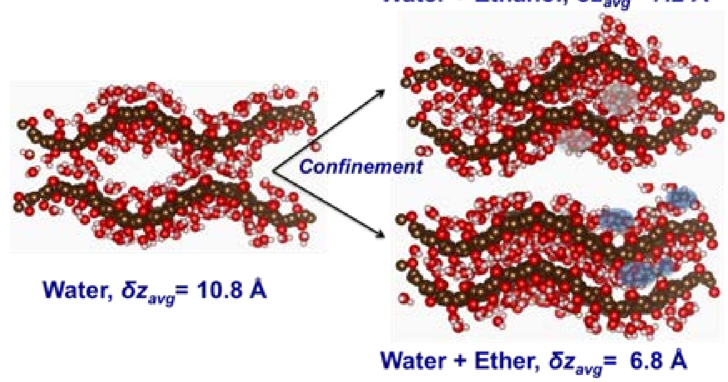
How: Accumulative roll-bonding

The "a-ha" moment: Until this discovery, it was thought that only thin film deposition techniques could provide control over interface structure to yield materials with incredible performance under extreme environments. We found that nanolayered composites made via a bulk, scalable thermomechanical processing technique could give similar control over interface structure, enabling manufacture of kilograms of damage-tolerant nanomaterial.

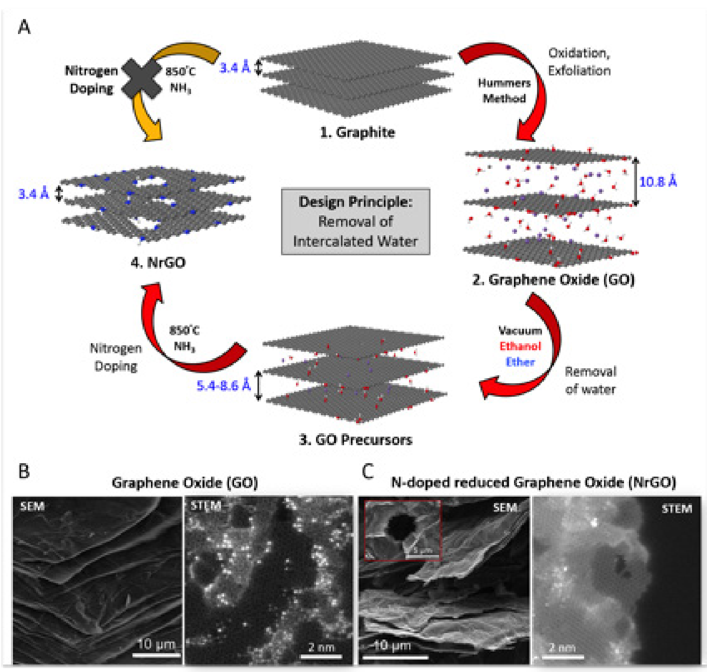
Water-removal technique boosts performance of carbon nanomaterials for energy applications

The key to designing next-generation carbon nanomaterials with enhanced performance for fuel cell and battery applications is to take the water out of the synthesis process. The findings by a Los Alamos-led team are based on a breakthrough in understanding the critical role of water in the formation of catalysts for oxygen reduction in materials.

Published in *Science Advances*, the research provides the first comprehensive understanding of intercalated water's role within graphene oxide nanosheets (GN). In general, graphene oxide is synthesized in aqueous solutions, and even "dry" graphene oxide films contain a substantial amount of intercalated water that organizes between the oxygen-functionalized nanosheets. The team demonstrated a simple solvent drying technique, based on Hansen's solubility parameters such as dispersion, hydrogen bonding character and polarity, to remove intercalated water within the graphitic sheets; it led to significant changes in the physical structure of GN, i.e., decrease in interlayer d-spacing, changes in the concentration of functional groups, and emergence of highly ordered structures. These observed changes play a direct role in forming active sites upon nitrogen doping, resulting in dramatically enhanced electrocatalytic activity.



Theoretical models of solvent-treated graphene oxide structures. Molecular dynamics relaxed structures for water, water/ethanol, and water/ether. Brown spheres represent carbon atoms, red spheres represent oxygen atoms, and white spheres represent hydrogen atoms. Addition of solvent molecules in between each layer leads to a decrease in d-spacing as observed from XRD data.



