Clusters: Strange Morsels of Matter

When metals or semiconductors are shrunk down to clumps only 10 or 100 atoms in size, they become a "totally new class of materials" with potentially valuable applications

A RAINBOW OF COLORS SHINES from the jars that AT&T Bell Labs chemist Louis Brus is displaying: red, orange, light green, black. The deep red powder, Brus explains, consists of cadmium selenium particles. The vivid orange powder, he says, also consists of cadmium selenium particles, as do the light green, the black, and other colors in between.

What's going on here? How can the powders in the different flasks be chemically identical, but visibly very different? The answer, Brus explains, is that the particles in each jar have slightly different sizes, although all are very small. The red powder, for instance, consists of cadmium selenium particles that are an average of 50 angstroms across and contain about 3000 atoms, while the clusters in the orange powder are 35 angstroms across and have about 1000 atoms. It is strange but true that the colors of the powders are changed dramatically simply by altering the particle sizes.

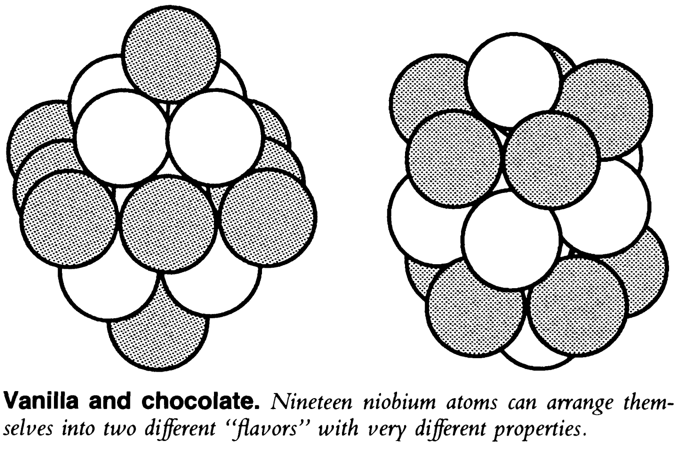
These chameleon-like powders are just one of the many surprises chemists and physicists are finding in the uncharted territory of clusters—groups of from two to several thousand atoms that fall outside the traditional bounds of both chemistry and physics. Clusters are not exactly molecules, at least not in the sense that chemists think of molecules; they usually consist of just one or two types of atoms packed into a roughly spherical shape. But neither are they like bulk materials, since they are too small for the atoms to settle completely into a periodic crystalline structure. "It's a totally new class of materials," says Ying Wang, a chemist at Du Pont in Wilmington, Delaware.

As such, clusters are forcing scientists to develop totally new techniques to study their structure and properties. But the effort should be worth it. Chemists, for example, believe that clusters of metal atoms could turn out to be much more effective catalysts than those in use today; physicists hope that clusters' optical properties will make them valuable in such areas as optical computing and optical switching; and materials scientists say that new classes of metals and ceramics assembled from clusters could be stronger and more flexible than those available today (see box on p. 1187).

The smallness of clusters leads to unique properties in two ways. First, a large percentage of a cluster's atoms are on or close to the surface, and surface atoms do not order themselves in the same way as do atoms on the inside of a bulk material. "They try to pull their heads in," explains Bell Labs' Walter Brown, and in small clusters that can completely overwhelm the urge of atoms to arrange themselves in a regular crystalline array, as they normally do in bulk materials. The ordering of atoms in a Si_{10} cluster, for instance, looks nothing like that of the familiar silicon crystalline structure.

Besides the consequences to its geometry, a cluster's small size also affects its electronic structure. In bulk materials, electrons can move freely in any direction, but in clusters they are confined to a space that is only a few atom widths across.

This "quantum size effect" results in, among other things, the amazing diversity of colors in the powders created by Brus and co-worker Mike Steigerwald. The color of a powder depends on which frequencies of light the clusters absorb, which in turn depends upon the clusters' electronic structure. The electronic structure is very sensitive to cluster size because the size determines how much room the electrons have to move around in and consequently the possible energy levels of the electrons.



