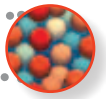


# BIG

SMALL

# THINGS

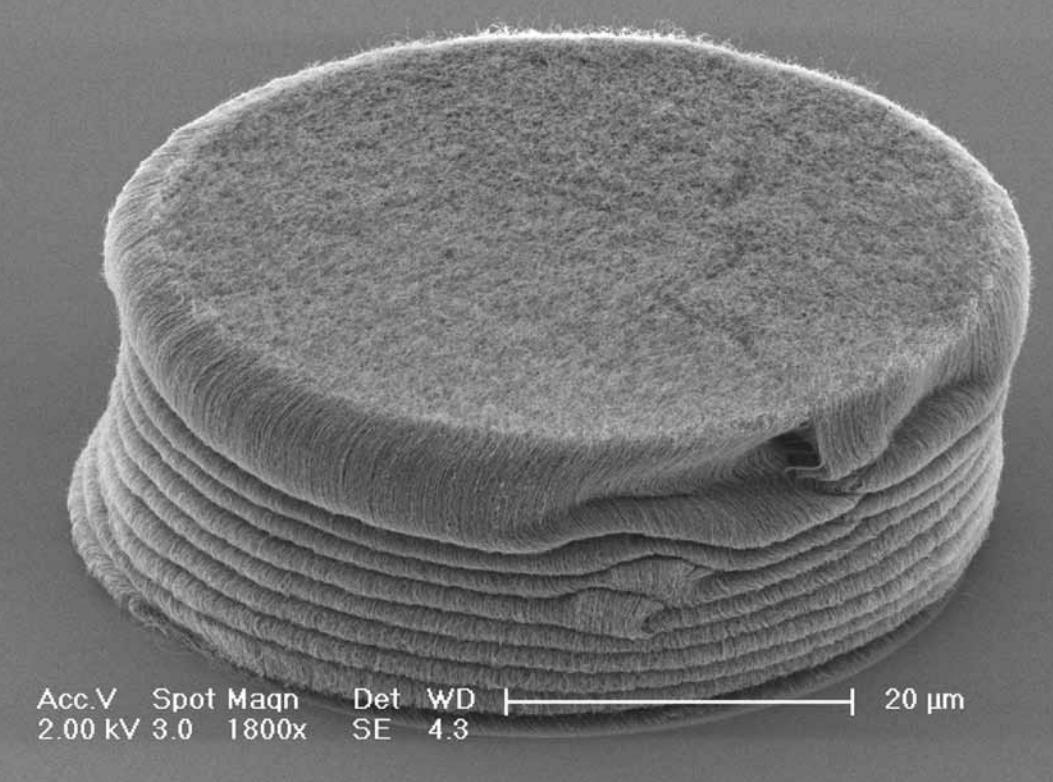




# HAPPENING HERE

By Kimm Fesenmaier

As scientists extend the limits of our knowledge of the universe, we ponder the limitless possibilities for discovery. But there's another, more subtle frontier: It's the science of materials—the transformation of the everyday into the truly extraordinary—and it's right at our fingertips. It's just *really, really* small. . . . ▶



Left: This micropillar, made up of millions of carbon nanotubes, has been compressed by a nanoindenter in the Greer lab. Its smooshed profile reveals localized buckles in the structure.

scales is the nanoindenter, a computer-controlled, spring-loaded shaft equipped with a diamond tip at the end, allowing it to probe tiny samples, sometimes smashing them to smithereens, all in the name of science. By exerting a precisely calibrated force, scientists can measure how much a sample deforms, how much energy it can absorb, and where its breaking point is.

A standard nanoindenter usually comes equipped with a vertically oriented optical microscope, which allows researchers to see relatively large structures, but which cannot distinguish features at the nanometer scale. It also lacks the ability to grab samples from above to test their breaking strengths or watch them deform. In order to overcome these limitations, Greer's lab built a souped-up version called the SEMentor (pronounced "cementor"), which is composed of a nanoindenter-like module inside a scanning electron microscope (SEM). The SEMentor allows researchers to grab the samples and watch deformation in real time.

"When you only have numerical data, the best you can do is hypothesize about what probably happened and then do a bunch of other indirect measurements to confirm or refute your hypothesis," Greer says. "But now we can say, 'Here's the data, and this is what really happened!'"

Equipping the SEMentor with custom-built grippers gives it the ability to not only poke or crush a sample, but also to stretch it. The Greer group's members have been stretching a

More than 50 years ago Richard Feynman posited in these very pages that "when we have some control of the arrangement of things on a small scale, we will get an enormously greater range of possible properties that substances can have." Researchers on campus are now gaining such control, which will lead to materials that are stronger, lighter, tougher . . . better.

