

Evidence Found for *d*-Wave Electron Pairing in High-Temp Superconductivity

Scientists at T.J. Watson Research Center and at State University of New York campuses in Buffalo and Stony Brook found evidence for *d*-wave electron pairing in high-temperature superconductivity. Their article in the January 19 issue of *Science* describes that the key to their experiments are four tiny rings (50 μm) of a high-temperature superconducting material in which the elements thallium and barium are interspersed between sheets of copper oxide ($\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$, or Tl2201). The rings were created on top of a strontium titanate substrate made of three wedges, each having a different crystalline orientation. The rings were placed so two of them spanned two crystalline orientations, one touched no crystal boundaries, and only one crossed all three crystal boundaries. Because the atomic spacings of Tl2201 are nearly equal to those of the substrate, the crystalline orientation of any part of the superconducting ring exactly matches that of the wedge beneath it and a transition region was forced above each wedge boundary.

The scientists then passed a sensitive, high-resolution magnetic sensor (a scan-

ning SQUID microscope) over the rings and recorded the observed magnetic fields. They detected a spontaneous magnetic field emanating only from the ring that crossed all three crystal boundaries. This ring had a total magnetic field (or flux) exactly half the fundamental unit that occurs in rings of conventional superconductors.

This "half-flux quantum effect" was a sign of *d*-wave pairing because *d*-wave superconductors with the specific crystalline orientations chosen in this experiment exhibit a "phase inversion" in the superconducting current that runs around the ring covering three orientation changes. Theory predicts that such a phase inversion produces an extra current—and an associated magnetic field equivalent to a half-flux quantum—to compensate. The rings with no change of crystalline orientation or two changes have no such inversion, and therefore show no spontaneous magnetization. Such phase inversions are impossible in superconductors having standard *s*-wave pairing, a well-understood cause of low-temperature superconductivity in which charge-induced vibrations in the material hold the pairs of electrons together.

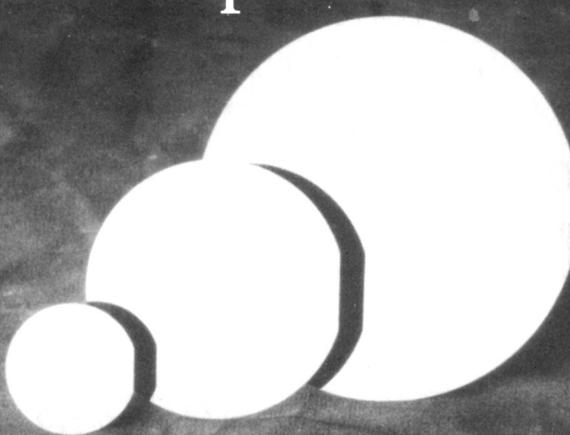
Phenothiazine Increases Efficiency of Molecular Solar Cells

Chemists at The Johns Hopkins University are developing solar-energy cells that work at the molecular level, fundamentally mimicking the way plants convert sunlight into usable energy. They prepared a light-absorbing synthetic dye, bonded with a chemical called phenothiazine, that increases the voltage production by 50% over similar cells.

For the molecular solar cell, small panels of glass are covered with tiny particles of titanium dioxide and then coated with the dye. When light shines onto the panel, the dye molecules are excited, injecting electrons into the semiconductor and creating an electric current. The key to sustaining the current is the addition of chemicals that inject electrons into the holes in the dye, in effect "regenerating" the dye molecules. That prevents the original electrons from recombining with the dye molecule and forces them to combine with the electron donor instead, delaying the recombination process and prolonging the flow of electrical current.

In similar cells, scientists use sodium iodide as an electron donor. The salt is dissolved in a solution sandwiched between the semiconductor and a plat-

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inum electrode. When the dye molecule loses an electron, the iodide quickly contributes one to the dye, turning into iodine in the process. Meanwhile, the electron originally from the dye molecule flows through the semiconductor and into a circuit where it can be useful. That electron recombines with the iodine, turning it back into iodide so that the cycle can start over again.

The scientists at Johns Hopkins University use two electron donors instead of one. The dye molecules act as molecular "electron pumps," said Gerald Meyer, an assistant professor of chemistry, who co-authored an article about the innovation, published November 29, 1995 in the *Journal of the American Chemical Society*. The dye molecules absorb light, inject an electron into the semiconductor, accept an electron from the donor and then start the cycle over again.

Instead of combining with the iodine, the electron in the semiconductor has to combine with the phenothiazine, which is located farther away from the surface of the semiconductor. As a result, the recombination process is slowed down dramatically: Instead of a microsecond, it takes closer to a millisecond for the electron-hole pair to recombine.

