

A Quantum Contribution to Technology

Quantum mechanics simulations help researchers design nanoscale materials and control manufacturing processes.

Members of the Quantum Simulations Group include (from left) Vincenzo Lordi, Trinh Vo, project leader Andrew Williamson, Sebastien Hamel, and John Reed.

AT the nanoscale, computer simulations are often the only way that researchers can learn about materials. Imagine the shaft of a human hair sliced about 50,000 times. One slice is about a nanometer, or one-billionth of a meter—a distance that can be spanned by just 3 to 10 atoms. This minute size range is the realm of nanoscale science, where materials typically measure between 1 and 100 nanometers (nm) across.

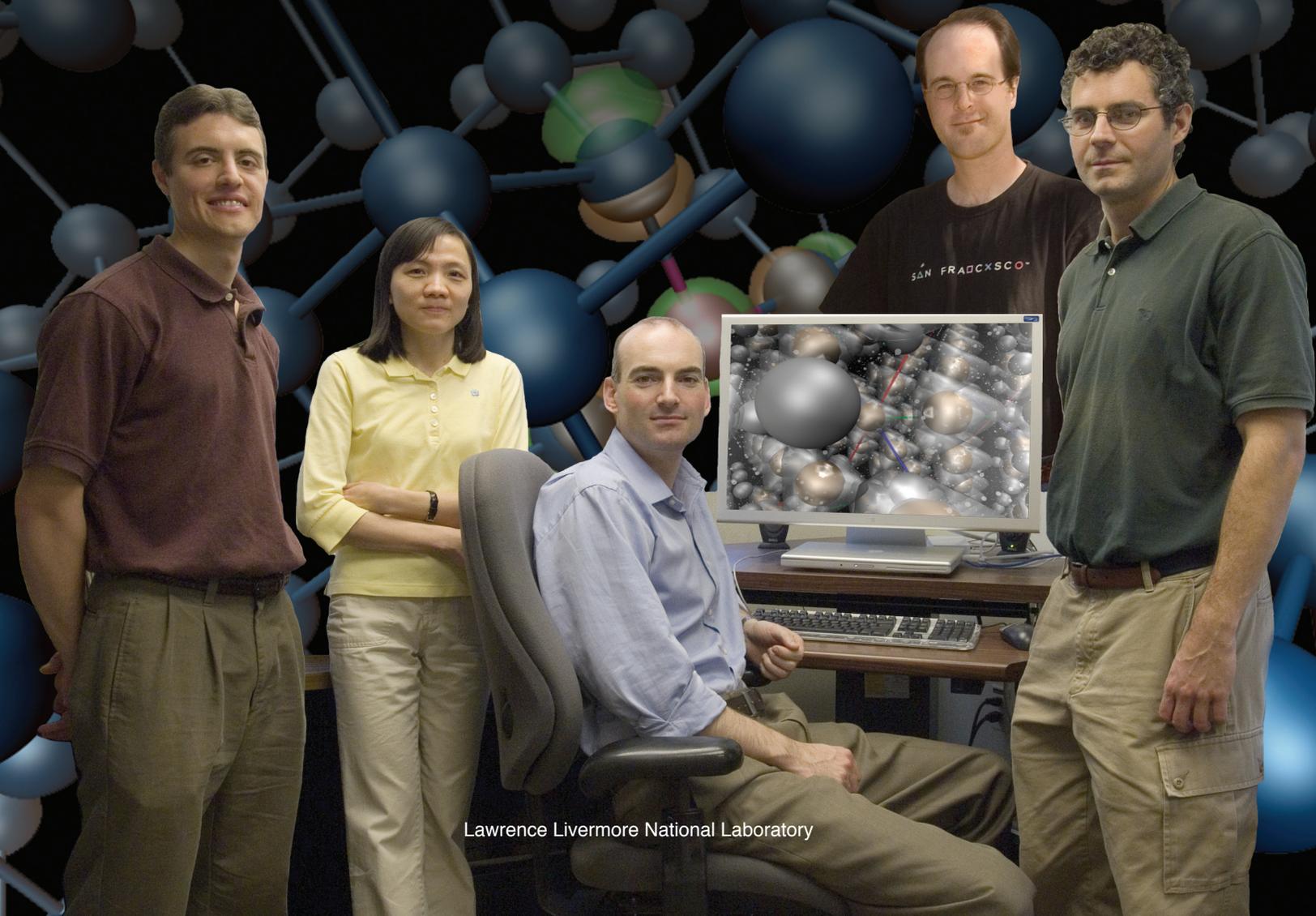
Accurate descriptions of nanoscale materials must account for the behavior of individual atoms and electrons: how they move, how they form bonds, and how those bonds break. In 1999, a Livermore simulation of such quantum behavior revealed the secrets of hydrogen fluoride