Think of it as modern-day alchemy—transforming existing matter into new materials by taking advantage of what happens at the micro- and nanoscales, where matter behaves in strange and wonderful ways. "We have to shift our way of thinking about creating new materials toward not being slaves to processing anymore," says materials scientist [Julia R. Greer](#). In today's world, you start with an atomic structure and a processing route, which then dictates the properties that the end product will have. So far, the design process has not been used the other way around.

Greer dreams of the day when she'll be able to type into a computer, "I need something lightweight like an aerogel, that won't corrode and will be as strong as steel," and have it tell her exactly which raw materials to use and how to structure them into a bulk-scale material with those

properties. Creating such a computer model, she says, is "the grand challenge in materials sciences."

Part of the reason this model doesn't already exist is that we don't know how to incorporate the vast range of different material scales—from atoms to nanometers to microns to the macro-level—nor how to account for the properties at each of these levels. In bulk materials—those at scales we deal with in everyday life—certain sets of properties tend to couple together. Strong materials tend to be heavy; bendy, or ductile, components tend to be weak. But materials that are really, really strong and extremely light? Or strong and tough? Those are lacking.

Things behave differently at the nanoscale, however. Greer has shown that, when reduced to the nanometer scale, a single crystal of gold becomes nearly as strong as steel, even though bulk gold is soft and malleable. Such "size effects" open up a grab bag of possibilities, but in order to be able to pick the right properties out of the bag, we need to learn a lot more about where they come from and—perhaps most importantly—how to build bulk materials with those same properties.

The tool of choice for measuring mechanical properties at these small



wide range of materials: small-scale samples made of metals, composites, carbon nanotubes, and metallic glasses, to name a few. Bulk metallic glasses, or metallic alloys that lack the crystalline structure of traditional metals, are normally quite brittle, but Dongchan Jang, a postdoc in Greer's group, found that tiny pillars of metallic glass that are 100 nanometers in diameter can stretch by about 25 percent—23 percent more than the bulk material can—without breaking.

This is important because a metallic glass's irregular jumble of atoms inevitably contains stronger regions and weaker ones. If there are enough weak regions in a narrow plane, a sufficiently hard tug will coalesce them into a so-called shear band, which then rips through the sample—a catastrophic failure.

This is where the size effect comes in: nanostructures have a lot more surface than interior. "In a small structure, you have surfaces everywhere. You don't have a constant supply of mobile crystal defects, or dislocations, so the crystals have to create new ones, which takes a lot of energy," Greer says. "Even the number of atoms is limited. So you're in this starved state. It's that starvation of defects and its consequences for the atomic features that give rise to interesting properties."

But you can't build an airplane or even a coffee mug out of nanopillars. To bring these size effects to a larger

