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Structural properties and glass transition in Al_n clusters

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We have studied the structural and dynamical properties of several Al_n clusters by the molecular-dynamics method combined with simulated annealing. The well-fitted *glue* potential is used to describe the interatomic interaction. The obtained atomic structures for $n = 13$, 55, and 147 are in agreement with results from *ab initio* calculations. Our results have demonstrated that the disordered cluster Al_{43} can be considered as a glass cluster. The obtained thermal properties of glass cluster Al_{43} are clearly different from the results for high-symmetry clusters, its melting behavior has properties similar to those of a glass solid. The present studies also show that the surface melting behavior does not exist in the studied Al_n clusters. [S0163-1829(98)08808-0]

I. INTRODUCTION

In the past decade, much attention has been paid to the studies of the thermal stability and melting behavior of metal clusters. Those studies have provided a deep understanding of thermal dynamical behavior in a small size system. On the basis of those studies, some interesting phenomena have been found.[1–8] For example, the coexistence of the solidlike and liquidlike phase was found over a finite range of temperature for both Lennard-Jones (LJ) clusters[1] and metal clusters.[2] The surface melting of clusters has been observed in both molecular-dynamics (MD) (Ref. 3) and Monte Carlo (MC) simulations.[7] The long-time dynamical behavior of small clusters has been studied recently.[8] Experimental observation clearly shows the reduction of melting temperature for some metallic clusters.[9–12]

Most of the theoretical studies on the melting of clusters concentrated on clusters with high symmetry. While the study and the characterization of structural and dynamical properties of clusters in the glass state are becoming an interesting field of research. The concept of a glass or amorphous cluster was introduced by Rose and Berry[13] based on the computer simulation studies of the structural properties of the alkali halide cluster $(\mathrm{KCl})_{32}$ with an empirical potential. According to the concept of bulk glass, they suggested that, if a cluster has a very large number of inherent disorder structures related to the number of its ordered structures, the cluster would have a glass phase. Very recently, the structural and vibrational properties of glass cluster Au_{55} have also been theoretically studied by Garzon and Posada-Amarillas,[14] in which the Gupta n-body potential was used. In the studies on the thermal behavior of metal clusters by Bulgac and co-workers,[15] they found that the magic Na_8 cluster can be transformed to the glass state upon heating. In fact, the existence of a disordered structure as the low-energy configuration of the metal cluster was also reported in other theoretical work.[16–19]

As a matter of fact, glasslike clusters were also observed in the experiments. With the high-resolution transmission election microscopy (HRTEM), gold and palladium nanoparticles were found to have glasslike structures in the particle size range of a few nanometers.[20] In other HRTEM experiments, the transition between the crystallinelike and glasslike structures in gold nanoparticles was also reported.[10,11]

However, to our knowledge, the understanding of the thermal properties of such glass clusters is very limited. It is interesting to study if the glass cluster behaves like a symmetrical cluster at finite temperature or if it shows a glass transition as in bulk glass. In this paper, we try to address these questions by the MD simulation on a few Al_n clusters. We find that the thermal behavior of Al_{43} cluster is much different from that of high-symmetry clusters, and some similarity to that of bulk glass, such as continuous changes of the volume and steplike changes in heat capacity, is clearly observed.

The rest of the paper is organized as follows: in Sec II, we sketch the main computational method used in the calculations. In Sec III, we present and discuss the obtained results on the structural and dynamical properties of Al_n clusters. Finally in Sec IV, we briefly summarize our conclusions.

II. COMPUTATIONAL DETAILS

In the present work, the recently developed *glue* potential,[21] which can correctly reproduce many basic properties of aluminum in crystalline and noncrystalline phases, is employed to model the atomic interaction in Al_n clusters. The standard microcanonical MD method without any boundary conditions is used in the calculation. The Newtonian equations of motion are integrated using the Verlet method with a time step of 4.0×10^{-15} s. Since the momentum of the center of mass and the total angular momentum of the system are carefully eliminated from the calculations, the temperature refers only to the vibrational modes; it is given by

$$T=\frac{2\langle E_k\rangle}{k_B(3N-6)}, \tag{1}$$

where $\langle E_k\rangle$ is the time average of kinetic energy, k_B is Boltzmann's constant, and N is the number of atoms in the cluster.

