

Why Do Gallium Clusters Have a Higher Melting Point than the Bulk?

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Density functional molecular dynamical simulations have been performed on Ga_{17} and Ga_{13} clusters to understand the recently observed higher-than-bulk melting temperatures in small gallium clusters [G. A. Breaux *et al.*, Phys. Rev. Lett. **91**, 215508 (2003)]. The specific-heat curve, calculated with the multiple-histogram technique, shows the melting temperature to be well above the bulk melting point of 303 K, viz., around 650 and 1400 K for Ga_{17} and Ga_{13} , respectively. The higher-than-bulk melting temperatures are attributed mainly to the covalent bonding in these clusters, in contrast with the covalent-metallic bonding in the bulk.

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Probing finite-temperature properties of clusters is a challenging task, both experimentally and theoretically. During the last few years a number of intriguing aspects of the melting properties of these finite-sized systems have been observed, such as a negative microcanonical specific-heat [1] and substantially higher melting temperatures than the bulk systems [2]. In a series of experiments on free sodium clusters (with sizes ranging from 55 to 357 atoms), Haberland and co-workers [3] observed a substantial lowering (by about 30%) of melting temperatures compared to bulk sodium, with rather large size-dependent fluctuations in the melting temperatures. This lowering is in qualitative agreement with old thermodynamic arguments [4] that a small particle should melt at a lower temperature than the bulk because of the effect of the surface. However, Shvartsburg and Jarrold [2] showed recently that small tin clusters (with sizes between 10 and 30 atoms) do not melt at least 50 K above the bulk melting temperature. Surprisingly, a very recent measurement on small gallium clusters by Breaux *et al.* [5] presented another example of a higher-than-bulk melting temperature. Their measurements indicated that Ga_{17}^+ does not melt up to about 700 K, while Ga_{39}^+ and Ga_{40}^+ have melting temperatures of about 550 K, all well above the bulk melting point [$T_m(\text{bulk}) = 303$ K]. While it might have been thought that tin was an exceptional case, these new measurements suggest that elevated melting temperatures could perhaps be a more widespread phenomenon. These authors also investigated the fragmentation pattern but were unable to find the existence of any particular stable building block, and they did not offer any explanation for the high melting temperatures.

Traditionally, classical molecular dynamics (MD) simulations have been used to understand the finite-temperature behavior of clusters [6]. For example, almost all simulations carried out to explain the thermodynamic

data of sodium clusters are based on classical MD employing a variety of parametrized interatomic potentials [7]. However, these attempts have fallen short of reproducing the crucial characteristics observed experimentally, such as the precise sizes at which maxima in the melting temperatures occur. Quite clearly, for reproducing the experimental results a more realistic treatment of interacting electrons is desirable. Recently, we have successfully demonstrated the power of density functional molecular dynamics (DFMD) by providing a detailed explanation of the experimentally observed phenomena of higher-than-bulk melting temperatures for tin clusters [8]. In particular, we have shown that the covalent bonding along with the existence of a highly stable tricapped trigonal prism (TTP) subunit is responsible for the higher melting temperature. For gallium clusters also, an *ab initio* treatment is quite crucial for simulating the finite-temperature behavior, especially since there is a possibility of a change in the nature of the bonding.

In this Letter, we provide an explanation and insight into the phenomenon of the higher-than-bulk melting temperature recently observed in small gallium clusters [5]. To this end we have carried out *ab initio* density functional simulations over a wide range of temperatures for the neutral clusters Ga_{17} and Ga_{13} . We present the calculated specific heat obtained via a multiple-histogram (MH) analysis [9]. We also present a detailed analysis of bonding in these clusters and contrast it with that of bulk. In an earlier density functional calculation by Jones, the bonds in small gallium clusters have been found to be shorter than those between the lighter atoms in the same main group, i.e., Al [10]. As we shall see, these clusters indeed melt at a temperature substantially higher than $T_m(\text{bulk})$, mainly due to the formation of covalent bonds.

Isokinetic Born-Oppenheimer MD simulations have been carried out using ultrasoft pseudopotentials within

the local density approximation, as implemented in the VASP package [11]. For Ga_{17} , the MD calculations were carried out for 23 temperatures, each of duration 75 ps, in the range of $150 \leq T \leq 1100$ K, which results in a total simulation time of 1.65 ns. The resulting trajectory data have been used to compute the ionic specific heat by employing the MH method [9,12]. For all the calculations, we have used only sp electrons ($4s^2$ and $4p^1$) as valence electrons, taking $3d$ as a part of the ionic core (represented by an ultrasoft pseudopotential). We have verified that the d electrons do not significantly affect the finite-temperature behavior and equilibrium geometries by recalculating the equilibrium structures, and performing three runs at finite temperature around the melting region, with the d electrons treated explicitly as valence electrons.

