the Lujan CENTER SCIENCE & PEOPLE

October, 2013
LA-UR 13-28262

INSIDE

2 JCP's 80th anniversary issue includes Lujan Center polymer study / "Shape-Setting" Mechanics for Shape Memory Alloy Actuators

3 New High Magnetic Field Capabilities

4 When quantum becomes magic

5 NR reveals helium bubble formation in radiation resistive materials

6 Stimuli responsive coating layers of medical importance

7 New discoveries on charge "stripes" in superconductors /New precision measurements of the ^{235}U neutron-capture cross section at DANCE

8 Ultrahigh resolution neutron crystallography at the Protein Crystallography Station

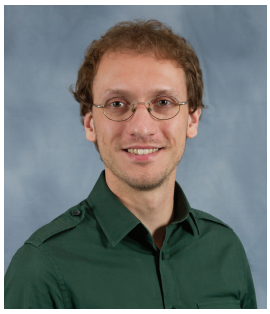
9 Los Alamos researchers author chapter in polymer science reference book

10 Hongwu Xu

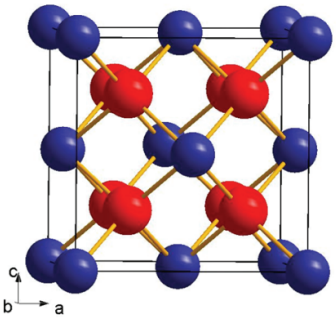
11 AISI Finalists Highlight Lujan Center Capability

13 Melvin Borrego

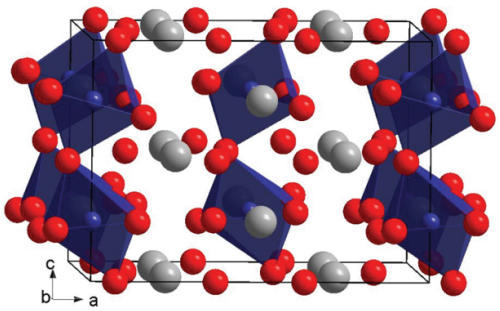
Los Alamos NATIONAL LABORATORY EST. 1943



Yb_3TaO_7



Average Structure:
Disordered Cubic Fluorite



Local Structure:
Yb/Ta and O/Vacancy Ordered Weberite

Insight on catalytic behavior in hydrogen catalyst weberites

Lujan Center Mission

"By exploiting the unique characteristics of intense beams of pulsed neutrons the Lujan Center enables innovative solutions for academia, national security, and industry."

Recently hired staff member, Graham King, used local structure analysis at the Lujan Neutron Scattering Center to determine the difference in water splitting catalytic activity between weberites and defect fluorites. (Weberite, Na_2MgAlF_7, is an orthorhombic mineral consisting of an aluminofluoride of sodium and magnesium.) La_3TaO_7 is an excellent catalyst for water splitting, while disordered Yb_3TaO_7 is not. By understanding why similar materials have different abilities to produce hydrogen from water, scientists could design new materials to enable a hydrogen - based economy. The team determined that the local structure of Yb_3TaO_7 is weberite - like with short range ordering of cations and vacancies with domain sizes ~30Å long. This is much larger than the size of water molecules. Therefore, structure alone cannot explain differences in catalytic activity between this compound and those with long - range weberite structures. The structures of La_3TaO_7 and Yb_3TaO_7 are nearly the same on short length scales, but La_3TaO_7 has much greater long range order. In Yb_3TaO_7 there are many different Ta-O bond lengths, whereas the Ta-O bond lengths in La_3TaO_7 are more similar. The bond length difference may be related to the water splitting difference. Other structural differences, such as the degree of distortion of the Ta coordination environment, could also be responsible for the catalytic differences.

Reference: " Local Structure of the Vacancy Disordered Fluorite Yb_3TaO_7 from Neutron Total Scattering," Journal of Materials Chemistry A1 , 10487 (2013); doi: 10.1039/c3ta12100c . Researchers include G. King and A. Llobet (Lujan Center, LANSCE - LC), C. M. Thompson and J. E. Greedan (McMaster University, Canada).

continued on page 2

King cont.

This work benefited from the use of NPDF at the Lujan Neutron Scattering Center at LANSCE.

Technical contact: Graham King

JCP's 80th anniversary issue includes Lujan Center polymer study

A landmark study of thin polymeric layers by Jarek Majewski (Lujan Neutron Scattering CenterJ) is featured in the Journal of Chemical Physics 80th anniversary collection alongside articles by such renowned scientists as Paul Flory (Nobel laureate), Edward Teller, Nicholas Metropolis, and others.

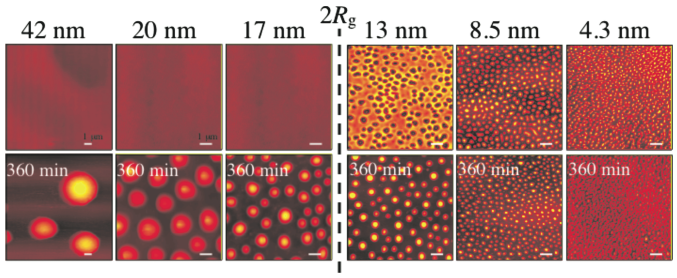
Co-authored with four scientists from Kyoto University in Japan, the 2009 paper presented new neutron measurements of polymer thin films. Widely used in everyday materials, polymer thin films consisting of single component and multicomponents are of great interest because their properties are quite different from bulk polymers. Polymer thin films can be useful as a coating, adhesive, surface friction, lubricants, and dielectric layer. Coatings can modify surfaces; for example, making them water repellant.

In this work, the scientist performed neutron scattering measurements to study the dewetting process of dPS/PVME (common polymers of polystyrene and poly-vinyl methyl ether) blend in the two-phase region. They used a time-of-flight (or energy dispersive) neutron reflectometer to study the details of phase separation in the depth direction before dewetting observed in previous measurements. In addition, they analyzed, for the first time, the off-specular data to demonstrate that the time-of-flight reflectivity measurements are very powerful to investigate kinetics of structure formation in the film plane in micrometer scale.

The study shows that the energy dispersive (or TOF) neutron measurements provide very unique information on the in-plane and out-of-plane polymer structure formation and can be used to address many other scientific problems.

Neutron studies require high neutron fluxes, and the Lujan Center, an international user facility, has one of the most intense sources of neutrons in the world. Majewski and Erik Watkins, his former student who is now at Institute Laue-Langevin in France, performed the measurements here with the surface profile analysis reflectometer (SPEAR), which can study even the thinnest organic and inorganic layers in a variety of environments.

This work benefited from the use of the Lujan Neutron Scattering Center at LANSCE funded by the DOE Office of Basic Energy Sciences and Los Alamos National Laboratory under DOE Contract DE-AC52-06NA25396. It supports the Lab's Energy Security mission and Materials for the Future pillar.



AFM images of blend thin films of dPS and PVME before and after annealing at 115 °C for 360 min for various initial film thicknesses above and below twice Rg (=17 nm). Scale bars in images are 1 μm.

JCP is the most cited journal in atomic, molecular, and chemical physics, according to Thomson Reuters.

"Time-resolved specular and off-specular neutron reflectivity measurements on deuterated polystyrene and poly(vinyl methyl ether) blend thin films during dewetting process," J. Chem. Phys. 131, 104907 (2009); dx.doi.org/10.1063/1.3224125. To view the 80th anniversary collection, please see jcp.aip.org/.

