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Thermal stability and structural transition in Be microclusters

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Thermodynamic stabilities of Be_{6-13} microclusters have been studied using Monte Carlo simulation and an *ab initio* many-body potential. The mean-square fluctuation of the interparticle distance and the heat capacity were monitored as a function of temperature to illustrate thermal softening of these microclusters. The melting temperatures were found to be a strongly nonmonotonic function of size with Be_6 and Be_{13} exhibiting unusual thermal stability while Be_9 and Be_{12}, on the other hand, were found to undergo structural transition at fairly low temperatures as a precursor to melting.

With the possibility that clusters can be used as sources of new materials, studies of their thermal stability have become important. To this end, one could ask a number of interesting questions: (1) What happens to the atomic structure of a cluster at elevated temperatures? (2) How does the thermal energy dissipate—by boiling off an atom or by cluster melting? (3) How does the melting temperature depend on cluster size? (4) Can a cluster undergo a structural transition (between two isomeric states) before it melts?

It has been difficult to answer these questions quantitatively since one is not sure how to define a precise criterion for melting of small clusters. At the smallest size, namely a molecule, there is no melting. As energy is fed into the system, the molecule passes directly from vibrational to the evaporative (dissociative) state. The concept of melting begins to have a meaning only when clusters grow in size, although other phenomena may need to be considered. For example, the initial thermal energy supplied to the cluster may result in atomic excitations causing the cluster to oscillate between different geometrical arrangements with nearly degenerate energies. Recent studies[1] have shown that melting of bulk materials starts from the surface layer or around grain boundaries. Atoms on surfaces or at grain boundaries have low coordination numbers and thus could initiate the melting process. Since clusters have most of their atoms on surfaces, one would think that they too would melt at temperatures well below the bulk melting point. Recent experiments[2,3] and computer simulation studies[4] on nanometer size particles tend to support this conclusion. One wonders if microclusters consisting of $2\sim50$ atoms would exhibit similar thermal characteristics (i.e., low melting temperatures) as nanoscale particles. No experimental or theoretical studies are available at these size ranges to address this issue.

Experimentally, thermal stability of clusters has been studied[2,3] through scanning tunneling microscopy or x-ray-scattering experiments. The melting temperatures were found to monotonically increase with cluster size. Precise interpretation of size dependence of melting is hard, however, not only because clusters used in the study are rather large, but the interaction of the cluster with the substrate on which it is deposited may obscure understanding of its real melting process. Theoretically, melting is studied[4-6] by carrying out simulations based upon empirical interatomic potentials. Thus, the validity of the calculated thermal statility is intimately linked to the validity of the potentials for simulating cluster dynamics.

It is well known from the studies on metal clusters[7] that the unique electronic structures of certain clusters can give them enhanced stability and these clusters can appear as magic numbers in the mass spectra. Calculation of energetics[8] at $T=0$ K support this picture. Could these clusters exhibit unusual *thermal* stability? Could there be a quantum size effect in the melting of clusters similar to that predicted[8] for the magnetism of particles in finite linear chains? In this paper we predict such an effect for the melting of microclusters. We show that the melting of very small clusters is *not* a monotonic function of size, and that some clusters can exhibit unusual thermal stability. In addition, we find that nearly degenerate ground states existing for certain cluster sizes can give rise to structural transitions and anomalous thermal response. Our results are based on Monte Carlo (MC) simulations of Be clusters consisting of six to thirteen atoms.