mixing with water at high temperatures and pressures. The motion being modeled lasted just 1 picosecond (a trillionth of a second), yet the calculation required 15 days and the entire resources of Blue Pacific, which at the time was Livermore's fastest supercomputer. (See *S&TR*, July/August 1999, pp. 20–22.) In the years since, computers have grown far more powerful, imaging devices can record even smaller features, and nanoscale science is thriving.

Livermore's Quantum Simulations Group in the Physics and Advanced Technologies Directorate is a leader in modeling material processes using quantum molecular dynamics methods. The group's early projects examined basic but poorly understood phenomena such as water under extreme pressure. (See *S&TR*, April 2002, pp. 4–10.) More recently,

quantum simulations revealed a new melt curve of hydrogen at extremely high pressures. (See *S&TR*, January/February 2005, pp. 4–13.) In 2006, a quantum simulation run on Livermore's BlueGene/L platform won the Gordon Bell Prize for Peak Performance.

More recently, the Livermore group has begun working on simulations for a diverse group of technological applications. For example, nanoscale materials could improve cooling technologies in military equipment and reduce the size of gamma radiation detectors being developed for homeland security. The Department of Energy (DOE) is funding research to dramatically improve storage systems



Lawrence Livermore National Laboratory

for hydrogen fuel on vehicles. In addition, computer chip manufacturers must ensure that their quality-control tools can detect defects in chips as their size continues to shrink. All of these applications require exploring materials at the nanoscale, a regime where simulations are often the most effective approach. “Nanoscale experiments are expensive,” says computational scientist Andrew Williamson, a project leader in the Quantum Simulations Group. “At this scale, simulations can be more cost effective.”

The computer codes for modeling dynamics at the molecular level are density functional theory and quantum Monte Carlo. Both types of code start from first principles—that is, with no laws other than quantum mechanics characterizing the system being studied. Density functional theory in quantum mechanics describes the electronic density of a molecular or condensed system. It can model atomic motion and the complex dynamics of material interactions. Quantum Monte Carlo also simulates these behaviors, but it uses a different technique. As the code’s name implies, the computer essentially “throws the dice” millions of times to select possible answers.

Quantum Monte Carlo codes are more accurate than density functional theory codes, but they can be extremely demanding of computational resources. Williamson and his colleagues have developed a linear scaling technique that greatly reduces the computing time for quantum Monte Carlo calculations. Still, for most problems, density functional theory is the first choice.

Refrigeration with Nanowires

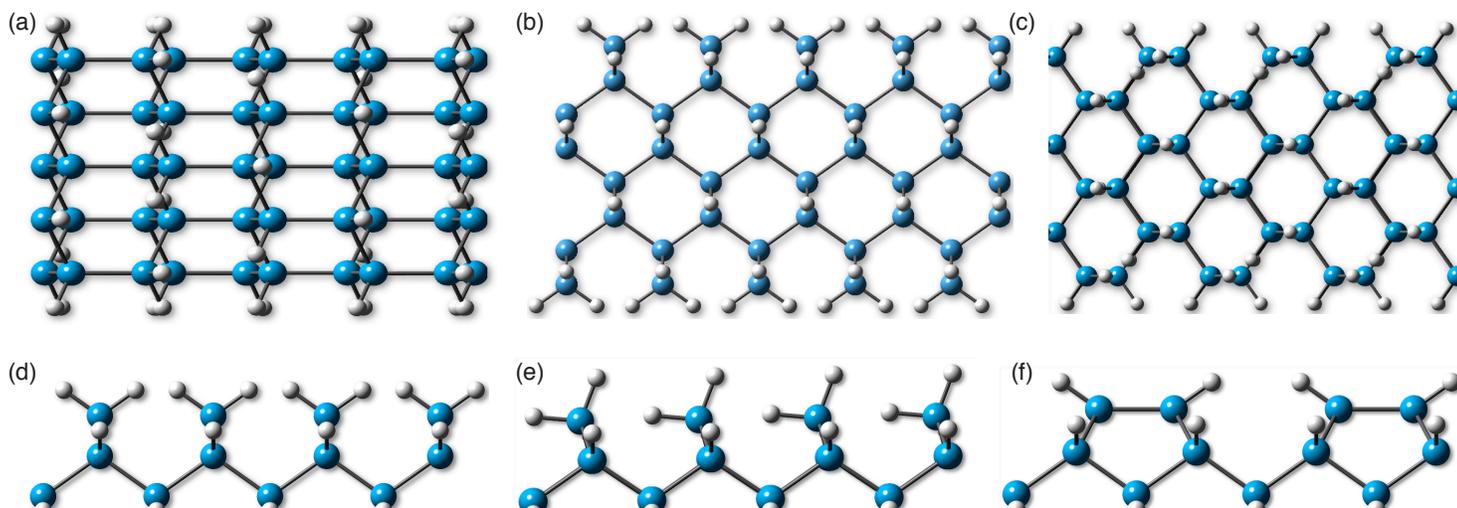
In one project, researchers in the Quantum Simulations Group are evaluating new materials to provide cooling for military applications. Their simulations, which are funded by the Defense Advanced Research Projects Agency (DARPA), indicate that a highly efficient thermoelectric material may be achievable using silicon germanium (SiGe) nanowires.