To characterize the structural changes with temperature, we have calculated the root-mean-square bond-length fluctuation at various temperatures[22]

$$\delta(T)=\frac{2}{N(N-1)}\sum_{i<j}\frac{(\langle R_{ij}^2\rangle-\langle R_{ij}\rangle^2)^{1/2}}{R_{ij}}, \tag{2}$$

where $\langle\rangle$ is the average over the entire trajectory, and R_{ij} is the distance between the atom i and the atom j.

The heat capacity per atom[23] is also calculated for the clusters:

$$C_p=\frac{3K_B(3N-6)(K_BT)^2}{2[(3N-6)(K_BT)^2-2(\langle E_k^2\rangle-\langle E_k\rangle^2)]}. \tag{3}$$

To study the cluster size changing with temperature, we calculate the average principal radii of gyration ($\langle R_1\rangle$,$\langle R_2\rangle$, $\langle R_3\rangle$) of the cluster. The principal radii of gyration R_i are given by

$$R_i=\sqrt{I_i/N}, \tag{4}$$

where I_i is the principal moment of inertia of clusters. From the principal radii of gyration, we can approximately define the volume of clusters,

$$V\approx\tfrac{4}{3}\pi R_1R_2R_3. \tag{5}$$

We have performed the MD run with 2×10^5 steps for Al_{13} and Al_{43}, 5×10^4 steps for Al_{147} at various temperatures far from the melting region. While at the temperature near the melting point (T_m), the system is allowed to propagate over 2×10^5 steps for equilibration and the trajectories are recorded in the next 5×10^5 steps. For Al_{43} cluster, at a temperature from 300 to 1200 K, we increased the number of steps to 10^6, and found that the results do not change.

III. RESULTS AND DISCUSSIONS

We have studied a few aluminum clusters that might have high [icosahedral (I_h) and octahedral (O_h)] symmetry. To determine the lowest-energy structure for each cluster, we employ the simulated annealing strategy. We find that, for Al_{13}, the lowest-energy structure is icosahedral-like, the octahedral structure has a higher energy, which is in agreement with the first-principles calculation[16,24] except for the absence of a small Jahn-Teller effect. For Al_{55}, the lowest-energy structure is also I_h like, but a distorted I_h isomer only 0.01 eV higher in energy has been obtained, in comparison with the first-principles calculation[16] in which the distorted I_h-like structure is the most stable. For Al_{147}, in agreement with the tight-binding model calculation,[19] we find that the I_h-like structure is also the most stable, although the energy difference between the icosahedral-like and octahedral-like structure becomes very small (0.03 eV per atom). These results suggest that the present potential can be used to describe the properties of Al_n clusters.