The interatomic potential used in the simulation was expressed in an analytical form whose parameters were determined by a simultaneous fit to the total-energy hyper surfaces of Be_2, Be_3, Be_4, and Be_5 clusters.[9,10] This potential has been shown to predict bulk properties at $T=0$ K, such as lattice constants, cohesive energy, and bulk modulus in quantitative agreement with experiment. To investigate the accuracy with which this potential can predict finite temperature properties, we have calculated the melting temperature of bulk Be by using molecular-dynamics simulation. We considered a slab of Be with its exposed (0001) surface and containing 420 atoms in 12 layers. In order to simulate the presence of a semi-infinite crystal, the two bottom layers were kept rigid. Periodic boundary conditions were imposed on the directions parallel to the surface and no constraints were applied on the direction perpendicular to the surface. Since melting originates at the surface,[11] and bulk characteristics are reached within the top five layers, the geometry used guarantees that the dynamics of the top layers is not affected by slab size. Melting is then monitored layer by layer by means of an order parameter defined for each layer. We chose to use as order parameter the absolute square of the structure factor, $S_1(\mathbf{G})$, where $\mathbf{G}$ is the reciprocal-lattice vector along the rows of atoms in each layer.[11] Starting from 0 K the system is heated up very slowly. At 1200 K vacancies start to appear in the surface layer. At 1500 K the surface layer is completely molten. The second and successive layers from the surface melt at 1600 and 1700 K respectively. From these simulations we estimate the melting temperature to be 1600±50 K, with the error being estimated based on the fluctuations of temperature. This agrees very well with the experimental melting temperature of 1562 K.

Having demonstrated the effectiveness of the *ab initio* many-body potential for finite temperature simulation, we turn to the study of finite temperature properties of clusters using MC simulation. Three sets of random numbers (R_1, R_2, R_3) ranging from -0.1 to $+0.1$ (in units of r_0) were generated. The energy difference, ΔE of the configurations (x,y,z) and $(x+R_1, y+R_2, z+R_3)$, was calculated. The new configuration is then accepted if $p=\exp(-\beta\Delta E)>R$, where R is a random number in the range between 0 and 1. For each temperature point, the initial 10 000 runs were discarded to allow the system to equilibrate. Then 100 000 MC steps per atom were used to get the thermal average of various physical quantities. Both heating and cooling runs (i.e., using different initial configurations) have been performed for small clusters and the agreement was found to be excellent, thus establishing the thermal equilibrium. We did not observe any hysteresis behavior for all the clusters studied.

The quantities we monitored (in addition to the average energy) were the root-mean-square fluctuation of the interatomic bond distances δ defined by

$$\delta=[2/N(N-1)]\sum_{i,j}(\langle r_{ij}^2\rangle-\langle r_{ij}\rangle^2)^{1/2}, \tag{1}$$

and the heat capacity per particle C which is related to the energy fluctuation by the relation

$$c=\beta^2/N(\langle E^2\rangle-\langle E\rangle^2). \tag{2}$$

The quantities δ and C are sensitive to the "melting" or other thermal softening mechanisms of a cluster and are monitored carefully as functions of temperature for clusters of different sizes.

In Fig. 1 we give our MC results for the temperature dependence of δ. The MC results were obtained with about 10^5-10^6 MC steps/atom. In most of the clusters we find that δ increases linearly with temperature (rather slowly except at very low temperatures when one expects a $\sqrt{T}$ dependence from simple equipartition arguments) and at a characteristic temperature T^* it begins to rise rapidly. We define T^* as the temperature at which the microclusters start to soften drastically, i.e., $d\delta/dT$ increases by more than a factor of 3. Figure 2 gives a plot of T^* as a function of the size.