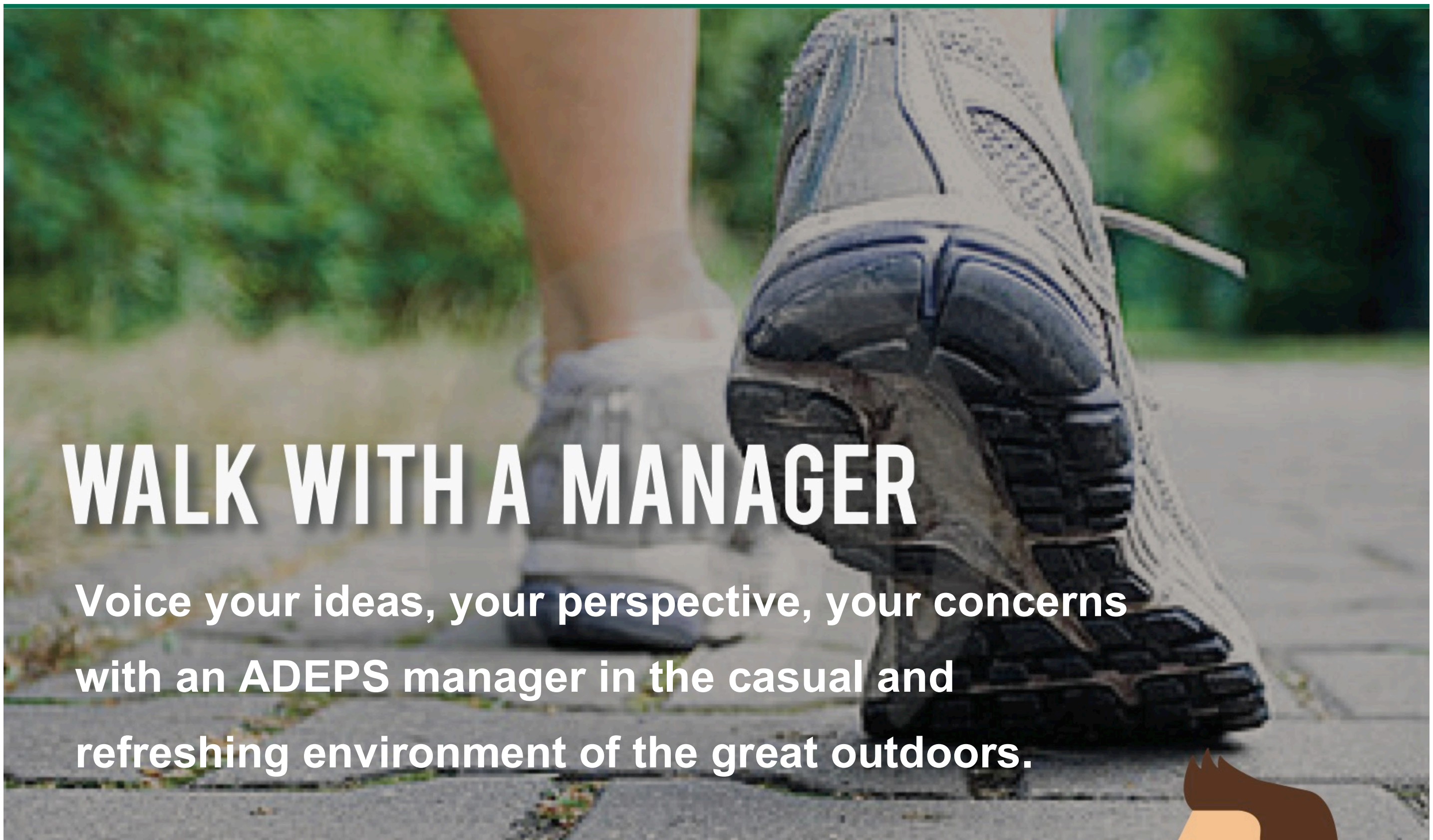
Synthesis of nitrogen-doped reduced graphene oxide (GO) catalysts. A) schematic of the process developed to make nitrogen-doped reduced graphene oxide catalysts. Natural graphite is chemically functionalized and exfoliated using potassium permanganate and sulfuric acid (modified Hummers method) to produce a GO powder with a d-spacing of ~1 nm. GO is then subjected to different solvent rinsing treatments followed by vacuum drying to effectively remove unbound intercalated water as indicated by the decrease in d-spacing. The resulting dried GO is doped with nitrogen leading to the formation of nitrogen-doped reduced graphene oxide catalysts with a final d-spacing of 3.4 Å. B) electron micrographs of GO, and C) nitrogen-doped GO (ether) showing oxidized and graphitic domains. Brighter atoms correspond to Si atoms, a common graphene impurity.

