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Second-Order Phase Transitions in Amorphous Gallium Clusters

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Ion mobility and calorimetry measurements have been used to probe the nature of the phase transitions in gallium clusters with 29−55 atoms. While most clusters appear to undergo a first-order transition between solidlike and liquidlike phases, a few show the signature of melting without a significant latent heat. These transitions appear to be the finite size analogue of a second-order phase transition, and they presumably occur for some cluster sizes because their solidlike phase is amorphous.

The structures and phase transitions of atomic clusters are topics of great current interest. Experimental studies[1−5] have now confirmed predictions[6−11] that clusters with tens of atoms can undergo the finite size analogue of a first-order phase transition, converting from an ordered solidlike phase to a disordered liquidlike phase as the temperature is raised. Most of the present experimental information on cluster melting has come from calorimetry measurements where the signature of melting is a peak in the heat capacity due to the latent heat. Large size dependent variations in the melting temperatures have been observed, and a lot of attention has recently been focused on understanding the cause of the variations.[12−16]

For more than a decade now, a growing number of theoretical studies have suggested that for some metal clusters high-symmetry ordered structures such as icosahedral and fcc are higher in energy than an amorphous or glassy phase (characterized by numerous nearly degenerate structures without any symmetry).[17−26] The melting of clusters with amorphous ground states has been examined by molecular dynamics simulations.[21,24,27] While ordered clusters melt with a substantial peak in their heat capacity (due to the latent heat) and usually a jump in their volume (due to the liquid clusters being less dense than the solid), the amorphous clusters are predicted to melt without a peak in their heat capacity and with an inflection in their volume (due to the liquid clusters having a larger coefficient of expansion than the solid).[21] This latter behavior is characteristic of a second-order phase transition.

In the work reported here, we have combined calorimetry and ion mobility measurements to probe the nature of the melting transitions in size-selected gallium clusters. The mobility measurements provide information on the volume and shape changes that occur on melting, and the information obtained from these studies complements that obtained from the heat capacities. We find three main types of behavior. Some gallium clusters undergo a normal first-order transition where a peak in the heat capacity is correlated with a jump in the volume. Other gallium clusters undergo a first-order transition where there is a peak in the heat capacity but only an inflection in the cross-sections. Finally, for a few clusters, the cross-sections show an inflection (which we take to indicate a melting transition), while the calorimetry measurements indicate that the transition occurs without a significant latent heat. This latter behavior is the signature of a second-order phase transition, which presumably occurs for some specific cluster sizes because their solidlike phase is amorphous.

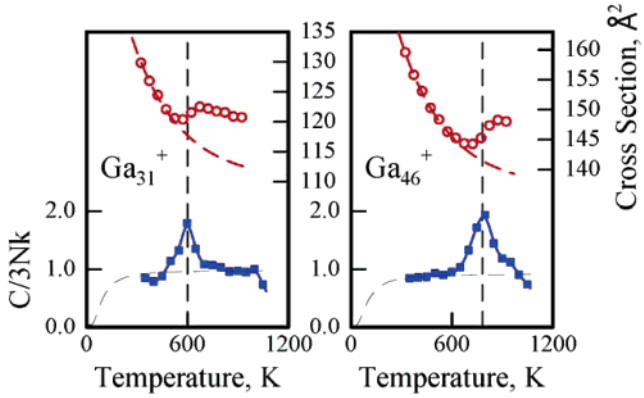

Figure 1. Phase transitions for Ga_{31}^+ and Ga_{46}^+. The solid blue points show the heat capacities which are normalized to $3Nk$ (the classical value), where k is the Boltzmann constant and $3N = 3n - 6 - {}^3/_2$ (n = number of atoms in the cluster, and $3n - 6$ and ${}^3/_2$ are due to the vibrational and rotational contributions, respectively). The thin dashed black line shows the heat capacities calculated from a modified Debye model. The open red points show the average collision cross-sections determined from ion mobility measurements in helium. The thick dashed red lines are fits to the cross-sections using a simple exponential function. The systematic decrease in the cross-sections occurs because the long-range interactions become less important and the collisions become harder as the temperature is raised. Average uncertainties (±1 standard deviation) in both the heat capacity and the cross-section measurements are less than the size of the points.

