THE ALCHEMISTS' HEIR

An unconventional crystal-growing technique provides an abundant supply of novel materials for materials research at the Ames Lab

By Diana Lutz

Bernd Matthias, a physicist who discovered thousands of superconducting compounds, was fond of pointing out that no theorist had ever predicted the existence of a new superconductor. Since theory provided no guidance in this area of physics, he preferred simply to explore the periodic table by means of the arc furnace.

Matthias made something of a sport of baiting theorists, and they retaliated in kind. German physicists called his method *schmutz* physics, or dirty physics. Others called it alchemy, a reference to the body of ancient lore concerned with preparing a substance called the philosophers' stone that would have the power of transmuting "base" metals, such as lead or iron, into "noble" metals, such as gold or silver.

Ames Lab physicist Paul Canfield takes a similar, empirical approach to his science. And with a contrarian pride Matthias would appreciate, he considers himself one of the alchemists' heirs. Instead of trying to prepare the philosophers' stone, however, he spends his time preparing single crystals of materials with new or exotic low-energy states.

"When I was in graduate school," Canfield says, "my dear old advisor used to say that if you want to do good physics, you have to have either novel techniques or novel materials. In my career, I've decided to go for novel materials.

"There are physicists who spend their lives making complex measurements on existing materials, and that's very important," he continues. "But they have to have specialized equipment, they have to be exceptionally smart, and they have to design complex experiments. The way I pursue physics is to try to design, grow or discover samples of new or exotic materials in single-crystal form and then do relatively simple measurements on them."

This approach paid off recently when Canfield and collaborators at Ames Lab won a 1995 DOE Materials Sciences Award for "outstanding scientific accomplishment" for measurements made on single-crystal rare-earth nickel borocarbide (RNi_2B_2C) superconductors grown in Canfield's lab. The borocarbides had attracted Canfield's attention because they are a freak of nature: unlike most materials, they can be magnetic and superconducting at the same time.

Canfield grows single crystals by flux growth, a synthesis technique he learned from Zachary Fisk during a postdoctoral fellowship at Los Alamos National Laboratory. According to Joe Thompson, group leader of condensed matter and thermal physics at Los Alamos, flux growth was "rediscovered by Joe Remeika, who worked for decades at Bell Labs, and refined by his close collaborator Zachary Fisk. The people who use this technique as an approach to materials physics have all been associated at one time with Remeika or Fisk."

Canfield points out that training in alchemy has always been by secret apprenticeship. According to an ancient treatise on Chinese alchemy: *The adept must ... learn the method directly from those skilled in the art. Books are inadequate. What is written in books is only enough for beginners. The rest is kept secret and is given only in oral teaching. Worship of the proper gods is necessary. The art can moreover only be learned by those who are specially blessed. People are born under suitable or unsuitable stars. Above all, belief is necessary. Disbelief brings failure.* Canfield declines to say whether he was born under a suitable star.

Flux growth is a comparatively simple technique: the crystals are grown out of a solvent that reduces the melting point of the desired compound. For example, beautiful crystals of alum, a white astringent mineral used in styptic pencils and pickle-making, can be grown out of the solvent water. "You can grow alum, which is sold in drugstores, just be making a supersaturated solution," Canfield says. "You boil water, dissolve in as much alum as you possibly can, and let the solution cook. If the solution cools slowly enough, the alum will form large single crystals." Dissolving the alum in water allows crystals to be grown at temperatures below alum's melting temperature; in other words, water acts as a flux for alum.

"Now, say I want to grow crystals of cerium antimonide, which has the largest magneto-optic rotation known," Canfield continues. "It turns out that this compound melts at a temperature near 1800 degrees Celsius, which is very high. At that temperature antimony has a large vapor pressure, and cerium has a significant one, so you can't grow the compound just by melting the elements together. However, it turns out that you can dissolve small amounts of cerium and antimony into tin, which has a relatively low melting point. If you heat this mixture up to a temperature of about 1200 C and then cool it down to about 700 C, beautiful single crystals of cerium antimonide grow out of the molten tin flux."

Flux growth is not widely used, Canfield says, because it is less predictable than conventional crystal-growing techniques. He estimates he has about a 30 percent chance of growing any intermetallic compound. "As you can imagine," he explains, "if you're adding an extra element, there's a possibility you might end up with a ternary compound instead of the binary one you're trying to make. And if you're working in a very linear research project, where you're only interested in the material you're trying to make, then flux growth may be more trouble than it's worth. On the other hand, if the discovery of new materials is part of your research agenda, then surprises are also opportunities."

"The advantage of flux growth," says Thompson, "is the variety of crystals that can be grown and the speed with which those crystals can be grown. It doesn't require elaborate apparatus; you're essentially limited only by the number of furnaces you possess. You can be growing any number of single crystals overnight while you're home sleeping, which is not how people generally grow crystals.

"Flux growth," Thompson continues, "is the preferred approach for any program that's interested in single crystals of new materials simply because of this ability to make so many materials rapidly. It allows you to explore so much phase space simultaneously that the probability of growing entirely new crystals is quite high."

