Hot and Solid Gallium Clusters: Too Small to Melt

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A novel multicollision induced dissociation scheme is employed to determine the energy content for mass-selected gallium cluster ions as a function of their temperature. Measurements were performed for Ga_n^+ ($n = 17$ 39, and 40) over a 90–720 K temperature range. For Ga_{39}^+ and Ga_{40}^+ a broad maximum in the heat capacity—a signature of a melting transition for a small cluster—occurs at around 550 K. Thus small gallium clusters melt at substantially *above* the 302.9 K melting point of bulk gallium, in conflict with expectations that they will remain liquid to below 150 K. No melting transition is observed for Ga_{17}^+.

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Melting and freezing are cooperative processes. In the thermodynamic limit of a macroscopic system they are first order phase transitions that occur at a single temperature. What happens to the phase transition when the size of the system is reduced into the nanometer regime has been the focus of studies dating back to the late 1800s [1,2]. In this work, we use a novel multicollision induced dissociation approach to perform calorimetry measurements on unsupported gallium cluster ions with 17, 39, and 40 atoms. A broad maximum in the heat capacity — a signature of a melting transition for a small cluster — was found for Ga_{39}^+ and Ga_{40}^+ at around 550 K, almost 250 K *above* the bulk melting point.

Early theoretical [3–5] and experimental [6–10] studies of the melting of small particles revealed a melting point depression that scales as approximately $1/r$. This behavior can be understood from a simple thermodynamic argument using the surface energy and the surface-to-volume ratio. The $1/r$ dependence breaks down for particles with less than around 500 atoms [11–16]. Theoretical studies have predicted many interesting phenomena for particles in this size regime, including size-specific melting temperatures [17–21], reduced heats of fusion [22–24], the coexistence of solidlike and liquidlike phases [17,22,25], and surface or core premelting [19,26–30]. Some of these predictions have been confirmed in a series of elegant experiments on sodium clusters [11–16].

Many liquids can be supercooled to well below their normal freezing points and held there almost indefinitely. The supercooling of some metals can be enhanced by finely dividing them into droplets. In classical nucleation theory a phase transition is initiated by formation of a critical nucleus. The rate of nucleus formation scales with the droplet size [31], so smaller droplets freeze more slowly and can be supercooled to a lower temperature. Thus, in addition to melting temperatures that are depressed for thermodynamic reasons, small particles may show freezing temperatures that are further lowered by supercooling. Bulk gallium has a strong tendency to supercool, and micron and submicron sized gallium droplets can be supercooled to 150 K (around half the normal bulk melting point) [32]. If the freezing temperature continues to scale with size, the small gallium clusters studied here are expected to remain liquid to significantly below 150 K.

In our experiments we search for a thermodynamic signature of melting for an ensemble of size-selected gallium clusters by measuring their internal energy as a function of temperature [11]. This is accomplished by setting the clusters' temperature, and then determining the amount of energy required to dissociate them. An increase in internal energy due to their heat capacity or to their heat of fusion (due to melting) will lead to a corresponding decrease in the dissociation energy. A steady systematic drop in the dissociation energy due to the cluster's heat capacity should occur over the entire temperature range examined, while a sharp step in the dissociation energy is expected at the melting transition.

The clusters are dissociated by shooting them into a high pressure helium buffer gas where they are heated by collisions until their kinetic energy is thermalized. This multicollision excitation process has previously been shown to lead to excited cluster ions with a relatively narrow distribution of internal energies (although broader than their initial thermal distribution) [33]. The fraction of the ions' initial kinetic energy that is converted into internal energy is small (see below). Thus small changes in the ions' initial internal energy lead to substantial changes in the initial kinetic energy required to cause dissociation. This amplification is a critical feature of the experiments. The fraction of the kinetic energy that is converted to internal energy is expected to be similar for liquid and solid clusters [34]. By using mass spectrometry, we are able to determine the number of atoms present in the cluster and ensure that the cluster is not contaminated (a common problem with supported clusters). The charge is not expected to be a significant perturbation for the larger clusters studied here [19].

