drimer family will be obtainable, which will facilitate practical applications for TPA molecules.

YUE HU

Anomalous Behavior Observed in the Magnetic State of Untwinned Lightly Doped $La_{2-x}Sr_xCuO_4$ Single Crystals

Researchers from the Central Research Institute of Electric Power Industry in Tokyo, Japan, have found unusual behavior in the magnetic susceptibility in detwinned $La_{2-x}Sr_xCuO_4$ (x = 0–0.03), or LSCO, single crystals. Parent insulating cuprates at high temperatures are considered to be two-dimensional (2D) Heisenberg antiferromagnets. The presence of doped holes introduces frustration into the spin system, and it has been postulated that, for the lightly doped region, the doped holes are distributed homogenously. A consequence of this homogenous picture is that once the long-range antiferromagnetic (AF) order is destroyed due to hole doping, the spin system must be isotropic. In the July 2 issue of *Physical Review Letters*, A.N. Lavrov, Y. Ando, S. Komiya, and I. Tsukada present a detailed study of the static magnetic susceptibility (χ) in LSCO crystals in the lightly doped region that demonstrates anisotropies in the "paramagnetic" state that are inconsistent with this picture of a 2D Heisenberg antiferromagnet. Their study of the low-temperature spin freezing in these untwinned crystals also reveals an anisotropic Curie constant and anisotropic "spin-glass" temperature.

Parallelepiped samples of LSCO single crystals (~40 mg) were prepared such that all faces coincided with the orthorhombic crystal planes to within 1°, and the samples were annealed in helium to remove excess oxygen. To obtain untwinned crystals, the samples were cooled slowly under a uniaxial pressure of 15–30 MPa. X-ray analysis and magnetic susceptibility measurements were performed to measure the detwinning in the bulk, and the fraction of misoriented domains was estimated to be below 5%. The researchers used a superconducting quantum interference device (SQUID) magnetometer at fields ranging from 0.2 kOe to 5 kOe applied along the orthorhombic crystal axes, *a* and *b* (*c* axis normal to the CuO_2 planes).

Magnetic susceptibility was measured as a function of temperature along the *a*, *b*, and *c* axes in undoped (x = 0) AF samples. While the χ_c data agreed with previous studies, the χ_a and χ_b data displayed unexpected results, including a temperature dependence below the Néel temperature (T_N) and a deviation of χ_a from χ_b above ~330 K in the "paramagnetic" state. These features reveal that suppression of the long-range Néel order in undoped LSCO does not make the system isotropic. For the lightly doped (x = 0.01) AF case, the researchers observed a similar deviation between χ_a and χ_b and no sign that an isotropic spin state was recovered above T_N. Furthermore, said Lavrov, this behavior is not limited to the AF samples. Lavrov said, "We are surprised that the unexpected anisotropy persists to higher doping levels (x = 0.02, 0.03) even after the long-range AF order is expected to be destroyed due to hole doping."

The researchers report that at low temperatures in the spin-glass state, the susceptibility is also anisotropic. Upon cooling below the spin-glass temperature, χ decreases steeply, but this freezing phenomenon is more complicated than was previously thought.

"While we are exploring several possibilities and plan to conduct further studies in order to arrive at a conclusive picture," said Lavrov, "it is clear that the magnetic state in lightly doped cuprates appears to be significantly different from a simple 2D Heisenberg antiferromagnet."

STEFFEN K. KALDOR

Soft Lithography Produces Well-Aligned Carbon Nanotubes

Carbon nanotubes' (CNTs) electronic, mechanical, and chemical properties make them potential candidates for various applications. For possible nanometer-scale integrated-circuit application, it is important to develop a controlled method to synthesize high-quality CNTs. Recent research using physical masks or photo-masks have limited resolution for the resulting nanotube patterns (in micrometer scale). A team of researchers from Fudan University, China, has synthesized well-aligned CNT patterns by a soft-lithographic technique.

The support material for the catalysts is key in determining the basic parameters of CNTs, including the number of walls, the diameter, and the graphitization. As reported in the July issue of *Chemistry of Materials*, the researchers combined the micromolding in capillaries (MIMIC) technique with three-dimensional (3D) cubic mesoporous silica films containing iron nanoparticles as catalysts to fabricate carbon nanotube patterns with aligned orientations. The researchers incorporated the transition-metal catalysts into the ordered mesopores. The molecularly well-defined mesoporous silicon materials have large pores that allow efficient diffusion of species involved in the reactions and lead to high yield and purity of the nanotubes.