Technical contact: Jarek Majewski

"Shape-Setting" Mechanics for Shape Memory Alloy Actuators

Scientists from NASA Glenn Research Center in collaboration with Don Brown and Bjorn Clausen from the Lujan Center turned to neutron diffraction to identify mechanisms associated with "shape setting" shape memory alloys (SMA). The measurements matched industry standard methods, while simultaneously tracking the underlying microstructure during realistic actuator conditions.

Shape memory alloys are used in applications ranging from medical (stents) to couplings in fighter jets to fluid control military (aerospace couplings) and industrial (automotive transmission fluid control). Shape setting determines the final configuration of shape memory alloy actuators. These data help optimize the load and temperature paths for optimal response, thus expanding the relevance of these materials to large-scale commercial applications.

While many studies have reported on the microstructure of NiTi and independently on the macroscopic behavior of shape setting NiTi, no experiments have been conducted to mimic the shape setting process while examining the microstructure and the macroscopic behavior simultaneously. A uniquely suited method for obtaining such concurrent analysis is in situ neutron diffraction. For this work in situ

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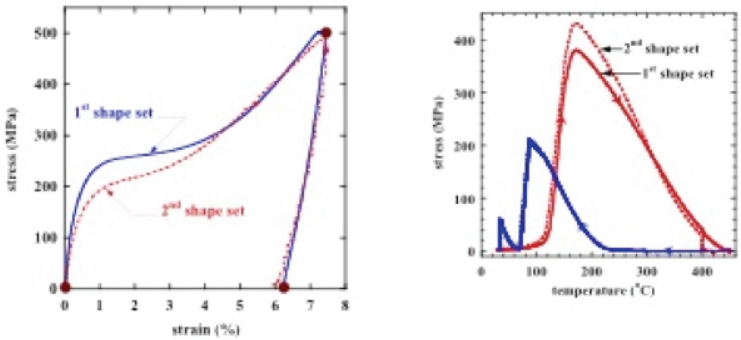


Stress vs strain for the first 2 shape setting cycles for NiTi. Stress vs. temperature for the first 2 shape cycles for NiTi

neutron diffraction experiments were conducted in the Spectrometer for Materials Research at Temperature and Stress (SMARTS) at Los Alamos National Laboratory. SMARTS employs a polychromatic beam from a spallation neutron source with two fixed banks of detectors.

The NASA Fundamental Aeronautics Program, Aeronautical Sciences Project funded the work. The Lujan Neutron Scattering Center at LANSCE is funded by DOE Office of Basic Energy Sciences.

Reference: "An in situ neutron diffraction study of shape setting shape memory NiTi," Acta Mater. 61, 10 (2013). Researchers include Don Brown and Bjorn Clausen (Lujan Neutron Scattering Center, LANSCE-LC), O. Benafan (University of Central Florida/NASA Glenn Research Center); R. Vaidyanathan (University of Central Florida); S.A. Padula II and R.D. Noebe (NASA Glenn Research Center).

Technical contacts: Don Brown and Bjorn Clausen

Lujan Center Offers New High Magnetic Field Capabilities

The Lujan Neutron Scattering Center, a national user facility at LANSCE, commissioned a new experimental capability that enables scientists to study electronic and magnetic properties of strongly correlated materials at low temperature and high magnetic fields. The team expanded the low temperature capability on the polarized neutron reflectometer (Asterix) by installing a helium-3 insert that can reach temperatures as low as 260 mK. That temperature is slightly above absolute zero, which is defined as -273.15°C. When used in conjunction with an 11-Tesla superconducting magnet at the Lujan Center, the reflectometer allows measurements of magnetic crystals, thin films, and nanostructured materials. Such extreme environments are crucial for investigating novel physical phenomena and the mechanisms needed to develop functional devices, such as sensitive magnetic field sensors, microwave filters, and spintronic devices.

Lujan Center and National High Magnetic Field Laboratory (NHMFL) scientists in collaboration with an external researcher used the Asterix instrument to perform a neutron diffraction study of a molecular magnet, $CoCl_2$-$2SC(NH_2)_2$. Their findings suggest a new route to multiferroic coupling and its feasibility in organic materials, which are easy to design and synthesize. Coupled ferroic orders create new functionality, such as better gyrators, low-power magnetic field sensors, spintronics devices, and antenna.

The 11-Tesla superconducting magnet used at the Lujan Center.

For the experiment, the NHMFL system revealed bulk magnetic and ferroelectric orders that are coupled below 820 mK with several different phases under the magnetic field. A complementary neutron diffraction experiment at the Lujan Center observed magnetic Bragg peaks that changed intensity as a function of temperature and magnetic field. These measurements enabled the team to determine the spin structure in each phase and elucidate the microscopic origin of the

Researchers include Jae Wook Kim, Eun-Deok Mun, and Vivien S. Zapf (Condensed Matter and Magnet Science, MPA-CMMS); Qiang Wang and Michael Fitzsimmons (LANSCE-LC); and Jamie Manson (Eastern Washington University). DOE's Office of Basic Energy Sciences, the National Science Foundation, and the State of Florida via the National
High Magnetic Field Laboratory user program within MPA-CMMS funded the work. The research supports the Laboratory's Energy Security mission area and the Materials for the Future science pillar.

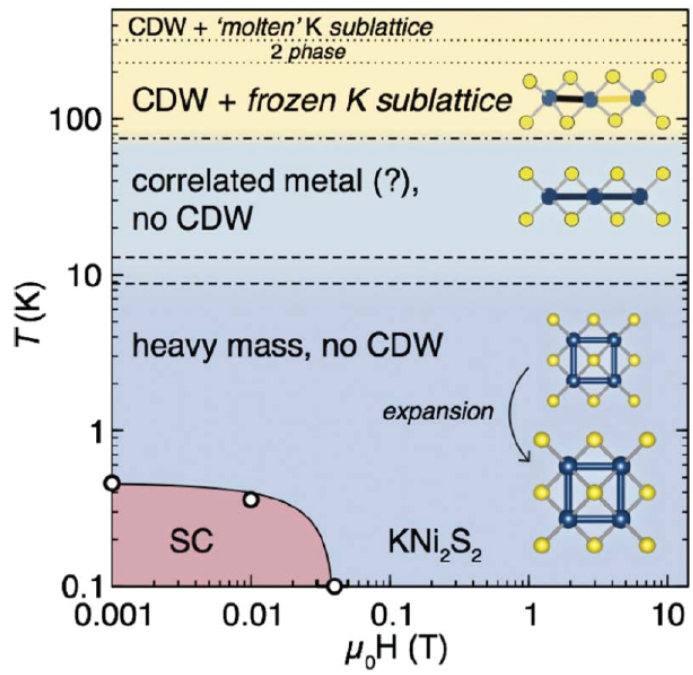
Technical contacts: Mike Fitzsimmons and Jae Wook Kim

When quantum becomes magic

Understanding the complexities of electronic and magnetic ground states in solids is one of the main goals of solid - state physics. Scientists from the DOE's Institute for Quantum Matter (Johns Hopkins University), LANSCE's Lujan Neutron Scattering Center, and Argonne National Laboratory discovered and studied a new mate rial exhibiting the richest and most unusual set of properties in a single system. KNi_2S_2 demonstrates charge density wave (CDW) fluctuations, heavy electrons, negative thermal expansion, and superconductivity, all in the absence of localized magnetism. Physical Review B published the work.

