MATERIALS SCIENCE

Hot Rumors, Blue Light, and Modern Art Shake Up Frisco

Though sandwiched between earthquakes and riots, the Materials Research Society's (MRS) spring meeting in San Francisco went on as scheduled. And when not following northern California's turmoil on TV, the more than 2400 attendees focused their attention on 27 symposia that addressed a wide range of topics, including superconductivity, corrosion-fighting polymers, smart materials, fullerenes, and materials issues in art and archeology. A few highlights follow.

180 K Superconductor–Is it or isn't it?

A few weeks ago, Tomoji Kawai's fax machine was humming as he sought to stem the buzz that he had created a 180 K superconductor, a material that would smash the current record by more than 50 degrees (*Science*, 17 April, p. 299). The rumor had materials scientists around the world agog—with good reason. If true, it would represent a major advance toward the dream of room-temperature superconductivity. But in a hastily composed fax, the Japanese researcher, whose lab is at the Institute of Scientific and Industrial Research in Osaka, declared, "The rumors are not true." He asked people to wait until the MRS meeting, where he would present his latest data, to judge his results.

That, at least, guaranteed a full room for Kawai's talk. But his presentation left those who showed up unclear about exactly what he has accomplished. Kawai first detailed the method with which he creates his possible superconductors. Using carefully controlled laser pulses in a chamber filled with gaseous NO_2, he vaporizes targets that contain the starting materials for the superconductors. The vaporized materials then deposit on a heated substrate, forming single molecular layers with whatever ratio of elements he desires. In effect, "we tailor the material layer by layer," explains Kawai, one of the world's experts in this difficult technique.

The painstaking effort was rewarded when his group began examining their layered materials for signs of superconductivity. Researchers usually claim superconductivity when a material's electrical resistance drops to zero and its magnetic susceptibility, which describes how a magnetic field penetrates the substance, experiences a significant transition. Kawai's first superconductors, consisting of alternating layers of copper oxide (the apparent backbone of most high-temperature superconductors) and strontium, showed both effects at 65 K. And they got a 25 degree improvement simply by lowering the temperature of the strontium titanate substrate on which the layers were deposited from 570 K to 500 K.

But it was the addition of calcium to the strontium layer [in a 1-to-4 ratio] that gave the greatest improvement. One such material showed a revealing shift in magnetic susceptibility at 120 K. Although Kawai presented only magnetic evidence, he did not hesitate to claim superconductivity for this material. "I have confidence about 120 K, it's very clear," he said. More important, the same compound, deposited on a slightly warmer substrate, showed both the required magnetic signal for superconductivity and a significant, but not complete, resistance drop at the astounding temperature of 180 K.

That's the result that has the materials community stirred up. Superconductivity is a field where exciting claims often do not pan out, explains Praveen Chaudhari, a materials scientist at the IBM T.J. Watson Research Center in Yorktown Heights, New York. But, Chaudhari continues, he has never seen claims for a material that displays both signs of superconductivity fizzle out.

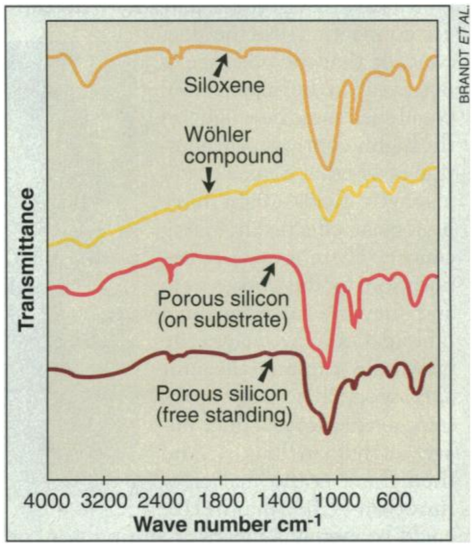
Other groups have also had success with the strontium-calcium-copper oxide approach. A team from the Institute for Chemical Research in Kyoto, Japan, reported in the 30 April *Nature* that it had demonstrated superconductivity at 110 K with such a material. But questions remain about the stability of these ceramic superconductors. Kawai's 4-to-1 strontium-calcium mixture falls apart after a few days, for example.

And even Kawai, who remembers past claims that went bust, is cautious, saying, "It's very dangerous for a scientist to declare superconductivity." He points out that his team has not yet reached zero resistivity at 180 K, and until they do, he won't claim superconductivity at that temperature. But if his materials live up to expectations, Kawai might just become the next superconductivity superstar to make headlines.

