Solid Clusters above the Bulk Melting Point

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The fact that the melting points of nanoparticles are always lower than those of the corresponding bulk material is a paradigm supported by extensive experimental data for a large number of systems and by numerous calculations. Here we demonstrate that tin cluster ions with 10–30 atoms remain solid at ~50 K *above* the melting point of bulk tin. This behavior is possibly related to the fact that the structure of the clusters is completely different from that of the bulk element.

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The melting of small particles attracted interest long before the early days of modern cluster science [1]. The first attempts at theoretical understanding of the melting of small particles were made within a macroscopic framework [2–4], using thermodynamic concepts such as surface energy. These analytical models predict a progressive depression of the melting point with decreasing particle size. While this approach is sound for mesoscopic particles with thousands of atoms, its applicability to much smaller clusters (where most if not all atoms are on the surface) is obviously tenuous. When computational resources became available, the melting of specific clusters was treated microscopically [5–13] using molecular dynamics simulations. Most of this work was for noble gas clusters using a Lennard-Jones potential [5–8], but lately metal clusters (sodium [8], copper [9], gold [10,11], beryllium [12], lead [13], and nickel [14]) have been studied as well. These simulations revealed that some features of cluster melting are qualitatively different from bulk melting, such as a difference between the melting and freezing points and the coexistence of "solid" and "liquid" clusters. The melting point depression predicted by microscopic simulations tends to exceed (often substantially) that given by macroscopic treatments [10].

The melting point depression in finite systems has been confirmed by extensive experimentation on particles of various materials usually deposited on surfaces [15–23]. For technical reasons, these investigations have been limited to metals with reasonably low melting temperatures: indium [16,17], bismuth [18], lead [19], gold [15,20,21], and tin [22,23]. All these studies dealt with particles containing at least hundreds and usually thousands of atoms. More recently, the melting of much smaller, size-selected clusters has been addressed in the gas phase. It is generally accepted that abundance maxima in liquid and solid clusters are governed by electronic and atomic shell structures, respectively. So the melting points of free clusters have been inferred by monitoring those maxima as functions of cluster temperature [24]. A more precise measurement of the melting points of free clusters has been performed by Haberland and collaborators [25,26]. In pioneering work they deduced the melting temperatures of sodium cluster cations from caloric curves obtained from photodissociation measurements. Notwithstanding strong local oscillations, all sizes melt at substantially lower temperatures than bulk sodium. In summary, it is now universally recognized that small particles have lower melting points than the bulk, and the inevitability of this melting point depression has never been questioned (except in recent calculations by Ho and co-workers [27] that were in part guided by the preliminary results of this work).

As any chemistry student knows, the usual way to measure a melting point is to put a small amount of the material into a glass capillary, place the capillary in a melting point apparatus, and slowly ramp up the temperature while monitoring the material by eye to observe the phase change. For a crystalline material the phase change is most easily identified by a change in shape: When the crystals melt they lose their angular shapes and become spherical or hemispherical (depending on how well the liquid wets the surface of the glass capillary). In the work described here we have employed a microscopic analog of this approach, where ion mobility measurements [28,29] are used to search for the shape change associated with the melting transition. An ion mobility measurement, where ions are pulled through a buffer gas by a weak electric field, provides a measure of the average collision cross section of the ion. We have recently used this approach to examine the room temperature structures of tin cluster cations with up to 68 atoms [30]. We found that $\mathrm{Sn}_n{}^+$ species with $15 < n \leq 35$ adopt prolate geometries with aspect ratios up to at least 3. These geometries are analogous to those found for silicon and germanium clusters in this size range. Comparison with detailed density functional theory calculations has shown that the prolate geometries of silicon [31,32] and germanium [33,34] clusters are stacks of stable tricapped trigonal prism units. In the experiments, the tin clusters follow the same growth pattern as silicon and germanium species and so they have similar structures. When clusters melt they are expected to adopt the roughly spherical geometry of a liquid droplet. While most liquid metal droplets in the nanometer size regime are expected to distort from being perfectly spherical because of electronic effects [35], the distortions are relatively small and quite difficult to detect by mobility measurements [36]. On the other hand, the transformation from the highly prolate geometries of the tin clusters to roughly spherical liquid droplets is easily detected. The appearance of a spherical geometry could also result from a structural transition between two solid phases (as actually happens for larger silicon clusters [31]). However, the retention of the prolate shape indicates that the clusters have not melted. So our measurements determine a rigorous lower limit for the melting point.

A series of mobility measurements was performed for tin clusters with a variety of drift tube temperatures up to around 555 K, the maximum temperature that can be attained with our existing injected ion drift tube apparatus. The tin clusters were generated by pulsed laser vaporization of a white tin rod. All experimental conditions besides the temperature remained the same as in our previous work [30]. The temperature gradient across the drift tube increased to around 10 K at the upper end of the temperature range studied. The signal falls substantially as the temperature is raised, because of the larger diffusional spread of the ion packet as it travels through the drift tube and the increased difficulty of injecting ions into the drift tube. At the highest drift tube temperature, we were not able to obtain data for some cluster sizes.