KNi_2S_2 , which is isostructural to the recently discovered electrostatically driven superconductor KNi_2Se_2 , displays a mobile K^+ sublattice at room temperature and a freezing transition temperature, T, of approximately 250 K. The system develops aperiodic incoherent charge density wave fluctuations above T ~ 75 K. This corresponds to the displacements of the Ni - Ni sublattice that evolve into a correlated metallic state with no CDW nor significant electronic mass enhancement. Further cooling (T less than 9K) leads to lattice expansion with concomitant significant enhanced electronic mass of approximately 24. The material becomes superconducting below T_c = 0.46 K.

Their research indicates that the origin of the heavy electron behavior in KNi_2S_2 lies in the hybridization of nearly localized and bonded states with conduction electrons and the absence of any evidence of localized magnetism. Crucial to this discovery was the pair distribution function analysis of neutron total scattering data taken at the Neutron Powder Diffractometer (NPDF) and High - Intensity Powder Diffractometer (HIPD) instruments of the Lujan Center and the X - ray powder diffraction analysis of experiments performed at Argonne National Laboratory. Reverse Monte Carlo (RMC) simulations of the experimental measurements produced atomistic configurations that are compatible with the average crystallographic symmetry and extended pairwise correlations. The RMC simulations demonstrate the existence of short and long Ni - Ni bonds randomly distributed throughout the lattice at room temperature. This result indicates that the CDW distortion is localized in nature, and thus likely dynamic. Such aperiodic incoherent CDW fluctuations disappear upon cooling, making the system become less distorted and effectively increasing the local symmetry without trivial charge ordering. The researchers attribute the negative thermal expansion of KNi_2S_2 at the lowest temperatures measured to the formation of a more delocalized, coherent electronic state. Quantitative analysis of the specific heat at higher temperatures reveals insight into the dynamic nature of the structural anomalies as charge density wave fluctuations. Upon cooling, most of the entropy of a 34(1) meV vibrational mode is released at a similar temperature scale to the disappearance of the CDW fluctuations. The entropy of the 7.47(3) meV mode is released at



The temperature/magnetic - field phase diagram of KNi_2S_2 reveals superconducting, heavy mass, intermediate but non-charge density wave, Ni - Ni charge density wave, and high K^+ mobility phases.

the same temperature scale as the observation of negative thermal expansion behavior T < 8 . 9 K. Analysis of the heat capacity is consistent with both the loss of a CDW around T ~ 75 K and the emergence of heavy electron physics at low temperature. The team suggests that the two phenomena are interrelated.

Reference: Charge Density Wave Fluctuations, Heavy Electrons, and Superconductivity in KNi_2S_2 ," Physical Review B 87 , 0 45124 (2013); doi : 10.1103/PhysRevB.87.045124. Coauthors include James R. Neilson, Tyrel M. McQueen , and Jiajia Wen (Johns Hopkins University) ; Anna Llobet (Lujan Center, LANSCE - LC); and Matthew R. Suchomel (Argonne National Laboratory). The DOE Office of Basic Energy Sciences (BES), Division of Materials Sciences and Engineering funded the research. The work benefited from the use of HIPD and NPDF at the Laboratory's Lujan Neutron Scattering Center and of beamline 11 - BM at Argonne's Advanced Photon Source, which DOE BES sponsors. The research supports the Lab's Energy Security mission area and the Materials for the Future and Science of Signatures science pillars.

Technical contact: Anna Llobet Megias

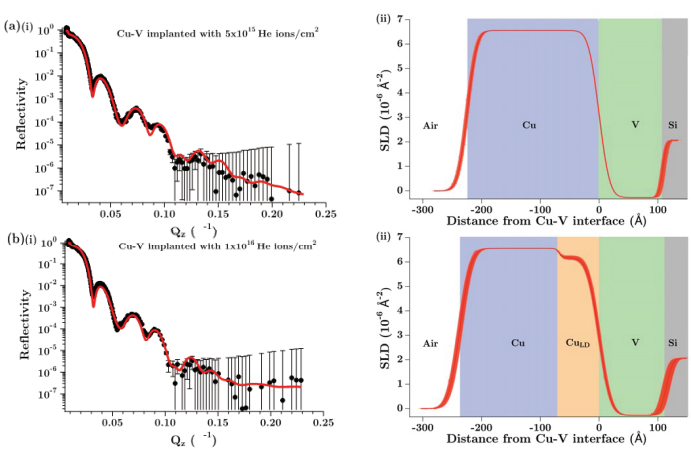
Neutron reflectometry reveals helium bubble formation in radiation resistive materials

Management of implanted helium (He) is crucial to the development of new fusion and fission reactor materials. Because of its insolubility in crystalline metals, implanted He immediately precipitates into 2–3-nm-diameter bubbles. Unlike He-free cavities, these bubbles are thermodynamically stable and are effective nuclei for the growth of larger voids, which in turn accelerate radiation-induced swelling and high-temperature embrittlement of grain boundaries. The current approach to reducing the deleterious effects of He in structural materials is based on delaying the so-called "bubble-to-void" transition. By reducing the concentration of radiation-induced vacancies and increasing the density of bubble nucleation sites, the critical fluence of implanted He required to transform stable bubbles into voids may be maximized.

Neutron reflectometry (NR) at Lujan Neutron Scattering Center at LANSCE has been used to find the critical He fluence required to form He bubbles at interfaces between fcc and bcc metals. Due to the excellent neutron scattering contrast between investigated metals (Cu, Nb, Mo and V), reflectometry is well suited to address the changes in the structural properties of such interfaces upon interaction with implanted He.

The findings, published in *J. Appl. Phys.*, are in agreement with previous experimental as well as modeling results and provide evidence for the presence of stable He platelets at fcc-bcc interfaces prior to bubble formation. The stable storage of He in interfacial platelets may provide the basis for the design of novel materials with increased resistance to He-induced degradation.

For this work, Abishek Kashinath, a PhD candidate from the Massachusetts Institute of Technology (MIT), who is currently with the Center for Integrated Nanotechnologies (MPA-CINT), received the Best Student Talk Award during the Department of Energy Office of Science 2013 Energy Frontier Research Centers PI meeting in July in Washington, DC. The citation highlighted use of neutron scattering to confirm his previous numerical calculation.

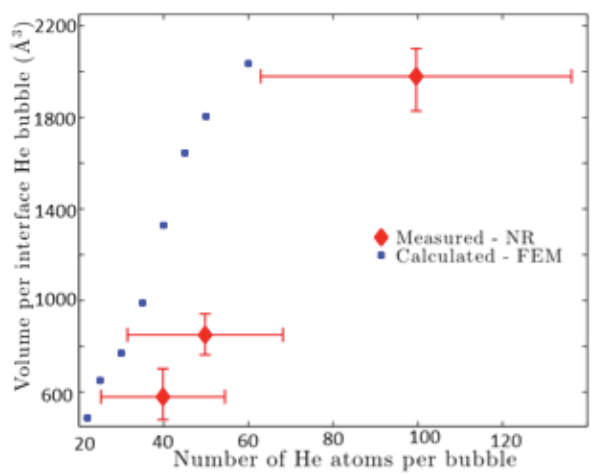


(a)-(b)(i) NR data (filled circles) from He implanted Cu-V bilayer samples and fitted curves (solid red lines). (a)-(b)(ii) SLD profiles from which the NR fits were obtained along with schematics of their interpretation in terms of composition.