Vanilla and chocolate. *Nineteen niobium atoms can arrange themselves into two different "flavors" with very different properties.*

The relationship between color and cluster size is well understood, Brus says. "Simple theories allow you to calculate—at least within a factor of 2—what size you want for a particular absorption." Indeed, right now the more difficult challenge for researchers is learning how to make clusters of a desired size in order to study their properties more closely. The potential practical applications of clusters will also depend on accurate control of cluster size.

Chemists have developed a variety of methods of forming clusters, each with advantages and disadvantages. The colored powders that both Brus and Wang produce are grown in solution to their desired size, coated with a thin layer of an organic molecule, such as benzene, and then precipitated out. Comparing the organic outer layer to the peel on an orange, Wang explains, "without the peel, they won't be stable." If two naked clusters come in contact, they will combine with each other to form a double-sized particle. Even with the coatings they must be kept in an inert atmosphere since they will react with the air.

Alternatively, the clusters can be precipitated inside porous glasses or polymers. The result is a solid that contains millions of the clusters, each isolated from the others. Other researchers have made clusters inside zeolites—the so-called "molecular cages" that are crystalline structures with relatively large empty spaces in which the clusters grow. However, once the clusters are grown inside the glass, polymer, or zeolite, they are stuck. They can be studied optically, but they can't be touched.

One problem with all the chemical methods is that they do not produce clusters of a single size. The clusters that are nominally 10 angstroms in size are in reality somewhere between, say, 8 and 12 angstroms, and the spread gets larger as the cluster size increases. Yet if researchers are to be able to engineer the properties of the clusters, they must be able to specify the cluster size.

That's where physical methods have the edge. In 1981, Richard

Smalley, a chemist at Rice University in Houston, discovered that he could create clusters of any material by firing a laser at a target made of that material. The laser knocks atoms and clusters of atoms off the surface, and when these single atoms and small groups are cooled in an inert gas, they coalesce into larger clusters. By ionizing the clusters to give them a positive charge, a researcher can electromagnetically separate the clusters into groups of different masses. For clusters with fewer than several dozen atoms, Smalley and others have been able to produce homogeneous samples where every cluster has the same number of atoms.

The drawback to this method is that it produces very few clusters, too few to use the usual techniques for analyzing molecular structure, such as x-ray crystallography. And the scanning tunneling microscope, which in special cases has been able to image single molecules, so far has produced only blurred pictures of clusters.

Instead, most workers in the field rely on such indirect measures as determining a cluster's electronic structure with laser spectroscopy. By shining laser light of different frequencies on a cluster sample and watching what happens, a researcher can measure the energy levels of the cluster's electrons. From such data, says Michael Duncan of the University of Georgia in Athens, scientists have inferred the precise structures of many two-atom clusters and several three-atom clusters. "Above about three atoms, there's just not any data [with which to infer the structures]," he says.

This doesn't mean that nothing is known about the larger clusters. Smalley at Rice, for instance, has studied the electronic structure of copper clusters of up to 410 atoms. He finds that by the time a cluster has several hundred atoms, its electronic structure is very similar to that of the bulk material, which leads him to believe that the insides of such large clusters probably have well-ordered crystalline structures.

At Argonne National Laboratory in Argonne, Illinois, Steve Riley is going at cluster structures from a different angle: with chemistry. For instance, he measured how many molecules of ammonia bind to cobalt clusters of different sizes and found that Co_{55} binds exactly 12 ammonia molecules, while clusters with either more or fewer than 55 atoms will grab onto more than 12 ammonia molecules. What does this say about the structure of Co_{55}?

Riley points out that "ammonia prefers to bind to a single atom, and the more that atom sticks out, the more it [ammonia] likes it." Since 55 atoms can arrange themselves into a perfect icosahedron with 12 corners, Riley argues that the ammonia-binding data are proof that the Co_{55} takes the shape of an icosahedron. With fewer or more atoms, the atoms do not fit together so nicely and there are more bumps on the surface for the ammonia to bind to.

Unfortunately, it's not usually that simple. In many cases, there is probably not a unique structure for a given cluster.

Take Nb_{19}^+, for instance. When Smalley created a sample of these positively charged clusters and measured how quickly they reacted with hydrogen gas, a funny thing happened. He got two answers. Some of the clusters ignored the hydrogen altogether, while others grabbed onto hydrogen molecules whenever they came in contact with them. Apparently, Smalley decided, Nb_{19}^+ comes in two flavors, which he calls "vanilla" and "chocolate."

