Superconducting Mechanism of MgB_2 Consistent with BCS Theory

Researchers R. Osborn and colleagues at Argonne National Laboratory have confirmed that the superconducting mechanism of MgB_2, a newly discovered non-copper-oxide superconductor with critical transition temperature (T_c) of 39 K, can be explained by the Bardeen–Cooper–Schrieffer (BCS) theory. As reported in the June 18 issue of *Physical Review Letters*, the researchers performed inelastic neutron-scattering measurement of the phonon density of states on an isotopically enriched polycrystalline sample of $Mg^{11}B_2$, using time-of-flight neutron spectroscopy. They found that boron vibration frequencies extend up to energies of 100 meV. The acoustic phonons extend in energy to 36 meV, and there are highly dispersive optic branches peaking at 54, 78, 89, and 97 meV. The frequencies of the main peaks are well represented by the Born–von Kármán force-constant model, and from which an electron-phonon coupling of ~0.9 was estimated from the Allen-Dynes equation. The measured values of the T_c and isotope effect are consistent with a conventional phonon mechanism for superconductivity with moderately strong electron-phonon coupling.

SHIMING WU

MgB_2 Crystallites Much Less Anisotropic than Cuprate HTS

Relatively high values of critical current density (J_c) and the absence of a grain-boundary weak-link problem have been observed for MgB_2, making it a potentially useful material for superconductive devices. However, the layered lattice structure of MgB_2 has made researchers wonder whether this compound is anisotropic like all the high T_c cuprates. In an article appearing in the June 25 issue of *Physical Review Letters*, direct measurements of upper critical field anisotropy and mass anisotropy ratio were made by O.F. de Lima and colleagues at UNICAMP in Brazil. The MgB_2 sample was weakly sintered from a stoichiometric mixture of pure boron and pure magnesium powders. It was then crushed and milled to crystallites. Small amounts of the crystallites were *c*-axis aligned on paper. The real component of ac susceptibility was measured with an external magnetic field *H* applied parallel and perpendicular to the sample *c*-axis.

The upper critical field H_{c2}, above which the superconductivity is destroyed, was calculated from the data taken in both orientations. The ratio between the upper critical field when *H* is applied parallel to the *ab* plane, and when it is along the *c* direction, was evaluated at different temperatures, producing a ratio of about 1.7. This ratio, in turn, implies an anisotropy of the coherence length of 1.7 and a mass anisotropy ratio of 0.3. Compared to the mass anisotropy ratio values found for the high T_c compounds Y-Ba-Cu-O (0.04) and Bi-Sr-Ca-Cu-O (10^{-4}), both of which are known to be highly anisotropic materials, MgB_2 is mildly anisotropic. In practical applications, the high T_c materials have to be textured to a maximum degree of *c*-axis alignment in order to obtain optimum J_c. While the texture might not be so important for the MgB_2 devices, its reported anisotropy value indicates that the use of texturization techniques to optimize J_c in polycrystalline MgB_2 would be advantageous.

SHIMING WU

Composition "Libraries" Designed for Structural Materials

High performance engineering applications require advanced structural materials, such as steels and superalloys, with properties superior to the constituent metals for the applications of interest. The high cost of traditional methods of iterative synthesis and testing greatly hinders progress in structural materials design. Ji-Cheng (J.-C.) Zhao has designed a technique to generate composition "libraries" for structural materials. As reported in a Communications in *Advanced Engineering Materials* **3** (2001) p. 143, Zhao first creates a "diffusion multiple" using thermal interdiffusion to form a bulk sample with continuous variations in multicomponent composition. Subsequently, he performs local measures of composition, phase, and properties across this sample, which provide an efficient chemical and mechanical survey of a range of multicomponent compositions. This technique is further described in a full-length article in *Journal of Materials Research* **16** (2001) p. 1565.

The concept of creating composition libraries is not new. Chemical libraries are perhaps best known for their applications in pharmaceutical drug design. More recently, combinatorial techniques have become increasingly popular for a wide variety of applications in functional materials.