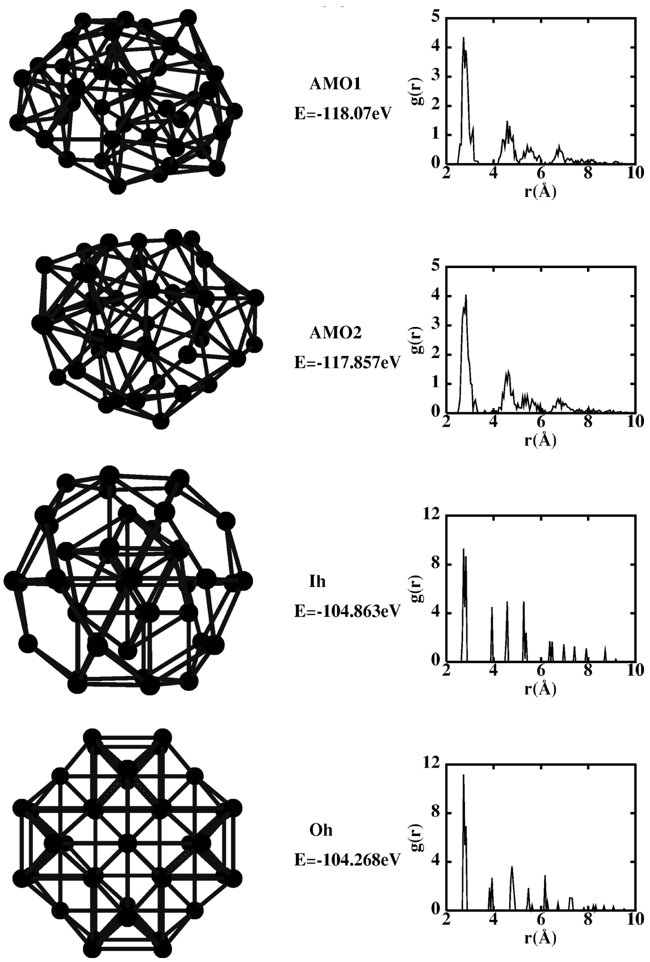

FIG. 1. Left: the stable isomers and their energies (eV) of the Al_{43} cluster, the upper two configurations correspond to glassy structures. The cluster shown on the top is the lowest-energy state. Right: pair-distribution function corresponding to the structures on the left.

Though the I_h-like structures are found to be the most stable for Al_{13}, Al_{55}, and Al_{147} clusters, however, it does not mean that the I_h-like structure is the most stable for all the clusters that could have the icosahedral symmetry. For Al_{43}, the obtained lowest-energy structure is found to be neither I_h like nor O_h like; it shows a highly disordered structure. The energy of the most stable disordered configuration is 3.11 eV and 3.70 eV lower than I_h-like and O_h-like structures, respectively. From our simulated annealing calculations, we find that the cluster Al_{43} has a very large number of inherent disordered structures relative to the number of its high-symmetry structures. In Fig. 1, we show the equilibrium structures of four isomers for Al_{43} along with their pair distribution functions (PDF). The structural differences between disordered and ordered isomers are well illustrated by PDF. For the disordered isomer, PDF has a clear tendency toward a more uniform distribution. The splitting of the second peak in the PDF, an indication of bulk glass metals, is already presented in the disordered cluster Al_{43}. To further show Al_{43} being glasslike, we present the energy of each atom versus its distance to the center of mass of cluster Al_{43} in Fig. 2. For comparison, the result for Al_{147} is also shown. We find that, for the high-symmetry cluster Al_{147}, atoms

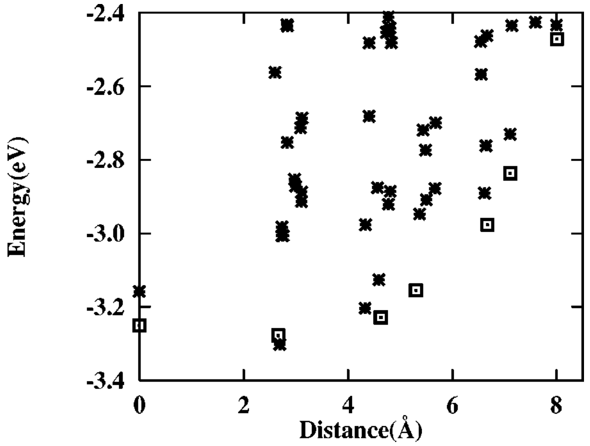

FIG. 2. The energy of each atom vs its distance to the center of mass of the cluster: Al_{147} (square) and Al_{43} (cross).

form shells, the atoms in the same shell have the same energy. However, for the glass cluster Al_{43}, different atoms have different energies. This characteristic energy distribution clearly shows the structural disorder in the cluster Al_{43}.

Usually, the stable structure of cluster is expected to have a high symmetry. However, since the structure of cluster is determined not only by the electronic effect and also by the geometric effect, not all the clusters with a high symmetry is favorable. For aluminum clusters, Al_{13}, Al_{55}, and Al_{147}, whenever they take the I_h or O_h structure, the surface atoms can form a compact shell structure, and it is energetically favorable. For Al_{43}, either with I_h or O_h structure, it would be energetically unfavorable since the compact shell structure cannot be formed. This is probably the reason why Al_{43} shows a disorder structure.

Since the adopted simulated annealing method does not guarantee the obtained lowest-energy disordered structure corresponding to the global minimum of the potential energy surface of cluster Al_{43}, it could be possible that other ordered or symmetrical structures other than the icosahedral or octahedral structures exist with a lower energy. However, none of the ordered configurations is observed in our annealing process. These results suggest that the topology of the potential-energy-surface of cluster Al_{43} is characterized by the low-energy configurations corresponding to disordered structures. Similar results have also been observed in the Au_{55} cluster.[14] In the quenching simulation of the $(KCl)_{32}$ cluster, an opposite behavior was found, in which the glass minima are at lower energies than those corresponding to a high-symmetry structure.