The gallium clusters for these studies were generated by laser vaporization of a liquid metal target and size-selected by mass spectrometry. Figure 1 shows results for gallium clusters with 31 and 46 atoms. The measured heat capacities, taken from our previous work,[4,5] are shown as the solid blue points. There are obvious peaks in the heat capacities at around 600 K for Ga_{31}^+ and at around 790 K for Ga_{46}^+. The melting temperatures of these clusters (which we take from the center of the peaks) are

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substantially above the bulk melting point (303 K). The elevated melting temperatures have been attributed to the clusters having different bonding than the bulk.[28]

The upper plots in Figure 1 show average collision cross-sections obtained from the ion mobility measurements.[29] These measurements are performed by determining the amount of time it takes for cluster ions to travel through a helium buffer gas under the influence of a weak electric field. A 7.6-cm-long high-temperature drift tube, constructed of molybdenum and alumina, was employed for these measurements. The drift tube was operated with a buffer gas pressure of 5 Torr and a drift voltage of 80 V. Drift time distributions are obtained by injecting 50-μs packets of ions into the drift tube and recording their arrival time distribution at the detector. Average collision cross-sections are determined from the drift times using standard methods.[30] The cross-sections provide information about the average size and shape of the clusters. If a cluster retains the same geometry, the cross-sections should systematically decrease as the temperature is raised, because the long-range interactions between the ion and the buffer gas become less important and the collisions become harder as the temperature increases. This decrease in the cross-sections can be fit by a simple exponential function shown by the thick dashed red lines in Figure 1. There are obvious discontinuities in the measured cross-sections, with steplike increases in the average cross-sections for Ga_{31}^+ and Ga_{46}^+ that are closely correlated with the peaks in the heat capacities.

The steplike increases in the average cross-section described above are due to volume and shape changes that occur when the clusters melt. The cross-sections are much more sensitive to small changes in the volume than to small changes in the shape. The mobility measurements determine the average cross-section, and an increase in the cross-section in one orientation due to a shape change is almost completely compensated by a decrease when the cluster is oriented orthogonally. Bulk gallium is unusual in that its volume *decreases* when it melts, so if a small, spherical gallium cluster behaved like the bulk material, we would see a steplike decrease in the average cross-sections on melting. None of the clusters examined here show such a steplike decrease. Liquid clusters are expected to be roughly spherical, so if a solid cluster is significantly distorted from spherical (and hence has a larger cross section); the cross-sections should show a steplike decrease when the cluster melts and attains a spherical geometry. The failure to observe a steplike decrease for any cluster size suggests that both liquid and solid clusters have roughly spherical geometries (as expected for metal clusters). It follows that the observed steplike increase in the cross-sections must be primarily due to a volume change. The steplike *increase* in the volume that occurs when the gallium clusters melt is the reverse of what occurs for the bulk material. This is almost certainly a consequence of the bonding in the clusters being different from in the bulk, a fact which has already been invoked to account for the clusters' elevated melting temperatures.[28]

Some clusters have a substantial step in their cross-sections (as in Figure 1), some have a small step, and some have no significant step. Examples of clusters that do not have a step are shown in Figure 2. Here, there is an inflection in the cross-section that is roughly correlated with the peak in the heat capacity. For clusters that do not show a step, it is possible that there is either no significant volume change associated with the phase transition or the volume change is compensated by a shape change due to the solidlike phase being significantly distorted from spherical. The inflection in the cross-sections presumably

