Solid-state NMR Central

BY KERRY GIBSON

Ames Laboratory's has an unusual concentration of nuclear magnetic resonance expertise

NUCLEAR MAGNETIC resonance spectroscopy is a complex, highly specialized field where researchers study the spin resonance of the atomic nuclei in materials to understand the molecular properties of those materials. That Ames Laboratory would use this technology in the characterization of new materials isn't surprising. But the fact that Ames Laboratory has three solid-state NMR research groups, especially for a research facility its size, is fairly unique.

The three groups – headed by Marek Pruski, Klaus Schmidt-Rohr and Yuji Furukawa – also have their own specialized uses for the technology. In Pruski's case, he's using it to study catalysts and other complex inorganic and organic materials. Schmidt-Rohr is applying the technology to understand the structure of fuel-cell membranes, nanocomposites, complex organic matter, and thermoelectric tellurides. For Furukawa, it's an important tool for understanding the magnetic and electronic properties of materials, such as low dimensional spin systems and superconductors, at extremely low temperatures.

It's all about spin

The technology is based on the principle that the nucleus of an atom of material that contains an odd total number of protons and neutrons will have a nonzero angular momentum, or spin, and a magnetic moment. This magnetic moment acts similar to a bar magnet in that it feels the effects of static and radio-frequency magnetic fields. It rotates around the field with a frequency that is directly proportional to the magnetic field at the nucleus. This frequency, which can be measured with an accuracy of better than 1 in 100 million, probes the local magnetic fields generated by surrounding electrons and other nuclear spins, and thus can provide detailed information about the physical and chemical properties of the material, such as the distance between nuclei and their specific positions at a particular point in time.

In liquids, the fast, random motion of the molecules averages out many of the interactions of the spins, resulting in narrow spectral lines. Solids, however, present more of a challenge because the molecules are basically locked in position, so anisotropic, or orientation-dependent, interactions affect the nuclear spins, resulting in broad spectral lines. To get better resolution, NMR specialists use some "tricks" to make the solid react more like a liquid, thereby producing high-resolution frequency spectra.

One such solid-state NMR technique mechanically spins the sample at high speed at the so-called "magic angle," which can effectively reduce some of the spin interactions, including the coupling between the magnetic moments of neighboring nuclei. Taking this a step further, researchers also use radio-frequency irradiation to achieve better control over the spin interactions. These strategies are used in various multiresonance and multidimensional schemes, which in concert with continuing advances in theory and instrumentation afford additional gains in sensitivity and resolution. And Ames Lab's NMR specialists are helping push the envelope.

Still evolving

"NMR is a fascinating field that, at 65-years-old, is still changing and evolving," Pruski says, "often on a monthly basis. We're not just users of fancy machines, we're helping advance the technology, and it's that constant push that keeps me excited about the work we're doing."

For example, Pruski's group is exploiting improved homo- and hetero-nuclear correlation experiments for spin-1/2 nuclei, where significant enhancements in resolution and sensitivity are accessible due to recent advances in ultrafast magic angle spinning. In this case, ultrafast means 3 million rpm! In fact the group is working with an equipment manufacturer on prototypes for new NMR probes that utilize this new technology.

Schmidt-Rohr's group has worked to tailor NMR techniques to specifically study nanocomposites using the exotically named HARDSHIP (HeteronucleAr Recoupling with Dephasing by Strong Homonuclear Interactions of Protons) and SUPER (Separation of Undistorted Powder patterns by Effortless Recoupling). Schmidt-Rohr's group has also introduced new methods for quantitative analysis of scattering data of nanostructured materials.

Sample holders that fit in the probe show only small amounts of material are required.

(opposite) The "business" end of a NMR probe. Samples are placed in the hole in the center and spun at ultra high speed. The probe mounts inside the bell-shaped magnetic field.