The experimental apparatus consists of a laser vaporization source, a quadrupole mass spectrometer (QMS) to select the cluster size, a high pressure collision cell, a

second QMS to analyze the products, and an ion detector. The laser vaporization source employs a liquid metal target. This provides a signal with both short- and long-term stability, which is difficult to obtain from rotating solid targets. The final temperature of the gallium clusters is set in an 8.9 cm long temperature-variable extension attached to the source. Measurements were performed with the diameters of the entrance and exit apertures varied so that the pressure in the extension changed by more than an order of magnitude. The results obtained with the different pressures were in excellent agreement, which indicates that the exiting clusters are in thermodynamic equilibrium with the walls of the extension. After leaving the extension, the cluster ions are size selected with the first QMS and then focused into the collision cell which contains helium buffer gas at a pressure of 1.00 Torr. As the ions enter the collision cell they undergo numerous collisions with the helium buffer gas, and may be heated to the point where they dissociate. Undissociated ions and fragment ions travel across the collision cell under the influence of a weak electric field and then exit through a small aperture. They are subsequently focused into the second QMS where they are mass analyzed and then detected.

Figure 1(a) shows an example of a mass spectrum recorded for Ga_{17}^+ with the extension set to 293 K and with an initial kinetic energy of 295.1 eV. The major products are Ga_{16}^+ and Ga_{15}^+ with small amounts of Ga_{14}^+ and Ga^+. The fraction of Ga_{17}^+ ions that dissociate is determined from the peak areas. Figure 1(b) shows this fraction plotted against the initial kinetic energy. The initial kinetic energy corresponding to 50% dissociation (IKE50%D) is determined as a function of the temperature of the source extension. This is normally done by measuring a narrower range of points around 50% dissociation and using a linear regression to determine the IKE50%D value. This procedure provides a measure of how the median internal energy changes with cluster temperature. The decision to track 50% dissociation is somewhat arbitrary, and tracking other values is expected to yield equivalent results.

Figure 2(a) shows the IKE50%D values for Ga_{17}^+ plotted against temperature from 90 to 720 K. The histogram in the lower half of Fig. 2(a) shows the numerical derivative of the measured IKE50%D points, which is proportional to the heat capacity. The proportionality constant depends on the fraction of the ions' initial kinetic energy that is converted into internal energy as they enter the collision cell. In previous work on the multicollision induced dissociation of silicon and germanium cluster ions, this fraction was estimated from a simple modified impulsive collision model [33,35]. For the gallium clusters studied here the model predicts a value of around 2%. The close agreement between the heat capacities determined using this expression and the values predicted by statistical mechanics (see below) further

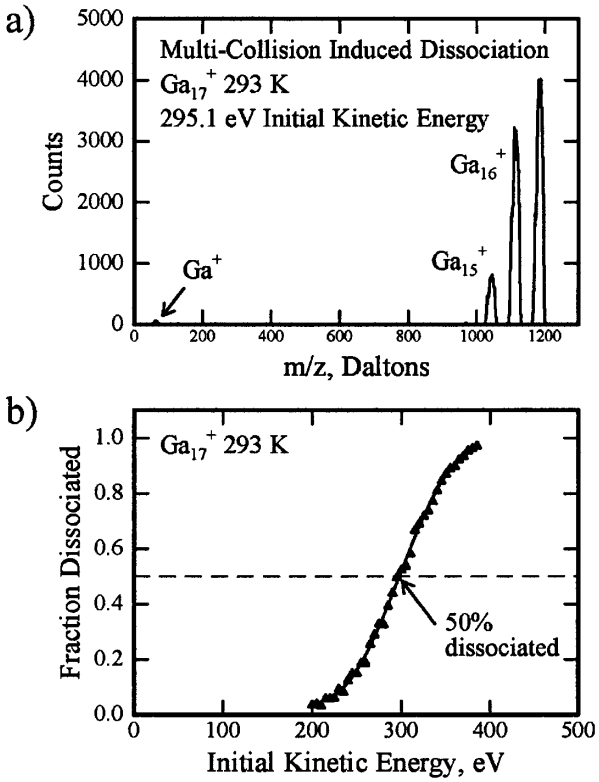

FIG. 1. Multicollision induced dissociation of Ga_{17}^+. (a) The mass spectrum measured for Ga_{17}^+ at 293 K with an initial kinetic energy of 293.1 eV. (b) A plot of the fraction dissociated against the initial kinetic energy.