There are many studies that were devoted to the dynamical properties of clusters, however, most of them were concentrated on the high-symmetry clusters. As it is known, the thermal properties of the crystalline phase and the glass phase are quite different. To look into the dynamical properties of high-symmetry and glass clusters, we have first studied the melting behavior of high-symmetry clusters. For Al_{13}, its melting behavior, similar to LJ 13-atom clusters,[1] has been observed. When the temperature increases, the cluster changes from a rigid (solidlike) to a nonrigid (liquidlike) state via an intermediate state in which both states coexist. The coexistence of the solidlike and liquidlike state is over a finite range of temperature of about 350 K.

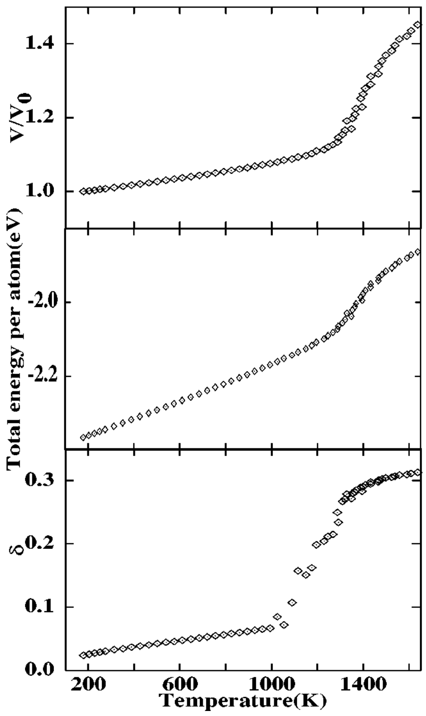

FIG. 3. The root-mean-square bond-length fluctuations, total energy, and volume as a function of temperature for Al_{13}, where V_0 is the volume at 0 K.

In the region of coexistence, the root-mean-square bond-length fluctuation δ and the volume of the cluster defined by Eq. (5) change significantly (see Fig. 3), but the changes occur continuously due to the finite-size effect. Similarly, the energy changes smoothly with the increase of temperature (Fig. 3). In addition, as we can see from Fig. 4, the λ-like peak in the heat capacity suggests a phase transition that can be identified with melting. This melting behavior is in accord with the picture of a first-order transition by the finite-size effects.[25,26] Similar behavior of other 13-atom clusters has been found by several authors.[4,6] For Al_{147}, the volume has a jump at $T=850$ K (Fig. 5), which can be characterized as the feature of a solid-liquid phase transition. An energy jump in caloric curves, which is the typical signature of melting for a crystal with the existence of latent heat, can clearly be

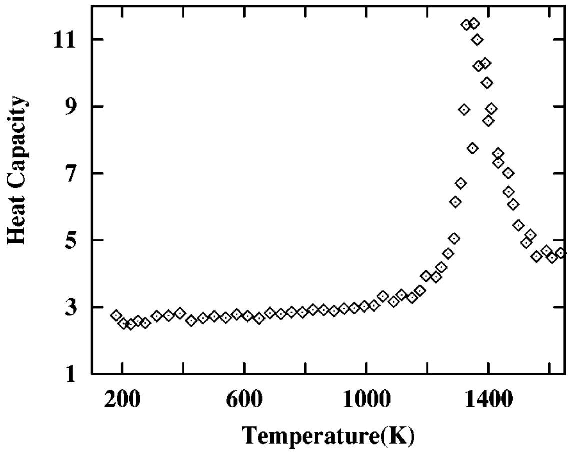

FIG. 4. Temperature dependence of heat capacity per atom for Al_{13}.

