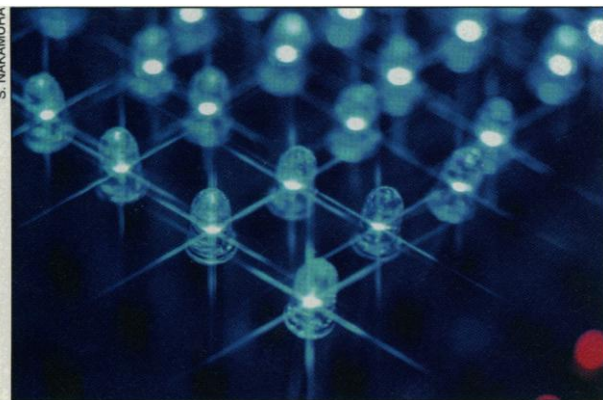


# Structure Meets Function at Materials Gathering

SAN FRANCISCO—Engineers, physicists, and other scientists interested in material behavior came together at the 1994 spring meeting of the Materials Research Society from 4 to 8 April. Among the 2200 papers given, researchers heard presentations on a variety of functional substances: a semiconductor suitable for a laser that gives off blue light, an improved magnetic refrigerator, and a method of keeping pollutants from forming in engine exhaust.

## Happy to See the Blues

Scientists don't ordinarily "ooh" and "aah" during a technical talk. But those were the sounds that greeted Japanese physicist Shuji Nakamura when he unveiled an array of blue light-emitting diodes (LEDs) in San Fran-



**Blue-light special.** These blue light-emitting diodes could be the first step toward a new type of laser.

cisco. And amidst the murmurs were undoubtedly a few groans of envy, because for years physicists have been chasing semiconducting materials that produce this true, bright blue.

The reason for this ardent pursuit is that such semiconductors are admirably suited for making blue-light lasers. And those lasers, in turn, have the potential to vastly increase optical storage capacity for computer memories and compact discs over that of the red and infrared-light lasers that are currently in use. But researchers have struggled to find substances that are durable enough and produce a bright enough blue light for laser applications. The semiconductor used in Nakamura's LEDs, called gallium nitride, looked to many in the audience as if it could fit the bill.

If Nakamura's LEDs—developed at his company, Nichia Chemical Industries—lead to a blue-light laser, that would be "a tremendously important step," says Asif Kahn, a physicist at APA Optics in Blaine, Minnesota, which is also trying to develop blue-light lasers. Researchers caution that

developing the lasers will probably take years, but in the meantime the LEDs have an immediate use: lighting up displays on outdoor billboards and in football stadiums, because they are more than 50 times brighter than those currently used.

The trick in getting semiconductors to emit blue light after plugging them into a wall socket is to coax electrons and oppositely charged particles called "holes" to combine within the material. Different sandwich-like layers in the semiconductor provide excess electrons and holes for this type of pairing. When jolted by an electric current, the electrons and holes move out of their layers and closer together, to a point where they can combine. When they do, they annihilate one another and give up a burst of energy that sometimes occurs as a photon.

The wavelength of the photon—and therefore its color—is related to the amount of energy an electron gives up in moving to meet its opposite number. A greater gap between the two requires a higher energy release, which produces a short—blue—wavelength photon. In most materials with appropriately sized gaps, however, such pairing actually occurs rather infrequently, and so the emitted light is dim.

To get brighter light, about 8 years ago researchers turned to materials such as zinc selenide, whose internal electronic properties make it more likely to bring electrons and holes together. But that material also contains structural defects. When electrons and holes pair inside these defects, they release heat instead of photons, which seriously damages the material. As a result, zinc selenide lasers typically break down after 20 seconds of use at room temperature, obviously rendering them useless for commercial applications.

Nakamura's semiconductor not only produces photons in the blue wavelengths, it also seems to be made of sterner stuff than its competitors. Gallium nitride is harder than

zinc selenide, and it resists deterioration due to heating. Nakamura's LEDs withstand thousands of hours of operation, and other researchers are hopeful that gallium nitride will prove just as robust in blue-light lasers.

Indeed, the blue LED "has convinced a lot of people that you can bring this material under control," says Kahn. "Getting the LED is the first step to getting the laser." Making a blue-light laser from gallium nitride is "definitely the way the R&D community is heading," adds Neal Hunter, the general manager of optoelectronics for Cree Research in Durham, North Carolina.

