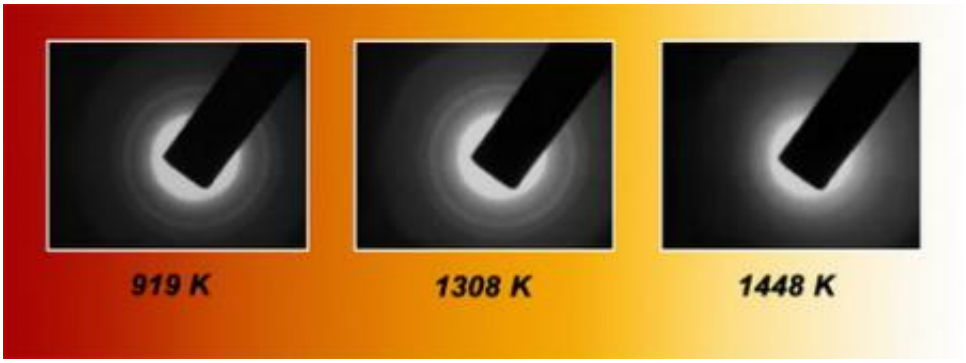
Nanocrystals Are Hot

October 9 2006

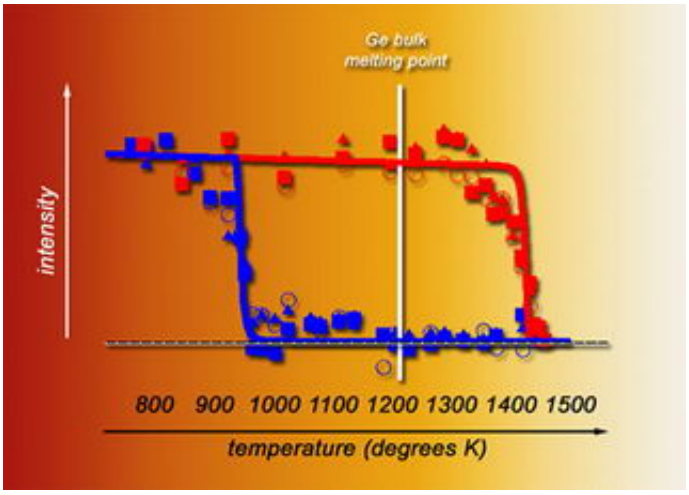


The melting point of germanium nanocrystals embedded in silica glass was measured inside a transmission electron microscope. Electron diffraction patterns from the crystalline lattice structure (bright rings) persist until the temperature is more than 200 degrees Kelvin above the melting point of germanium in bulk, which is approximately 1211 K. When the nanocrystal melts, the diffraction patterns disappear.

Scientists at the Department of Energy's Lawrence Berkeley National Laboratory have discovered that nanocrystals of germanium embedded in silica glass don't melt until the temperature rises almost 200 degrees Kelvin above the melting temperature of germanium in bulk. What's even more surprising, these melted nanocrystals have to be cooled more than 200 K below the bulk melting point before they resolidify. Such a large and nearly symmetrical "hysteresis" — the divergence of melting and freezing temperatures above and below the bulk melting point — has never before been observed for embedded nanoparticles.

Phase transitions between solid and liquid or liquid and vapor are familiar phenomena in the everyday world, for example between solid water ice, liquid water, and water vapor, or steam. Eugene Haller of Berkeley Lab's Materials Sciences Division (MSD), who is also a professor of materials science at the University of California at Berkeley, uses an epicurean example: "When a solid piece of chocolate melts in the mouth, it releases a burst of flavors."

Haller explains that beyond broad scientific interest, the properties of germanium nanoparticles embedded in amorphous silicon dioxide matrices have promising applications. "Germanium nanocrystals in silica have the ability to accept charge and hold it stably for long periods, a property which can be used in improved computer memory systems. Moreover, germanium dioxide (germania) mixed with silicon dioxide (silica) offers particular advantages for forming optical fibers for long-distance communication."