We begin our discussion by noting some interesting features of the electronic structure of bulk Ga, which has been investigated by Gong *et al.* [13]. The α -Ga lattice, which is stable at ambient pressure, can be viewed as base-centered orthorhombic with eight atoms in the unit cell. The peculiarity of this structure is that each atom has only one nearest neighbor connected by a short bond at a distance of 2.44 Å (see Fig. 1). The six other neighbors are at distances of 2.71 and 2.79 Å, in two sets of three. These six atoms lie on strongly buckled parallel planes connected by the short bonds, as shown in Fig. 1. Electronic structure calculations by Gong *et al.* [13] reveal this short bond to be covalent in nature. The density of states shows a pseudogap, which has been related to this covalent bond [14], and the weak bonding in the buckled planes leads to an observed metallic behavior. Thus, two kinds of bonds coexist in bulk Ga: one a molecular bond between the nearest neighbors and the other a metallic bond within the buckled planes.

Now we present and discuss some relevant features observed in the equilibrium structures of Ga_{17} . We have relaxed many structures, randomly chosen from high-temperature DFMD runs. In this way, we have found more than 20 different equilibrium structures spanning

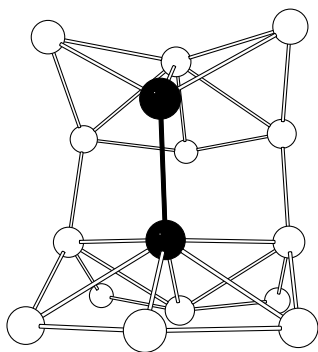


FIG. 1. A part of the bulk structure of α -Ga (not a unit cell). It shows two buckled planes. The dark line joining the black atoms corresponds to the interplanar covalent bond discussed in the text.

an energy range of about 0.83 eV with respect to the ground-state energy. In Fig. 2, we show some low-lying structures relevant to the present discussion. A common feature observed in all these geometries, except one [Fig. 2(d)], is the presence of a trapped atom, that is, a single atom contained within a cage formed by the remaining atoms. The lowest-energy structure that we have found [Fig. 2(a)] is a highly asymmetric structure, which can be thought of as formed out of a decahedron with serious distortions and asymmetric capping. Interestingly, this structure can also be viewed as composed of two near planar rings, as discussed further below.

We have also analyzed the nature of bonding by employing the electron localization function (ELF) [15], which is defined such that values approaching unity indicate a strong localization of the valence electrons and covalent bonding. The isosurface of the ELF for the neutral Ga_{17} and charged Ga_{17}^+ are shown in Figs. 3(a) and 3(b), respectively. A striking feature seen in these figures is the existence of strong localized bonds giving rise to two ringlike structures. Further, these rings are also bonded to each other via the atoms at the edge of each ring and with the trapped atom at the center. The existence of an isosurface of the ELF with such a high value clearly indicates the covalent nature of the bonding. This is also substantiated by examination of the corresponding charge-density isosurface (not shown). Calculations of the ELF for the excited isomers in Fig. 2 and for other small Ga clusters show similar features. Generally, most atoms have two covalent bonds in a roughly linear arrangement, with a tendency to link neighbors together into rings or ring fragments; extra covalent bonds on some atoms then join these structures together. The bonding here is thus seen to be in sharp contrast to the one observed in the bulk α -Ga, where, as discussed earlier, only a single strong interlayer bond between two Ga

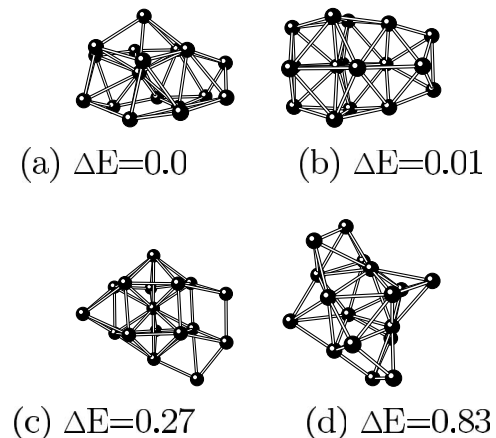


FIG. 2. The ground-state geometry and some of the the low-energy structures of Ga_{17} . The structures are arranged in increasing order of the energy. (a) represents the lowest-energy structure and (d) represents the highest-energy structure studied. Energy differences ΔE are in eV.

atoms exists (see Fig. 1). An analysis of the bond lengths reveals that each atom in the cluster has at least two nearest neighbors at a distance of 2.5 Å or less. Indeed, it is this difference in bonding that is primarily responsible for the higher melting temperature of the small clusters.