The team demonstrated state-of-the-art performance of nitrogen-doped reduced graphene oxide in acidic environments and demonstrated the best electrochemical stability reported thus far for GN-based catalysts. An onset potential of ~0.9 V, half-wave potential ($E_{1/2}$) of 0.71 V, and selectivity for 4-electron reduction of oxygen >95% (<5% H_2O_2) was observed in acid-media.

A Los Alamos Directed Research Grant funded the work, which supports the Lab's Energy Security mission area and Materials for the Future science pillar. The work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the DOE Office of Science by Los Alamos and Sandia national laboratories.

Reference: "Critical Role of Intercalated Water for Electrocatalytically Active Nitrogen-Doped Graphitic Systems," *Science Advances*, **2** (2016). Los Alamos authors: Ulises Martinez, Joseph Dumont, Geraldine Purdy, Akhilesh Singh, Piotr Zelenay, Andrew Dattelbaum, Aditya Mohite, Gautam Gupta (Materials Synthesis and Integrated Devices, MPA-11): Edward Holby (Metallurgy, MST-6) and Nathan Mack (Nuclear Nonproliferation and Security, GS-NNS), with collaborators from University of New Mexico, Oak Ridge National Laboratory, and Rutgers University.

Technical contact: Gautam Gupta



WALK WITH A MANAGER

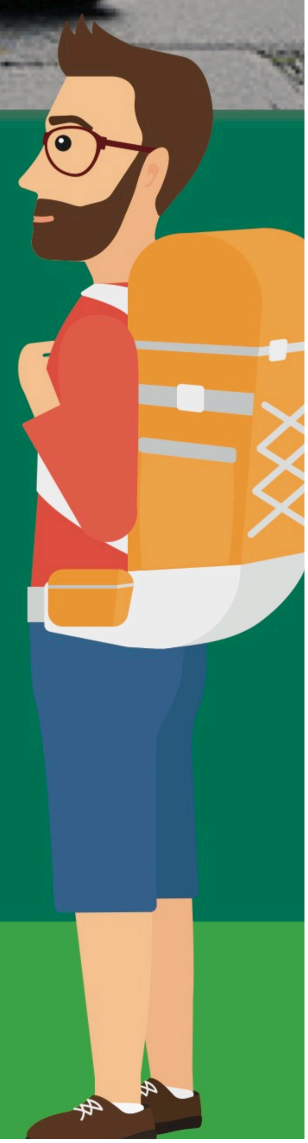
Voice your ideas, your perspective, your concerns with an ADEPS manager in the casual and refreshing environment of the great outdoors.

During the months of July and August, ADEPS managers are available to staff interested in getting together for informal walking and talking meetings.

The event is part of the directorate's health and wellness initiative aimed at promoting a healthy, safe, and productive workforce.

Nothing is off the table; topics are yours to decide.

So don your sensible shoes, bring a water bottle, and walk with a manager!



To make an appointment, contact the following:
ADEPS: Tina Varela, cvarela@lanl.gov, 665-4454
MPA: Susie Duran, susiew@lanl.gov, 665-1131
MST: Monica Roybal, mgr@lanl.gov, 665-1535
P: Gerri Barela, gbarela@lanl.gov, 667-4117
SIGMA: Brenda Espinoza, bme@lanl.gov, 667-4368

ECS recognizes Rangachary Mukundan for sensor achievements

Rangachary Mukundan (Materials Synthesis and Integrated Devices, MPA-11) has won the 2016 Sensor Division Outstanding Achievement Award, presented biennially by the Sensor Division of the Electrochemical Society (ECS). The award is the highest recognition the division can bestow on a member.