Figuratively, the cells work like chlorophyll in plants. Although plants do not produce electrical current from sunlight, they do efficiently produce energy from sunlight at the molecular level by preventing the recombination of electrons and holes.

Sn, Zr, Si, and Alkali Elements Stabilize Glass Structure for Storage of Plutonium

A form of glass that could provide safe long-term storage of plutonium from dismantled nuclear weapons has been developed by scientists at Argonne National Laboratory. Designed by scientist Adam Ellison, the glass is made of tin, zirconium, silicon, and alkali elements such as sodium. Neutron absorbers prevent the plutonium from undergoing an uncontrolled nuclear reaction. The alkali elements help dissolve the plutonium. Tin, zirconium, and silicon stabilize the glass's structure.

The glass melts at a low temperature and dissolves more than five percent of its own weight in plutonium, scientist John Bates said. It can hold high concentrations of scrap metals and resists reaction with water under storage conditions.

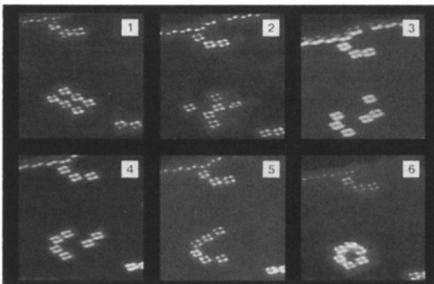
"The trick is to develop a solid waste form that doesn't break down under the influence of the radioactive material inside it," said Bates. "At the same time, it

must keep the plutonium from accidentally forming a nuclear chain reaction and retain the plutonium during any long-term contact with any groundwater that might invade a repository."

To evaluate its behavior over long time periods, the researchers exposed the glass to hot, caustic vapors that simulate thousands of years of natural reaction in a few months. Early results indicate that the glass does not readily break down to form new mineral products and that it firmly retains the plutonium, uranium, and neutron absorbers. Additional tests and composition developments are in progress to confirm these conclusions.

Individual Molecules Positioned at Room Temperature

Scientists at IBM's Zurich Research Laboratory have moved and precisely positioned individual molecules at room temperature, using the extremely fine tip of a scanning tunneling microscope (STM). This innovation, published in the January 12 issue of *Science*, is an important step toward being able to do a wide range of engineering on the nanometer scale.



Sequence of images that illustrate the manipulation of individual molecules: a group of six molecules (1) is first disordered (2) by cruising through the group with the STM tip. Subsequently, one molecule after the other is pushed by the tip in a precisely controlled manner (2-5). This allows a ring to be formed (6) that would not normally be found in nature. Note that the process does not interfere with other molecules visible at the top of the images. Their positions remain unchanged.

The molecules have to stick tightly enough to remain at their position but not so tightly that they cannot be moved. The chemical bonds within the molecule, on the other hand, must resist being changed or broken when the molecule is pushed by the STM tip (see Figure). The scientists evaluated a wide range of molecules as possible candidates in experiments and performed elaborate molecular mechanical simulations in collaboration with col-

leagues at the French National Center for Scientific Research (CNRS) in Toulouse. They selected Cu-tetra-(3,5 di-tertiary-butyl-phenyl)-porphyrin (or Cu-TBP-porphyrin), an organic molecule having a total of 173 atoms. Its core consists of a porphyrin, a stable ring of atoms. Four strongly but flexibly bonded hydrocarbon groups attached vertically to the ring make the molecule, which has a diameter of approximately 1.5 nm, ideal for displacement experiments because its position and structure are easily identified by STM imaging, and the four hydrocarbon groups act as legs that lift the body of the molecule from the atomically flat copper surface. Computer simulation revealed that when pushed by the STM tip the molecule walks in uncorrelated, slip-stick-like steps and exhibits exactly the desired degree of stickiness.

Polymer Filtrations Decontaminate and Recycle Waste

At the annual meeting of the American Association for the Advancement of Science (AAAS), held in Baltimore, Los Alamos scientist Gordon D. Jarvinen of the Nuclear Materials Technology Division reported on polymer filtration systems that show promise for decontaminating materials; concentrating radioactive metals for analysis; and recycling precious metals used by the electroplating, mining, and other industries.

The system consists of water-soluble polymers and a compact, pumping and ultrafiltration apparatus that mixes the polymers with liquid wastes. The polymers bind with metal ions in the liquid waste stream, which then is pumped through a cartridge packed with ultrafiltration membranes shaped into hollow fibers. The metal-bound polymers are too large to pass through the filter, but water and smaller, unbound components of the solution such as calcium and sodium ions pass through the membrane. The polymers can be reused by changing the solution conditions to release the metal ions. The metals then are recovered in concentrated form for recycling or disposal.