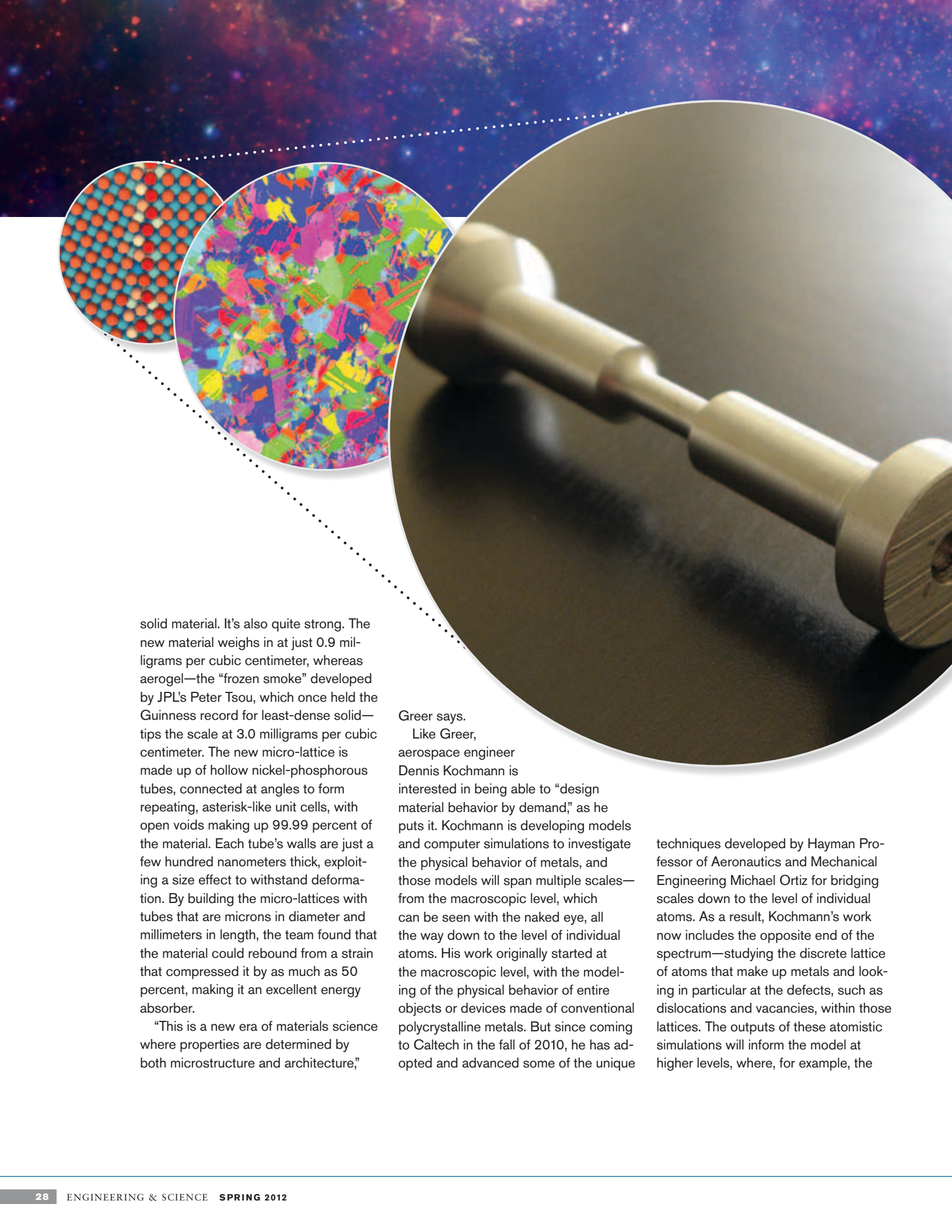
scale, Greer's lab is creating what she calls hierarchically structured materials. A hierarchical material consists of tiny structural elements whose properties bring certain advantages to the material; those elements are then aggregated into larger structural elements that preserve the advantages. The larger elements can then be aggregated themselves, leading to a whole new set of beneficial properties, and so on.

In this way, Greer and her colleagues are taking a page from Mother Nature's book. Nacre, the iridescent lining of many seashells, is a hierarchical material. Also known as mother-of-pearl, it is 95 percent aragonite, by volume, but 3,000 times tougher than nacre alone. The reason: the densely packed, microns-long tablets of aragonite are stacked like bricks, with nanometers-thick layers of proteins and chitin acting as mortar. When a crack gets started, the brick-like structure prevents the flaw from propagating. It might extend through one brittle aragonite tablet, but the surrounding organic layer will keep it from destroying the entire shell. Also, under stress—from the pounding surf, for example—the organic mortar gives, allowing the tablets to slide past one another and distributing the power of the blow.

Inspired by this hierarchical notion, Greer's lab recently collaborated with UC Irvine and HRL Laboratories, LLC, in Malibu, to develop a "micro-lattice" that now ranks as the world's lightest



This hierarchically structured microlattice, which Greer helped develop, is now considered the world's lightest solid material.



solid material. It's also quite strong. The new material weighs in at just 0.9 milligrams per cubic centimeter, whereas aerogel—the “frozen smoke” developed by JPL's Peter Tsou, which once held the Guinness record for least-dense solid—tips the scale at 3.0 milligrams per cubic centimeter. The new micro-lattice is made up of hollow nickel-phosphorous tubes, connected at angles to form repeating, asterisk-like unit cells, with open voids making up 99.99 percent of the material. Each tube's walls are just a few hundred nanometers thick, exploiting a size effect to withstand deformation. By building the micro-lattices with tubes that are microns in diameter and millimeters in length, the team found that the material could rebound from a strain that compressed it by as much as 50 percent, making it an excellent energy absorber.

“This is a new era of materials science where properties are determined by both microstructure and architecture,”

Greer says.