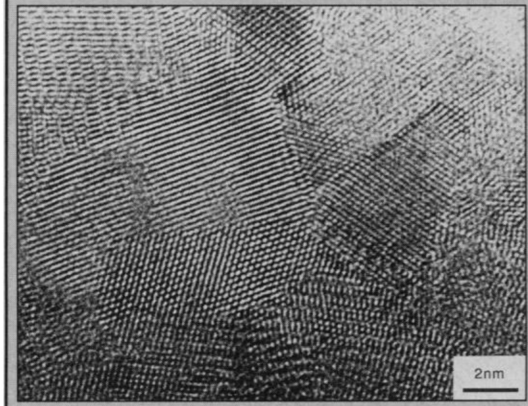
Smalley attributes the difference in reactivity to different structures. The 19 atoms in the cluster can arrange themselves either in an eight-sided double pyramid or a "capped icosahedron"—a 13-atom icosahedron with a 6-atom cap (see figure, p. 1186). The double pyramid has flat sides, and flat surfaces react very poorly with hydrogen molecules, so Smalley guesses that this structure is "vanilla." The capped icosahedron has bumpy sides and plenty of places to react with hydrogen, so it is "chocolate."

This sensitive dependence of chemical reactivity upon structure has many catalysis chemists excited about clusters. Andy Kaldor and Don Cox of Exxon Research in Annandale, New Jersey, are two of them. They are studying the catalytic activity of small clusters of metal atoms, and they find

Clusters of Clusters: Double Strange

Clusters are not only strange individually, they are also strange when assembled in groups, says Richard Siegel of Argonne National Laboratory, who studies "cluster-assembled materials"—metals and ceramics that are pieced together cluster by cluster into substances that look like patchwork quilts. And that can give the materials some very unusual properties indeed.

Take the ceramic TiO_2, for example. In normal form, it is quite brittle, but forming it from clusters that are about 100 nanometers across increases its ductility by a factor of 4 or 5, Siegel says. Indeed, the cluster-assembled TiO_2 is no more brittle than some metal alloys. And there is "some evidence," Siegel says, that at 800°C the material becomes superplastic—capable of being deformed with little stress. If this is the case, "it would revolutionize ceramic-forming techniques," he says. Making ceramics is now a time-consuming process, in which the ceramic precursor is molded into shape and then fired to harden it. Ceramics that could be formed as easily as plastics would be both more versatile and much less expensive than current ceramics.



George Thomas/Sandia National Laboratories

Patchwork palladium. *Electron micrograph reveals tiny grains in cluster-assembled Pd.*

In experiments on cluster-assembled metals, Siegel has found that palladium in which the individual grains are between 50 and 100 angstroms across is four times harder than the same metal with grain sizes of 100 micrometers. He found a similar improvement in tensile strength.

To a certain extent, such improvements were to be expected. Materials scientists have known for a long time that decreasing the grain size in a metal increases its hardness. But the conventional explanation of why this happens probably doesn't apply to cluster-assembled materials, Siegel says. The interaction between grains 50 angstroms across is likely to be qualitatively different than the interaction between grains that are 1000 times larger. For example, a significant percentage of the atoms in cluster-assembled materials are within a few layers of a grain boundary, while only a tiny percent are in normal materials, and this means that grain boundary structures should play a larger role in determining the properties of the new materials. "I suspect," Siegel says, "that we're going to find some new physics here." ■ R.P.

that in this size range, the addition or subtraction of a single atom can make all the difference.

Most industrial catalysis is now done with small metal particles held in place on a substrate, with sizes ranging from a few hundred angstroms down to as little as 20 angstroms. "The regime that is really unexplored is what happens when you go below this size," Kaldor says. The hope is that making the particles smaller and smaller will increase both the activity and the selectivity of their catalytic behavior. And experiments that test the reactivity of clusters with such simple molecules as hydrogen and methane encourage that hope.