Reference: "Detection of helium bubble formation at fcc-bcc interfaces using neutron reflectometry," A. Kashinath (MIT); P. Wang, J. Majewski (LANSCE-LC); J. K. Baldwin (MPA-CINT); Y. Q. Wang (Materials Science in Radiation and Dynamics Extremes, MST-8), et al., *J. Appl. Phys.* **114**, 043505 (2013); doi: 10.1063/1.4813780.

This work was supported by the Center for Materials in Irradiation and Mechanical Extremes (CMIME), an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Award No. 2008 LANL1026. This work also benefited from the use of the Lujan Neutron Scattering Center at LANSCE, funded by the DOE Office of Basic Energy Sciences and Los Alamos National Laboratory under DOE Contract DE-AC52-06NA25396.

Technical contact: Jaroslaw (Jarek) Majewski



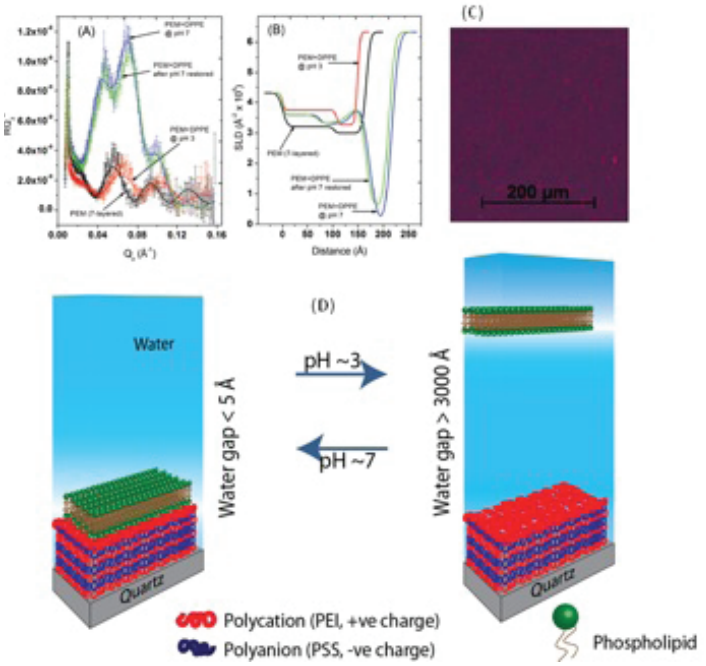
Red diamonds—volume per He bubble at Cu-Nb interfaces determined from NR data. Blue squares—volumes of stable interfacial He bubbles calculated from a reaction-diffusion model using finite element method.

Stimuli responsive coating layers of medical importance

Stimuli responsive mesoscale systems are of great potential for many applications, e.g., in material science for sensing molecular architectures, creation of medical nanodevices, molecular electronics, permselective membranes/scaffolds, and the bottom-up fabrication of functional molecular devices.

However, their fabrication poses many engineering challenges. Frequently, employed preparation techniques result in incomplete structures of limited functionalities, which are too fragile to sustain significant mechanical stress or to endure changing environmental conditions required for most practical applications.

Structures of importance include ultra-thin coating layers, which are friendly towards biological objects, e.g. cells, and can be easily applied and manipulated. Imagine a way to grow artificial tissue, or a layer of stem cells, of macroscale dimension that have the ability to be easily detached from a support and applied into malfunctioning organs! Or, envision self-cleaning surfaces that can shed any unfavorable residues via application of an external stimulus.



Polyelectrolyte multilayers as a platform for pH-responsive lipid bilayers. (A) Neutron reflectivity profiles and corresponding (B) scattering length density profiles of lipid bilayer deposited on PEM revealing that the separation distance between the polymeric cushion and the DPPE bilayer can be reversibly adjusted by varying the pH of the aqueous environment. (C) Fluorescence micrographs of lipid bilayer deposited on PEM showing intactness of the lipid bilayer in acidic environment. (D) Schematic depicting the pH responsiveness of the bilayer deposited on a polymeric cushion.

Scientists from the Lujan Center at LANSCE were able to fabricate such stimuli responsive mesoscale films: thin lipidic membranes that could reversibly be de-attached from polymeric cushions by changing the environmental conditions. Neutron reflectivity and other complementary techniques showed that decreasing the pH of the surrounding liquid separated the lipidic film and the polymeric cushion due to electrostatic repulsion. Returning to the original pH reconstitutes the initial configuration, with little or no change in the film structure.

Hence, they were able to create a free-floating lipid film (sheet of self-assembled lipid molecules of many cm^2 in the lateral dimension, but only couple of nanometers thick) that can serve as a platform for many bio-applications. For example, a sheet of cells could be fabricated on such polymeric cushions and efficiently be transferred to an implant for better immune-acceptance.

As another possibility, tubes could be coated with such films making them self-cleaning. Such stimuli responsive free-floating films are not only of interest for smart materials, but also for the study of biomembranes and associated proteins, which is very important for drug targeting or designing new types of antibiotics.

In work published in *Soft Matter*, Lujan Center scientists Ann Junghans, Saurabh Singh and Jarek Majewski, in collaboration with Jianhui Tian and S. Gnanakaran (Theoretical Biology and Biophysics, T-6) as well as Jerzy Chlistunoff (Materials Synthesis and Integrated Devices, MPA-11), used a combination of techniques to understand the reversible pH-responsive behavior of lipid bilayers deposited on polyelectrolyte multilayer (PEM) cushions. Structural characterization using neutron reflectivity revealed that the separation distance between the polymeric cushion and the lipid bilayer can be reversibly adjusted by varying the pH of the aqueous environment.

These observations were further supported by fluorescent microscopy, electrochemical impedance spectroscopy measurements and molecular dynamics simulations. Experimental and modeling results suggest that coulombic forces play a key role in affecting the separation distances between the polymeric support and the lipid bilayer.

This novel system offers great potential for fundamental biophysical studies of membrane properties decoupled from the underlying solid support, but also is a promising tool for tissue engineering applications.

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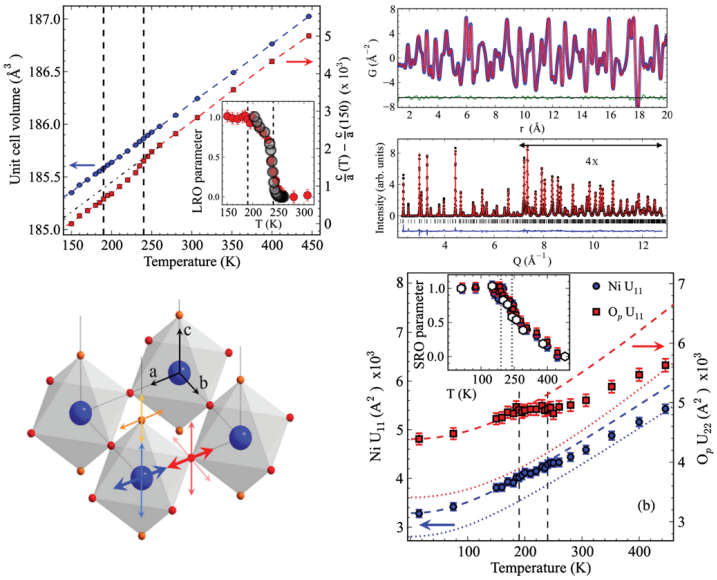
Reference: “Polyelectrolyte Multilayers as a Platform for pH-responsive Lipid Bilayers,” Soft Matter, DOI:10.1039/c3sm51651b.This work benefited from the Lujan Neutron Scattering Center at Los Alamos Neutron Science Center funded by the DOE Office of Basic Energy Sciences and LANL under DOE Contract DE-AC52-06NA25396.