Thermoelectric materials convert heat into electricity and vice versa. They have no moving parts and release no pollutants into the environment. A few niche markets have used them for decades to cool electrical parts or generate power. Researchers have considered using thermoelectric-based refrigerators

to replace current heat-pump-based refrigerators that compress and expand a refrigerant such as Freon. However, despite extensive research, the efficiency of these materials has remained low.

A highly efficient thermoelectric material must exhibit a combination of properties that do not coexist in conventional materials. It must have the high thermoelectric power of semiconductors, the high electrical conductivity of metals, and the low thermal conductivity of insulators. By measuring these features, scientists can determine a material’s efficiency or figure of merit, which is known as its ZT . The highest ZT achieved in the past 40 years is 1. A thermoelectric material designed to replace a conventional Freon-gas refrigerator must have a ZT of at least 3.

A semiconductor nanowire is an ideal thermoelectric material. Nanowires are so thin they are often considered to have only one dimension: their length. This extreme thinness restricts electrons and holes in a process called quantum confinement, which increases electrical conductivity. A nanowire’s small size also increases the influence of its surfaces, reducing



Livermore’s Quantum Simulations Group evaluated silicon nanowires with lattices grown in the (a) [111], (b) [011], and (c) [001] direction and with (d) symmetric, (e) canted, and (f) reconstructed surfaces.

thermal conductivity. To date, the best thermoelectric materials are superlattice nanowires with a ZT of 2.5 to 3.

For the DARPA project, Livermore scientist Trinh Vo, a postdoctoral researcher, developed simulations to compare the growth direction, surface structure, and size of silicon nanowires and determine the optimal properties for electrical conductivity. Vo studied silicon with lattices grown in directions known as [001], [011], and [111], and with symmetric, canted, and reconstructed surfaces. Starting with bulk silicon, she computationally constructed 1-, 2-, and 3-nm cylinders of silicon “terminated” with hydrogen on their surfaces. She then optimized their atomic structure using a density functional code called QBox. The [011] growth direction showed the highest electrical conductivity and thermoelectric power, two parameters that increase ZT .

The effect of the wire’s size was mixed. For wires with canted surfaces grown in the [001] and [111] directions, effective mass increased as the wire’s diameter decreased. (As effective mass decreases, electrical conductivity increases and, thus, improves ZT .) However, for the [011] growth direction, where straight channels allow easy electron transport along the wire, effective mass remained the same regardless of the wire’s dimension. “These findings indicate that we can tune the electron mass and mobility to optimize a wire’s electronic conductivity,” says Vo.

Canted nanowires grown in the [001] direction can achieve a ZT of 3.5 but require considerable doping with either phosphorus or boron. “I doubt that the wires could be doped strongly enough for this surface to work,” says Vo. “Wires grown in the [011] direction will probably be the best compromise.”

