MEETING BRIEFS

Chemists Cluster in Chicago to Confer on Cagey Compounds

Shrink a clump of matter to a few hundred atoms, and it enters a curious netherworld. Neither ordinary solids nor conventional small molecules, such atomic clusters have unique chemical, optical, and electronic properties. Since the mid-1970s, when advances in synthesizing and analyzing clusters first enabled researchers to explore this netherworld in earnest, clusters have nucleated a sizable field. Many of its participants gathered in Chicago on 15 to 22 September for the Sixth International Symposium on Small Particles and Inorganic Clusters, the first of the series to be held in the United States. At the top of the agenda for the 300 attendees were the field's old stalwarts, various kinds of metal clusters; its current darlings, the carbon clusters known as fullerenes; and a possible future superstar, silicon clusters.

A New (Russian) Doll of Fullerene

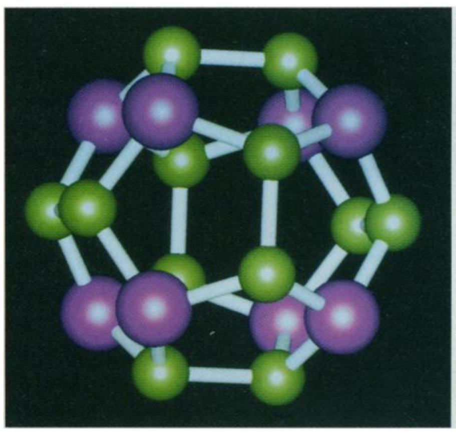
Plain old buckyballs are starting to look a little drab next to their showy offspring. In the past year, the cagelike carbon molecules have been upstaged by progeny flaunting metal atoms on the inside, metals on the outside, and side groups of urethane, oxygen, and hydroxyl, to name a few. Then there are the buckytubes, in which the linked carbon atoms roll up into cylinders instead of spherical cages. Now come Daniel M. Ugarte and Dietrich Reinhard of the Ecole Polytechnique Federal de Lausanne with a report on the latest addition to this pageant: the bucky onion, a Russian doll-like cluster of concentric carbon cages.

Putting together such intricate clusters sounds like painstaking work, but Ugarte and Reinhard told the conference that they happened on them by luck, as the two researchers tinkered with the conditions used to make ordinary buckyballs and buckytubes. They grew their onions on a carbon electrode heated by an electric arc—the same setting in which other fullerenes are spawned. Substituting A.C. current for D.C. and filling the reaction vessel with helium instead of argon, says Ugarte, was enough to transform the product from single cages and sheets to concentric clusters.

Ugarte, an electron microscopist, says that the first batch of onions have an outer cage of 540 carbons holding successively smaller ones, with the innermost cage consisting of just 45 to 50 carbons. The clusters are objects of beauty, he says, and they seem to be quite durable as well. But their discovery may also solve a longstanding mystery: the composition of the dust found in interstellar space. Astrophysicists have long suspected that the dust is made up of carbon clusters, but the dust's spectrum didn't match that of any known carbon compound. Even the original buckyball didn't live up to hopes that it might be the long-sought constituent of the dust. The spectra of the newly discovered clusters, Ugarte and Reinhard say, indicate that researchers may have finally found their interstellar dweller.

A Met-Car Assembly Line

For buckyballs, a key step along the way from the status of curiosity to that of darling of materials scientists and chemists was the development of a technique for making the molecules in quantity. Chemist A. Welford Castleman of Pennsylvania State University hopes to pull off the same feat for the metallo-carbohedrenes, or met-cars, a new class of cagelike clusters containing both metal and carbon atoms that he and his colleagues reported earlier this year (*Science*, 13 March, p. 1411 and 24 April, p. 515). At first, Castleman could build only a few of these metal-carbon molecules, which take the form of both single and multiple cages—too few to test their potential as catalysts or superconductors. But at the meeting, he discussed a production scheme that could open the way to making all the met-cars an eager cluster chemist could want.


A. WELFORD CASTLEMAN

Now in production. A met-car cluster, with eight titanium atoms *(purple)* interspersed among the 12 carbons.

Castleman produced his first met-cars by playing a laser across a metal rod to vaporize its surface and allowing a burst of helium to sweep a few hydrocarbon molecules, such as methane and benzene, through the metal vapor. The metal atoms and hydrocarbons reacted to form clusters—but no matter how Castleman and his colleagues adjusted the reaction, it could yield no more than a smattering of met-cars.