validates this approach. The dashed lines in Fig. 2 are derived from the clusters' vibrational and rotational heat capacities. The vibrational heat capacity is obtained from a modified Debye model which incorporates a low frequency cutoff to account for the finite cluster size [36]. The rotational heat capacity is assumed to be classical. The calculated heat capacities are in reasonable agreement with the measured values at high temperatures, and reproduce the decrease in the heat capacities at low temperatures due to quantum effects. However, the quantitative agreement for Ga_{17}^+ is rather poor at low temperatures.

Bulk gallium melts at 302.9 K, so if Ga_{17}^+ behaved like the bulk there would be a sharp drop in the IKE50%D values (and a spike in the heat capacity) at 302.9 K due to the heat of fusion. The bar on the left-hand side of Fig. 2(a) shows the size of the drop expected in the IKE50%D values if Ga_{17}^+ had the same heat of fusion (per atom) as the bulk metal (5.59 kJ mol^{-1}). While clusters are expected to have a reduced heat of fusion, it is evident that it should be possible to discern a transition with a heat of fusion that is a small fraction of the bulk value. Even if the heat of fusion becomes vanishingly small, a melting transition should still be detectable by a step in the heat capacity (liquids are expected to have larger heat capacities than solids) [16]. For Ga_{17}^+, it appears that there is no

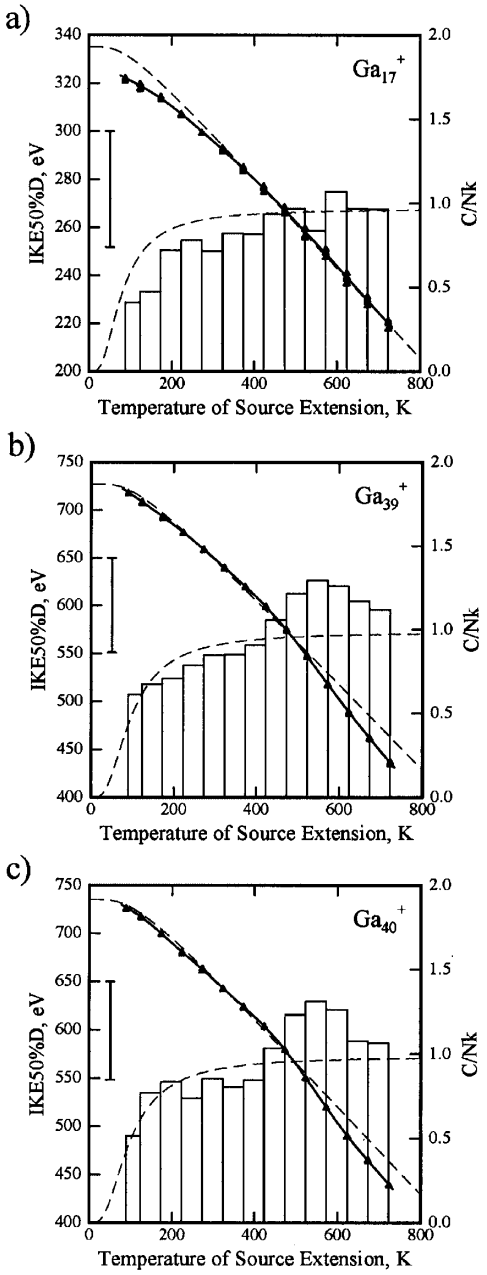

FIG. 2. Plot of IKE50%D against temperature for Ga_{17}^+, Ga_{39}^+, and Ga_{40}^+. The solid lines are spline fits which are provided as guides. The histograms show the numerical derivative of the measured points, which is proportional to the heat capacity, C/Nk (where N is $3n - 6 + 3/2$ and n is the number of atoms in the cluster). The dashed lines are derived from the vibrational and rotational heat capacities calculated using statistical mechanics (see text). The bar on the left-hand side of the figures shows the heat of fusion expected if the clusters have the same value (per atom) as bulk gallium.

evidence for a melting transition over the temperature range examined.