Technical contacts: Jerzy Chlistunoff and Jaroslaw (Jarek) Majewski

New discoveries on charge “stripes” in superconductors

Experiments performed on the Neutron Powder Diffractometer (NPDF) at Los Alamos have allowed scientists from Brookhaven National Laboratory to identify a series of clues that particular arrangements of electrical charges known as "stripes" may play a role in superconductivity—the ability of some materials to carry electric current with no energy loss. Stripe-like modulations of electronic states are presumed to be responsible for the superconductivity in Cu-based superconductors. Uncovering the detailed relationship between these stripe patterns and the appearance or disappearance of superconductivity has been extremely difficult, particularly because the stripes that may accompany superconductivity are very likely moving or fluctuating.



Subtle changes in the c/a lattice parameter ratio in tetragonal LSNO at temperature TCO identify a structural signature sensitive to development of long-range static charge stripe order. On the other hand, excess magnitude of the ADPs above the canonical Debye characteristics correlates well with the pseudogap temperature evolution and is sensitive to short range ordered/fluctuating stripe correlations. Mean square displacements of Ni and O (extracted from Rietveld and PDF) along the Ni-O in-plane bond unveil a way to identify the existence of fluctuating stripes above T_{CO}.

This work represents the first powder diffraction scattering evidence for fluctuating charge stripes above the temperature where static stripes develop. The polycrystalline sample—La1.67Sr0.33NiO4 (LSNO)—is known to show robust charge-stripe order below 240 K. These results provide support for the idea that short-range-ordered, and presumably fluctuating, stripes could underlie electronic features, such as pseudogap and nematic and smectic phases seen in the related cuprates. Physical Review Letters published the work.

"One of the most critical aspects of this experiment is that we had lots of different data points, lots of temperatures—so you can catch small deviations," said co-author Emil Bozin of Brookhaven. He also noted how improvements in detector technology made it possible to collect a lot of data within a fixed amount of time. "Ten years ago we would have needed a couple of weeks of beam time to do this experiment; we collected all our data in just a few days.”

The Lujan Neutron Scattering Center is a national user facility that attracts scientists from around the world. After a 2001 upgrade, NPDF became the first instrument of its kind designed specifically for pair distribution function analysis—a way of characterizing local atomic structure—and at the same time, it is among the best powder diffractometers in the United States.

Reference: “Evidence for Short-Range-Ordered Charge Stripes Far above the Charge-Ordering Transition in La1.67Sr0.33NiO4,” A.M.A. Abeykoon (Brookhaven National Laboratory) et al, Physical Review Letters 111, 096404 (2013); DOI: 10.1103/PhysRevLett.111.096404
This work was supported by the Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, US Department of Energy. This work benefited from the use of NPDF at the Los Alamos Neutron Science Center, funded by DOE Office of Basic Energy Sciences.

Technical contact: Katharine Page

New precision measurements of the ^{235}U neutron-capture cross section at DANCE

The capture cross section for neutrons reacting with ^{235}U is of fundamental importance for understanding nuclear technology, including criticality and reactors, defense systems, and transmutation technologies.

Many measurements have been made over the past 60 years, yet this important quantity is still poorly known in the neutron energy range from 1 keV to 1 MeV, which corresponds to the energies with which roughly half of the neutrons from fission are produced. The uncertainties are

estimated to range from 15% to 30%, far above what is needed for precise calculations of nuclear systems.

The main reason for this uncertainty is that capture is usually detected from the gamma-rays it produces, but the probability for creating fission, which also produces gamma-rays, is from 2 to 10 times higher than capture in this energy range. The probability for neutrons to scatter from ^{235}U into the detector is about 10 to 30 times larger than the capture probability, and these neutrons can also produce gamma rays that interfere with the measurement.

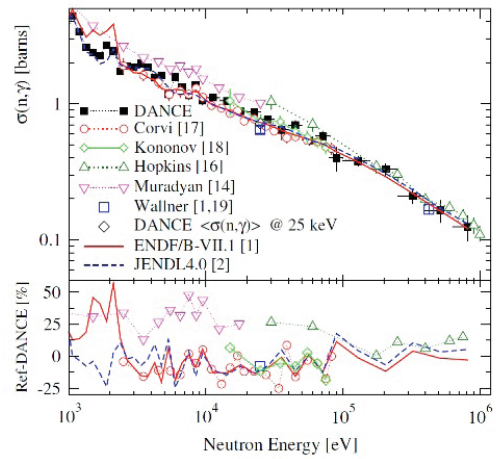
For accurate measurements of the cross section, it must be determined which reaction produced the gamma rays that are detected. Fission reactions can be identified using a "fission chamber" to tag the reaction, but a thin target (less than 0.5 micrometers thick) is required.

However, for good capture measurements, targets from 10 to 100 times thicker are needed.

However, in a new experiment, recently published in *Physical Review Letters* (M. Jandel, et al., *PRL* **109**, 202506 [2012]), LANL and LLNL researchers led by Marian Jandel (Nuclear and Radiochemistry, C-NR), using the Detector for Advanced Neutron Capture Experiments (DANCE) at LANSCE, used two innovations to make measurements with 2% to 5% uncertainties. Both innovations are unique to detectors such as DANCE, which measure the total gamma-ray energy released during a reaction. In addition, the unique high segmentation of the DANCE detector (160 individual crystal detector elements) enables counting the number of individual gamma rays.

The first innovation involved measuring the fission gamma-ray spectrum as a function of neutron energy using a thin target, and then measuring the capture reaction using a thick target. The fission gamma rays were subtracted from the thick-target gamma ray spectrum by normalizing the fission gamma-ray spectrum to the thick-target spectrum for events with more than 6 gamma rays, a signature of fission.

The second innovation involved measuring the spectrum of gamma rays due to neutrons scattering into the detector by using a ^{208}Pb target, which has a very small probability for neutron capture. The fission gamma-ray spectrum was measured using a 130 μg/cm^2 ^{235}U target mounted in a parallel-plate avalanche counter, which gave a signal for a fission event. The capture gammas were measured using a 26 mg/cm^2 self-supporting ^{235}U target, and the gamma spectrum from scattering was measured using a 120 mg/cm^2 ^{208}Pb target. Finally, since fission and capture were measured in the same target, the capture data were normalized to the very well known fission cross section, eliminating uncertainties due to target thickness and neutron flux measurement. More details of the experiment were given in the publication.



The top panel shows the ^{235}U(n,γ) cross section measured at the DANCE detector (black squares) compared to the ENDV/B-VII.1 and JENDL4.0 data evaluations, and earlier experimental measurements. The lower panel shows the percent difference between the current measurement and the earlier values.