For some waste streams containing plutonium or americium, it may be cheaper to use the polymer once and then treat the polymer concentrate for disposal in a repository.

Jarvinen said the technology offers several advantages over commonly used ion-exchange resins and other extraction techniques. "Polymer filtration can be scaled up readily to a higher capacity when necessary," he said. "Rapid binding, high selectivity and low energy and pressure require-

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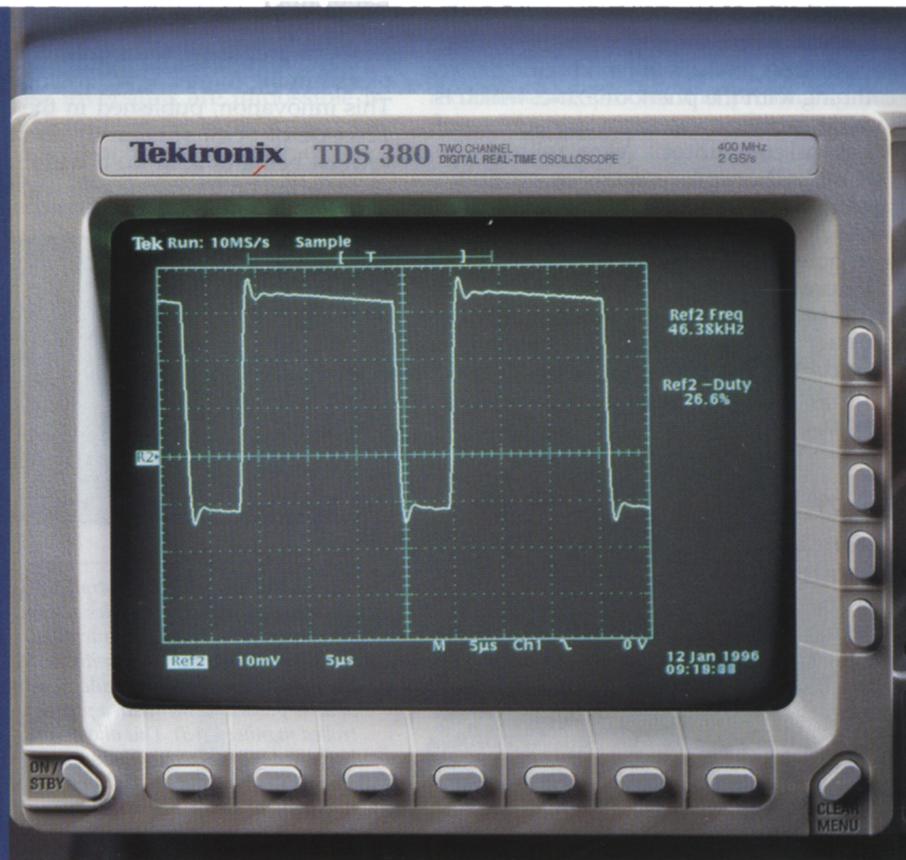
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ments are among the other advantages."

In electroplating, an object is passed through a bath of metal ions such as zinc or nickel that form a protective coating. The plated object then is washed in a series of rinsing baths. Electroplating metals that remain in the rinse water typically are precipitated, collected, and buried as toxic sludge, which creates an environmental hazard and wastes valuable materials. The polymer filtration system minimizes electroplating waste by recovering the metal ions directly and recycling them to the electroplating bath. The process eliminates sludge byproducts.

Internal Donor-Acceptor Heterojunctions Enhance Efficiencies of Polymer Photovoltaic Cells

By means of a photoinduced charge transfer effect in a nanoscale, bicontinuous donor-acceptor (D-A) network, researchers at the University of California—Santa Barbara have fabricated polymer photovoltaic (PV) cells with carrier collection efficiency (η_c) of ~30% electrons per photon and energy conversion efficiency (η_e) of ~3%. Both are two orders of magnitude higher than those in devices made with pure polymeric materials, and become comparable to those of a-Si PV cells. Operated under reverse bias as photodiodes, the quantum efficiencies of these devices are over 50% electrons per photon, which is as good as that of ultraviolet-enhanced silicon photodiodes.