Phase transitions are expected to become more clearly defined as the number of atoms in the system increases. Figure 2(b) shows a plot of IKE50%D against temperature for Ga_{39}^+. As expected, for a larger cluster with more internal degrees of freedom, the IKE50%D values are shifted to higher energies and show a steeper slope with temperature than those for Ga_{17}^+. In addition, for Ga_{39}^+ there is a step in the IKE50%D values and a broad maximum in the heat capacity at around 550 K. This feature is reproducible. The IKE50%D values in Fig. 2(b) actually consist of *three* data sets lying virtually on top of each other [37]. One of these data sets was recorded after the apparatus was completely disassembled, cleaned, and reassembled. Figure 2(c) shows analogous results for Ga_{40}^+, which also shows a maximum in the heat capacity at around 550 K. Liquid-liquid phase transitions are common in multicomponent systems and liquid crystals, but very rare in pure isotropic liquids. At present, phosphorus appears to be the only example of a pure isotropic system exhibiting a transition between two liquid phases [38,39]. Even in this case, exceedingly high pressures are required to access the second liquid phase. So the most reasonable interpretation of the peaks in the heat capacities for Ga_{39}^+ and Ga_{40}^+ is that they result from a melting transition.

The melting transitions for Ga_{39}^+ and Ga_{40}^+ are expected to be broad because the clusters have so few atoms. In addition to the spike (or bump) in the heat capacity due to the heat of fusion there should also be a step in the heat capacity at the melting transition due to the heat capacity of the liquid being enhanced over that of the solid by configurational entropy. It appears in Fig. 2 that the heat capacity is higher after the melting transition than before. An estimate of the heat of fusion can be obtained by integrating the bump in the heat capacity. Using a simple linear interpolation to account for the heat capacity difference between the solid and liquid clusters, we estimate the heat of fusion for Ga_{39}^+ and Ga_{40}^+ to be around 7.1×10^{-20} J and 8.0×10^{-20} J (0.44 and 0.50 eV), respectively. These are around 20% of the bulk values (on a per atom basis) so the clusters have substantially reduced heats of fusion.

The most striking feature of the results presented here is that the maxima in the heat capacities occur at well above the bulk melting point of 302.9 K. Melting temperatures are expected to *decrease* with decreasing particle size. Furthermore, gallium has a strong tendency to supercool, and the nanometer-sized gallium clusters studied here are expected to remain liquid to at least 150 K. This evidently does not occur. There has been one other experimental observation of small clusters with elevated melting temperatures: tin clusters with 20–30 atoms have been found to remain solid to at least 50 K above the bulk melting point [40]. In these studies, the melting transition was never observed, and the elevated melting temperatures were inferred from the cluster's shape. Elevated melting temperatures have also been found in several theoretical studies of small clusters [41–44]. In the case of tin, the elevated melting

temperatures were attributed to the clusters having geometries that are different from the bulk, and, in particular, to the stability of the Sn_{10} tricapped trigonal prism unit [43,45]. It seems likely that the elevated melting temperatures for Ga_{39}^+ and Ga_{40}^+ also have a structural origin, and that these clusters adopt geometries that are substantially different from the bulk material. However, the fragmentation pattern for the gallium clusters does not reveal the existence of a particularly stable building block like the Sn_{10} unit that is evident in the fragmentation pattern of tin clusters [46].

In summary, calorimetry measurements performed on size-selected gallium clusters using a novel multicollision induced dissociation scheme reveal broad maxima in the heat capacities of Ga_{39}^+ and Ga_{40}^+ centered around 550 K. The maxima are attributed to melting transitions, which, surprisingly, occur at substantially above the bulk melting point. The heats of fusion estimated from the experimental results are around 20% of the bulk values. The cause of the elevated melting transitions is most likely structural: the clusters having geometries that are substantially different from the bulk material.

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