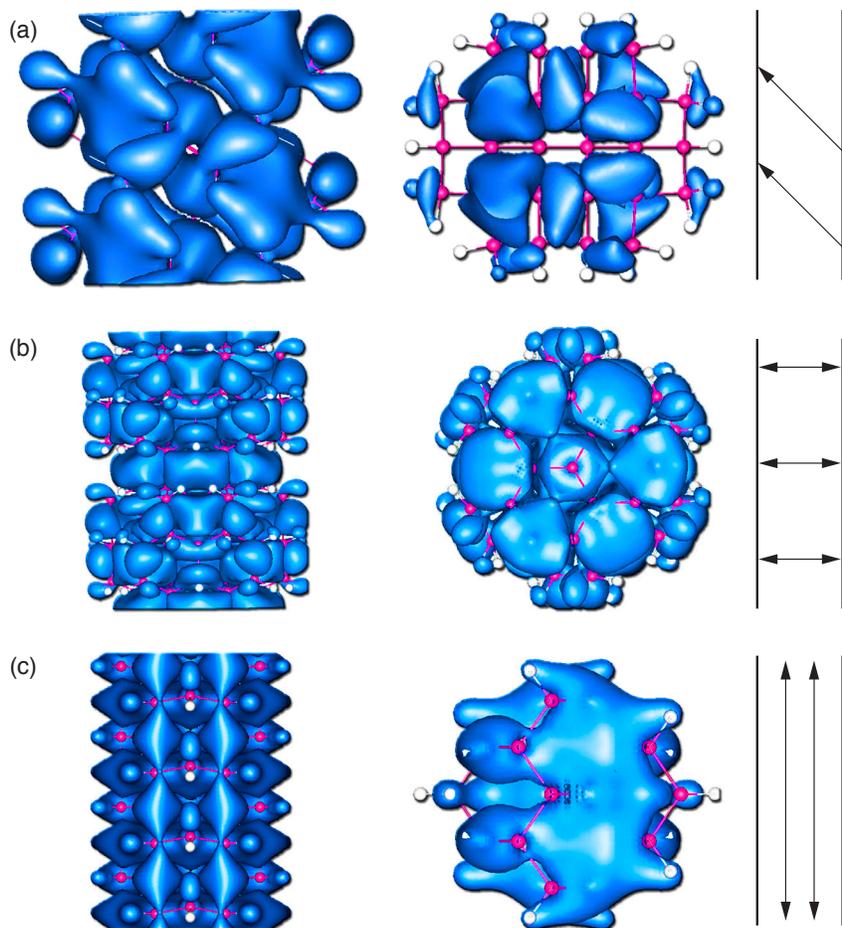
Although the low effective mass of silicon increases electrical conductivity, it also contributes to a high thermal conductivity. Thermal conductivity must be low for a thermoelectric material to be efficient. One solution is to

change the material used for the wires. Vo’s simulations indicate that a SiGe combination will reduce lattice thermal conductivity by as much as five times without affecting electrical conductivity. She is now working with Livermore scientist John Reed, who also is a postdoctoral researcher, to optimize wires made of silicon and germanium.

In collaboration with colleagues at the Massachusetts Institute of Technology (MIT), Reed is using classical molecular dynamics techniques to calculate the

thermal conductivity of wires with various configurations of silicon and germanium atoms. The goal is to create a SiGe wire with the lowest possible thermal conductivity.

Optimizing the SiGe wire involves an iterative scheme. Reed extracts fluctuations in heat current from the results of his molecular dynamics calculations, and the MIT team inputs these data into a cluster-expansion-based optimization method. The cluster-expansion algorithm produces candidate structures. The



Simulations indicate that when canted nanowires have lattices grown in the (a) [001] and (b) [111] directions, the wire’s effective mass increases as its diameter decreases. These configurations will increase electrical conductivity in thermoelectric materials. (c) When silicon nanowires are grown in the [011] direction, electron states are oriented along the wire. In this configuration, effective mass does not change when the wire’s diameter changes.

thermal conductivities of these structures are then calculated by Reed's code and plugged back into the MIT optimization calculation. This iterative process can also be used to optimize the thermal properties of semiconductors similar to silicon and germanium.

"The cluster-expansion method could propose a configuration for silicon and germanium that is impossible to fabricate," says Reed. Consequently, potential configurations must be evaluated to ascertain whether they can be fabricated and doped appropriately, and whether they are stable.