The researchers blended composite films of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) as donor with C_{60} as acceptor. Using either a Ca or Al contact on the surface of a blend film on a glass substrate, coated with transparent indium-tin-oxide (ITO), the MEH-PPV: C_{60} films were spin-cast from 0.3 to 0.5 wt% xylene solutions. The films were typically 1,000 to 2,000 Å, with the Al or Ca electrode vacuum-evaporated to a thickness between 1,000 and 5,000 Å. When substituting xylene with 1,2-dichlorobenzene, high-quality MEH-PPV:[6,6]PCBM films were cast with methano-fullerene compositions up to 1:4 weight ratio, that is, about one acceptor for every polymer repeat unit.

As reported in the December 15, 1995 issue of *Science*, the researchers said that both contact metals "automatically extract electrons from C_{60} and holes from MEH-PPV. Even though the low-work-function metal is in direct contact with the donor, holes will not be extracted at this interface because the internal field forces the holes toward the high-work-

function contact." According to the report, the separated carriers are then collected by the electrode so that external work can be done. The researchers reported that the "enhancement in η_c achieved with the bicontinuous D-A network material results from the large increase in the interfacial area over that in a D-A bilayer and from the relatively short distance from any point in the polymer to a charge-separating interface."

Food Container Made with Multiaxially-Oriented Liquid-Crystal-Polymer Layers

Superex Polymer, Inc. announced a type of multilayer food container using a high oxygen and water vapor barrier layer of liquid crystal polymer (LCP) to improve performance and reduce cost compared with existing designs. The design uses an LCP layer sandwiched between two layers of conventional packaging plastic sheet, such as poly-

ethylene terephthalate or polypropylene. A very thin layer of LCP can be used, resulting in cost savings. In a humid environment the oxygen barrier of LCP is over eight times better than ethylene vinyl alcohol (EVOH), an alternative barrier polymer, therefore less than 10 μm of LCP will provide the same level of barrier as 50 μm of EVOH.

Superex plans to manufacture the multilayer containers using a proprietary coextrusion and thermoforming method which imparts orientation to the LCP layer, allowing the LCP to be made very thin, strong, and uniform.

Other LCP materials have not been used in multilayer packaging because conventional processing results in uniaxial orientation which causes streaks, pinholes, and transverse weakness which impair the barrier layer. Scientists at Superex overcame these problems with multiaxially oriented LCP layers which achieve high performance in layers less than 10 μm thick.



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SBIR Update

Structured Materials Industries, Inc. (SMI) (Piscataway, New Jersey) received two SBIR awards from the Ballistic Missiles Defense Organization. One, signed together with **Stevens Institute of Technology** (Hoboken, New Jersey) and **Lehigh University** (Lehigh, Pennsylvania), is for a Phase II contract for \$500,000 to continue its efforts to develop and implement carbon nitride as an advanced tribological coating material. The other award is for over \$79,000 for a six-month Phase I contract for the development of advanced transparent conductive coatings for display applications using an advanced metal-organic-chemical-vapor-deposition (MOCVD) approach.

Advanced Refractory Technologies, Inc. (ART) (Buffalo, New York) was awarded Phase II SBIR funding of \$574,000 by the U.S. Army for research on diamondlike nanocomposites as tailorable, hard, low-friction coatings.

Plasma Polymerization Produces Functional Surfaces

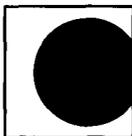
Using plasma technology, researchers at the Aachen Fraunhofer Institute for Laser Technology (ILT) have developed a technique which allows rapid and cost-effective sterilization of the aluminum foils used in food packaging. Initially the foils, which are partially contaminated with rolling oil, are continuously passed through a field of passive discharges. A voltage is then applied between the foil and an electrode, generating many small plasma flashes which convert the contaminants on the foil into volatile substances.

Beyond just cleaning surfaces, scientists at the Bremen-based Fraunhofer Institute for Applied Materials Research (IFAM) have been employing a technique known as plasma polymerization in which a suitable substance placed in a plasma is polymerized and redeposited as a polymer coating on the surface. By this method, functional surfaces can be produced on almost any type of work piece. Compared to conventional polymerization processes the deposited layers are more strongly

intermeshed and adhere well because of the number of chemical bonds broken and reformed. A polymer can be produced in a plasma from methane even though this molecule lacks the requisite conventional, structural basis. Such thin polymer layers can, for example, render synthetics particularly shock and scratch proof or serve as a bonding agent between substances which usually do not adhere to one another well.

Researchers at the Dresden-based Fraunhofer Institute for Electron Radiation and Plasma Technology (FEP) are investigating how large surfaces, such as plastic foils or metal plates, can be coated cost-effectively. Thin synthetic films which, for example, are used as packaging for food must be impervious to moisture and aromas. This is achieved with the application of oxides which must first be vaporized and then deposited as a thin transparent film on the foil surface. In addition, the research team has developed types of plasma sources and further techniques for coating various materials.