Gold, for instance, is inert to most materials, but becomes very reactive with both hydrogen and methane when it is in the form of positively charged clusters with less than 15 atoms, Kaldor says. And as for selectivity, researchers have found one example after another of how a cluster's reactivity can depend closely on its size and composition. Co_9 is almost completely inert to hydrogen or nitrogen gas, while Co_{10} reacts any time it comes in contact with either gas. Co_{13} is very reactive with hydrogen, but if one of the cobalt atoms is replaced with vanadium, a closely related element, it is not reactive at all.

Eventually, Cox notes, chemists will have to learn how to attach clusters to a surface, without breaking them up, if they are to be used in commercial catalysis, which normally involves running hot gases of reactants over a catalyst. But the work has a long way to go. Cox and his colleagues recently managed "soft landings" for platinum clusters on a silica surface and showed that clusters with up to six atoms remained intact after sticking to the surface. "After six, we got [so few clusters] that we couldn't see them on the surface," he says. The researchers don't know yet how much the presence of the surface deforms the structure of the clusters since they don't know what those structures are, and they don't know how putting clusters on a substrate will affect their reactivity with other chemicals. But they know that clusters have opened up a whole new field of science. ■ ROBERT POOL

ADDITIONAL READING

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Watching the Dietary Detectives

Isotope ratios offer archeologists a firmer grip on prehistoric diets, helping to resolve key evolutionary questions

Carnegie Institution

Bone of contention? *Probably not. Marilyn Fogel (left) and Noreen Tuross are isotopists on excellent terms.*

IN A LABORATORY AT THE UNIVERSITY OF CAPE TOWN in South Africa, archeologist Julia Lee-Thorp spends some of her time carefully extracting carbon dioxide from the tooth enamel of a 1.5-million-year-old hominid tooth and then running the mineral through a mass spectrometer. Because the instrument measures the precise ratio of two carbon isotopes from a substance called apatite in the enamel, it can show Lee-Thorp just what this early hominid, *Australopithecus robustus*, was eating as it roamed the savanna in southern Africa. The answer, based on the ratio of carbon-13 to carbon-12: fruits, nuts, and grasses. The results are at odds with current thinking about the diet of *robustus*; if they hold up, they will contradict theories that the hominid was actually a vegetarian.

That dietary evidence in turn might provide an important clue about why *robustus* went extinct while its omnivorous contemporary, *Homo habilis*, survived to become the ancestor of modern humans. "The punch line is that the diet of early hominids can tell us about evolution—about their subsistence and why some species went extinct," says Lee-Thorp, a research archeologist in the lab of Nikolaas van der Merwe.

The use of isotope analysis to study the diet of hominids and early humans is among the latest applications of a technique that is rapidly becoming an important archeological tool. It was first tried in the early 1970s, when a few archeologists saw how geochemists used isotope ratios of carbon (and other elements) to date sediments. But only recently have archeologists begun to make full-scale use of such ratios to help answer central evolutionary questions, including which human groups were farmers and which remained hunter-gatherers, how different species coexisted at a single site, and how climate changes affected life on Earth.

This ambitious agenda for isotopy, as the field has come to be called, was described last week at the annual meeting of the International Council for Archaeozoology, held at the Smithsonian Institution. At the meeting, two dozen or so isotopists (who also call themselves isotopeteers, isotopologists, or archeisologists) described the areas in which they are putting their methods to work. Many members of the little band present at the meeting are among the pioneers in the field.

Regardless of what they're called, these scientists are essentially dietary detectives. Their aim is to reconstruct ancient food webs, working with the scant evidence provided by isotopes found in bones, teeth, horns, and other human or animal tissues of dead humans or animals. The reason the method works, the isotopists are fond of saying, is because "you are what you eat, plus a few per mil" (a measurement of isotopes, equal to a few parts per thousand).

Every food leaves a distinctive isotopic signature in its consumer. The reason is that different types of plants metabolize carbon and nitrogen differently during photosynthesis; hence plants from different environments have distinct carbon and nitrogen isotope ratios. The animals that eat those plants—and the animals that in turn eat *them*—maintain similar ratios. Those isotopic differences make it possible to distinguish animals that ate seafood from those that grazed in savanna or browsed in woodlands.

Unfortunately, the process isn't perfectly straightforward, partly because the isotopic ratios are altered by a creature's metabolism