Success would be welcome news for the optical storage industry, which currently uses red and infrared lasers to store and retrieve data on compact discs and laser video discs. Lasers using shorter wavelengths of light can be focused into narrower beams. These beams are used to burn a pattern of dots into the plastic data storage material. Since the narrower beams can burn more dots into the same amount of space, they can store more information. In fact, the payoff for compact discs using blue light would be a four-fold increase in storage capacity over today's models, says Kahn.

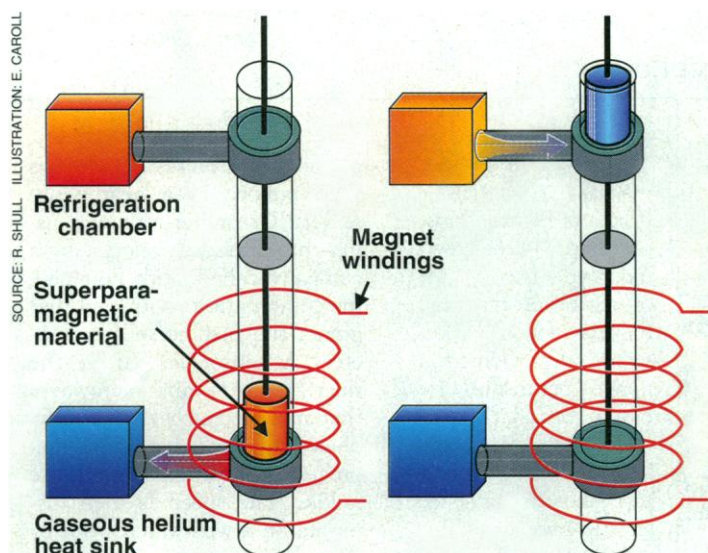
Researchers have many steps to take before putting entire anthologies of B. B. King on a single compact disc, though. The next step, says Nakamura, is getting gallium nitride to emit additional light and directing it into a single beam instead of shooting it out in all directions. To do so researchers must fashion what amount to tiny mirrors in the material to channel the emitted photons in one particular direction. If that can be accomplished—and it's no mean feat—then eventually we may not just be seeing more blues, but hearing more, too.

## Birth of the Cool

The coolest presentation at the meeting may well have come from Robert Shull, a metallurgist at the National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland, who outlined his efforts to create a class of supercooling magnetic materials that can plunge themselves to temperatures only a fraction of a degree above absolute zero.

Similar magnetic materials, known as "paramagnetics," have been used for years by industry to chill helium gas in order to liquefy it (liquid helium is a common coolant for sensitive optical and magnetic detectors). But Shull's "superparamagnetic" materials can provide the same cooling more efficiently, he says. In the long run, Shull hopes these materials will replace ozone-destroying chemical coolants such as CFCs and find a place in everything from kitchen refrigerators to living room air conditioners.

Many meeting participants gave Shull's cool work a warm reception. "What Bob has



**Cool attraction.** "Superparamagnetic" materials are cooled by magnets (left) and then used to chill a refrigeration chamber (right).

been doing is very exciting," says Gan-Moog Chow, a research physicist at the Naval Research Laboratory in Washington, D.C. "If what he is doing works, the payoff will be big." University of Connecticut chemist Kenneth Gonsalves, who collaborates with Shull, says that "if we can do this, it would be a big step toward getting a real alternative to chemical refrigerants."

Shull's materials, along with more conventional paramagnetics, work because they contain atoms whose electrons behave in a way that gives the atoms a tiny magnetic field with a positive and a negative pole. The direction of these "atomic magnets" can be oriented by an external field, in much the way that Earth's magnetic field makes a compass needle point north. When an external field performs such an alignment—lining up these atomic magnets in the same direction—it increases the overall temperature of the magnetic material. The reason: This type of organization requires energy, and energy translates into heat. Pull the material out of a field, and both the atomic magnetic alignments and the material's temperature drop. These fluctuations can be used to cool a chamber in a magnetic refrigeration system (see diagram, this page).

The problem with current paramagnetic materials is that they require strong magnetic fields to keep these atomic magnets in line. Manufacturers who need to liquefy helium, for instance, presently need to use expensive superconducting magnets to generate strong enough fields to drop the temperature to 4 degrees Kelvin. But 5 years ago, Shull and his colleagues at NIST figured out that they could use a weaker external field if they could encourage the atomic magnets in the material to help align one another.