Castleman has since learned, however, that the technique is unnecessarily complicated. The hydrocarbons contain both hydrogen and carbon, but spectra of the product molecules showed that the hydrogen is driven off in their synthesis. So Castleman decided to simplify his recipe. He now uses titanium and graphite powders as the raw material. When the ratio of the two elements is just right, vaporizing the mixture with a laser beam yields abundant titanium-carbon met-cars.

The success of the new technique for making met-cars should not only open the way to detailed studies of the clusters; it also offers clues about how stray metal and carbon atoms could assemble into the unlikely geometry of multiple-cage met-cars, says Castleman. "It suggests what the essential building blocks are" by hinting that the carbon and metal atoms gather directly into simple cages, which then assemble into the more complex forms.

The Sparkle of Silicon Clusters

Carbon-containing compounds like the met-cars and the fullerenes may rule the roost in cluster chemistry just now. But a new leader may be waiting in the wings: clusters of silicon. Not that silicon wants for glory; in bulk form, the element already dominates the microelectronics industry. But researchers suspect that when the dimensions of a piece of silicon shrink to a few billionths of a meter, its tightly confined electrons start exhibiting new, quantum behaviors. The resulting electronic and optical properties could open the door to entirely new technologies—and two teams of researchers have now developed ways to make silicon clusters in bulk and put that promise to the test.

For both groups, led by Louis Brus of AT&T Bell Labs in Murray Hill, New Jersey, and Jim Heath of the IBM Thomas J. Watson Research Center in Yorktown Heights, New York, one goal was to follow up on hints that finely divided silicon can respond to an electric field or ultraviolet radiation by emitting light. The luminescence, which was discovered 2 years ago in silicon wafers etched to create pores, raised hopes that silicon might make inroads into the optoelectronic technologies that have been the domain of more expensive and hard-to-handle semiconductors. But researchers weren't sure whether the light was coming from the silicon itself, or from some compound created by the etching process.

To find out whether silicon itself can luminesce, researchers need a supply of pure silicon clusters. At the conference, Brus and his colleague Karl Littau described a technique for making them from a gaseous compound of hydrogen and silicon: Heat the gas until it decomposes to form a haze of pure silicon clusters. Heath, in contrast, forms his clusters in solution. He heats a solution of silicon-chlorine compounds to high temperatures, then adds sodium metal to the reaction vessel. The sodium snares the chlorine, forming table salt and leaving behind silicon atoms that gather into clusters.

The verdict on luminescence: Brus' pure silicon clusters, at least, do sparkle, suggesting that the glow of his silicon really is a quantum effect in the element itself. Brus is confident only of his own samples, not necessarily of the porous silicon tested by others. But silicon's star seems to be on the rise.

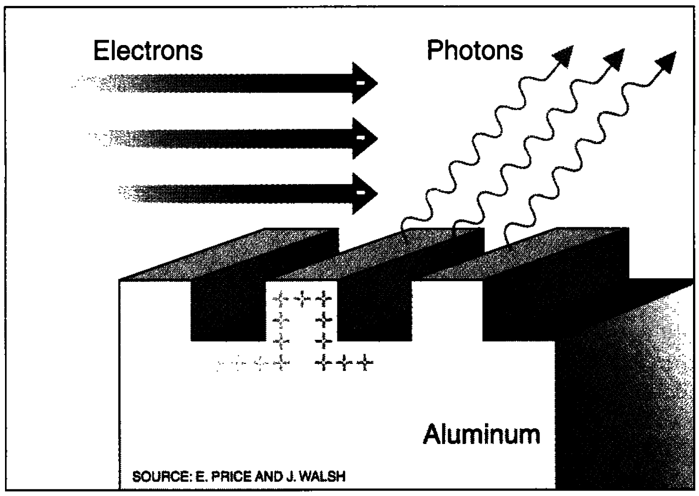
–Anne Simon Moffat

TECHNOLOGY

An Everyman's Free-Electron Laser?

Some lasers generate their light in a crystal, others in glass, gas, or semiconductors. Still others, so-called free-electron lasers, generate light from a beam of electrons, usually by snaking it through a gauntlet of magnets. Now recent research suggests that still another kind of laser may be on the horizon: a free-electron laser (FEL) in which far-infrared light would be coaxed from a washboard-shaped metal surface by a beam of electrons zooming just above it.