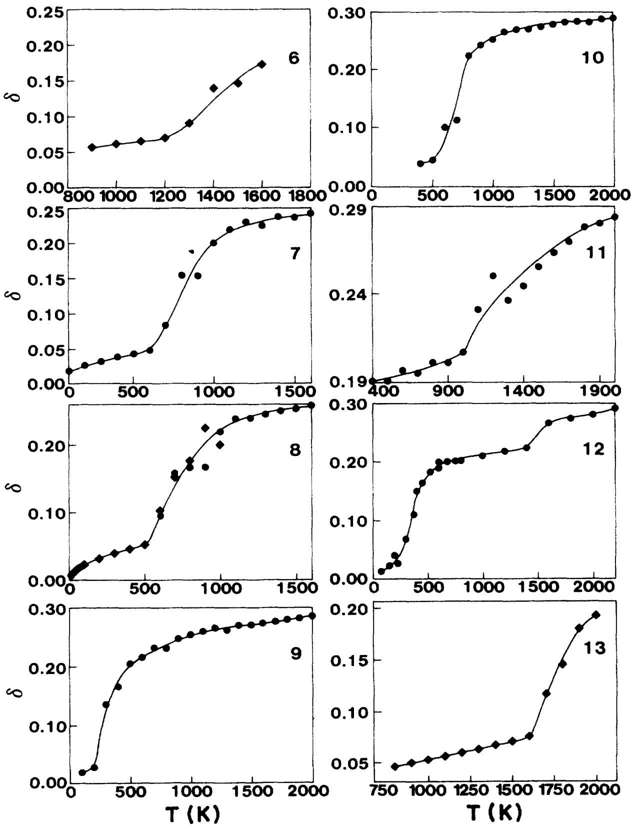

FIG. 1. Temperature dependence of the thermal-expansion parameter δ for different Be_n microclusters.

Depending on the values of T^* we can divide these clusters roughly into three main groups (see Table I). The first ones consisting of Be_6 and Be_{13} are unusually

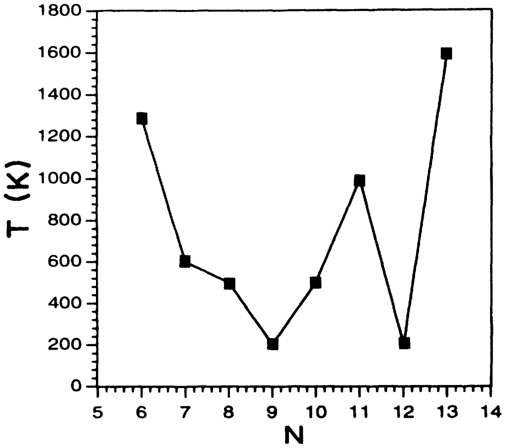

FIG. 2. The temperature T^* where the parameter δ measuring the thermal increase in the interparticle separation [see Eq. (1) of the text] for different Be_n microclusters.

TABLE I. Binding energy per atom and T^* for Be_n clusters.

N	$E(N)/N$ (a.u.)	T^* (K)
6	−0.0585	1300
7	−0.0595	600
8	−0.0614	500
9	−0.0624	200
	−0.0622	
10	−0.0653	500
11	−0.0684	1000
12	−0.0717	200
13	−0.0777	1600

stable, and these clusters do not soften until the temperature is increased well beyond 1000 K. Be_{13} is the most stable cluster and starts to show a rapid increase in δ at about 1600 K, which can be thought of as its "melting" temperature. The second group consisting of Be_7, Be_8, and Be_{10} has $T^* \simeq 500$ K and can be categorized as ones with intermediate stability. Be_{11} appears to fall between these two groups. The third group consisting of Be_9 and Be_{12} appears to be unusually soft, i.e., δ increases rapidly at $T^* \simeq 200$ K.

To understand the physical origin of this unusual low-temperature thermal behavior, we concentrate our attention on the Be_9 cluster. We note that Be_9 has two isomeric states whose binding energies per atom are nearly degenerate (1.697, 1.692 eV). The geometries of these two isomers are given in Fig. 3. In Fig. 4 we give a more detailed T dependence of δ and the heat capacity C for Be_9. The peak in the heat capacity (λ like) suggests some sort of phase transition which cannot be identified with "melting" due to such low values of the peak temperature. We ascribe this peak and the concomitant rapid increase in δ to a "structural transition." This peak in C, we believe, has the same origin as the well-known Schottky specific heat of a two-level system.