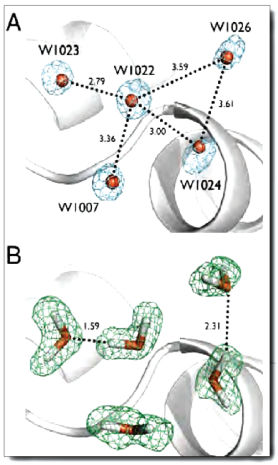
The results of the experiment are shown in the figure. The data from this measurement (black squares) are compared to two different data evaluations, the ENDF/B-VII.1 evaluation and the JENDL4.0 evaluation., as well as to other experimental results. The new data resolve the difference between the evaluations near 2 X 10^3 eV, and confirm the earlier data and evaluations above 10^4 eV. The uncertainty of the new measurement from 10^4 eV to 5 X 10^5 eV varied from 5% to roughly 10%. This data will provide new confidence in simulations for nuclear technology.

This work benefitted from the use of the LANSCE accelerator facility and the moderated neutron source at the Lujan Neutron Scattering Center. NNSA Defense Programs support the LANSCE accelerator, and the Defense Programs Science Campaigns funded the DANCE spectrometer and experimental work.

Technical contact: John Ullmann

Ultrahigh resolution neutron crystallography at the Protein Crystallography Station

Ultrahigh resolution neutron crystallography at the Protein Crystallography Station X- ray crystallography has been used to determine the atomic structure of many protein molecules and macromolecular complexes, but only a small fraction of the hydrogen (H) atoms in these molecules can be located using this technique. In contrast, neutrons are scattered well by hydrogen (or its isotope deuter ium, D), allowing determination of the position of these atoms in a protein molecule. Most of these assignments are made at approximately 2 Å resolution. Los Alamos scientists and collaborators have used the Protein Crystallography Station (PCS) at the Los Alamos Neutron Science Center (LAN-



Resolving the details of hydrogen - bonded water networks using X - ray a nd neutron crystallography. (a) Water molecule oxygen atoms are shown as red spheres, electron (X - ray) density are shown in cyan mesh, with inferred H - bonds as dashed lines; (b) Neutron data (nuclear density maps in green mesh) reveal the full structure of waters and their interactions with other waters. "Real" H -bonds are shown as dashed lines and are very different from what the researchers would infer based on X - ray data alone.

SCE) to determine the highest resolution neutron structure of a protein ever recorded. They determined the structure of a protein, crambin, including the positions of its hydrogen/deuterium atoms, defined to an ultrahigh resolution of 1.1 Å. The scientists located nearly 95% of the hydrogen atoms in the protein at this resolution, and readily observed the hydrogen bonds that help determine the Science Highlights (03 - 06 - 13) 9 three - dimensional structure of the folded protein. The journal Proceedings of the National Academy of Sciences (U S A) published the research.

Approximately one - half of all atoms in a protein are H atoms. These atoms play a variety of critical roles in proteins, including hydrogen bonding, electrostatic interactions, and ca talysis. Unfortunately, H atoms are difficult to visualize in a three - dimensional context. In most crystal structures, H locations are inferred from the position of their neighboring heavy atom (C, N, O, S). Hydrogen bonding networks that are ambiguous in the 0.85 Å ultrahigh resolution X - ray structure can be resolved by accurate orientation of water molecules using ultra - high resolution neutron crystallography. The neutron scattering data quality allowed the researchers to visualize most H and D atoms with in the protein and to the first and second hydration shells. The scientists inventoried all H bonding interactions within the protein, determined their categories, and suggested strengths of H bonds in the system. This research demonstrates the power of ul trahigh resolution neutron diffraction to resolve ambiguous hydrogen bonding networks and to reveal unconventional structural features and interatomic interactions, information that scientists could not collect previously . This milestone will improve the u nderstanding of the activity and structure of many enzymes. Ultrahigh resolution data will guide computational structural modeling and refinement of future enzyme structures.

Reference: "Direct Observation of Hydrogen Atom Dynamics and Interactions by Ultrahigh Resolution Neutron Protein Crystallography," Proceedings of the National Academy of Sciences (U S A) 109 , 15301 (2012); doi: 10.1073/pnas.1208341109. Authors include Julian C. - H. Chen and B. Leif Hanson (University of Toledo, Ohio), S. Zoë Fisher and Andrey Y. Kovalevsky (Bioenergy and Biome Sciences, B - 11), and Paul Langan (University of Toledo and Oak Ridge National Laboratory). The DOE Office of Biological and Environmental Research funds the Protein Crystallography Station. The National Instit ute of General Medical Science of the National Institutes of Health and the Laboratory Directed Research and Development (LDRD) Program funded different aspects of the Los Alamos research. The work supports the Lab's Energy Security mission area and the Science of Signatures science pillar.

Technical and PCS instrument contact: Zoë Fisher

Los Alamos researchers author chapter in polymer science reference book

Four Los Alamos scientists have written a chapter on fuel cell applications for the second edition of the book, Polymer Science : A Comprehensive Reference . After more than 20 years since the publication of the first edition, Elsevier has issued the second edition of the handbook as a 10 - volume set, edited by Kris Matyjaszewski and Martin Möller. Polymer science, also called macromolecular science, is a subfield of materials science. It is highly related to chemistry and extends into physics, chemical engineering/material science and biochemistry/biology. The book covers all aspects of polymer science, including synthesis, theory, properties, characterization, and use. The Los Alamos team wrote the chapter, "Polymers in Membrane Electrode Assemblies." It highlights the important role of polymers in membrane electrode assemblies of fuel cells, describing the details of structure, properties, and function of polymers that are critical for fuel cell applications.

The fuel cell chapter authors include Yu Seung Kim (Sensors and Electrochemical Devices, MPA - 11), Dae Sik Ki m (formerly MPA - 11), Cindy Welch (Polymers and Coatings, MST - 7), Rex Hjelm (Lujan Neutron Scattering Center, LANSCE - LC), and M. D. Guiver (National Research Council, Canada and Hanyang University, Korea). Reference: Polymer Science : A Comprehensive Reference Vol. 10 , pp. 691 - 720 (2012); Amsterdam: Elsevier BV. The DOE Fuel Cell Technologies Program funds the Los Alamos research, which supports the Lab's Energy Security mission area and the Materials for the Future science pillar.

Technical contact: Yu Seung Kim

Hongwu Xu

Using minerals and neutrons to unearth geologic solutions to global challenges

By Diana Del Mauro, ADEPS Communications

Hongwu Xu likes dreaming up new ways to use neutrons to solve problems in earth and environmental sciences. As he's simulating the planet's deep water cycle or reproducing the realms of buried nuclear waste, he uses neutrons to probe water-bearing minerals or complex oxide materials. His research often demands high-pressure, high-temperature conditions, nearly as extreme as what's found in Earth's mantle.

"Neutrons are ideal for detecting light elements, especially hydrogen," said Xu, who uses the Lujan Neutron Scattering Center at Los Alamos for his neutron diffraction studies. The community of geoscience researchers using neutron techniques is small, Xu said, partly because neutron facilities are in short supply compared with x-ray facilities.

The Mineralogical Society of America named Xu a 2013 fellow, paying tribute to his talents in neutron diffraction, conventional x-ray scattering, and synchrotron x-ray studies—complementary methods of exploring the atomic structures of materials and revealing their properties.