Intensity of electron diffraction rings reveals whether the germanium nanocrystals embedded in silica glass are solid (high intensity) or liquid (low intensity). Solid curves show what the theory predicts during heating (red) and cooling (blue); the symbols are the experimental measurements. Superheating and supercooling are clearly observed, forming a nearly symmetrical hysteresis

loop about germanium&acutes bulk melting temperature.

To exploit these properties means understanding the melting/freezing transition of germanium under a variety of conditions. The researchers embedded nanoparticles averaging 2.5 nanometers in diameter (a nanometer is a billionth of a meter) in silica. What they encountered when they heated and cooled this system was completely unexpected. Their results are published in the October 13, 2006 issue of *Physical Review Letters*.

How Materials Melt and Freeze

For almost a hundred years, theorists and experimenters have studied how the size of a crystal affects melting and freezing, the transition between the liquid and solid state of a material. For most crystalline materials, the smaller the size, the lower the melting temperature. The melting temperature of a free-standing metal or semiconductor nanocrystal, typically comprised of a few hundred to a few thousand atoms, may be more than 300 degrees Kelvin below the melting temperature of the same material in bulk.

The reason for this, says Joel Ager of MSD, a coauthor of the *Physical Review Letters* report, is that "the smaller a solid object gets, the larger the percentage of its atoms residing at the surface. If it keeps shrinking, eventually it's practically all surface." Inside a crystalline solid the atoms are constrained by the crystal lattice, "but at the surface the atoms have more freedom to move. As the temperature increases, they begin to vibrate; when the vibration of the surface atoms reaches a certain percentage of the bond length between them, melting begins and then starts to propagate through the solid."

Beginning in the 1950s, methods for accurately measuring the melting of crystalline solids were developed, and at the same time theories of melting and freezing became more sophisticated.

"Melting and freezing begin at the interface between the surface of the solid and its surroundings," says theorist Daryl Chrzan of MSD, also a professor of materials science at UC Berkeley. "The solid phase has a certain free energy, the liquid another, vapor yet another, and interfaces between these phases have their own characteristic energies. The likelihood of a phase transition occurring in one direction or the other can be calculated based on the free energies of the material phases themselves and their interface energies, taking into account volume, geometry, density, and other factors."

For most materials, interface energies between solid and vapor — for example, a bar of gold in air — favor the formation of a liquid surface layer as the temperature increases, which continues to grow until the entire object is melted; this liquid layer forms more readily at lower temperatures as the proportion of surface to volume increases. Haller notes that "if you make free-standing nanoparticles of gold small enough, they melt at room temperature."

Embedded nanocrystals occasionally behave differently, however. Superheating has been observed in the case of nanocrystals embedded in a crystalline matrix, for example nanoparticles of lead embedded in an aluminum matrix. This is attributed to the lattice structures of the two crystals "locking up," suppressing the vibration of the nanoparticles' surface atoms that would lead to melting.

But germanium nanocrystals in silica glass are quite a different matter: the glass matrix has no lattice structure to lock with the surface of the germanium crystal. Ager says that "because there was no lattice structure in the matrix, we had naively expected the germanium crystals to behave

more like free-standing nanoparticles — that is, we expected the melting temperature to be much less than in bulk germanium. Instead, to our surprise, germanium nanocrystals in glass had to be superheated to melt."

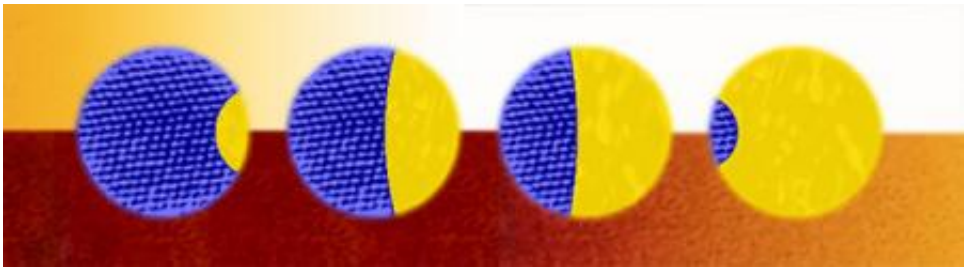
That was only the first surprise. In bulk materials, the interface energy between solid and vapor, which allows the transition from solid to liquid at the melting temperature, creates a roadblock in the opposite direction, an energy barrier to freezing.