A Better Radiation Detector

Quantum simulations are also helping researchers develop a lightweight, high-resolution gamma radiation detector. A portable detector that can identify specific threat agents while ignoring the many legitimate sources of radiation has been a long-term goal to enhance security in the U.S. and worldwide. Such units would allow security personnel at cargo ports, airport terminals, and border crossings to quickly and easily detect threat agents before they enter the country. Improvements in the detection of weapons-grade nuclear materials are also critical to the effectiveness of the U.S. nonproliferation program.

The challenge in designing a portable gamma radiation detector is that high-purity germanium, the best material to date, cannot be used at room temperature. It must be cooled to remove its inherent background noise so the detector can read the signal emitted by gamma rays. Because of the cooling required with current technology, a high-resolution germanium-based radiation detector is typically a heavy, fragile unit.

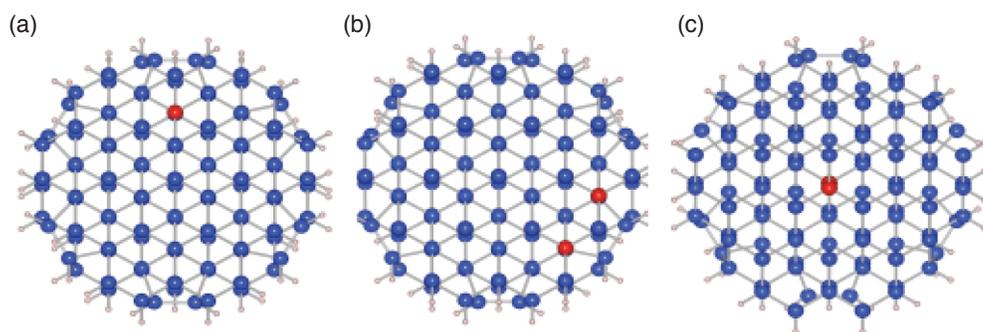
Researchers have proposed about 20 semiconductor elements and alloys as substitutes for germanium. Unfortunately, many of these materials have not performed as well as expected. Experimental investigations of every possible material would be prohibitively expensive. Now that computers can accurately predict material properties, computer scientists have joined the search for a new detector material.

When a semiconductor material interacts with gamma radiation, it produces electron-hole pairs that are detected as an electrical signal. A candidate material should therefore have highly mobile electrons (and holes) and long electron-hole recombination times to maximize the signal from each absorbed gamma ray. For use at room temperature, the material must also have an energy band gap large enough to preclude thermal excitations.

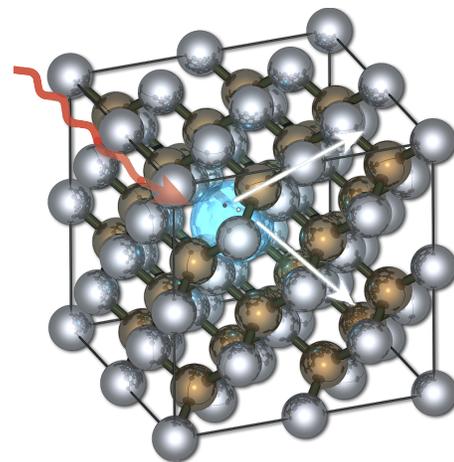
These features are controlled both by the intrinsic electronic properties of the semiconductor, such as its band structure and effective masses, and by the purity of the material. Structural defects in the material can trap electrons, reducing their mobility and increasing the probability of recombination, which in turn reduces the resolution of the detector.

Lawrence Fellow Vincenzo Lordi is performing first-principles studies to characterize the microscopic properties of materials and determine which ones are the best for semiconductor alloys. "Our research focuses on material impurities and ways to eliminate them," says Lordi. His simulations first provide an atomistic view of potential detector materials such as bulk gallium telluride and aluminum antimonide. Using density functional theory, he models the microscopic mechanisms by which defects degrade mobility. He then can calculate the intrinsic limits of mobility. Defects may be either native to the material or nonnative, for example, from a dopant.