Probing Catalysts

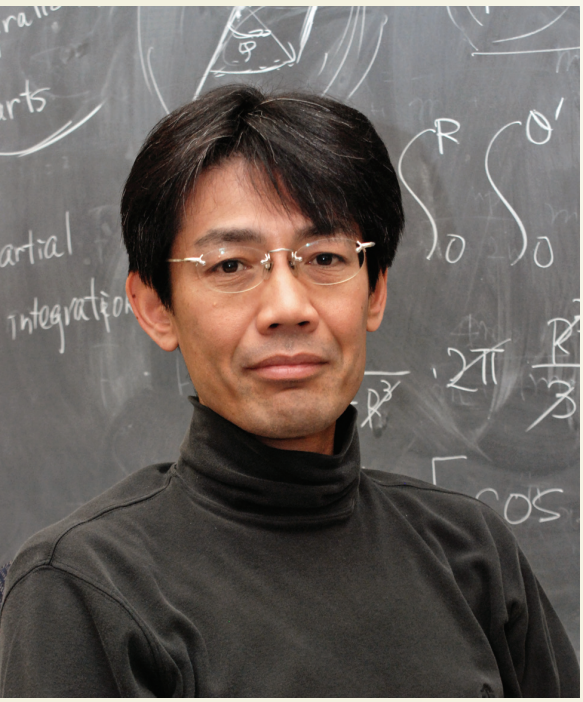
Pruski, an Ames Laboratory senior scientist, and his group, which currently includes Ames Lab associate scientist Jerzy Wiench and graduate students Kanmi Mao and Stacey Althaus, have focused on the chemical and physical properties of materials involved in heterogeneous catalysis, surface science and materials science. The work on catalysts, done primarily in collaboration with Ames Lab senior chemist and Chemical and Biological Sciences Program director Victor Lin, focuses on studying the properties of surfaces, as well as the molecular structure, dynamics and reactions of the adsorbed species.

Lin's research involves mesoporous silica nanoparticles, sponge-like spheres only about 200 nanometers in diameter. They have thousands of parallel channels running through them. They can be filled with chemotherapy drugs and "capped" so they selectively release their payload only inside cancer cells. They can also carry thousands of particles of a catalyst, dramatically increasing the overall surface area of the catalyst over the same amount of catalyst produced in larger particles.

"We're working on characterizing the mesoporous silica nanoparticles, with the underlying motivation of designing them for various applications from nanocatalysts to algal oil harvest and drug delivery," Pruski says. "We want to find out precisely what the surface structure is, which molecules attach, how they're oriented and even what's taking place during catalysis. Advancement in sensitivity and resolution of solid-state NMR techniques is essential to study these materials quickly and without isotope enrichment."

The group also has worked with Ames Lab senior scientist Vitalij Pecharsky on characterization of novel materials for hydrogen storage, mainly complex metal hydrides synthesized by means of a solvent-free technique (mechanochemistry) or by chemical approaches (self-assembled micelles).

Marek Pruski



Yuji Furukawa

Nanoscale Molecular Magnets and Superconductors

The most recent addition to Ames Laboratory's cadre of NMR specialists is associate physicist Yuji Furukawa, who joined the Materials Sciences and Engineering program earlier this year. Furukawa, who was on the faculty in the Department of Physics at the Hokkaido University, Japan, spent a year at Ames Lab roughly a decade ago as a visiting scientist working with physicist Fernando Borsa. When Borsa retired a year ago, Furukawa jumped at the chance to return to Ames.