Los Alamos has performed pioneering research in understanding the working principles of mixed potential electrochemical sensor leading to patented novel sensor designs. Currently, the Laboratory is working to commercialize these sensors for hydrogen safety and automotive emissions control applications with Industrial partners.

Mukundan (Mukund), graduated from the Indian Institute of Technology, Roorkee, India with a bachelors degree in metallurgical engineering and received his Ph.D. in materials science and engineering under the supervision of Profs. Wayne Worrell and Peter Davies at the University of Pennsylvania. His thesis was awarded the S. J. Stein Prize for superior achievement in the field of new or unique materials in electronics. He joined Los Alamos in 1997 as a postdoctoral fellow and has been a staff scientist there since 1999. His research interests include electrochemical gas sensors, fuel cells, and energy storage devices. He leads several projects related to sensors and fuel cells funded by the Department of Energy. His work on sulfur tolerant anodes for fuel cells was recognized as *Scientific American*'s Top 50 Science and Technology Achievements for 2003. His work was also recognized by the J.B. Wagner Award of the High Temperature Materials Division of the Electrochemical Society in 2005. He is the co-inventor on 6 U.S. patents and has authored more than 125 papers including more than 50 in peer-reviewed journals that have been cited over 4,000 times. He is the technical editor in the area of sensors and measurement sciences for the ECS journals.

The Electrochemical Society is a U.S.-based professional association with more than 9,000 members in more than 75 countries. Its mission is to advance theory and practice at the forefront of electrochemical and solid-state science and technology, and allied subjects. Mukundan will receive the award at the 230th ECS Meeting in Honolulu in October.

Technical contact: Rangachary Mukundan

Quantum criticality in a low-carrier system

The easily tuned balance among competing interactions in Kondo lattice metals allows access to a zero-temperature, continuous transition between magnetically ordered and disordered phases, a quantum-critical point (QCP). Indeed, these highly correlated electron materials are prototypes for discovering and exploring quantum critical states. Theoretical models proposed to account for the strange thermodynamic and electrical transport properties that emerge around the QCP of a Kondo lattice assume the presence of an indefinitely large number of itinerant charge carriers.

In research appearing in the *Proceedings of the National Academy of Sciences of the United States of America*, Los Alamos researchers and collaborators report that pressure- and field-induced zero-temperature magnetic phase transitions in $CeNi_{2-d}As_2$ emphasize the previously unappreciated importance of a low-carrier density on the nature of quantum-phase transitions and signatures of quantum criticality. Conditions leading to a local type of quantum criticality have remained uncertain since evidence for it was discovered nearly 20 years ago.

Their study of $CeNi_{2-d}As_2$ reveals—for the first time—that a sufficient condition for local quantum criticality is a low-carrier density and that consequences of this condition should be considered explicitly in models of criticality.

An unconventional quantum-critical point involves a critical destruction of the Kondo entanglement and a reconstruction of Fermi surface topology. A description of such quantum criticality requires a broader experimental basis and a theoretical model that includes critical fermionic degrees of freedom.

Their research provides a rare example of peculiar quantum-critical behavior in the low-carrier density limit. Most significantly, the similarity between our $CeNi_{2-d}As_2$ and the well-known quantum-critical Kondo lattice system $CeCu_{6-x}Au_x$ indicates that a condition favorable for the unconventional quantum criticality is a “small” Fermi volume that disfavors the conventional Hertz–Millis-type spin density-wave criticality. This insight provides new guidance for where new examples of unconventional quantum criticality could be found.

