Exploring the New Material World

There may be a dire shortage of undiscovered continents, but intrepid chemists are pursuing their own quests in laboratory reaction vessels

FRANCIS J. DISALVO DOES A LOT OF PREACHING these days: Woe unto those who neglect unworn pathways through the periodic table of chemical elements, he thunders, for there wait material treasures of unimagined wonder.

"Every material that can possibly come our way is sitting there in the periodic table," says DiSalvo, a solid-state chemist at Cornell University. "It's a puzzle that has been given to us by God...and it's one of the most exciting brain teasers that science will ever have."

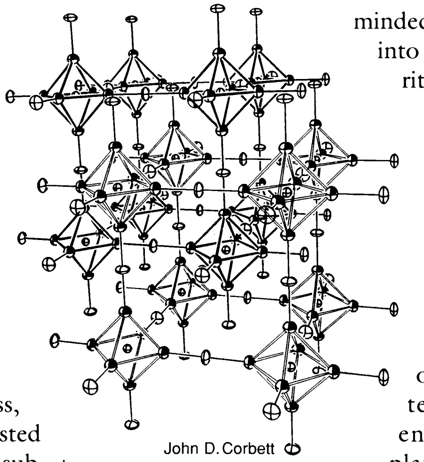
Who can argue? Every gemstone, every metallic alloy, every superconductor, every speck of dust, every semiconducting crystal, every piece of biological tissue, absolutely every material that ever was, is, or will be remains latent within the periodic table until someone or something puts its atomic building blocks together.

And yet all those undiscovered materials, silent in their potential, could easily remain unrevealed forever. Unless, that is, natural processes—either unassisted or aided by chemists—give the nascent substances physical reality by putting a never-before-considered set of atoms together. DiSalvo, for one, has made that his personal business.

He and a small band of fellow solid-state chemists practice what they call exploratory synthesis, treating the periodic table as a pantry full of ingredients for culinary invention. Guided by experimental rules of thumb and seat-of-the-pants intuition, they have cooked up hundreds of previously unimagined inorganic solids. The cook-offs most often produce worthless sooty muck, but there is always the possibility of a new catalyst that could revolutionize the petroleum industry, a new superconductor, or something with entirely unprecedented properties—perhaps the solution to a problem that hasn't even arisen yet.

One might think that this approach would be standard operating procedure in materials science—after all, creating useful new materials is the grail of the field. But at least in the United States, DiSalvo has little company in his endeavor—so little that he worries the country will miss out on the discovery of potential bonanza materials. Many U.S. researchers have concentrated on finding new ways to process or alter existing materials—to turn carbon into diamond films, say, or to improve the crystal structure of superalloys by slightly changing their atomic composition or their processing. Others have focused on analyzing known materials, trying to understand the basis of their properties. But few have followed DiSalvo and likeminded chemists into virgin territory.

Yet it's an effort other materials scientists applaud. "Exploratory synthesis is where all of the great discoveries come from," says chemist M. Frederick Hawthorne of the University of California at Los Angeles, who is editor of the journal *Inorganic Chemistry*. The Rensselaer Polytechnic Institute's Leonard V. Interrante, who edits *Chemistry of Materials*, seconds that view: "A lot of the work in solid-state chemistry tends to be derivative and unimaginative....These efforts are not as likely [as exploratory synthesis] to lead to large breakthroughs."



John D. Corbett

Diamonds in the rough? *A newly synthesized arrangement of zirconium atoms.*

For chemist and materials scientist Arthur Sleight, a practitioner of exploratory synthesis at Oregon State University in Corvallis, the discovery of the high-temperature superconductors is a case in point. The roots of the current research frenzy surrounding these ceramic materials, Sleight is fond of pointing out, actually stretch back to the mid-1970s, to the kind of exploratory chemistry he and DiSalvo are now advocating. That was when Bernard Raveau and his coworkers at the University of Caen in France began synthesizing unassuming electrically conductive compounds composed of lanthanum, barium, copper, and oxygen atoms.

Raveau never bothered to chill them to the exquisitely frigid temperatures required for the superconducting metals known at the time. But in 1985, after reading papers by Raveau's group, K. Alex Müller and J. Georg Bednorz of IBM's Zurich Research Laboratory noticed that the same unassuming compounds contained copper atoms possessing exactly the chemical characteristics that they suspected might lead to high-temperature superconductors. As all the world knows, their hunch was correct.