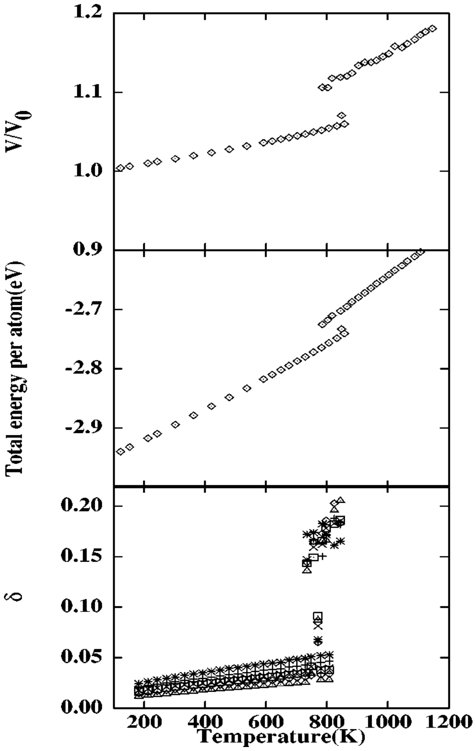

FIG. 5. The root-mean-square bond-length fluctuations of each shell, total energy, and volume as a function of temperature for Al_{147}, where V_0 is the volume at 0 K.

observed for Al_{147} cluster from Fig. 5. Different from Al_{13}, δ increases abruptly at $T=850$ K for cluster Al_{147} indicating the melting. Comparing with cluster Al_{13}, the cluster Al_{147} changes from a solidlike to a liquidlike structure directly upon heating and no intermediate state is observed during a finite temperature range in the melting process. The abrupt change of the volume and total energy is similar to the case in bulk material as the melting occurs. In a word, for high-symmetry Al_{13} and Al_{147} clusters melting can be unambiguously identified.

To study the thermal properties of the disordered cluster Al_{43}, we first calculate δ changing with temperature as shown in Fig. 6. From the figure, we can see that δ increases linearly at low temperature. At $T\sim 400$ K, it begins to rise rapidly, up to 900 K, then the changes become slow. It is interesting to note that the rapid increase of δ happens in a wide range of temperature, namely from 400 K to 900 K. At $T=400$ K, the sharp increase of δ indicates the onset of the diffusive movement of atoms, and the structure begins to change. At $T=900$ K, δ approximately reaches 0.29, and above this temperature, δ almost saturates. According to the Lindemann rule,[22] the cluster has become liquidlike when T >900 K. In Fig. 6, we also present the results for the temperature dependence of the energy per atom. In contrast to high-symmetry clusters, there is no jump or a sharp change in the caloric curves from low temperature to very high temperature, at which the cluster has melted. It means that the latent heat is absent for glass cluster Al_{43}. In Fig. 7, we show the heat capacity as a function of temperature, there is no clear peak as observed for Al_{13}, while the heat capacity has only a steplike jump from 400 K to 900 K. In terms of the changes of the total energy and the heat capacity, the melting of glass cluster Al_{43} cannot be classified into the first-order phase transition as observed in high-symmetry cluster Al_{147}. However, these behaviors are very similar to the glass transition in the bulk glass. The characteristic behavior of the heat capacity is an especially important property of the melting of a glass cluster. In fact, the continuous changes of volume with temperature shown in Fig. 6, which is the basic feature of bulk glass-liquid transition, provides further evidence for the glass transition. Again, the change of volume indicates that the melting of disordered Al_{43} is quite different from the high-symmetry clusters.

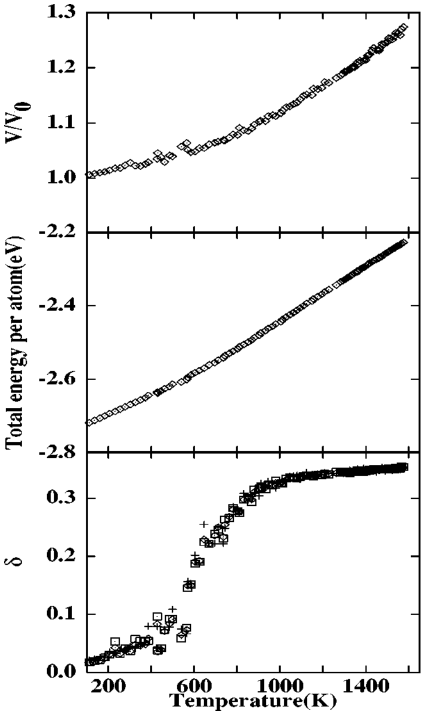

FIG. 6. The root-mean-square bond-length fluctuations of each shell, total energy, and volume as a function of temperature for Al_{43}, where V_0 is the volume at 0 K.