Like Greer, aerospace engineer Dennis Kochmann is interested in being able to “design material behavior by demand,” as he puts it. Kochmann is developing models and computer simulations to investigate the physical behavior of metals, and those models will span multiple scales—from the macroscopic level, which can be seen with the naked eye, all the way down to the level of individual atoms. His work originally started at the macroscopic level, with the modeling of the physical behavior of entire objects or devices made of conventional polycrystalline metals. But since coming to Caltech in the fall of 2010, he has adopted and advanced some of the unique

techniques developed by Hayman Professor of Aeronautics and Mechanical Engineering Michael Ortiz for bridging scales down to the level of individual atoms. As a result, Kochmann's work now includes the opposite end of the spectrum—studying the discrete lattice of atoms that make up metals and looking in particular at the defects, such as dislocations and vacancies, within those lattices. The outputs of these atomistic simulations will inform the model at higher levels, where, for example, the

Spanning multiple scales.

Far left: An atomistic model showing the boundary between grains in vanadium, an elemental metal.

Middle: The different orientations of the grains in this polycrystal of stainless steel are indicated by the image's various colors.

Right: A standard macroscale specimen made of aluminum.

different orientations of grains—groupings of lattices—and the boundaries between them also affect a material's properties.

"It's very important to study what is going on at these lower scales: How do these defects interact? What do they do? What is their energy? How do they move?" Kochmann

says. "We try to model how these defects interact to give rise to the very specific behaviors we observe at the macroscale."

And understanding leads to prediction. "If you design a completely new structure or aircraft, let's say, you want to be able to predict how much load it will be able to carry, when it will break, and so forth," Kochmann says. "Once we understand the connection between microscale and macroscale, we should be able to use that in order to design new materials with the beneficial properties we want."

Kochmann isn't just interested in modeling, though. As a graduate student in Roderic Lakes's lab at the University of Wisconsin–Madison, he helped develop a composite material with an unusual combination of properties—extremely high stiffness *and* high damping, which is the ability to absorb energy. This combo would be useful for

such things as an airplane wing that doesn't bend but absorbs vibrations, or an armor plate that soaks up the energy of a projectile. The key to this material is that it's tunable by temperature: near 120 degrees Celsius, the material becomes extremely stiff and highly damping; much above or below that temperature, the material is less stiff and only moderately damping.

high electron mobility, such as metals, conduct both electricity and heat; insulating glasses, in which the electrons are firmly bound to their atoms, conduct neither. But a semiconductor rod that is a thermal insulator *and* an electrical conductor can convert heat into electricity; heating the rod on one end causes charge carriers—electrons

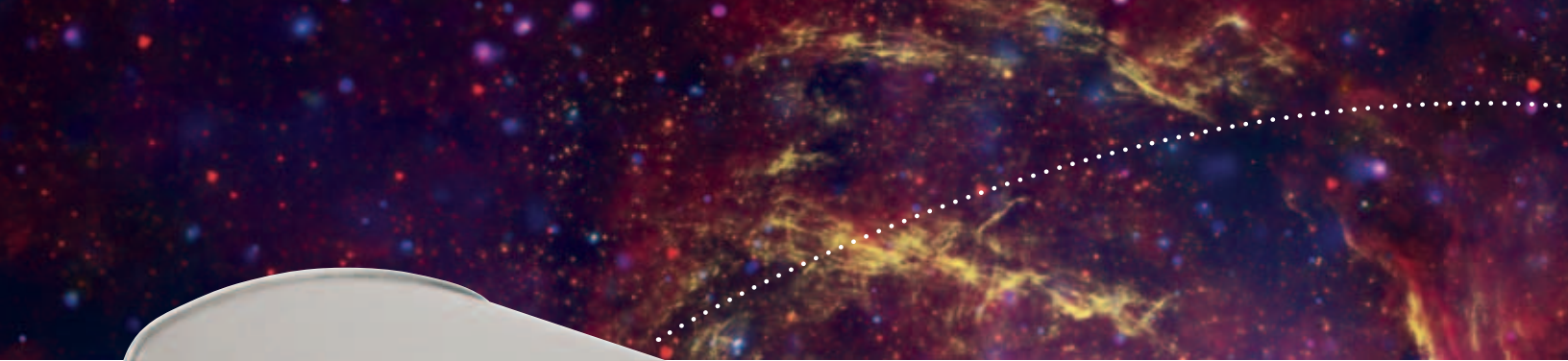
"It's very important to study what is going on at these lower scales: How do these defects interact? What do they do? What is their energy? How do they move?"

Now that he's at Caltech, Kochmann plans to make similar composites that transform through other mechanisms. It might be possible, for example, to use materials that change under electric fields, like certain piezomaterials. "The idea is to eventually have a material that changes its properties at the push of a button," Kochmann says.