Shining New Light on an Old Material

About a year ago, researchers from Great Britain and France startled the materials science world by announcing that they had achieved something that had eluded other researchers for decades: They induced silicon to photoluminesce—to emit light when light was shined on it. Their discovery spurred dreams that the versatile and cheap semiconducting material would lead to an easy marriage of optical and electronic circuits, a union that promises faster communication devices, better computers, and more. But, while the initial observations have been confirmed by many groups, materials scientists still don't understand what causes silicon's light emission (*Science*, 20 December 1991, p. 1731). Several theories have emerged, however, and one, put forth by a group at the Max Planck Institute for Solid-State Science in Stuttgart, Germany, has attracted so much attention that it even drew its own special session in San Francisco.

Most theorists have assumed that the light-emitting property has something to do with



Identical twins? Infrared spectra of siloxene samples *(two upper lines)* and porous silicon match closely.

the size of the fine pores that researchers have to etch into silicon with a combination of an electrical current and acid to make it luminescent. But Martin S. Brandt, a doctoral student in the Max Planck lab directed by Manuel Cardona and Hans Joachim Queisser, laid out his group's evidence for an alternative explanation: that the material's ability to luminesce is due to the presence of layers of siloxene ($Si_6O_3H_6$), a compound whose light-emitting capabilities were first discovered more than a century ago by the German chemist Friedrich Wöhler. Among other experiments, the Max Planck researchers compared the infrared transmittance spectra of samples of siloxene and of porous silicon and showed that two siloxene and two porous silicon samples all showed luminescence peaks around 750 nanometers (red). They matched in many other details as well, Brandt says.

And even more interesting, at least to those who dream of silicon-based optical electronics, Brandt detailed techniques that may improve the versatility of siloxene and make it easier to use. The Max Planck workers have shown that it's possible to build up layers of siloxene on silicon. They do this, Brandt explained, by first growing calcium disilicide on crystalline silicon and then adding hydrochloric acid to remove the calcium. Siloxene layers created this way stack up more than 400 nanometers thick and can luminesce just like porous silicon.

As a final touch, Brandt showed that modifying siloxene's structure can cause a shift in the type of light emitted. Depending on the atoms attached to the material's six silicons, siloxene could be made to emit a surprising blue light, instead of the more typical red or green-yellow light. On seeing this rainbow of colors, Eicke Weber from the University of California at Berkeley, who organized the late-night meeting, remarked to the audience, "I think we have all seen something new—blue light from silicon."

But despite Brandt's demonstration of siloxene's light-emitting abilities, not everyone was ready to accept the idea that it's the cause of porous silicon's luminescence. One problem with the siloxene theory, says Mike Tischler of the Watson Research Center, is that it does not explain why unoxidized, freshly made porous silicon, which should have little or no siloxene in it, also luminesces efficiently.

And many who might have argued for a competing theory, called "quantum confinement," which holds that it's the small pore size that makes porous silicon luminescent, were not at the hastily arranged session. One such researcher, Leigh Canham of the Royal Signals and Radar Establishment in Malvern, England, later told *Science*: "We still believe that's it's basically a size-related phenomenon." But Canham also admits that, to his knowledge, no one has produced blue light from porous silicon.

The morning after his provocative talk, Brandt said that his group does not "want to conduct a crusade against quantum confinement." Instead of arguing over the porous silicon mechanism, he says, they now plan to focus their efforts on exploiting siloxene's versatile optical behavior. Several problems, including the instability of the materials, will have to be solved before any applications of either porous silicon or siloxene approach reality. But if history is any judge, watch out for more dazzling material from Germany.