Müller and Bednorz's discovery spurred a herd of solid-state researchers to embark on exploratory synthesis of a limited sort. They have been cooking up new high-temperature superconductors, largely by varying recipes for the compounds—such as yttrium-barium-copper-oxide in proportions of 1 to 2 to 3 to about 7 atoms—that are already known to work. But DiSalvo, Sleight, and a few other researchers are much less constrained in their search. If a new ceramic happens to be a superconductor, well and good, but they'll still celebrate if it has entirely unexpected properties.

"Exploring what materials are possible in the solid state is a natural intellectual goal," says John D. Corbett, a well-known practitioner of exploratory synthesis at the Iowa State University at Ames. Indeed, Corbett sees it as somewhat akin to cataloging the world's biological species.

For exploratory chemists, unlike globe-trotting biologists who at least know what countries are likely to host new animal species, there are very few maps—not even theoretical ones to point the way to brand new chemical species. But they do have a few rules of thumb to guide their journeys. Sleight, for example, relies mostly on mild conditions and cheap materials to keep down the cost of the synthesis—and of any practical material he might create. Corbett, on the other hand, often opts for high temperatures, which reduce the number of chemical products and simplify subsequent analysis. And all explorers, DiSalvo says, need to apply a decent dollop of chemical wisdom that comes only from years of benchwork and knowledge of their fellow explorers' work.

As for their molecule-making techniques, these intrepid explorers don't exactly win the most elegant chemical synthesis award. They often employ synthetic methods that Corbett suspects are perceived as low-brow by many other chemists. Even Corbett uses the nicknames "heat and beat" and "shake and bake" chemistry to describe what he does. And the irreverent descriptors aren't far off the mark when you consider a typical exploratory synthesis in his lab.

Reactants—metals and metal compounds, in various proportions—go into vessels of tantalum or niobium, which can withstand the high processing temperatures without contributing their own atomic constituents to the reaction. After allowing a good long bake, sometimes lasting weeks, the investigators sift through the contents of the vessel to harvest the result: small crystals of metallic clusters never before made by human beings and probably by nothing else.

"We are just continually amazed by what nature can provide in terms of unexpected solids," Corbett says. When the vessels are loaded with cobalt and zirconium powders and zirconium tetrachloride, the reaction yields octahedral clusters consisting of 6 zirconium atoms, one at each vertex, surrounded by a halo of 18 chloride ions. A cobalt atom somehow finds its way inside each octahedron, where it seems to buttress the assembly. When other metals are substituted for cobalt, the buttressing atom changes, and with it the shape and size of the cluster.

The clusters—each an individual molecule—assemble into solid forms like powders and crystals. But more recently Corbett coaxed his clusters to share edges, linking them into chains. In some cases these chains also weave into sheets, which can then stack on top of one another like the carbon layers of graphite—an arrangement that could endow the resulting materials with electrical conductivity or lubricating properties.

Not that Corbett set out to produce those qualities. He simply chose a patch of chemical territory and searched it for intriguing properties. "The blind squirrel eventually will find a nut," Corbett says in defense of his methods.

DiSalvo has been looking for his nut mainly in the largely unexplored class of materials known as ternary nitrides (see accompanying box). But, like Corbett, he also investigates small metal clusters surrounded by nonmetal atoms. DiSalvo has succeeded in linking together the clusters to form minuscule wirelike structures just 6 angstroms—a few atomic widths—thick. "We not only know how to make the world's thinnest wire," he says, "it's also the thinnest insulated wire!"

To Sleight of the Oregon State University it's this kind of surprise that makes exploratory synthesis worthwhile. In his own laboratory's exploration of oxides containing four atomic constituents, Sleight says, "We recently came across a new material that has the ability to double the frequency of light passing through it." Solids with that property will be central to the emerging photonics technologies, which manipulate light signals the way electronic technologies manipulate electrical ones.

In spite of the adventure and the potential payoff, only a minority of solid-state chemists have exploratory synthesis on their research agendas. The reasons for its absence are many. The sheer vastness of possibility can be paralyzing, DiSalvo says. "If you try to make all possible compounds by combining 10 different elements, and if every person on Earth were a solid-state chemist, it would take a period equal to the age of the universe to examine all of the compounds," he suggests.