The researchers—Dartmouth College physicist John Walsh and his colleagues at the Universities of Oxford and Essex—have so far succeeded only in generating the infrared light, not in amplifying it into a laser beam. But if they can transform their basic research, reported in the 21 September *Physical Review Letters*, into a working laser, they will have equipped researchers in many fields with a powerful new tool. Since most kinds of lasers can't generate coherent, intense beams of far-infrared light, the promise of this spectral region for such areas of science and technology as chemical analysis and surgery has remained largely untested. Only FELs can open the blinds on this region, but they have been off limits to most researchers because of their size and cost.



C. FABER SMITH

Ripple effect. As electrons speed over a corrugated metal surface, they induce "image" charges, which oscillate and emit radiation.

Walsh and his colleagues speculated that a phenomenon first observed 40 years ago, known as Smith-Purcell radiation, might bring FELs within reach. In conventional free-electron lasers, an intense beam of electrons from an accelerator passes through a periodic magnetic field, or a wiggler. As the electrons wiggle through the field, they emit radiation at wavelengths that depend on their velocities, enabling researchers—in principle, at least—to tune the laser to virtually any region of the spectrum, including the far infrared. But that advantage has been offset by the size and complexity of an FEL's accelerator and wiggler.

Smith-Purcell radiation could pave the way to an everyman's FEL, Walsh says, because it eliminates the wiggler. The principle is straightforward. Electrons speeding above a metal grating induce an oscillating charge in the grating, which, in turn, emits radiation, much as a stick dragged over a washboard generates a rat-a-tat sound. And like the radiation generated by a conventional FEL, Smith-Purcell radiation can be tuned—in this case by adjusting the period of the grating or the velocity of the electrons passing over it.

Previous experiments by other workers had produced Smith-Purcell radiation at visible wavelengths—but at intensities far too low for a laser. Walsh, John Mulvey of Oxford, and their colleagues reasoned, however, that they could generate more intense far-infrared radiation by increasing the energy of the electron beam. When they commandeered an obsolete Van de Graaff electron accelerator at Oxford and used it to fire electrons over an aluminum grating at nearly the speed of light, they observed a broad range of far-infrared Smith-Purcell radiation. The intensity, they say, was satisfyingly high—roughly one-tenth the far-infrared intensity generated by synchrotrons, massive accelerators in which electrons emit radiation as they speed around a ring.

Turning that success into a far-infrared FEL, Walsh admits, will require several advances. For one, since the grating emitted radiation at many different wavelengths, each going off at a different angle, it was not behaving like a laser, which gives off radiation at only one or a small ensemble of wavelengths. The solution: Flank the grating with mirrors that would capture a specific wavelength and send it back and forth over the grating. Theoretically, Walsh says, this arrangement should, in laserly fashion, stimulate the grating to emit more radiation at exactly the same wavelength, thereby amplifying it. A tiny hole in one of the mirrors would allow the amplified coherent radiation to stream out as a laser beam for research or technical jobs.

Another must is to miniaturize the apparatus. Even though the setup did away with the bulky magnets of a conventional FEL, it did include an accelerator that towers several stories—not exactly standard lab bench equipment. But calculations suggest to Walsh and his colleagues that a compact linear accelerator (linac) a few meters long could elicit far more intense far-infrared radiation from a grating than the Oxford accelerator was able to generate. Walsh says he is already arranging with Robert Palmer, director of the Center for Accelerator Physics at Brookhaven National Laboratory, to test those calculations with a real linac.

If all of this effort ever yields a no-frills benchtop FEL, says Harvard University chemist William Klemperer, it could give chemists a better means of probing weak and experimentally elusive intermolecular interactions such as the hydrogen bonding between water molecules. Such a laser might also serve military or medical roles—as a means of sizzling sensitive electronic components on missiles, say, or as a laser bone saw—adds Phillip Sprangle, head of the beam physics branch of the Naval Research Laboratory in Washington, D.C., who is also trying to develop compact FELs. Physicist Frank Delucia of Ohio State University speculates that a powerful beam of far-infrared radiation could even serve for remote sensing and air traffic control, since such radiation is little affected by clouds and haze. If a small, inexpensive FEL were available, concludes Klemperer, "I would buy one."

–Ivan Amato