That could be done, the scientists calculated, by grouping magnetic atoms in the

material into nano-meter-sized clusters. "The orientation of one atomic magnet doesn't care what its neighbors are doing"—as long as that magnet is alone, Shull says. But when they are clumped together, if one atomic magnet in a cluster changes its orientation, it takes a neighbor with it. The overall effect, explains Shull, is that it doesn't take as strong an applied field to produce the same magnitude of alignment within the material.

It took several years for Shull and his colleagues to engineer materials that cluster the atoms close enough to produce the desired effect. A mixture of iron and gadolinium-gallium-garnet finally turned out to be the right combination; in tests it has proven three to four times as efficient as current paramagnetics for cooling at 15 K. The payoff: "With these materials [manufacturers] may be able to switch to non-superconducting magnets," says Shull.

Of course, 15 K is a little chilly for household applications. But above this temperature, in paramagnetics, the atomic magnets no longer align, since the extra heat bounces atoms around in the material, throwing off their magnetic field orientations. Shull's superparamagnetics can get up to 70 K, and he hopes to push them still higher by squeezing the nano-sized clusters in the material even closer together. By doing so, he predicts the clusters will help align one another, which will help the materials maintain their magnetic alignment—and therefore maintain their cooling effect—at higher temperatures.

If he and his colleagues can engineer new composites that produce their cooling effect near the freezing point of water—another 200 K higher—people could be putting their refrigerator magnets on nonpolluting magnetic refrigerators.

## Riding the Precycle

You've heard of recycling, of course; everybody has in this green decade. Well, get ready for "precycling." That's a fancy term for reducing pollution by making less of it in the first place. It's also the idea behind Robert Farrauto's drive to change the way stationary engines, such as those used by power plants and industry, generate power. In San Francisco, Farrauto, a chemist at Engelhard Corporation in Iselin, New Jersey, described

new catalytic materials that combust fuel, allowing those engines to burn so cleanly that they churn out almost no nitrogen oxides and gaseous hydrocarbons, the chief villains in urban smog.

In engines that burn gasoline, natural gas, or other hydrocarbons, nitrogen oxides are formed when the temperature goes above 1400 degrees Celsius—and that's a problem, because conventional engines regularly reach temperatures of around 2500°C. Because of the catalyst, however, engines using Engelhard's catalyst reach a maximum temperature of only 1400°C, preventing the pollutants from forming in the first place. The result: nitrogen oxide levels of only 2 parts per million (ppm) in the exhaust, compared with a level of 200 ppm for conventional power plants.

The new catalyst is made of palladium oxide, stabilized by a series of other compounds and deposited on a heat-resistant honeycomb structure at the entrance to the engine's combustion chamber. Conventional gas-burning engines inject a mixture of fuel and air into this chamber, where it ignites, creating heat and pressure to drive the turbines. In the Engelhard-modified engine, the fuel-air mixture first passes through the honeycomb, where the palladium oxide breaks down some of the hydrocarbons in the fuel into carbon dioxide and water, giving off heat and preheating the remaining gas to as much as 800°C. Such preheated mixtures can ignite with far lower concentrations of fuel. The engines use a mixture containing only 40 percent as much fuel as a conventional engine, says Farrauto. This keeps the engine's overall temperature down, because less fuel burning in the combustion chamber generates less heat—but still enough to drive turbines efficiently.

The idea for this catalyst was patented in the 1970s, but it has only been since the advent of new federal clean-air regulations in 1990 that industrial researchers have had the incentive to test it in a real engine. Whether industry will be similarly tempted is another question, however. "It's an interesting idea," says Kathleen Taylor, a catalyst expert at General Motors Research and Development in Warren, Michigan. But its success is likely to rest as much on economics as on science, she adds. Industrial companies such as utilities and chemical plants have already spent millions of dollars redesigning their burners to filter nitrogen oxides from their exhaust. It will take a huge economic incentive to replace their current engines. "After-treatment [of nitrogen oxides] may sound expensive," she says. "But it's cheap compared to rebuilding your plant."

And if that's the case, then precycling has some high hurdles to leap before it, like recycling, becomes a household word.

—Robert F. Service