An examination of the molecular orbitals and the eigenvalue spectrum (not shown) brings out some notable features. The eigenvalue spectrum is divided into two groups, which are separated by about 1.18 eV. The lower 15 states forming the first group are the bonding states formed out of atomic 4s orbitals. Almost all the upper states are formed out of pure atomic *p* orbitals and show no *sp* hybridization. The only exception to this is the bonding between the trapped atom and its three nearest neighbors, where a weak *sp*² hybridization is observed. This picture is also confirmed by a site-projected spherical harmonics analysis of the orbitals, which does not show any significant mixing of *s* and *p* character in these states. All the bonds seen are of predominantly σ type, formed out of atomic *s* and *p* orbitals. The lack of *sp* hybridization explains the tendency to form covalent bonds at approximately 180° or 90° angles, as observed in Fig. 3.

The calculated specific-heat curve for Ga₁₇ is shown in Fig. 4. A clear peak is observed in the specific heat with a maximum around 650 K, well above the bulk melting point of 303 K. Following the discussion in Ref. [8], we expect the statistical uncertainty in our peak position to be up to 15%. Now, a novel multicollision induced dissociation scheme has recently been used to measure the caloric curve of small, charged Ga clusters [5]. For Ga₁₇⁺, no evidence was found for melting (in the sense of a peak in the specific heat) over a temperature range 90–720 K. Our simulations are consistent with this finding. Note that there is likely to be some shift of the melting temperature between the neutral and charged cluster.

While the thermodynamic simulation has been carried out for neutral Ga₁₇, calculations of the ELF in Ga₁₇⁺ reveal a similar network of covalent bonds [see Fig. 3(b)]. The ground-state geometry changes to a more symmetric form (which is a low-lying isomer for Ga₁₇), and the HOMO-LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) gap increases

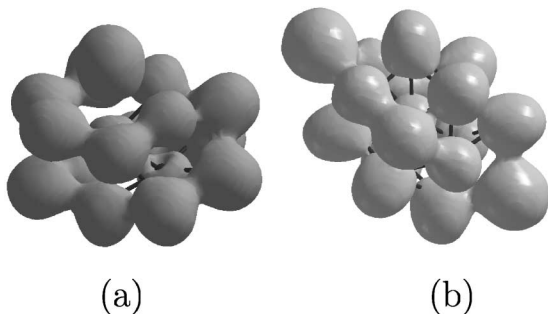


FIG. 3. The isosurface of ELF for (a) Ga₁₇ at the value 0.68 and (b) Ga₁₇⁺ at the value 0.65.

from 0.76 eV for the neutral to 1.07 eV. The low-lying isomers span an energy range of order 0.8 eV for both Ga₁₇ and Ga₁₇⁺. Therefore, we expect Ga₁₇⁺ to have similar melting properties to Ga₁₇. The larger HOMO-LUMO gap for Ga₁₇⁺ may imply that it has a slightly higher melting temperature.

Our specific-heat curve shows no premelting features in the temperature range studied, and that the peak is quite broad, as expected for the finite-sized systems. A detailed examination of the ionic motion at different temperatures sheds more light on the nature of melting. Around 225 K, we observe the occurrence of the first excited state [Fig. 2(b)]. As the temperature rises further, the system visits a variety of isomers all of which contain a trapped atom. It is only above 550 K that the isomer shown in Fig. 2(d) is observed. Evidently, the peak in the specific heat is associated with the diffusion of the trapped atom out of the enclosing structure. Interestingly, in the trajectories at all temperatures below 600 K, the trapped atom is seen to bond itself to atoms in both rings. This confers stability on the caged structure. We have also carried out the analysis of the melting properties via traditional parameters such as the root-mean-square bond-length fluctuations and the mean square atomic displacements (not shown). Their behavior is consistent with the above observations.