Although alternative methods for determining solid-state continuous phase diagrams have been previously achieved, Zhao's method provides a significant step forward by allowing simultaneous determination of structural properties such as plastic hardness, toughness, and elastic stiffness—crucial features in materials applications. Previous methods using thin-film libraries cannot investigate such features because the thin-film nature of the sample often significantly alters the properties from those of the bulk materials.

This technique may offer significant potential for practical advances. If realized, not only would this technique allow faster concept-to-market turnaround in structural materials design, it should also permit more informed "fine-tuning" of complex materials composition. The nature of the diffusion sample allows investigation of a continuous multicomponent phase diagram rather than discrete modifications on sample tiles or production of macroscopic homogenous samples for analysis. This technique may also generate contributions in the realm of fundamental scientific interest. In particular, the rapid, *in situ* property measures may provide feedback very useful for modeling of complex materials.

Zhao initially applied his technique to study a Ni-NiAl diffusion couple. Armed with the success of this relatively simple test case, he went on to explore the much more complex, multicomponent sample Ni-Mo-Fe, for which he plotted the multicomponent phase diagram and *in situ* measures of hardness and elastic modulus as a function of Mo content. Zhao ascertains that this method can be used to map multicomponent phase diagrams, look for novel compounds in multicomponent systems, determine diffusion coefficients, evaluate precipitation kinetics, study the effects of compositional modifications in complex systems, and map composition–structure–property data.

"It is exciting to contemplate the advances this new technique will make possible," Zhao said. "This method should provide a significant speed-up over traditional synthesis and testing of structural materials."

EMILY JARVIS

Separating and Probing Carbon Nanotubes for Advanced Nanoelectronics

Carbon nanotubes, cylinders of graphene approximately 1–2 nm in diameter, may someday serve as interconnects in molecular electronics or as transistors that are 500 times smaller than current devices. Two teams of researchers—one from the IBM T.J. Watson Research Center in Yorktown Heights, NY, and the other from Harvard University in Cambridge, MA—have been separately investigating two of the fundamental issues associated with nanotubes to help achieve these goals. Both multiwalled nanotubes (MWNTs) and single-walled nanotubes (SWNTs) in bundles are complex conductors that incorporate many coupled tubes/shells that each

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possesses either metallic (m) or semiconducting (s) electronic structures. Although s-nanotubes can be switched on and off as field-effect transistors (FETs), no method exists for selectively preparing or separating out s-nanotubes from m-nanotubes; this has been seen as the primary hurdle to nanotube-based electronics. IBM researchers have been studying how to selectively modify nanotubes to achieve tube separation and attain specific electrical properties. In the April 27 issue of *Science*, P.G. Collins, M.S. Arnold, and P. Avouris describe novel techniques carried out at IBM for converting MWNTs into either metallic or semiconducting conductors and for fabricating arrays of FETs from SWNTs. While classifying nanotubes as either metallic or semiconducting is common, considerable work has been performed to determine if "metallic" SWNTs are true metals. Featured in the same issue of *Science* is an article by Harvard University researchers, M. Ouyang, J.-L. Huang, C.L. Cheung, and C.M. Lieber, that reports measurements of the local electronic density of states (DOS) in various "metallic" SWNTs and elucidates this point.

Collins and co-workers employed an approach that uses current-induced electrical breakdown to remove individual carbon shells. Even though nanotubes can withstand very high current densities ($>10^9$ A/cm^2) at low bias voltage, at high bias the tubes fail. For a SWNT rope, an electrostatically coupled gate electrode was used to select the s-SWNTs and deplete them of their carriers, thus protecting the semiconducting tubes during high current passage; only the metallic tubes were destroyed due to rapid oxidation of the carbon nanotube, while the s-tubes remained undamaged. Using lithography, an array of electrodes (source, drain, and gate) was deposited on top of a layer of SWNT ropes. By forming FETs from the ropes linking source and drain electrodes and destroying all other stray connections through selective breakdown, the researchers were able to fabricate small arrays of independently addressable SWNT FETs; previously, only individual SWNT FETs could be generated. This demonstration of the self-assembly of SWNT FET arrays is unprecedented, and, said Collins, "we have shown that arrays of molecular devices can be produced without a need for actual control at the nanometer scale—an absolute requirement if devices such as these are ever to be manufactured."

