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Nanoclusters of Niobium Display Nonmetallic Properties at Ultracold Temperatures

While searching for signs of superconductivity in nanometer-scale clusters of the metal niobium, researchers at the Georgia Institute of Technology found that the material stops behaving as a metal when the clusters—of up to 200 niobium atoms—are cooled to low temperature. The electrical charges in the clusters suddenly shift, forming dipoles, as the temperature is lowered below a transition temperature that depends on cluster size.

“This is very strange, because no metal is supposed to be able to do this,” said Walter de Heer, a professor in the School of Physics at the Georgia Institute of Technology. “These clusters become spontaneously polarized, with electrons moving to one side of the cluster for no apparent reason. One side of each cluster becomes negatively charged, and the other side becomes positively charged. The clusters lock into that behavior.” In bulk metals—including niobium clusters at room temperature—electrical charge is normally distributed equally throughout

the sample unless an electric field is applied to them.

This ferroelectric phenomenon has so far been observed in clusters of niobium, vanadium, and tantalum—three transition metals that in bulk form become superconducting at about the same temperature that the researchers observe formation of dipoles in the tiny clusters. De Heer believes this discovery will provide insights into superconductivity.

For the smallest clusters, as reported in the May 23 issue of *Science* by de Heer and collaborators R. Moro, X. Xu, and S. Yin, the strength of the dipole effect varies dramatically according to size. Clusters composed of 14 atoms display strong effects, while those made up of 15 atoms show little effect. Above 30 atoms, clusters with even numbers of atoms display stronger dipole effects than clusters with odd numbers of atoms.

De Heer attributes the size sensitivity to the quantum size regime, which is related to restrictions on how electrons can move in very small clusters.

To produce and study the clusters, the researchers use a custom-built apparatus that includes a detector able to count and characterize several million particles per hour. First, a laser beam is used to vaporize the niobium, creating a cloud of metal-

lic vapor. A stream of ultracold helium gas is then injected into a vacuum chamber housing the vapor, causing the niobium gas to condense into particles of varying sizes. Under pressure from the helium, the particles exit through a small hole in the chamber’s wall, creating a 1-mm-wide jet of particles that passes between two metal plates before hitting the detector.

At intervals 1 min apart, the metal plates are energized with 15,000 V, creating a strong electrical field. The field interacts with the polarized niobium nanoclusters, causing them to be deflected away from the detector. Unpolarized clusters remain in the beam and are counted by the detector.

By comparing detector readings while the plates are energized against the readings when no field is applied, the researchers learn which clusters carry the dipole. By varying the temperature and voltage, the research team can study the impact of these changes on the effect.

“By studying several different metals, we found that those that are superconducting in bulk have this effect, and those that are not superconducting do not have it. That strengthens our belief that this is connected to superconductivity in some way that we don’t yet understand,” de Heer said.

Radiotracer Diffusion Measurements of Isotope Motion in a Metal Alloy above the Glass-Transition Temperature Support Mode-Coupling Theory

The discovery of alloys formed from bulk metallic glass has offered a host of applications ranging from casings for mobile phones to golf clubs. Like conventional glasses, these alloys are processed by supercooling the melt though the glass transition. Much effort has been made into understanding the atomic motion in the supercooled melt and the dynamics of the glass transition. Recently, researchers at Kiel University have measured diffusion and the isotope effect in a Pd-based metallic alloy from the glassy state to the equilibrium liquid. The scientists said that the results, reported by V. Zöllmer, K. Rätzke, F. Faupel, and A. Meyer in the May 16 issue of *Physical Review Letters*, provide direct evidence of the decay of activation barriers due to the onset of liquidlike motion.

According to Faupel, who holds the Chair for Multicomponent Materials at Kiel, the most striking result is that the onset of liquidlike motion upon heating the metallic glass is not observed at the caloric glass-transition temperature,

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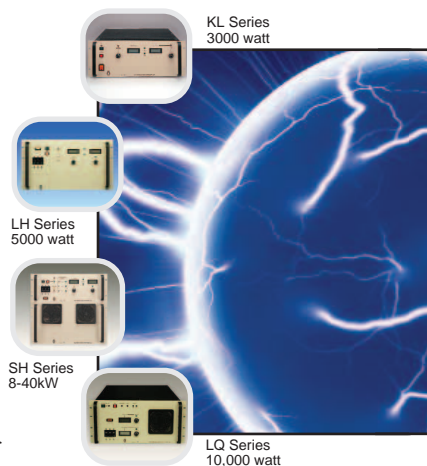
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where macroscopic softening sets in, but at a much higher critical temperature.