To summarize, our *ab initio* MD simulations have shown that the elevated melting temperature of Ga₁₇ is due mainly to the formation of covalent bonds. The stability of the cluster is further enhanced by the role of the caged atom. These observations should have implications for the melting characteristics of clusters of smaller sizes, such as Ga₁₃. The ground-state geometry of Ga₁₃ is decahedral, a more compact structure having a greater average number of covalent bonds per atom than Ga₁₇. Further, our bonding analysis shows that the bonding is strongly covalent, similar to Ga₁₇. We therefore expect this cluster to melt at a higher temperature than Ga₁₇. To

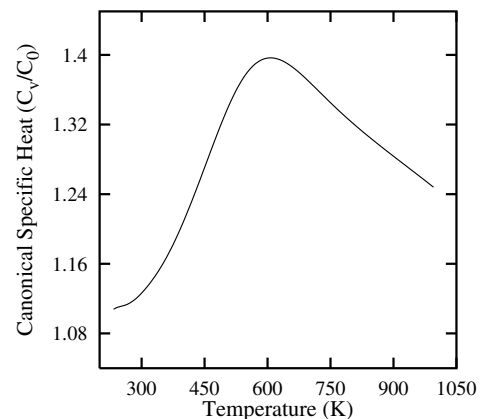


FIG. 4. Normalized canonical specific heat of Ga₁₇ cluster. $C_0 = (3N - 9/2)k_B$ is the zero temperature classical limit of the rotational plus vibrational canonical specific heat.

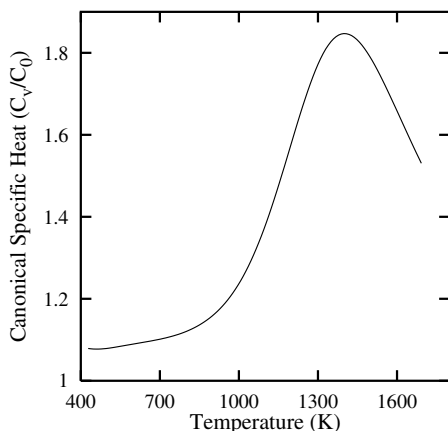


FIG. 5. Normalized canonical specific heat of Ga_{13} cluster.

verify this conjecture, we have carried out extensive DFMD simulations for 30 different temperatures in the range $40 \leq T \leq 1750$ K, with a total simulation time of about 2.7 ns. The resulting specific heat is shown in Fig. 5. Indeed, the peak is around 1400 K, a much higher value than the peak position of Ga_{17} or the bulk melting point. The detailed analysis will be published elsewhere.

Finally, we note that Ga_{39}^+ and Ga_{40}^+ have been measured to have a broad maximum in the specific heat around 550 K [5]. Unfortunately, the large sizes of these clusters prevent us from making a complete thermodynamic study at this stage. However, we have found and analyzed some low-lying equilibrium structures of Ga_{40} . We believe that a mechanism similar to that in Ga_{17} is operative in Ga_{39}^+ and Ga_{40}^+ . In Fig. 6 we show an isosurface of the ELF for the value of 0.64 for Ga_{40} . The ringlike structures of covalent bonds are once again clearly evident. However, it may be noted that at this value of the ELF no contours are seen between the inner core atoms and the outer surface, and not all the atoms on the surface are bonded. Therefore, it is not unreasonable to expect this cluster to melt at a somewhat lower temperature than Ga_{17} , but still higher than that of the bulk.

In conclusion, we have carried out extensive density functional thermodynamical simulations on Ga_{17} and Ga_{13} with the aim of understanding the observed higher-than-bulk melting temperatures. The analysis of the specific-heat curve indicates the melting temperatures (defined as the peak of the specific-heat curve) to be around 650 and 1400 K for Ga_{17} and Ga_{13} , respectively. This result is consistent with the recent experimental observations of Breaux *et al.* [5]. We find a significant change in the nature of bonding between bulk Ga and small Ga clusters. The strong covalent bonds in the small clusters, along with the stabilizing role of the trapped atom in Ga_{17} , are responsible for the higher-than-bulk melting temperatures. While the structural details for Sn and Ga clusters are very different, the common feature

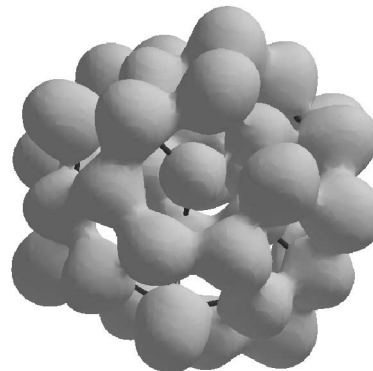


FIG. 6. The isosurface of ELF for Ga_{40} at the value 0.64.

between these two systems is thus seen to be the development of strong covalent bonding in the small clusters.

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