The researchers deposited well-aligned patterned CNTs on this catalyst film by chemical vapor deposition (CVD) with high yield (400%). Scanning electron micrographs (SEMs) show that the CNTs are almost pure and also demonstrate that the distribution of the catalyst controls the growth of CNTs. Different patterns were obtained, including striplike, petal-like, and square and hexangular patterns, by using a variety of stamps.

The CNT arrays are perpendicular to the substrate. High-resolution SEM shows that the arrays are composed of thousands of CNTs compacted together. These CNTs have a length of ~10 μm and outer diameter of about 20–40 nm. Formations of CNT arrays are related to the pore structure. On the 3D cubic-ordered mesoporous silica SBA-16 with nanopores perpendicular to the substrate, perpendicular CNTs are obtained, while the 2D hexagonal structure SBA-15 with 1D channels parallel to the substrate promotes parallel growth.

Interior and wall structure information has been acquired by transmission electron microscopy of some of the typical thinner CNTs. They have a structure with multilayer graphitized carbon walls. An increase in the amount of iron catalysts leads to a large yield of CNTs, but does not modify the diameters. Finding new catalyst support materials for CNTs with smaller diameters is still the future goal.

LI ZENG

Bubbles Simulate Atomic-Scale Contact at Surfaces

Using a raft of soap bubbles to simulate the behavior of atoms, researchers at the Massachusetts Institute of Technology (MIT) have built a macroscopic system that can provide insight into the characteristics of nanoscale contact at surfaces.

In a communication published June 7 in *Nature*, Subra Suresh, the R.P. Simmons Professor and Head of the Department of Materials Science and Engineering at MIT and his graduate students, Andrew Gouldstone and Krystyn Van Vliet, described how they created the raft of bubbles a single-layer thick to represent an atomic layer of a material's surface. Using a high-resolution digital camera, the researchers monitored, in real time, the evolution of asperity-level contact and defect nucleation when they indented the surface from the side. They then compared data from the bubble simulation with data from nanoindentation of a variety of metals.

The experiments provide quantitative information about the location beneath the contact surface where defects nucleate

https://doi.org/10.1557/mrs2001.166 Published online by Cambridge University Press

and its dependence on crystallographic orientation and surface roughness on the atomic scale. They also reveal how repeated contact between surfaces leads to nucleation and progression of damage at the nanoscopic dimensions, and why real crystals exhibit unusally high local strength for defect nucleation beneath a free surface when subjected to nanoscale contact.

With such insights gained from the bubble model, the researchers formulated a mechanistic theory for defect nucleation at surfaces during nanoindentation. The researchers have since used the bubble system to explore how defects form for a variety of surface conditions.

They have experimentally simulated the effects of atomic-level surface roughness on defect nucleation at surfaces. Although soap bubbles have long been used to study deformation of bulk metals, this work attempts the quantitative simulation of nanoscale contact deformation and defect nucleation at surfaces. By monitoring the defect nucleation characteristics in the bubble experiments as a function of surface asperity dimensions and the radius of the indenter tip, Suresh and his colleagues were also able to identify the conditions governing the nucleation of defects either at surfaces or in the interior for different local contact geometries. With the information obtained on homogeneous defect nucleation beneath the surface when the asperity dimension is comparable to or larger than the indenter tip radius, they were then able to rationalize why many metals exhibit unusually high local strengths near surfaces prior to the onset of defect nucleation during nanoindentation when the surface is penetrated by an indenter to a depth of only a few tens of nanometers.

"Our ultimate goal is to use them to predict how defects will form on the nanolevel, because such defects can affect the performance of these surfaces and nanoscale devices," said Suresh.

$LiNbO_3$ Crystals Reduced in Vacuum Show a Photorefractive Response Time in the Order of 100 ms

Photorefractive crystals have different applications in optics including optical storage, coherent optical amplification, and phase conjugation. In many photorefractive materials, it is possible to write a holographic grating with a response time of less than a second. However, in the case of lithium niobate, the response time is slow, of the order of several minutes, in contrast with predictions from theoretical calculations. A group of researchers from Nankai University in China has demonstrated a method that improves this condition in $LiNbO_3$. According to their latest results published in the July 1 issue of *Optics Letters*, the application of a reducing treatment on a near-stoichiometric crystal significantly decreases its response time in the order of 100 ms.