In order to confirm the two-level analogy mentioned above, we have constructed a simple anharmonic potential model given by

$$V(x)=x^2-bx^4+cx^6\,, \qquad (3)$$

where the constants b and c can be adjusted to control the spatial separation and the energy difference between the two minima (one at $x=0$, and the other at $x=x_0$ or $-x_0$). We identify the two minima with the two stable structures of the Be_9 cluster (see Fig. 3). We calculate δ, C, and the probability distribution function $P(x)\alpha\exp[-V(x)/k_BT]$ as functions of T for a typical case $b=\frac{10}{9}$ and $c=\frac{1}{3}$. We plot in Fig. 5 the T dependence of δ, C, and P for this potential model. Note that these results are similar to those seen for Be_9 in Fig. 4. The increase in δ and the peak in C coincides with the increased population of the $x=x_0$ configuration in the anharmonic model, thus confirming our idea of a structural transition in Be_9. Although the low-temperature thermal behavior of Be_9 clusters can be understood qualitatively in terms of an anharmonic potential model, the actual thermodynamic and dynamic properties of these microclusters are much more complex and interesting. For example, in Fig. 4, the heat-capacity peak is rather sharp and more λ like in shape. The exact shape of the heat-capacity peak and its proper understanding needs more investigation. Although we have not carried out a detailed study for the Be_{12} cluster we believe that its thermal properties are similar to the Be_9 cluster.

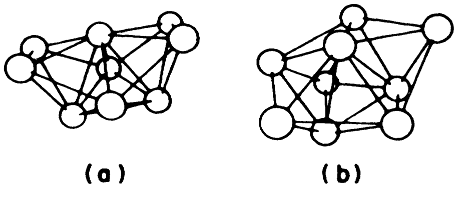

FIG. 3. The nearly degenerate configurations of a Be_9 cluster.

It is interesting to compare the stability of clusters at elevated temperatures to their stability at 0 K. In this regard the binding energy per atom calculated at 0 K can serve as a useful guide. It is known that alkali-metal clusters exhibit odd-even alternation[8] in their stability and ionization potential and these variations are explained on

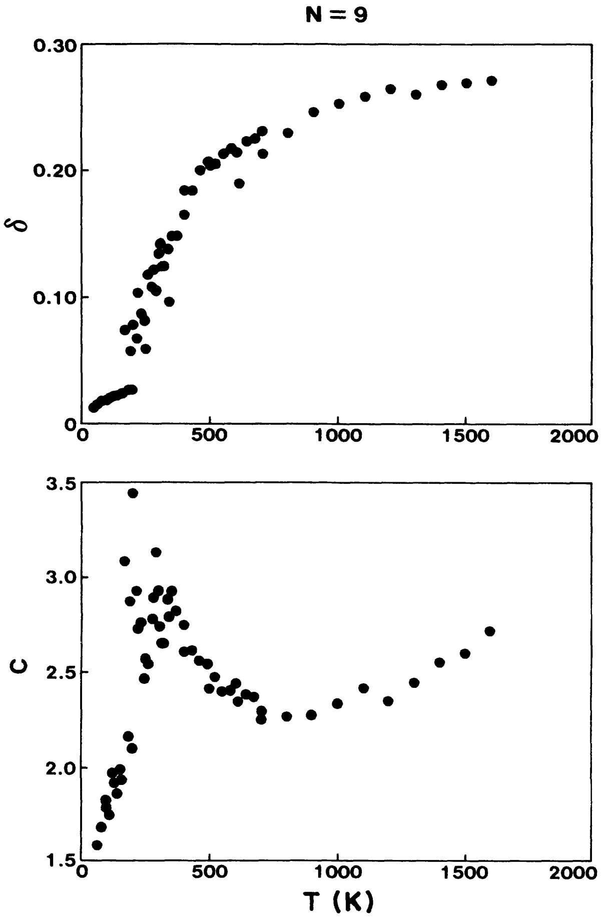

FIG. 4. Temperature dependence of thermal-expansion parameter δ and heat capacity for the Be_9 cluster.