We have noted that there are some fluctuations appearing in the heat capacity (Fig. 7). To see if the fluctuation comes from the small numbers of steps, we have recalculated the heat capacity with many more time steps up to 10^6 steps at temperatures from 300 K to 1400 K, and run 3.0×10^6 steps

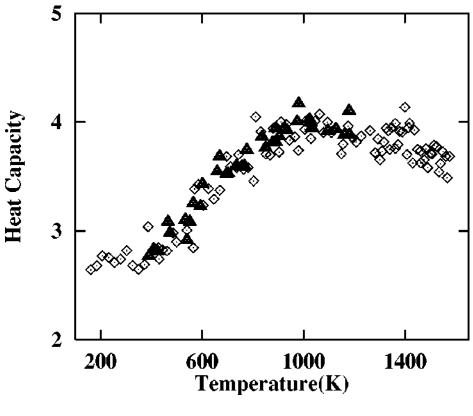

FIG. 7. Temperature dependence of heat capacity per atom for Al_{43}. Square, data collected throughout 2×10^5 MD steps; triangle, data collected throughout 10^6 MD steps.

at a few temperatures. The obtained results are also plotted in Fig. 7 (triangles); we find that the fluctuation does not significantly decrease. These results suggest that the fluctuation in the properties of Al_{43} is intrinsic, which may be due to its complicated potential surface, and it is difficult to reduce the fluctuation just by increasing the number of steps.

According to the discussion above, we find that the thermal behavior of glass cluster Al_{43} has the basic features similar to the bulk glass transition. However, because of the size effect in cluster Al_{43}, the transition is over a very wide range of temperatures up to 400 K; it is difficult to exactly determine a transition temperature for the glass cluster Al_{43}. Similar to bulk glass, the transition region will probably also depend on the heating rate.

For a long time, people are interesting in the behavior of surface melting for bulk materials. Although the standard argument was that the surface premelting could always take place, recent experiments have shown that the overheated surface can be observed. Since the Al(111) and Al(100) surface can be overheated,[27] it is interesting to know if the surface melting can exist in the cluster, even though the surface melting of the I_h cluster has been observed in some metal clusters (Ni_{55} and Cu_{55}) and LJ clusters.[28] For Al_{13}, the root-mean-square bond-length fluctuation for the total cluster and outermost 12 atoms have similar behavior (see Fig. 3), there is evidently no surface melting in agreement with previous studies.[4,6] For Al_{147}, the root-mean-square bond fluctuations for each shell has very small differences below 800 K (see Fig. 5), it begins to change significantly at the same time, which indicates that melting happens simultaneously in the whole cluster. In fact, as discussed in Au clusters by Ercolessi, Andreoni, and Tosatti,[3] surface melting should not exist in aluminum icosahedral structure where only (111) facets are present, since it is shown that Al(111) has a lower surface free energy than the liquid surface at T_m.[27] However, it needs to be pointed out that we have also observed the emergence of floater-vacancy pairs as mentioned in previous papers about surface melting of cluster,[28] but we have not observed the significant diffusion of the surface atoms before the overall melting. Therefore, we do not think that the surface melting really occurs in Al_{147}. For Al_{43}, from the change of δ of each shell (Fig. 6), no surface melting can be observed too, it implies that the surface melting will not occur in the glass clusters, since in the glasslike cluster, the energy difference between the surface atoms and the inner atoms becomes small.

IV. SUMMARY

In summary, we have studied the structural and thermal properties of Al_n clusters by MD and the simulated annealing method with the *glue* atomic potential. We find that, for Al_{13}, Al_{55}, and Al_{147} the lowest-energy structures are icosahedral like, in agreement with previous studies. While for Al_{43}, the structure is glasslike. For the high-symmetry clusters, the results of thermal and melting behavior are similar to those observed previously. The size effect in the small cluster is important, which can lead to the coexistence of a liquidlike state and a solidlike state. In the large high-symmetry cluster, the melting process is similar to the first-order solid-liquid phase transition. However, in the glass cluster Al_{43}, the continuous change of the volume and the steplike change in heat capacity, which are very similar to glass transition in bulk, are found. Because of the size effect, the change of energy, volume and heat capacity are even smoother than that observed in bulk glass. The melting of the glass cluster is inherently different from the melting of high-symmetry clusters. Contrary to what is observed in Ni_{55} and Cu_{55}, we have not observed the surface-melting behavior in all studied Al_n clusters.

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