Raising the anxiety level even further, Sleight notes, is the fact that "you can't get

One Man's "Night Ride" Through Nitride Country

Explorer DiSalvo

How can you make a material with all the electronic benefits of the new ceramic superconductors but none of the brittleness and processing challenges? Francis DiSalvo doesn't have the answer, but he thinks he knows where to look, and he's taking what is (for the United States) an unorthodox approach. Where your party-line materials scientist is changing this or changing that in the recipe for known superconductors, the Cornell University solid-state chemist has been practicing exploratory synthesis—a way of discovering new materials (see main text) that has been yielding breakthroughs in Europe for decades but is little practiced in the United States.

DiSalvo is applying the method to a largely uncharted class of materials called ternary nitrides, which consist of nitrogen and two other atomic constituents—often calcium and nickel, in DiSalvo's experiments. The right combination of those ingredients, DiSalvo thought, might have nickel atoms poised to shuttle electrons in that fashionable superconductive way.

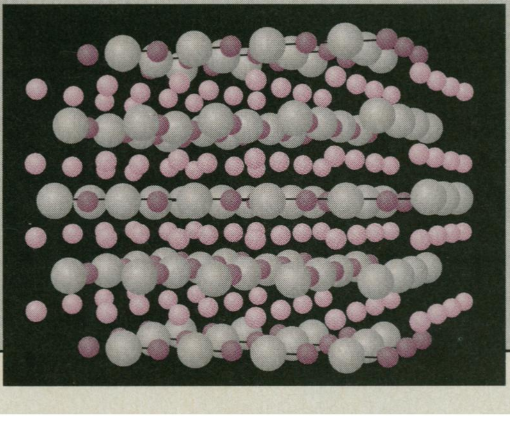
Hoping to hit the jackpot, he has been concocting lots of nitrides but changing the proportions and processing details each time. Some products have shown an atomic layering reminiscent of known high-temperature superconductors—and a structural versatility that might lead to new superconductors far more tractable than existing ones.

But DiSalvo is not out to prove he's a candidate for Gambler's Anonymous. He concedes that the odds are long against finding the perfect nitride-based superconductive solid. So he's hedged his bets. "Hardly anybody has done chemistry on the nitrides," he says. "I knew we would get new solids no matter what."

Indeed, DiSalvo's basic recipe of mixing calcium nitride and nickel powders and heating them under nitrogen gas has yielded a variety of curious layered structures. Nickel and nitrogen atoms link into chains that line up like "shish kebabs on a grill," DiSalvo says. Successive shish kebab layers criss-cross, held apart by layers of calcium ions.

DiSalvo has found that the shish kebab stacking has odd effects on the electronic structure of the nickel atoms. The nickel atoms' outer electrons reshuffle so that they resemble those of the copper atoms in known high-temperature superconductors. And that reshuffling, DiSalvo hopes, might open routes to an entirely new class of materials displaying useful electronic properties.

Then again, it might not. Many of the new nitrides inevitably will turn out to be no more interesting than the dirt in a dustpan. But that doesn't discourage DiSalvo: Buried in the debris, he figures, there might just be a candidate for *Science's* "Molecule of the Year," Edition 1992. ■ **I.A.**



Shish kebab chemistry. *A route to new superconductors?*

guidance from theorists." Without such pointers, a chemist might randomly assemble atoms until death does him part and still never happen upon an important new compound. As a result, many scientists, particularly young, untenured ones whose jobs and grants depend on successful research, can't risk committing to exploratory synthesis even if they wanted to, says Hawthorne of the University of California at Los Angeles.

DiSalvo acknowledges the risk of wandering through unknown territory without a theoretical map, but he defends exploratory synthesis with the bravado of a New World explorer. "This lack of understanding is a source not only of great challenge, but also of surprise, wonder, and excitement about the intricacy of nature," he wrote last year in an issue of *Science* devoted to new materials. He also notes that chemical and physical theories do play crucial roles after an initial discovery, by helping exploratory chemists understand how their products formed and how they might prove useful.

Before other chemists can take up the challenge, some institutional and sociological barriers will have to be lowered. For one thing, Sleight notes, few chemistry departments have specific programs in solid-state chemistry. For another, each elaborate new analytical tool has spawned a cadre of chemists skilled in analysis, drawing people away from other fields such as exploratory synthesis. "We need fewer people making measurements and more people making things to measure," Sleight says.

That synthesis-centered approach has been the modus operandi of chemists in Europe. The high-temperature superconductors, Corbett adds, are but the latest of a long list of solids that had been made first in the Old World, then characterized and harnessed in new technologies in the United States and Japan. But the United States should not get in the habit of relying on foreign scientists to supply them interesting new solids, DiSalvo and Sleight warn.