the energetics ground. We plot in Fig. 6 the binding energy per atom of Be_n clusters for $6 \le n \le 13$. Note that the binding energies increase monotonically in this range—a pattern in sharp contrast with the thermal stability curve in Fig. 2. This indicates that the thermal stability of clusters is strongly influenced by atomic vibrations and by excursions made by clusters between various isomeric states at high temperatures. Thus the marked stability of a cluster at $T=0$ K by no means guarantees

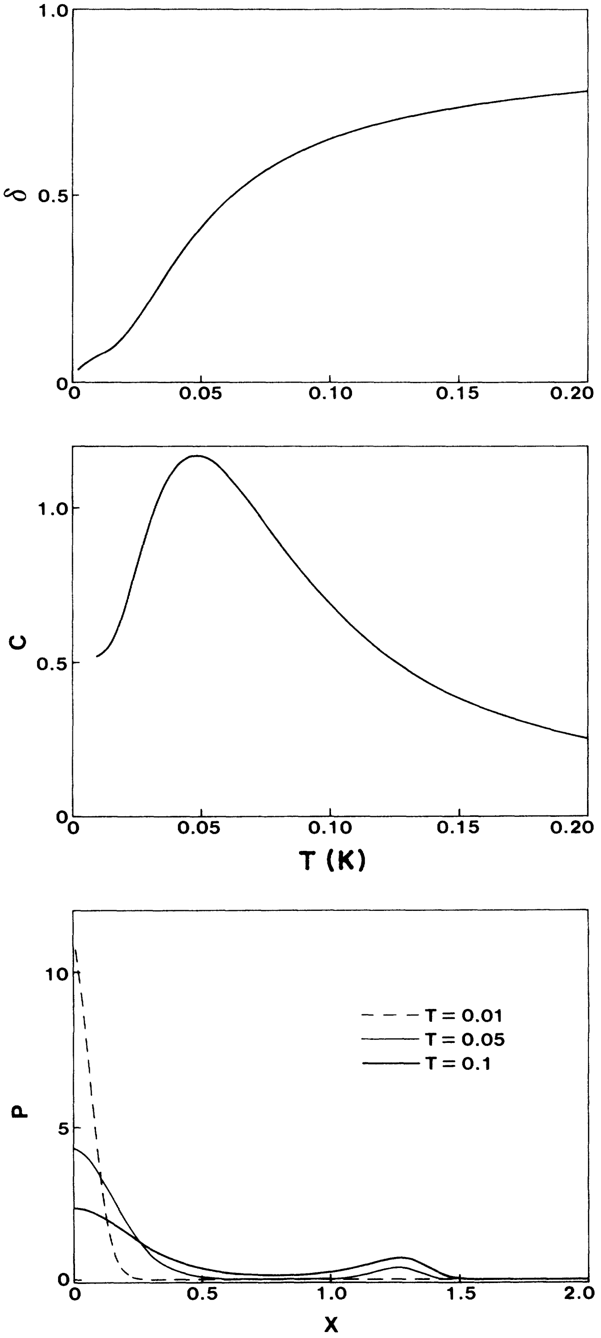

FIG. 5. Temperature dependence of the thermal-expansion parameter and the heat capacity for a model anharmonic system [see Eq. (3) of the text].

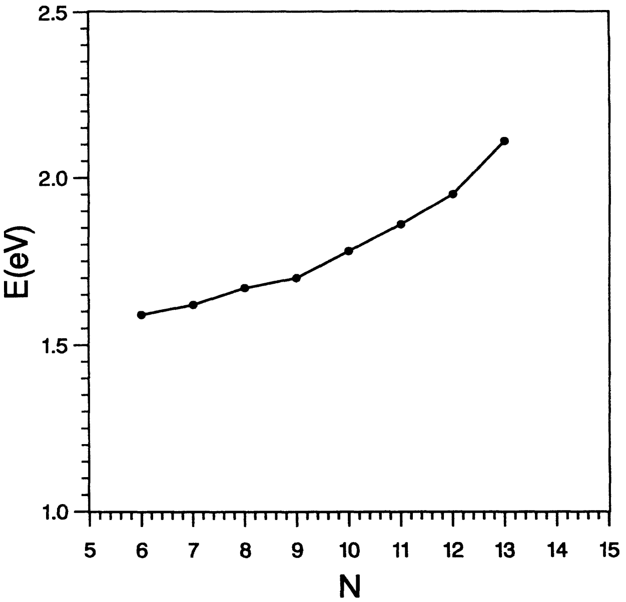

FIG. 6. Binding energy per atom of Be_n clusters for $6 \le n \le 13$.