The rare-earth nickel borocarbides are one example. The discovery of these compounds was announced in January 1994 by a large collaboration led by researchers at the Tata Institute in India and, independently, by a Bell Labs research group led by Bob Cava. "Cava's group identified the composition and crystal structure," Canfield says. "They also showed that the crystal structure existed not only for yttrium, which is an honorary rare earth, but also for elements in the lanthanide series, which are true rare earths. This was extremely interesting because most of the rare earths are magnetic.

"I saw the announcement of this stuff," Canfield recalls, "and I said to myself, it's an intermetallic, it looks interesting, I have a chance of growing it, let's go." Although flux growth is a simple technique, it does have one tricky part, which is figuring out what flux to use. The flux can be one of the elements in the system, a mixture of the elements in the system, or an additional element. Canfield tried several fluxes a day for weeks before he figured out that di-nickel boride (Ni_2B) would work as a flux for the nickel borocarbides. But within two months he had single crystals, and for the next year and a half Ames Lab was the sole source of single crystals of these materials.

What is so interesting about the nickel borocarbides? Canfield replies that he's interested in phase transitions -- transitions from disorder to order or from one type of order to another. As the borocarbides are cooled, they can undergo two basic types of phase transitions. The first is the phase transition of the conduction electrons, the electrons that have enough energy to zip freely through the material, at the superconducting transition temperature. At this temperature the conduction electrons begin to move through the material in a "quantum phalanx" that cannot be easily disrupted by thermal vibrations or defects. The second phase transition is the transition of the rare-earth element's magnetic moments at the magnetic transition temperature. At a typical magnetic transition (there can be more than one), the magnetic moments suddenly assume a regular pattern that extends throughout the material.

Magnetism usually kills superconductivity. Pure lanthanum, for example, conducts electricity without resistance at temperatures below 6 Kelvin. But if just a fraction of a percent of the magnetic rare-earth element gadolinium is added to the lanthanum, it destroys the superconducting state. In a magnetic superconductor, however, there is only weak coupling between the moments of the rare-earth elements that give rise to the magnetism and the conduction electrons that give rise to the superconductivity. Because the couple is so weak, the material can be simultaneously superconducting and magnetic.

A nickel borocarbide that includes the rare-earth element holmium, for example, becomes superconducting at 8.5 Kelvin. Then, starting at 6 Kelvin, it undergoes a cascade of transitions between magnetic states. But instead of killing the material's superconductivity, magnetic ordering causes novel features to appear in its superconducting parameters.

Flux growth is more central to the physics of the nickel borocarbides than one might suppose. In the late 1970s and early 1980s several other families of magnetic superconductors -- the rare-earth rhodium borides and the rare-earth molybdenum selenides and sulfides -- created a stir in the physics community. According to Brian Maple, the Bernd T. Matthias professor of physics at the University of California at San Diego, this "early work was done on polycrystalline material. What Paul Canfield did was to devise a method of growing single crystals of the new magnetic superconductors. This then made possible much more meaningful studies of the interplay of superconductivity and magnetic ordering."

Access to single crystals is important for two reasons. One is that it is much easier to study the anisotropic, or directionally dependent, properties of a material in a single crystal. Just as the appearance of a cornfield depends on whether one is looking down or across the rows, the properties of many crystalline materials depend on the axis along which they are measured. "For example, some materials are thought to be metallic (conducting) along one axis and insulating along another," Canfield says. "A polycrystalline sample of such a material might appear to be conducting, because the anisotropy would be hidden by the variable orientation of the crystallites of which the sample was composed." Largely because they were available in single-crystal form so soon after their discovery, the borocarbides are the first magnetic superconductors whose anisotropies have been systematically examined.

The second reason access to single crystals is important is that single crystals do not exhibit artificial effects due to strain or impurities. Crystals can belong to one of several crystal systems, each of which is characterized by certain symmetries. A polycrystalline sample of a material that belongs to one of the noncubic crystal systems can have significant built-in strain. The nickel borocarbides have tetragonal symmetry and their electrical and magnetic properties seem to be highly strain and pressure dependent. "So if you're not looking at a single crystal," Canfield says, "you may not be looking at intrinsic properties."

According to Maple, "materials synthesis is one of the most important and most underrated activities in science, especially in the United States. The activity Paul Canfield is involved in is very important, and the materials he's been making are highly sought after by other people at Ames and throughout the world."

Canfield's group has done extensive magnetic and electrical resistivity measurements on the borocarbides. And they have established collaborative research projects on the properties of these novel materials with other national laboratories, university laboratories and research groups in England, France, Switzerland, Japan and Korea.

"I think Paul Canfield has done a nice service to condensed matter physics by pushing the rare-earth magnetic superconductors," Thompson says. "He deserves a lot of credit not only for developing a technique for growing high-quality single crystals of these materials but also for pushing the interest and science that's developed around them."

Although the alchemists of old sought to turn lead into gold, today's alchemists search for new materials with properties as precious as gold's. As one of these practitioners, Paul Canfield and his apprentices continue the search for the modern versions of the philosophers' stone (or crystal).

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