Inspired by time-tested minerals, Xu studies synthetic copies or analogues—mostly polycrystalline powder or ceramic chunks—of minerals. His studies, for example, potentially can be used for turning liquid nuclear waste into a rock-like ceramic that, when placed in a metal canister and buried, won't leach into the environment.

"We learn from nature," said Xu, of Earth System Observations (EES-14).

Since joining Los Alamos National Laboratory in 2004, Xu has fostered collaborations between the Earth and Environment Sciences Division and the Lujan Center. "New discoveries occur at the boundaries of different disciplines," he said. For five years, he has been a part-time instrument scientist assisting researchers at the national user facility and developing new research techniques. He is the only EES scientist who maintains an office at the Lujan Center.

For HIPPO, the High-Pressure Preferred Orientation Diffractometer, Xu and his colleagues developed capabilities that combine high pressure–up to 20 GPa–with temperatures ranging from a low of 8 to a high of 1800 K. The benefits are two-fold: researchers can simulate situations deep in the Earth or other planets, or they can create new materials with new properties. "Only a few places in the world have these kinds of high-pressure neutron capabilities," Xu said.

Xu's knowledge of minerals and materials science, stemming from his PhD in geosciences from Princeton University, made him a key player on the Lujan Center team that pioneered in situ high-pressure neutron diffraction methodologies. Using high-pressure fluid cells, for instance, his team studies the stability and structures of clathrate hydrates, a family of ice-like solids filled with various gases that are stable at high-pressure, low-temperature conditions. Found in the ocean floor sediments, methane clathrate is a potential energy resource, however, during landslides or earthquakes methane release can negatively affect climate. Xu is unraveling the mechanisms and kinetics of how different gas clathrates are formed.

Xu plans to expand the capabilities of other Lujan instruments and apply the techniques to broader earth, energy, and environmental studies. For example, through neutron scattering and imaging measurements coupled with multiscale modeling, his team may assess the suitability of salt repositories, such as WIPP, for storing high-level nuclear wastes—an urgent challenge for sustainable nuclear energy.

As well, his work on high-pressure conditions could be applied to research at MaRIE (Matter-Radiation Interactions in Extremes), the Laboratory's proposed experimental facility for the discovery and design of advanced materials. "Broadly speaking, pressure is an effective tool for designing new materials or tuning existing materials for new properties," he said.

Xu has authored 82 publications in notable scientific journals and serves as an associate editor of *American Mineralogist*.

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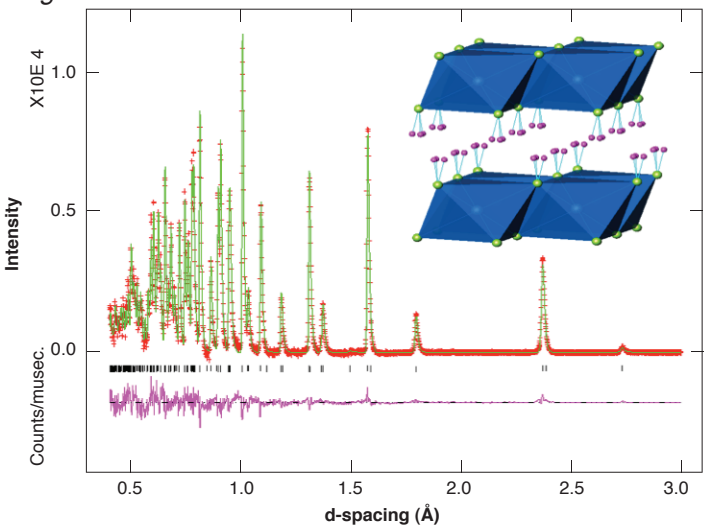

Neutron diffraction pattern and crystal structure of deuterated brucite, $Mg(OD)_2$. Brucite occurs as a component unit in the structures of complex hydrous minerals, which are potential hosts for water in the Earth's mantle. Since neutrons are sensitive to light elements, particular hydrogen, neutron diffraction is a powerful technique for studying hydrogen-bearing phases. Determination of the structures and phase equilibria of hydrous minerals at elevated pressure and temperature provides insights into mechanisms of water storage and transport in Earth's interior.

Paul Gibbs (left), Bjørn Clausen (right) are recipients of an American Iron and Steel Institute 2013 Finalist medal for research benefitting the development of high strength steels.

AISI Finalist Medal spotlights Lujan Center capability

Bjørn Clausen (Lujan Center, LANSCE-LC) and Paul Gibbs (Materials Science: Metallurgy, MST-6) are among the recipients of an American Iron and Steel Institute (AISI) 2013 Finalist Medal for their paper that drew upon the Lujan Neutron Scattering Center's neutron diffraction capability and set forth a methodology for producing a family of transformation-induced plasticity (TRIP) steels with desirable austenite stability conditions.

Since 1927, AISI has given awards for technical papers having special merit and importance in connection with the activities and interests of the iron and steel industry. Papers are judged on the potential value to future prosperity of the industry, technical excellence and originality, effective communication, and breadth of interest to AISI members.

There is an interest in developing new advanced high strength steel (AHSS) grades to meet the evolving demands of the automotive industry. It is anticipated that these so-called "Third Generation AHSS" microstructures will consist of high volume fractions (20-40 vol pct.) of metastable retained austenite (i.e., austenite that transforms to a harder phase with deformation) displaying controlled deformation-induced transformation to martensite in a high strength matrix.

The authors developed a methodology for the work to utilize manganese enrichment of austenite from ferrite during annealing to produce a set of steels with systematically varied microstructures. The resulting structures are shown in figure (a)-(c) for a 7.1 wt% Mn steel annealed between 575°C and

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AISI cont.