Edited from Uta Bilow in *The German Research Service: Science Reports*, 11, Oct. 1995.



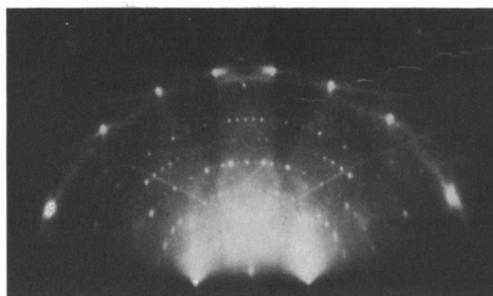
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Williams, Ceder Receive Honors from TMS

David B. Williams, a professor of materials science and engineering at Lehigh University, received The Minerals, Metals & Materials Society's (TMS) high rank of TMS Fellow during the 1996 TMS Annual Meeting and Exhibition in February in Anaheim, California. He was recognized for the development of high resolution microscopy and microanalysis techniques. Williams received his BA, MA, and PhD degrees in metallurgy and materials science from the University of Cambridge.

During the same meeting, Gerbrand Ceder, an Alcoa Assistant Professor in Materials Science at the Massachusetts Institute of Technology, was named recipient of TMS Robert Lansing Hardy Award for 1996. This award recognizes a young person in the broad field of metallurgy for exceptional promise of a successful career. Ceder received his MS degree in metallurgy and materials science from the Catholic University of

Leuven, Belgium, and his PhD degree in materials science from the University of California—Berkeley. He has also received numerous awards which includes The André Deruyttere Prize. This prize is awarded every two years for the best publication in an area of research that is of interest to the Materials Science Department at the Catholic University of Leuven.

Charles Kuen Kao to Receive 1996 Japan Prize

The Science and Technology Foundation of Japan has announced that Charles Kuen Kao, vice-chancellor and president of The Chinese University of Hong Kong, has won the 1996 Japan Prize, which includes a cash award of \$500,000. Kao was recognized for his prediction on the potential capability of optical fiber for low-loss, broadband information transmission. Kao has extensively contributed to this theory through his own verification studies on the exploration of optical fiber communications

which are currently finding worldwide applications.

He will be honored during a Prize presentation ceremony scheduled for April 26 at the National Theatre in Tokyo.

The Japan Prize was created in 1983 by The Science and Technology Foundation of Japan with the endorsement of the Japanese Cabinet. The award was created to commend scientists throughout the world for major scientific and technological achievements that advance peace and prosperity of humankind.

Synthesized Chromophore Leads to Polymer Film with High Electro-Optic Coefficient

An international team of researchers reported in the January 19 issue of *Science* the synthesis of a series of chromophores that has led to a polymer film yielding a large electro-optic coefficient. Such materials are needed for telecommunications and signal processing applications requiring light to be routed within a fiber optic network.

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Relying on the strong acceptor 3-(dicyanomethylidene)-2,3-dihydrobenzothiofen-2-ylidene-1,1-dioxide, which contains two electron withdrawing groups dicyanomethylidene and sulfone, the researchers synthesized a series of chromophores. A polycarbonate film consisting of 20 wt% of one of the chromophore compounds was spin-coated onto a glass substrate coated with indium-tin-oxide, and a thin film of Au was deposited on top of the polymer as the second electrode. The composite, poled at 80°C with an applied field of 150 V/ μm , yielded an electro-optic coefficient (r_{33}) value of 55 pm/V at a wavelength of 1.3 μm , which is nearly twice that of lithium niobate, an inorganic crystal, whose r_{33} value is 30.8 pm/V at telecommunication wavelengths 1.3 and 1.5 μm . □

New Horizons in Quasicrystal Research and Applications Ames Laboratory at Iowa State University August 19–23, 1996

This international conference is being organized in collaboration with the International Institute of Theoretical and Applied Physics (IITAP) at Iowa State University.

The three main topics of the conference are existing and potential applications of quasicrystals, surface and interface properties of quasicrystals, and potential new quasicrystalline materials.

The co-chairs of the conference are Jean Marie Dubois (CNRS-Ecole des Mines de Nancy, France) and Alan Goldman, Dan Sordelet, and Patricia Thiel from Iowa State University. For further details, contact Todd K. Watson, Conference Secretary, IITAP, 123 Office and Laboratory, Iowa State University, Ames, IA 50011-3022; 515-294-5686; fax 515-294-9933; or e-mail qcames@iastate.edu.

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