In order to compare data measured at different buffer gas temperatures, one has to eliminate the systematic temperature dependence of the mobility (which carries no structural information). This is achieved by expressing the measured values as relative mobilities, K_{rel}. The standard procedure to accomplish this is to divide the measured mobility by K_{sph}, the mobility calculated for a hypothetical sphere of the volume equal to nV_a, where V_a is the atomic volume of the bulk element [30,31,33]. Relative mobilities close to unity are obtained for compact, near-spherical geometries, while the prolate morphologies are characterized by lower values of K_{rel}. The collision radius of He used to evaluate K_{sph} is adjusted such that the relative mobilities of small clusters ($n \sim 10$) remain independent of the temperature, as they should be because these species are near spherical in both the solid and the liquid state [30]. The relative mobilities determined at 300, 378, and 555 K are plotted in Fig. 1. The results at all three temperatures are identical within the experimental error margin. This fact indicates that tin cluster cations retain their size-specific, highly prolate geometries [30] at least up to $\sim$555 K. While no rigorous definition of cluster "melting" exists, all known criteria for this process involve the loss of well-defined rigid geometry and conversion into a fluxional near-spherical drop. Hence we are compelled to conclude that all tin clusters studied here remain solid up to at least $\sim$555 K, that is $\sim$50° above the melting temperature of bulk tin (505 K). Impurities are known to affect the melting points of bulk materials. However, the measured mass spectra rule out the presence of impurities in the clusters. Figure 2 shows a plot of the melting points as a function of radius for our clusters with 19 to 31 atoms and for mesoscopic tin particles [22,23] with several thousand to tens of millions of atoms. The melting point depression and then the increase in the small size regime are clearly apparent.

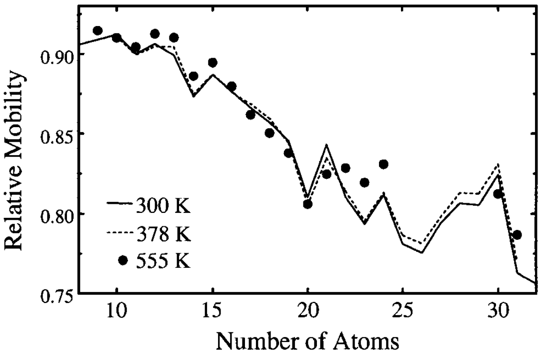

FIG. 1. Relative mobilities of tin cluster cations at different drift tube temperatures. The relative mobility is the ratio of measured mobility to that calculated for a spherical cluster with the same number of atoms (see text). Relative mobilities significantly less than 1.0 indicate geometries that deviate substantially from spherical.

Since the tricapped trigonal prism-based structures of tin clusters in the size range addressed here [30] have little in common with the body-centered tetragonal habit of white tin (or the "diamond" lattice of its grey allotrope) it seems appropriate to question whether this reconstruction is responsible for the elevated melting points. While the reconstructed clusters are expected to have larger cohesive energies than bulk fragments, their cohesive energies (per atom) are still expected to be substantially less than the bulk value. So the mechanism by which the melting points become elevated is not clear. It may result indirectly from changes in the nature of the chemical bonding, through, for example, differences in coordination numbers, directionality, and rigidity. The elevated melting points do not result because the clusters are charged; calculations show that charged and uncharged clusters in this size regime usually have similar structures and cohesive energies [32,34].

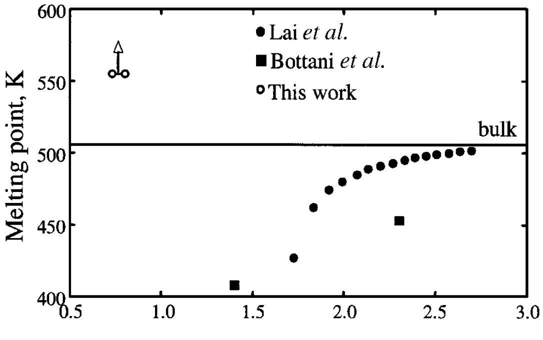

FIG. 2. Melting points of tin clusters as functions of the average cluster radius. ● Lai *et al.* [22] and ■ Bottani *et al.* [23] for mesoscopic tin particles, and ○ this work for clusters with 19–31 atoms.

Once the tin clusters rearrange their interior to resemble the bulk, the melting behavior will presumably become "normal." We cannot presently pinpoint the size at which this transition occurs, other than to say it is beyond 31 atoms.

If the physical basis for the elevated melting points in small tin clusters is their heavily reconstructed geometries, then the same phenomenon may occur for other clusters that are heavily reconstructed, including perhaps silicon and germanium species. The melting points of these elements in bulk (1687 K and 1210 K, respectively) are both much higher than the 555 K attainable with our current experimental configuration, and so we cannot yet determine if this is indeed the case. Recently, Ho and co-workers [27] have modeled the melting of Si, Ge, and Sn clusters with up to 13 atoms using Carr-Parrinello *ab initio* molecular dynamics simulations. The melting points calculated for tin species in this size range are all above 900 K. The calculated values for silicon and germanium clusters similarly exceed the melting points of the bulk elements, although by a smaller margin. Our finding of a substantial melting point elevation in clusters of certain sizes may have important technological implications. For example, it means that nanodevices manufactured from such materials may retain structural integrity and functionality at a much higher temperature than anticipated. Obviously, this is of particular significance for silicon and germanium nanostructures.

In summary, we have found that, in contrast to the accepted paradigm, tin clusters with tens of atoms are solid above the bulk melting point. Since mesoscopic tin particles are known to have depressed melting points [22,23], our results provide a striking illustration of how properties can change in the nanometer size regime. The cause of the abnormally high melting points of small tin clusters may be their heavily reconstructed geometries. The melting points of other reconstructed clusters, like small silicon and germanium species, are also expected to be above their bulk values, and this has important technological implications.

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