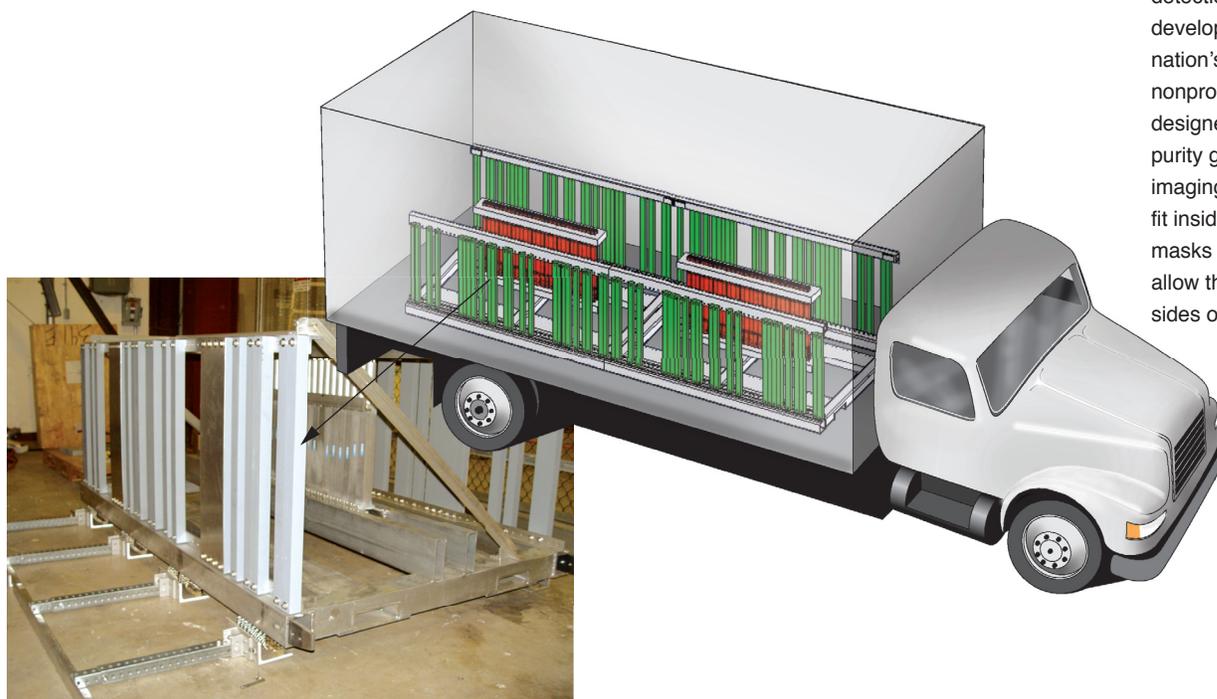
Kuang Jen Wu, a scientist in the Chemistry, Materials, and Life Sciences Directorate, is experimenting with



The cluster-based optimization method can be used to determine which configuration of silicon (blue) and germanium (red) produces the best thermal conductivity in a nanowire. (a) Germanium at one site increases thermal conductivity. (b) Having coplanar sites reduces thermal conductivity. (c) When sites are parallel to the wire, thermal conductivity increases.



This schematic of aluminum antimonide, a potential material for gamma radiation detectors, shows a defect (blue) in its lattice. Arrows indicate electron scattering.



High-resolution gamma-ray detection techniques are being developed to support the nation's homeland security and nonproliferation efforts. A detector designed at Livermore uses high-purity germanium for gamma-ray imaging and is small enough to fit inside a truck. Coded-aperture masks (the gray bars in the inset) allow the instrument to image both sides of a road.

aluminum antimonide, but the crystals produced to date have not been pure enough for use in a detector. Wu has tried annealing the crystals to repair some of the defects and is using Lordi's recent calculations to guide the annealing procedures.

Lordi and Williamson have also begun to develop a first-principles computational toolkit that will predict the structural, electronic, and transport properties of different semiconductor detector materials. The toolkit will evaluate a candidate material, determine the formation energies for a range of structural defects and dopants, and identify the most commonly formed defects. It will then predict how the concentration and distribution of defects will affect the material's electronic band structure, effective mass, and charge carrier mobility, lifetime, and scattering rate.

Ultimately, the toolkit will be used to create a database of fully characterized candidate materials for semiconductor detectors. With extensive information

showing how the sensitivity of transport properties is affected by imperfections in a material's structure, the team can more easily identify promising materials. "The database will also allow us to evaluate methods to improve a material's performance by modifying the synthesis process," says Lordi.

A high-resolution room-temperature radiation detector has other potential applications in addition to homeland security and nonproliferation. For example, astrophysicists are interested in using these detectors to better study gamma-ray bursts, the most luminous events to occur since the big bang. Orbiting satellites now detect a gamma-ray burst somewhere in the universe about once a day.