The selective breakdown technique is also very effective in studying individual carbon shells in MWNTs. In a MWNT, the current tends to favor the outermost shell since it is in direct contact with the external electrodes. When the MWNT is subjected to a high current density, the outer shell carries the majority of the current and leaves the inner shells almost current-free. Thus, only the outer carbon shell is destroyed by oxidation, and the inner shells remain undamaged. Since shells alternate randomly between metallic and semiconducting in MWNTs, the researchers were able to eliminate shells one by one and study the electrical properties of individual shells.

Ouyang and co-workers have shown that the finite curvature of the graphene sheet comprising nanotubes modifies the electronic properties of m-SWNTs possessing certain chiral angles (θ). Using low-temperature atomically resolved

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scanning tunneling microscopy (STM), the researchers examined "metallic" zigzag ($\theta = 0$) and armchair nanotubes ($\theta = 30$). While it has been postulated that curvature effects alter the overlap of π electron wave functions creating small energy gaps in "metallic" zigzag and chiral ($0 < \theta < 30$) SWNTs at the Fermi energy (E_f) and that intertube interactions can break the rotational symmetry of armchair SWNTs, there has been no experimental verification of these points. STM measurements were carried out in ultrahigh vacuum at ~5 K on SWNT samples supported on Au(111) substrates. The SWNT indices (n,m), which are related to the tube diameter and chiral angle and are typically used to describe nanotubes, were assigned from the STM images. Tunneling conductance data were obtained by tunneling spectroscopy simultaneously with the STM images, and the DOS was calculated using a π-only tight-binding calculation for the assigned indices. For the "metallic" zigzag structures, the researchers' spectroscopy data showed previously unobservable gaplike structures at E_f that demonstrate that these tubes are small-gap semiconductors and not metals. As predicted, the gap magnitude was seen to depend inversely on the square of tube radius indicating that these gaps arise from curvature in the graphene sheet. Armchair nanotube experiments were performed both on a SWNT in a bundle and on an isolated tube on a Au(111) surface. Tunneling spectra on the isolated nanotube did not show any gaps but rather behaved as true metals as expected because of the crossing of π and π^* bands at E_f. However, measurements on the nanotube in a bundle showed a gaplike feature that arose due to interactions between multiple tubes; this feature, termed a pseudogap, differs from the curvature-induced gaps seen in the zigzag SWNTs, because the DOS are suppressed but not reduced entirely to zero at E_f. The measurements being carried out by Ouyang and co-workers will help clarify the nature of nanotube electronic DOS near the Fermi level and thus increase the understanding of electrical transport through "metallic" SWNTs.

"The absence of gaps and pseudogaps in isolated armchair SWNTs," said Ouyang, "indicates that through control of the local environment of these tubes, it will be possible to maximize their conductivity, possibly as interconnects in nanoelectronics."

STEFFEN K. KALDOR

Chalcogenide Glasses Show Photoinduced Second-Harmonic Generation

Researchers at the Shanghai Institute of Optics and Fine Mechanics, the Japan Science and Technology Corp., and Kyoto University have observed photoinduced stable second-harmonic generation (SHG) in chalcogenide glasses. As reported in the June 15 issue of *Optics Letters*, J. Qiu, J. Si, and K. Hirao optically encoded SHG in 20Ge-20As-60S (mol%) glass with nanosecond laser pulses. The glass exhibits excellent photoinduced SHG conversion efficiency and stability compared to tellurite and bismuth oxide glasses.

The glass was prepared by heating a 50-g mixture of Ge, As, and S in a silica ampule in a rocking electric furnace at 800°C for 2 h under 0.1-Pa vacuum. The sample was quenched to room temperature and annealed at the glass-transition

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