"It always costs energy to form a surface," says Chrzan. "In the bulk, in fact, it's possible to supercool many materials and maintain them in a liquid state well above their normal freezing/melting point. In order to freeze, a material must overcome that slight energy barrier so as to form a critical solid nucleus."

In the case of germanium nanocrystals embedded in glass, the same large interface-energy barrier that leads to superheating before the solid crystal can melt means the melted inclusions must be supercooled before they freeze.

"While these results were unexpected," Chrzan says, "it turns out they can be explained in a straightforward way. We modified the traditional theory of nucleation developed by David Turnbull in the 1950s. Even though in our system, the ratio of surface to volume is far greater than in the bulk materials Turnbull was working with — and even though, instead of a solid-vapor interface, we are working with a solid-glass interface — we saw that we could apply his theory in this new regime."

Says Chrzan, "Typically in bulk materials, surface premelting means there's no need for nucleation before melting occurs. But in our case, the large proportional surface area of the germanium nanoparticles, plus the interface energy of the solid-glass interface, creates a calculable nucleation barrier in both directions."



A germanium nanocrystal with a radius of 2.5 nanometers embedded in silica glass doesn't form a critical nucleus for melting until 199 K above the bulk melting point (as suggested by the upper panel). But the critical nucleus for resolidification of the same nanocrystal forms at 255 K below the bulk melting point (as suggested by the lower panel)

As the nanoparticle heats up, a liquid nucleus, its lens shape partly determined by the confining spherical cavity in the glass, must achieve a critical size before it can spread and entirely melt the nanocrystal. Conversely, as the temperature drops, a solid nucleus forms and starts to grow from the surface of the liquid sphere — a nucleus that will eventually cause the entire nanometer-sized liquid globule to freeze into a solid crystal. The Turnbull theory as modified by Chrzan correctly predicted the temperatures at which both events would occur.

Manipulation Under the Microscope

To perform these experiments, the researchers made silica glass samples 500 nanometers thick by oxidizing pure silicon in steam. They implanted germanium ions in the amorphous silicon and then annealed the sample at 900 degrees Celsius to form nanocrystals. The transparent glass allowed characterization of the embedded nanocrystals by Raman spectroscopy; the glass was also readily etched away for examination of

the nanocrystals with an atomic force microscope.

Heating and cooling of the samples were performed in situ in a transmission electron microscope at the Department of Energy's National Center for Electron Microscopy, based at Berkeley Lab. By thinning the samples to less than 300 nanometers and looking straight through them with the microscope's electron beam (with the beam itself masked off so as not to hit the camera), the researchers could observe the electron diffraction rings produced by the crystal lattices of the embedded particles. When the particles began to melt, the diffraction rings weakened and finally vanished, allowing precise measurement of the temperature at which the embedded particles melted. As the temperature was lowered again, the appearance of the diffraction rings signaled resolidification.

"Melting and freezing points for materials in bulk have been well understood for a long time," says Haller, "but whenever an embedded nanoparticle's melting point goes up instead of down, it requires an explanation. With our observations of germanium in amorphous silica and the application of a classical thermodynamic theory that successfully explains and predicts these observations, we've made a good start on a general explanation of what have until now been regarded as anomalous events."

Citation: "Large melting point hysteresis of Ge nanocrystals embedded in SiO_2," by Q. Xu, I. D. Sharp, C. W. Yuan, D. O. Yi, C. Y. Liao, A. M. Glaeser, A. M. Minor, J. W. Beeman, M. C. Ridgway, P. Kluth, J. W. Ager III, D. C. Chrzan, and E. E. Haller, appears in the October 13, 2006 issue of *Physical Review Letters*.

Source: Berkeley Lab