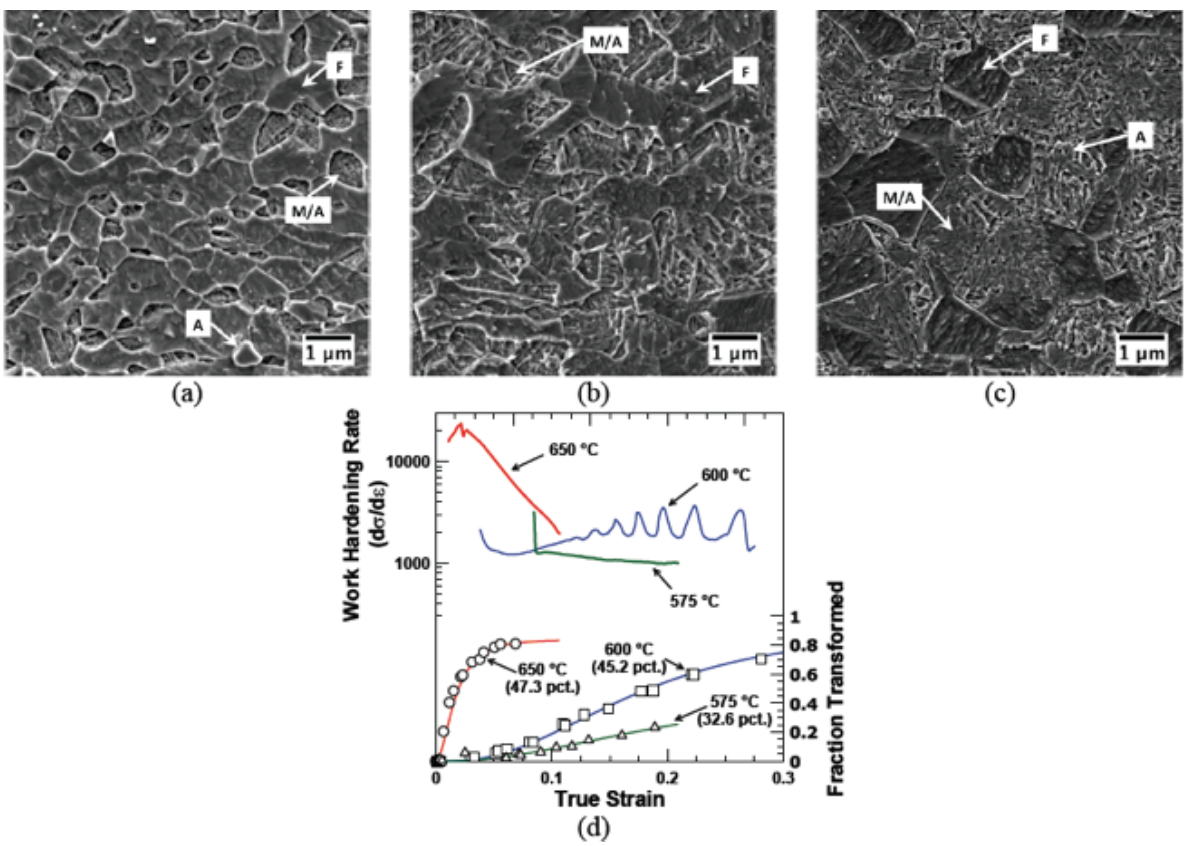
Using the SMARTS (Spectrometer for Materials Research at Temperature and Stress) instrument at the Lujan Center, the researchers measured the mechanical stability of the austenite during deformation using in situ neutron diffraction. A correlation between austenite stability for each of the annealing conditions and the mechanical behavior was observed, as shown in figure (d), leading them to conclude that the development of new steels to meet Third Generation AHSS demands must take into consideration the mechanical stability of austenite, as well as the total amount of austenite in the steel.

Co-authors included researchers from the Advanced Steel Processing and Products Research Center at the Colorado School of Mines (CSM), of which MST-6 is an active sponsor institution, and the United States Steel Corporation Research and Technology Center. Gibbs, who participated in the Lujan Center's 2009 Neutron Scattering School, performed the work as a CSM graduate student.

The National Science Foundation supported Gibbs's PhD work under award CMMI-0729114. The Lujan Neutron Scattering Center at the Los Alamos Neutron Science Center (LANSCE) is funded by the Office of Basic Energy Sciences (DOE) contract No. DE AC5206NA25396. Donald W. Brown and Thomas A. Sisneros (Materials Science in Radiation and Dynamics Extremes, MST-8) assisted with neutron experiments. The work is in alignment with the Laboratory's Energy Security mission and Materials for the Future pillar.

Reference: "Austenite Stability Effects on Tensile Behavior of Manganese-Enriched-Austenite Transformation-Induced Plasticity Steel," *Metallurgical and Materials Transactions A*, **42** 12 3691-3702 (2011).

Technical contacts: Bjørn Clausen and Paul Gibbs



Secondary electron scanning electron micrographs of 7.1 wt% Mn steel annealed at (a) 575°C, (b) 600°C and (c) 650°C for 168 hr. and water quenched. Representative phase regions are labeled ferrite (F), martensite (M), austenite (A), and mixed martensite and austenite (M/A). The figure in part (d) shows a comparison between instantaneous hardening rate (dσ/dε) and austenite transformation as a function of sample deformation for the three structures highlighted in parts (a-c). Significant austenite transformation occurs where high strengthening is observed. The initial amount of metastable austenite in the steels is listed below the annealing temperature.

Melvin Borrego

Serving the nation through neutron science and National Guard missions

By Diana Del Mauro, ADEPS Communications

For one year in Iraq, Melvin Borrego drove the lead five-ton cargo truck in convoys that delivered food, ammunition, and other logistical supplies to United States soldiers. On the road, he braced for sniper attacks, ambushes, and home-made bomb explosions. He also provided a secured area for all soldiers at Camp Cook in Taji, a village just north of Baghdad that was under constant mortar attack. He mourned the deaths of five close friends from the Arkansas National Guard.

With life-threatening dangers weighing on his mind, Borrego said he was glad he didn't have to worry about his wife and two children back in Española. "My family was taken care of," said Borrego, of the Lujan Center Neutron Scattering Center (LANSCE-LC). "They had the support of family, friends, the New Mexico Army National Guard Family Support Program, and Los Alamos National Laboratory."

For 16 of the 18 years that Borrego has served with the National Guard, he has worked at the Lujan Center, winning awards in both positions. To show his gratitude to the Laboratory for years of support, Borrego nominated Los Alamos National Laboratory for the 2013 Secretary of Defense Freedom Award, which recognizes employers for outstanding support of National Guard and U.S. Army Reserve members. Los Alamos received an Above and Beyond Award, but did not advance to the national competition.

"When I was deployed, they went above and beyond," Borrego said. "It's like a family over here—you're not just a number."
Every payday, a member of the group office would call his wife, Angela, to confirm she had received Borrego's Laboratory paycheck, which supplemented his National Guard wages. The Lujan Center and the Laboratory sent care packages of New Mexico green chile, salsa, and beef jerky. "Somebody sent me slippers," Borrego said, "a very nice comfort of home after wearing boots for many hours."

Fortunately, all 103 soldiers of the 1115th Transportation Company of the New Mexico Army National Guard returned home to their families in 2005.

Borrego said he found it reassuring to still have the job he loved at the Lujan Center. He is 1 of 2 technicians for 12 scientific instruments at the national user facility. If something breaks down or needs on-the-spot fabrication on the beam lines, he must react promptly, even if it's at 2 a.m. "It's my job to see that every user and every scientist at the Lujan Center gets a positive experience from a mechanical perspective," he said.

When he enlisted in the U.S. Army in 1991, he was a seasonal construction worker seeking steady work with health benefits for his young family. Borrego, who received a Combat Action Badge and other awards from his Iraq tour, is now a 1115th Transportation Company first sergeant, overseeing operations and training for 126 soldiers in the Taos-based unit. He performs two weeks of annual National Guard training and responds to federal and state emergencies. During the Las Conchas Fire, for instance, his unit spent two weeks providing security in Los Alamos by assisting local police and fire departments.

Whenever Borrego is on military leave, his Lujan Center colleagues step in, ensuring tasks get done and maintenance operations stay on schedule.

Now eyeing military retirement, Borrego is glad Los Alamos National Laboratory received recognition for what it has done for him and all employees in the National Guard or U.S. Army Reserve. Nearly 900 Laboratory workers have military affiliations. "I want to make sure everyone knows the Lab is a strong supporter of our civilian soldiers," Borrego said. "Without the Laboratory's strong support, we cannot do our jobs and fulfill our obligations in the military effectively."

The Lujan Center Science & People is a publication of the Lujan Neutron Scattering Center for those interested in the research and activities of the national user facility at the Los Alamos Neutron Science Center of Los Alamos National Laboratory. It includes news produced by the Experimental Physical Sciences Communications Team. Questions, comments, and suggestions, please send e-mail to lujan-highlight@lanl.gov

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