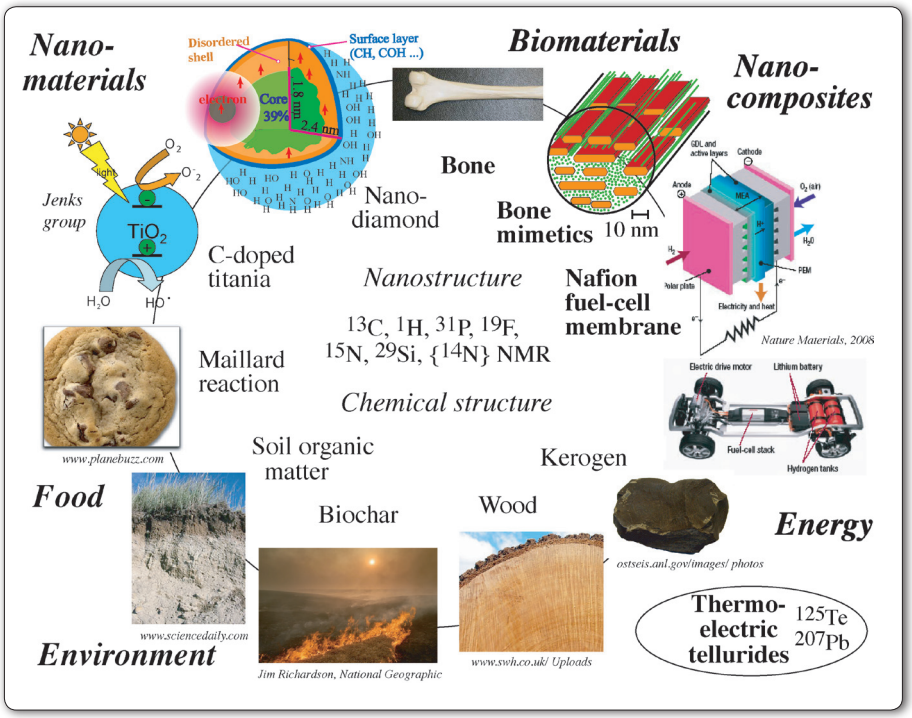
"There's an excellent research environment here," Furukawa says. "The collaboration is very strong, much more so than in Japan. You work as a team."

Furukawa is still in the process of setting up his research laboratory, awaiting the installation of a dilution refrigerator that will allow him to study materials down to 0.05 Kelvin. He also has equipment that allows him to vary both temperature and magnetic field strength.

"When you study materials at extremely low temperatures, even small changes in temperature can sometimes lead to dramatic changes in properties," Furukawa says.

He, along with many researchers in Ames Laboratory's Materials Sciences and Engineering program, is involved in studying nanoscale molecular magnets and the new class of iron-arsenide superconducting materials.

Schmidt-Rohr's group is working on a variety of materials and techniques.



Polymers, Nanocomposites and Thermoelectrics

Klaus Schmidt-Rohr

Senior chemist Klaus Schmidt-Rohr's group studies the composition and nanoscale structure as well as dynamics of polymer materials, nanocomposites, natural organic matter, and thermoelectric tellurides, using a variety of selective or two-dimensional NMR experiments, many of which they developed.

One of the first was a study of Nafion®, a proton-exchange membrane widely used in fuel cells. Despite its popularity as a fuel-cell membrane, little was known about the molecular structure that separates water into its component parts of hydrogen and oxygen and at the same time releases electrons that generate power from the fuel cell. Through NMR and scattering studies, Schmidt-Rohr developed a model in which the polymer forms long, parallel water channels randomly dispersed throughout the material.

A variety of nanocomposites has also been studied by the group, including work on the loading-bearing nanocomposite found in bone. This material consists of 3-nanometer-thick apatite (calcium phosphate) platelets imbedded in a collagen matrix in a ratio of 40-to-50 with the remaining 10 percent being water, which in part forms a monomolecular layer at the interfaces between phosphate and collagen, coupling the components of the composite like viscous glue. A relatively new research focus, pursued by Schmidt-Rohr and co-principal investigator Eugene Levin in collaboration with Ames Lab associate scientist Bruce Cook, is ternary and quaternary thermoelectric tellurides.

"Tellurium has been considered an exotic isotope in NMR," says Schmidt-Rohr, "but in fact there are many technologically interesting tellurium compounds. By elucidating the local structure and charge-carrier concentration, $_{125}$Te NMR can make important contributions to establishing structure-property relaxations in partially disordered tellurides."

Schmidt-Rohr's group is also involved in several other projects looking at the structure of natural organic matter from soil to biochar, a byproduct of gasification of biorenewable crops.