Researchers are Y. Luo, F. Ronning, N. Wakeham and J.D. Thompson, (Condensed Matter & Magnet Science, MPA-CMMS), with collaborators X. Lu and Z.-A. Xu (Zhejian University, China) and T. Park (Sunkyunkwan University, South Korea). The work, funded by the DOE Division of Materials Sciences and a Director's postdoctoral fellowship supported through Los Alamos's Laboratory Research and Develop-

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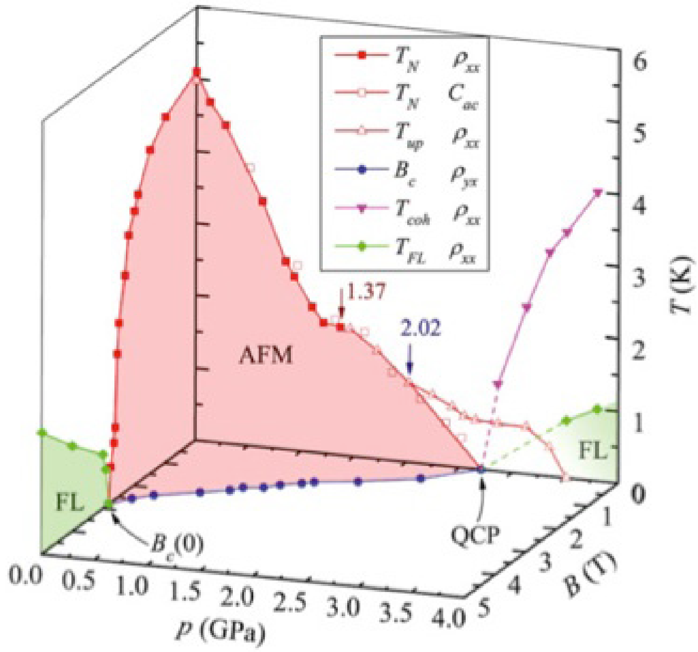
Quantum cont.



Temperature (T)-pressure (p)-field (B) diagram for $CeNi_{2d}As_2$. The Neel temperature (T_N(p,B)) is determined by resistivity (ρ_{xx}) and specific heat (C_{ac}) and the T=0, p-B boundary by Hall resistivity (ρ_{xx}). The Hall effect implies a very small carrier density of ~0.03 electrons/formula unit. At the quantum-critical pressure (QCP) of 2.7 GPa, C_{ac}/T diverges as $-\ln T/T_0$, and at the T=0, p=0, quantum critical field $B_c(0)$, $C_{ac}/T|_{T\text{-}0}$ is a maximum. These are expected signatures for a local-type of quantum criticality, but the transport signature for criticality at the QCP is unusual due to the low carrier density.

ment program, supports the Laboratory's Energy Security mission and the Materials for the Future science pillar.

Reference: "Pressure-tuned quantum criticality in the antiferromagnetic Kondo semimetal $CeNi_{2-\delta}As_2$," *PNAS*, **112** 13520 (2015).

Technical contact: Yongkang Luo

Celebrating service

Congratulations to the following MPA Division employees recently celebrating a service anniversary:

Michael Pacheco, MPA-CMMS................................45 years
Eric Brosha, MPA-11..25 years
Alex Lacerda, MPA-CINT..20 years
Anatoly Efimov, MPA-CINT...................................... 15 years

HeadsUP!

Be mindful of risks for new workers

Many new and returning students, as well as new employees, have joined the Laboratory this summer. According to the National Safety Council, new employees are more vulnerable to injuries. Data from the Institute for Work and Health and the Bureau of Labor Statistics indicates that new workers are three times more likely to suffer an injury on the job than employees who have been on site for one year. Additionally, 8% of all non-fatal occupational injuries reported involved an employee who was on the job for less than a year, and those injured were out of work for a month or more as a result of the kind of injuries they sustained.

In order to reduce the chances of injury to new hires and students employees can:

- Ensure proper training for new hires
- Communicate clear safety rights, pause work procedures, and questioning-attitude practices
- Reinforce safety concepts until new employees become comfortable.
- Assign lower-risk tasks first and gradually work toward to higher-risk tasks.
- Mentor or assign a mentor or buddy system for new employees.
- Check in with new employees in detail about a month after they start work, reinforcing key concepts and ensuring their familiarity and comfort with their work

MPA Materials Matter

Materials Physics and Applications

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To submit news items or for more information, contact Karen Kippen, ADEPS Communications, at 505-606-1822 or adeps-comm@lanl.gov. To read past issues see www.lanl.gov/orgs/mpa/materialsmatter.shtml.

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