A high-purity $LiNbO_3$ single crystal grown by the Czochralski method and with 49.6 mol% Li_2O was reduced in vacuum at 950°C for 5 h. The resultant, near-stoichiometric sample had blue-shifted absorption edge as compared with the as-grown crystal. Holographic gratings were written in the sample using an argon ion laser of 514.5-nm-wavelength light at an optical intensity of ~1.6 W/cm^2. Measurements of the diffraction efficiency as a function of the intensity of an incident He-Ne laser beam and the correspondent diffracted beam were performed. The diffraction efficiency quickly increased to a maximum when the experiment started and after the beams were turned off it decreased to zero as the light-induced grating decayed. The corresponding time constants for grating and dark decay were 122 ms and 182 ms. The incident light caused a temperature increase during the holographic grating that increased the dark conductivity, and also reduced the diffraction efficiency. The dependence of the diffraction efficiency with light intensity showed that the maximum value increased with increasing light intensity and the stationary value had an optimal point. Under the effect of an external electric field, the diffraction efficiency was greatly increased. In these conditions, the potential for the use of $LiNbO_3$ crystals in optical applications is significantly enhanced.

SIARI S. SOSA

Parameter-Free Quasi-Particle Calculations Reveal CaB_6 as a Semiconducting Material

The materials classification of CaB_6 has been shifted from semi-metal to semiconductor by a group of researchers from the University of Twente, Catholic University of Nijmegen, and Eindhoven University of Technology. The most commonly accepted electronic structure model for this alkaline-earth hexaboride has been so far provided by the full-potential linearized augmented plane-wave (FLAPW) method. CaB_6 is classified as a semi-metal by this model, due to a small overlap between the valence and the conduction band in the χ direction.

When CaB_6 is doped with minute amounts (~1%) of lanthanum, the system displays unexpected ferromagnetic behavior. This material has a particularly high Curie temperature of 900 K. Because this is an odd behavior for a semi-metal matrix, the research team reexamined the validity of the semi-metal model for CaB_6. As reported in the July 2 issue of *Physical Review Letters*, using the GW approximation (expanded Green's function and Coulomb screening in a perturbation series) and applying the quasi-particle condition, very good overall agreement with the FLAPW model was obtained. The results indicated lower electron and hole effective masses by an average of 10%. However, at χ, the conduction band shifted upward while the valence band moved downward, opening a small bandgap of ~0.8 eV. According to the research team, CaB_6, instead of being a semi-metal, is a semiconductor. The researchers reported experimental phenomena that also support this new finding. For example, resistivity in CaB_6 increases as the temperature decreases, which is identified as classical semiconductor behavior.

According to the researchers, ferromagnetic behavior in La-doped CaB_6 is especially encouraging because it opens the possibility of creating a new class of devices using magnetic semiconductors. $Ca_{0.99}La_{0.01}B_6$ is an especially good candidate for studies, they said, due to its room-temperature stability as suggested by the extraordinarily high Curie temperature.

JUNE LAU

Generalized Titanate Ceramic Waste Form Developed for Processing Radioactive Waste with Various Compositions

A titanate ceramic phase assemblage has been developed to immobilize a wide range of nuclear-waste stream compositions. As reported in the May issue of the *Journal of the American Ceramic Society*, waste loadings of 42–50 wt% were achieved for a variety of waste-stream compositions, with leach rates comparable to those of reference grade Synroc C.

According to Ewan Maddrell, a research associate with British Nuclear Fuels at Sellafield, United Kingdom, the processing method that the research team used led to dissolution of significant amounts of the fuel assembly components together with the fission products. This resulted in waste streams rich in zirconium, iron, chromium, and nickel and gave rise to variable waste-stream compositions depending on the fuel assembly design of each reactor.

To reduce the large volume of highly active waste generated by the process, the researchers blended some of these waste-

https://doi.org/10.1557/mrs2001.166 Published online by Cambridge University Press