"This means that there is a temperature range, extending over almost 200°C, where the atoms still move exclusively like in a solid by local hopping over thermal barriers, although macroscopically the system already behaves like a viscous liquid. As in the glassy state, this hopping involves the coordinated motion of many atoms," said Faupel.

Faupel said that the critical temperature was found to be exactly located at the temperature T_c where the so-called mode-coupling theory predicts the freezing-in of liquidlike motion upon cooling. The T_c was obtained from quasi-elastic neutron scattering by A. Meyer at the Munich University of Technology.

"Moreover, our isotope-effect measurements, which are the first measurements of this kind near T_c in any material, demonstrate that even in the equilibrium melt of the novel bulk-glass-forming alloys, the atomic dynamics are highly coordinated and far away from the hydrodynamic limit of uncorrelated binary collisions," Faupel said. "This seems to be a prerequisite of the exceptional glass-forming abilities."

Nature Designs Hard and Tough Materials at the Nanoscale

The nanoscale size of mineral particles in bone, teeth, and other biological materials may have evolved to ensure optimum strength and maximize tolerance of flaws, according to a research team from the Max Planck Institute for Metals Research (MPI), the Austrian Academy of Sciences, and the University of Leoben. While it is clear that the composite character of biological materials plays an important role in determining their strength, little is known about the role of the nanometer scale of mineral particles. The research team reports in the May 13 issue of the *Proceedings of the National Academy of Sciences* that there exists a critical nanometer size at which the particles found in biocomposites become insensitive to flaws: They maintain strength equivalent to a perfect crystal

despite inherent defects. This phenomenon also suggests that the engineering concept of stress concentration at flaws is no longer valid for nanoscale design.

Biomaterials like bone are molecular composites of proteins and biominerals. While the stiffness of biocomposites is similar to that of the mineral, their fracture energy can be several orders of magnitude higher than the mineral. For example, the composite shell of nacre shows a fracture strength that is 3000 times higher than its mineral constituent CaCO_3 . Despite the complicated hierarchical structures of biocomposites, the smallest building blocks in biological materials are generally on the nanometer length scale and aligned in a generic structure of mineral platelets staggered in a protein matrix.

H. Gao of MPI, I.L. Jäger of the Academy and the University of Leoben, and co-workers have found that this generic nanostructure of biomaterials may be the key to the high fracture strength of these materials. Their analysis demonstrates that the mineral crystals carry the tensile load while the protein matrix transfers the load between mineral crystals by shear. The mineral crystals have large aspect ratios in order to compensate for the large differences in stiffness between mineral and protein. In order to ensure integrity and strength of the composite structure, the mineral crystals must be able to sustain large tensile stress without fracture. The tensile strength of mineral crystals is the key to the composite strength.

Using a simple model, the scientists illustrated that cracked mineral crystals below a critical nanometer size, estimated at 30 nm, have fracture strength identical to that of a perfect, defect-free crystal. They further developed a finite element method to demonstrate that the stress field near a growing crack becomes more and more uniform as the thickness of the structure decreases, eventually reaching the theoretical strength at the critical size. A particle smaller than this size becomes insensitive to cracklike flaws. The findings may explain why bone, which has

particles a few nanometers thick, is stronger than shell, which has particles a few hundred nanometers thick. The scientists suggest that because materials become insensitive to flaws at this critical nanometer size, the engineering concept of stress concentration at flaws is no longer valid for nanoscale design. □

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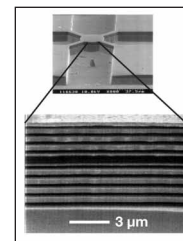
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Corrections

An article in the February 2003 issue of *MRS Bulletin*, "Cosmic-Ray Neutrons on the Ground and in the Atmosphere," by P. Goldhagen, contained two incorrect entries in Table I: Cosmic-Ray Neutron Fluence Rates Measured at Various Locations (p. 134). In the column under " $E > 10$ MeV Fluence Rate ($\text{cm}^{-2} \text{s}^{-1}$)," the correct entries for the second and third rows are 2.5 and 2.3, respectively, not 6.9 and 6.2.

On the cover of the May 2003 issue of *MRS Bulletin* on Photonic Materials for Optical Communications, an incorrect scale was included in the micrograph of the photon wave resonator (right bottom image on the cover). The correct version is reproduced here. See LETTERS TO THE EDITOR in this issue for a detailed explanation from H. Hillmer, guest editor of the May 2003 issue, of the parallel between quantum electronics and quantum photonics as represented on the cover of the issue.



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