Squeezing Hydrogen from a Sponge

Another quantum simulation project is looking at material optimization, this time to allow auto manufacturers to scrap the internal combustion engine and make

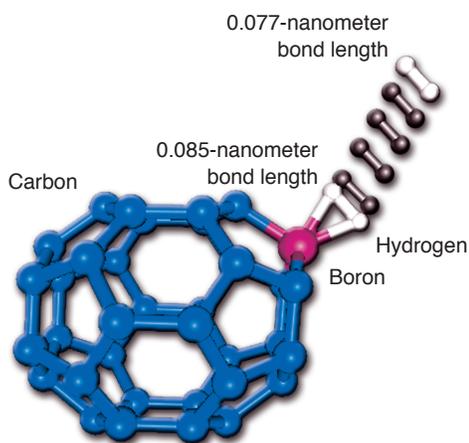
the move to hydrogen-fueled vehicles. "Fuel storage is a major stumbling block to further development of hydrogen vehicles," says Williamson. "With current storage technology, a tank holding enough hydrogen to travel 480 kilometers would be much too big and heavy for a car." Scientists have been trying to solve this conundrum for more than 30 years.

Williamson is working with researchers Julie Herberg and Ted Baumann from the Chemistry, Materials, and Life Sciences Directorate to determine if spongelike materials made of carbon can be used to soak up hydrogen and efficiently store it on cars. This project, which is funded by DOE's Office of Science, also includes computer scientists from the National Renewable Energy Laboratory (NREL) in Boulder, Colorado. Williamson likens the team's research to Thomas Edison's hunt for the best light bulb filament. Edison experimented with thousands of materials before settling on carbon.

The ideal storage material cannot react with hydrogen but must weakly bind to it so that hydrogen can be easily drawn off when a vehicle needs more power. In other words, the binding must be reversible. The optimal storage material will be very light so that more of the weight of the full tank is taken up by hydrogen, rather than by the tank itself. Before Williamson joined the project, the NREL scientists conducted experiments with boron and boron-doped carbon ($C_{35}B$) fullerenes. Their research showed that pure boron would have to be heated to release hydrogen, but $C_{35}B$ remains a possible choice.

These materials absorb hydrogen by the Van der Waals intermolecular force. This force, which is much weaker than a chemical bond, arises when molecules polarize into dipoles. These intermolecular forces may be feeble, but life as we know it would not exist without them. For example, the Van der Waals force provides just enough attraction to hold water molecules together in the liquid state.

Density functional theory does not capture Van der Waals forces. Instead, Williamson and his colleagues at NREL are using diffusion quantum Monte Carlo. By also incorporating Livermore's faster,



Livermore researchers calculated the binding energy of a boron-doped carbon fullerene to determine if it is a suitable material for hydrogen storage systems in vehicles.

linearly scaled version of quantum Monte Carlo, they have performed the first highly accurate quantum Monte Carlo studies of potential hydrogen storage materials. Calculations of the Van der Waals binding energy for hydrogen and carbon fullerenes doped with either boron or beryllium showed both materials to be adequate for reversible hydrogen storage. The team is now investigating other possible carbon-based storage materials, such as calcium-intercalated graphite.

These preliminary results will be augmented by a new coding capability. Williamson and the NREL researchers are modifying density functional theory to explicitly include the nonlocal correlation effect particularly tailored for the Van der Waals interactions. This new tool and diffusion quantum Monte Carlo complement one another and should firmly establish the binding energy and reversibility of hydrogen in candidate materials. Having these data is crucial because DOE is considering whether to continue research on carbon-based storage materials for hydrogen-fueled vehicles.

Quality Control for Chip Manufacture

Each year, computers become faster and more powerful because chip manufacturers can fit more features on a silicon wafer. As silicon chips get smaller, they become more difficult to make. Manufactured chips now have features measuring 65 nm, and in the laboratory, features can be made as small as 25 nm. Experts predict that features will be less than 10 nm by 2015.