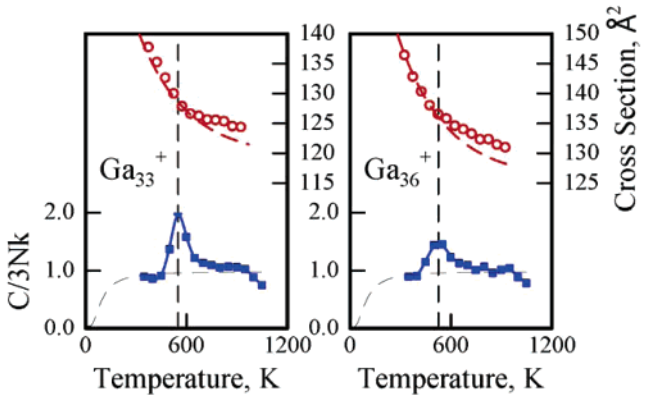

Figure 2. Phase transitions for Ga_{33}^+ and Ga_{36}^+. See caption to Figure 1 for a detailed description.

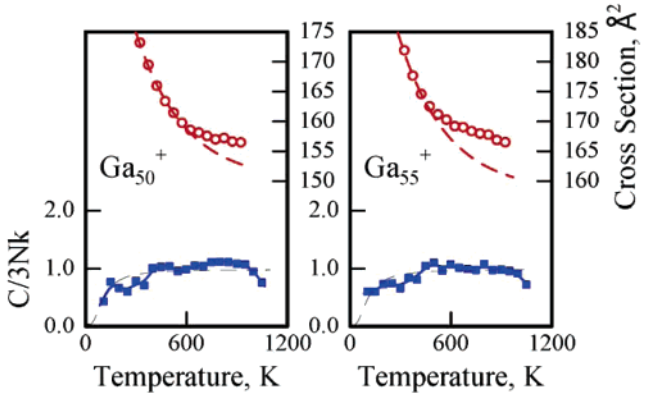

Figure 3. Phase transitions for Ga_{50}^+ and Ga_{55}^+. See caption to Figure 1 for a detailed description.

results because the coefficient of thermal expansion is larger for the liquid clusters than for the solid (liquids usually have larger coefficients of thermal expansion than solids). This increase in the thermal expansion coefficient is also evident in the results for clusters that show a step in the cross-sections. For example, in Figure 1, in addition to the step in the cross-sections for Ga_{31}^+ that is due to the change in volume when the clusters melt, there is also a change in the slope which is consistent with the liquid clusters having a larger expansion coefficient than the solid.

For a few clusters, for example, Ga_{50}^+ and Ga_{55}^+, there is no peak in the heat capacities. There is, however, an inflection in the cross-sections as the temperature is raised (see Figure 3). This behavior is identical to that found in computer simulations of the melting of amorphous clusters, and it is characteristic of a second-order phase transition. The inflection again presumably results because the coefficient of thermal expansion is larger for the liquid clusters than for the solid. In the melting of the amorphous clusters, the inflection in the cross-sections can be taken to roughly indicate the melting temperature. The inflection is at around 620 K for Ga_{50}^+ and at around 520 K for Ga_{55}^+. These melting temperatures are significantly smaller than for gallium clusters with 46−48 atoms (which melt at ~800 K) but comparable to the melting temperatures of clusters with 31−44 atoms (all clusters with 31−48 atoms show first-order transitions with peaks in their heat capacities).

In order for a cluster to melt without a latent heat, the energy of the solidlike phase must be similar to the energy of the liquidlike phase. Figure 4 shows the relationship between the internal energies of liquid, amorphous solid, and ordered solid clusters. The jump in the internal energy on going from the ordered solid to the liquid is the latent heat (the energy decrease

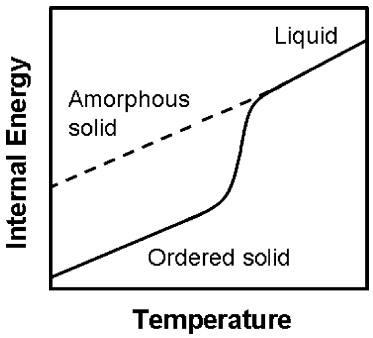

Figure 4. Schematic diagram of internal energy plotted against temperature showing relationship between the liquid, ordered solid, and amorphous solid phases.

that normally results from forming an ordered structure). The latent heat (and the corresponding peak in the heat capacity) are absent when the amorphous clusters melt. The entropy change on melting of the amorphous clusters is also expected to be much smaller than for the melting of the ordered clusters, because the amorphous clusters retain much of the disorder present in the liquidlike phase. In order for a cluster to show a first-order transition, there must be an ordered structure with an energy significantly below that of the amorphous structures, so that the system falls into the ordered structure when it freezes.