Meanwhile, researchers elsewhere on campus are pursuing materials that would be able to conduct electricity well while protecting against heat conduction. Substances with

and "holes" (which carry a positive charge)—to migrate toward the cool side, creating an electrical flow.

Such thermoelectric generators are nothing new. NASA used them in the Apollo program and on the Viking landers, and such generators are keeping the twin Voyager spacecraft fueled on their epic journey. The generators are also headed to Mars, where they will power the *Curiosity* rover. But earthbound thermoelectrics are returning to the limelight these days as well, because they have the



potential to turn otherwise wasted heat, such as that in car exhaust or factory emissions, into usable energy.

In the last year or so, materials scientist Jeff Snyder has made major advances in the “recipe” for lead-telluride-based thermoelectrics—descendants of the type used in the Apollo instrument packages. He has significantly improved their electronic properties, and, most recently, has come back to the idea of including nanostructures in them to decrease thermal conductivity.

Snyder’s lab first started experimenting with this concept of nano-inclusion nearly a decade ago. One way to produce such nano-inclusions is to add a secondary material such as silver telluride into the melted original semiconductor and then carefully cool the mixture. The idea is that if the particles are the right size, they will disrupt the motion of the phonons—heat-carrying packets of thermal vibrations akin to photons, which are

packets of light—without disrupting the material’s electrical conductivity.

But after making some really complicated materials along these lines, the researchers identified a problem—they couldn’t say for certain that the improvements they were seeing were purely because of the nano-inclusions. So they stepped back and started working with simpler materials. “What we discovered was that everybody,

including ourselves, was comparing our nanostructured materials against reports from 1960 that relied on an inaccurate thermal conductivity measurement,” Snyder says. When they went back to the lab, they found that the measurement for lead telluride was off by about 30 percent.

Once Snyder’s team pinned down this pervasive error, they saw that there was room for improvement with lead telluride. The measure of efficiency in thermoelectrics is a dimensionless unit called the figure of merit,  $zT$ , and for nearly 50 years, the highest  $zT$  of lead-telluride-based thermoelectrics was thought to be 0.8. But by carefully selecting which elements to add to the lead telluride, Snyder’s lab improved the electronic properties to achieve a peak  $zT$  of nearly 1.8—an enormous increase. Most recently, the team has shown

It’s still early days when it comes to investigating the bizarre properties that can arise at the smallest of scales.

Waste not: Thermoelectric materials, which convert heat directly into electricity, have been improved by changing things at the nanoscale.

that nanoinclusions can improve a material even further by improving its average  $zT$ . For a thermoelectric to be useful in the real world, it needs to operate at a range of temperatures—in a car's muffler, for example, it would need to work anywhere between 50°C and 600°C. That means the average  $zT$ —the efficiency of the thermoelectric—needs to be high across all those temperatures. "So," says Snyder, "even though the exciting papers are the ones where the peak  $zT$  is very high, the important ones are really the ones where the average  $zT$  is boosted."

To make his thermoelectrics better, Snyder realized, it is the spacing between the particles that really matters. According to theory, about 20 percent of phonons in lead telluride have a mean free path—the distance they can travel without being disrupted—of longer than 100 nanometers. So by spacing nanoinclusions 100 nanometers apart, the team can increase scattering and reduce the material's overall thermal conductivity. Thus, while many teams have focused on making ultrasmall nanoinclusions—on the order of five or 10 nanometers in diameter—Snyder's group uses particles 50 nanometers in length, or even larger. Indeed, Snyder sometimes jokes that his is "the *large* nanoparticle research group."

As all three of these scientists point out, it's still the early days when it comes to investigating the bizarre properties that can arise at the

smallest of scales. And we're only just beginning to take advantage of the nanorealm to conjure up materials never before considered.

Still, the situation looks quite different today than it did in 1959, when Feynman told *E&S*, "We have been content to dig in the ground to find minerals." These

days, instead, we're burrowing down to the nanoscale, and finding new possibilities. **e&s**

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*Julia Greer is an assistant professor of materials science and mechanics. Her work on nanopillars and with the SEMentor is funded by the National Science Foundation and the Office of Naval Research, and utilizes the fabrication and characterization facilities of the Kavli Nanoscience Institute at Caltech.*

*Dennis Kochmann is an assistant professor of aerospace. He joined the Caltech faculty in 2011. His research is supported by the Haythornthwaite Foundation, as well as by Caltech.*

*Jeff Snyder is a faculty associate in applied physics and materials science. His thermoelectrics research is supported by NASA-JPL, the DARPA Nano Materials program, and the Chinese Academy of Sciences.*