Silicon at 10 nm may behave differently than it does at 50 or 100 nm. At the larger, bulk scale, silicon's behavior follows the rules of classical molecular dynamics. At smaller scales, however, quantum mechanics rules behavior. The Quantum Simulations Group is working to better understand the optical properties of this important material. Postdoctoral researcher Sebastien Hamel is using quantum simulations in a project funded by Intel Corporation and KLA-Tencor to determine

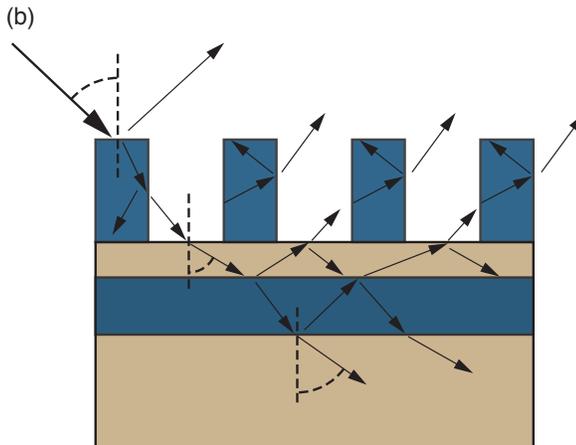
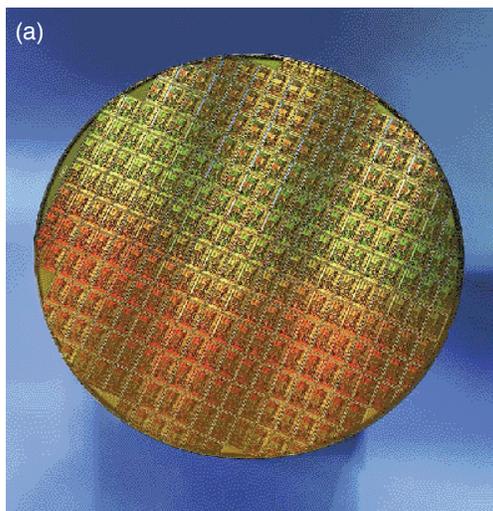
the transition point between bulk and nanoscale behavior.

Semiconductor manufacturers such as Intel use optical scatterometry equipment made by KLA-Tencor to control the quality of their silicon wafers. In scatterometry, light shone on a wafer at a specific angle bounces off the wafer's features. Measurements of the scattered light reveal critical structural parameters of the wafer's nanoscale features. As feature size shrinks, KLA-Tencor must adjust its algorithms to account for the changed properties of silicon. At 65 nm, the refractive index of silicon is the same as that of bulk silicon, but at 10 nm, its refractive index is unknown.

"We know something about the properties of silicon nanowires and have plenty of information on bulk silicon, but we don't know much at all about silicon at dimensions in between," says Hamel. "We need to determine how characteristics such as width, height, and rounded corners will affect the material's properties. The big question is how small can a feature be and still behave like bulk silicon? Or at what point does quantum behavior kick in?"

In Hamel's simulations using density functional theory, he looked for the distribution of electrons and the material's dielectric response. He found that a slab of silicon only 2.5 nm thick responds the same as bulk silicon. Silicon nanowires are different because they have so much surface area. For them, 5 nm is the limit for bulklike behavior. In the Intel laboratories, researchers have produced features as small as 5 nm by 25 nm, which Hamel predicts will have a dielectric response the same as bulk material.

His next research effort will examine the frequency dependence of the dielectric response—or absorption spectrum—of silicon nanostructures. The KLA-Tencor equipment uses a broad spectrum of light for the optical scatterometry experiments, but some parts of the absorption spectrum may be more sensitive to size than others. "KLA-Tencor wants to determine how



Manufacturers use optical scatterometry as a quality-control tool to ensure that semiconductor chips are free of defects. (a) A silicon wafer 30 centimeters in diameter is covered with thousands of minute features. (b) Scatterometry measures light as it bounces off a wafer's features. The scattering pattern indicates if a chip has been manufactured precisely as designed.

long the scatterometry technology will be effective," says Hamel. "At what point will chip manufacturers need a new quality-control technology?"

Quantum Coming of Age

The University of California recently selected Williamson as an Executive Management Discovery Fellow. Each year, the university chooses one fellow

per campus and offers resources for these people to establish strategic partnerships and collaborations with industry, particularly small businesses, to spur the California economy. That a quantum simulations expert was selected as the Laboratory's Discovery Fellow reflects the growing importance of the quantum world in the private sector.

—Katie Walter

Key Words: density functional theory, hydrogen storage, optical scatterometry, quantum molecular simulations, quantum Monte Carlo, silicon chip manufacture, silicon nanowires, thermoelectric materials.

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