Laser Replication of Rare Art

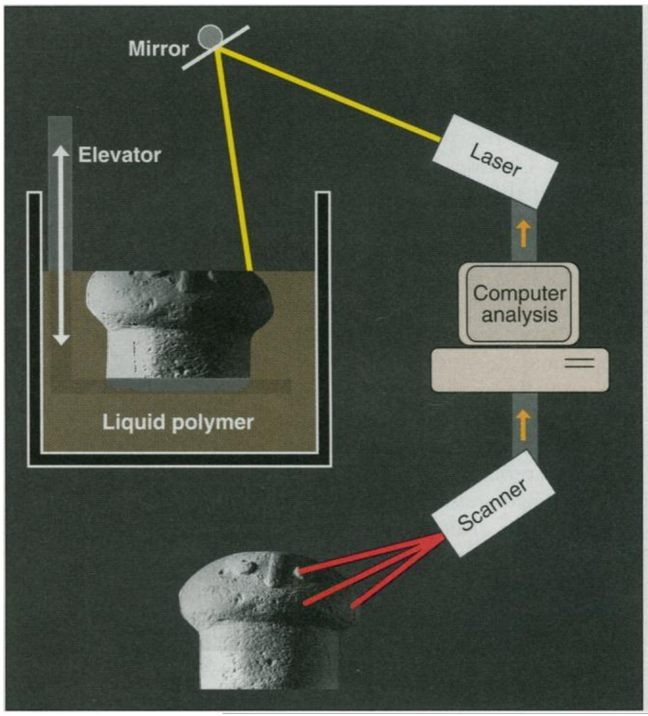
Among the many prized possessions at the J. Paul Getty Museum in Santa Monica, California, is a rare idol, a fertility goddess dating back to 2500 B.C. Scholars are eager to study the tool marks on this relic for clues to the instruments and techniques that were used to make it. But there's a problem: The idol, which is made of soft, easily damaged limestone, is too fragile to be handled extensively. Now, however, thanks to a blend of lasers and materials science, the museum may have found a way to enable scholars anywhere in the world to perform the studies they want on this and other fragile statues—without actually touching them.

The trick, Jerry Podany, the Getty museum's conservator of antiquities, explained at the materials science meeting, is a new method for producing exact replicas of three-dimensional objects. Normally, to provide copies of a statue, a museum would make a mold of it with plaster or other materials. But that runs the risk of damaging the object's surface. "The challenge was to produce a sufficiently detailed replica without touching the object," Podany said.

The task sounds impossible, but by borrowing on the latest in industrial laser technology, the Getty museum may have found a solution in a process known as "rapid prototyping." Already popular in such fields as medicine and aerospace, rapid prototyping translates computer data on the exact dimensions of an object into a solid, real-life copy. In this instance, the museum collaborated with Hughes Aircraft Co., 3-D Systems Inc., and LaserDesign Inc. to use a particular prototyping process called stereolithography that not only translates dimensions but also reproduces surface details. Since this was their first trial of the method, they tested it on a plaster copy of another idol, instead of the rare figure itself.

In the first step of the process, the plaster statue was scanned by a laser to build up a point-by-point representation of the object in the computer. From those data, the computer generated a wire-frame image of the idol and then converted that into a detailed surface model by filling in the grid with small triangles.

The next step was to transform the computer surface model into reality with the aid of an ultraviolet laser. A beam of ultraviolet light, following the computer's directions, copies the object from the bottom up by solidifying thin layers of photosensitive polymer, which are held on an elevator platform in a vat of the liquid polymer. After the first layer is traced by the laser, the platform dips down into the vat and picks up another layer, which is then "squeegeed" to the desired thickness. The laser then solidifies the new layer, welding it to the one below, and this process is repeated until the statue is recreated. A final dose of ultraviolet light further hardens the complete replica.



Modern art. Two lasers, one to scan the original statue and one to solidify the liquid polymer, produce a detailed copy.

PHOTOS: J. PAUL GETTY MUSEUM ILLUSTRATION: D. DEFRANCESCO

First attempts at copying the plaster reproduction of the idol proved disappointing, says Podany. The surfaces of the replica were much too coarse for study and many computer-generated features could have been mistaken for tool marks. However, by decreasing the slice size when the object was scanned by the laser and doing additional computer filtering, the researchers were able to generate an excellent copy of their test figure. They plan to try their method on the rare idol later this year.

Despite the success of this experiment, the inaccessibility and the cost of the equipment put this marriage of art, laser, and polymers out of the reach of most museums. But Podany predicts that the cost of rapid prototyping will decrease dramatically.

What's more, the Getty museum was not the only beneficiary of this unique experiment. To gain the needed accuracy to reproduce a stature, complete with tool marks, the research team pushed the stereolithography equipment past its specified limits, working with slices the width of a piece of paper. Says Timothy Thelander, a project engineer at Hughes Aircraft: "It was an opportunity to work with something totally out of the normal. I can't stress how much we learned from this." Nor, perhaps, how much future art scholars will be able to learn.

–**John Travis**