So far, U.S. funding policy has not favored a large homegrown exploratory synthesis crowd. Federal agencies have not been apt to place bets on blind squirrels, notes Sleight. "People don't get excited when you say, 'I'm going somewhere and I don't know what I'll find,'" he says. But there have been signs that this may be changing. The National Science Foundation has requested an additional $25 million for a 1992 initiative in materials synthesis and processing. And other high-level decision makers are considering launching a far more comprehensive national initiative that would boost exploratory synthesis. In time, DiSalvo may find himself preaching to the converted.

■ IVAN AMATO

Buckyballs, Hairyballs, Dopeyballs

The 60-carbon spherical molecules called buckyballs rolled back onto center stage last month with the report that the fullerene materials made from C60 molecules can be transformed into superconductors (see *Science*, 26 April, p. 512). But just outside the spotlight other buckyball curiosities that offer hints of practical promise or theoretical significance were emerging. Like biologists learning the ways of a new life form, buckyball researchers are poking and prodding their new creature to see how it responds.

Like the geodesic dome invented by namesake Buckminster Fuller, buckyballs are proving to be extraordinarily sturdy. They can survive colliding with targets of metal and other materials at 20,000 miles per hour—an impact that would tear other molecules apart. "Nothing else can do that," according to Robert Whetten of the University of California in Los Angeles, who mentioned the result during a press conference on April 17 at a meeting of the American Chemical Society (ACS) in Atlanta. Such durability adds to the molecule's appeal for use as a potential lubricant and for other uses in which ruggedness comes in handy.

As tough as they are, buckyballs still can't resist fraternizing with their chemical brethren. Fred Wudl of the University of California at Santa Barbara and others reported at the press conference and later that night during a 5-hour symposium that buckyballs react readily with many organic chemicals. The work capitalizes on the tendency of C60, the most studied fullerene, to accept electrons.

"For a while, it was crazy in our lab. No matter what we pulled off the shelf, it would react," Wudl recalls. C60's symmetrical architecture, coupled with its reactivity, led to some elaborate chemical constructs. Wudl calls one of them a "hairyball": a C60 soccer ball festooned with a dozen or more ethylene diamine components, whose nitrogen atoms have electrons to spare. This buckyball derivative is soluble in water, Wudl found—to the surprise of other researcherss, who so far have been able to dissolve the carbon molecules only in organic solvents such as benzene. In water, fullerenes might be able to take part in an even wider range of reactions.

"This opens up a huge area of organic chemistry," Wudl says. A good analogy for the potential of C60, he says, may be benzene—a highly stable 6-carbon form whose ring-shaped structure forms the dominant motif in countless organic molecules. Like the discovery of the benzene structure in the 19th century, the synthesis of C60 has given chemists "a new architecture to play with."

While other people have been building onto the C60 structure, Smalley has been building a new element into it—boron. The trick of doing so, he told the ACS audience, is to vaporize a mix of carbon and boron nitride with a laser and then rapidly cool the resulting vapors. As many as four boron atoms seem to integrate themselves into the buckyball structure as it takes shape. Braving groans, Smalley called the boron-doped buckyballs "dopeyballs."

Dopeyballs may not be the harbingers of any new technology, but they may help researchers address the basic question of how buckyballs form. A nascent buckyball could well look like a patch of chicken wire—a "hot graphitic net," as Smalley puts it—that curls and closes up into a sphere as it incorporates more and more carbon atoms. If this picture holds, stray atoms such as boron could join the fun by bonding into the growing nets of carbon atoms before they curl into fullerene molecules.

The spectacular shape that is the end result of the growth process had been known only indirectly, from strong circumstantial evidence, but now there is little room for doubt: the buckyball is for real. The ACS session saw direct evidence of the shape, in the form of data from x-ray crystallography. Getting the spherical molecules to stand still for their picture was apparently no mean feat, as Joel Hawkins of the University of California and others told the ACS session. Under standard conditions C60 molecules rotate like ball bearings, becoming moving targets for incoming x-rays.

As researchers' familiarity with the fullerenes grows, thoughts are naturally turning to commercial applications. So far, the carbon spheres have turned up on the market only in the form of a specialty chemical for sale by a pair of startup companies. Still, meeting participants spoke of possible applications ranging from rocket propellants to electronic materials to precursors for synthetic diamond. But specifics are hard to come by. As Smalley suggests, "People who know where they want to go with this are no longer talking."

■ IVAN AMATO