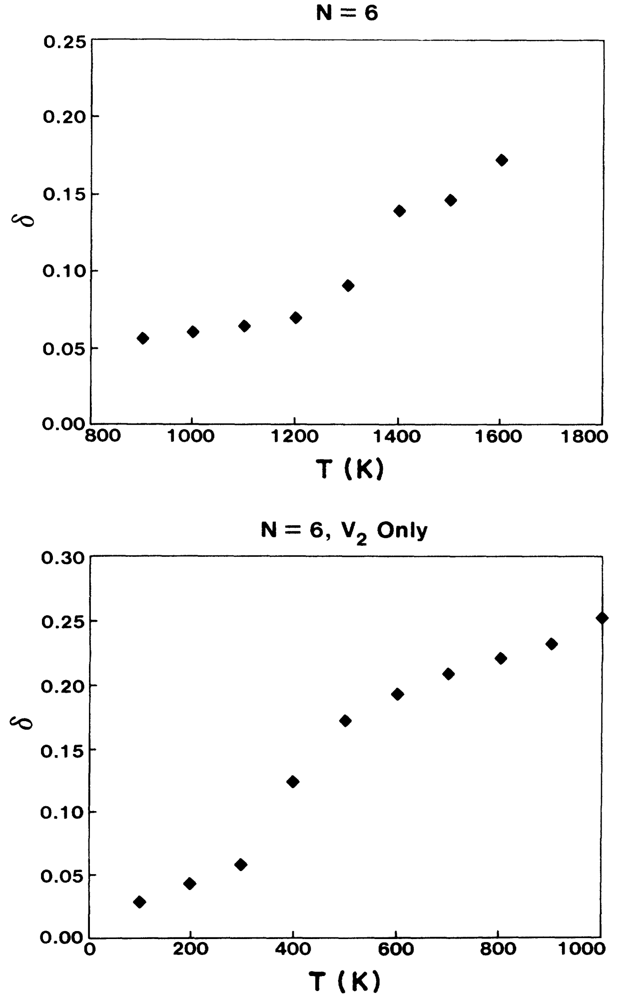

FIG. 7. Temperature dependence of the thermal-expansion parameter δ and the heat capacity C for Be_6 with ($V_3 \neq 0$) and without ($V_3 = 0$) the three-body potential.

that it would have a higher melting temperature.

Finally, we would like to make some remarks about the importance of the three-body terms in the potential V_3 on the melting properties. To this end, we show in Fig. 7 the temperature dependence of δ and C for a Be_6 cluster obtained with ($V_3=0$) and ($V_3\neq0$) terms by using the *ab initio* interatomic potential. The three-body term increases the scale of the temperature as it must because its inclusion increases the cluster binging energy. But the more interesting observation is that the relative sharper "melting" transition for the $V_3=0$ case becomes smoother (broad) for the $V_3\neq0$ case. Thus it appears that the three-body terms tend to smooth out the cluster "melting" transition.

In conclusion, we have demonstrated that the melting characteristics of clusters are not a monotonic function of size and that certain small clusters can exhibit unusually high thermal stability. Recent discovery[12] of the C_{60} fullerene has already illustrated that its thermal stability exceeds that of other forms of carbon. Clusters with nearly degenerate isomeric states can undergo structural transition as a precursor to melting. Anomalous thermal response of the interparticle distance and specific heat can provide a signature of cluster melting.

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