Could the behavior we observe for Ga_{50}^+ and Ga_{55}^+ be due to the melting of an ordered cluster with a number of structural isomers rather than the melting of an amorphous cluster? For simplicity, consider a cluster with a high- and low-energy isomer. The entropy change on melting is approximately the same for both isomers (and much larger than for the amorphous cluster). As the temperature is raised, the higher-energy isomer (which has a smaller latent heat) melts first. However, both isomers share a common liquid phase, and the liquid produced by melting the higher-energy isomer will refreeze into the lower-energy isomer (because the clusters are in a buffer gas at a fixed temperature). For small clusters, the metastable liquid phase is short-lived, and refreezing should occur on a sub-microsecond time scale.[31,32] Hence, the melting of the higher-energy isomer leads to annealing into the lower-energy isomer. As the temperature is raised, the lower-energy isomer will eventually melt with a peak in its heat capacity that reflects the latent heat for this isomer. It follows that a small, ordered cluster will have, experimentally, only one true melting transition (corresponding to the melting of the lowest-energy isomer) and that all isomers will convert into the lowest-energy isomer before the cluster melts (we ignore premelting phenomena here, which complicate, but do not change, the picture). Note that conversion into the lowest-energy isomer does not require the higher-energy isomer to melt; it can occur through a solid−solid transition if the barrier between the two isomers is low enough. The conversion of the higher-energy isomer to the lower-energy isomer causes the energy of the system to decrease (the energy required to cause dissociation increases) which leads to an apparent dip in the measured heat capacity. This signature of isomerization (the dip) has been observed in studies of the melting of sodium chloride clusters[32] and aluminum clusters.[33] Thus, melting of an ordered cluster with structural isomers is expected to show a characteristic behavior that is different from what is observed here.

Amorphous clusters can result from either a kinetic effect (where lower-energy ordered structures exist, but they cannot be accessed on the relevant time scale) or from a thermodynamic effect where the ordered structures are destabilized relative to the disordered ones (so that the ordered structures are not thermodynamically favored even at low temperatures). As mentioned above, theoretical studies have already suggested that the lowest-energy structures of some metal clusters are disordered. For Au_{55}, for example, hundreds of disordered structures are predicted to be lower than the Mackay icosahedron, and the number of disordered structures increases rapidly with energy.[23] What destabilizes the ordered structures relative to the amorphous ones? It appears that the main features that drive the amorphization of metal clusters are the contraction of the bonds at the cluster surface because of decreased coordination and the low energetic penalties associated with bond length and coordinational disorder in metals.[34] For the gallium clusters studied here, the amorphous structures appear to be stable. If the amorphous clusters crystallize as the temperature is raised, there would be a dip in the heat capacity due to the formation of the lower-energy structures. Since there is no dip, the amorphous clusters must persist up to the melting temperature. It is worth noting that gallium is the only metal where the metal core of inorganic clusters (i.e., clusters with ligands) show structural isomers. The Ga_{22} core, for example, has recently been shown to have at least four different arrangements.[35] This structural flexibility is consistent with the amorphous behavior indicated by our results for some (naked) cluster sizes.

In conclusion, we have used ion mobility and calorimetry measurements to probe the nature of the phase transitions in gallium clusters with 29−55 atoms. The calorimetry measurements show that most clusters undergo a first-order transition between solidlike and liquidlike phases. For a few clusters, however, the ion mobility measurements show a signature of melting, while the calorimetry measurements indicate that the transitions occur without a significant latent heat. These transitions are probably the finite size analogue of a second-order phase transition, and they occur for some cluster sizes because their ground state is amorphous.

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