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Magic numbers in supported metal clusters

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Relative stabilities of Ag clusters supported on a Ag(001) substrate have been studied using both the self-consistent Korringa-Kohn-Rostoker–Green's function technique as well as molecular dynamics. Total-energy calculations reveal that unlike in the gas-phase clusters, the relative stability of the supported clusters are governed by the underlying geometry of the substrate leading to completely different magic numbers in two-dimensional systems. [S0163-1829(97)07135-X]

One of the most striking features of clusters that has attracted considerable attention in the last two decades is the existence of conspicuous peaks in their mass spectra.[1] The clusters with pronounced peaks are generally considered to be more stable than others and are referred to as magic numbers. The origin of the magic numbers depend on their size as well as on the chemistry of atoms. For rare-gas atoms, the magic numbers are governed by close packing criteria and clusters consisting of 13,55, . . . , atoms corresponding to complete icosahedric shells exhibit unusual stability. For simple metal clusters such as alkali metals, the origin of the magic numbers depends on cluster size. For small clusters the magic numbers at 2,8,20,40, . . . , were attributed to closure of electronic shells[1]—the same effect that renders rare-gas atoms their chemical inertness and gives the magic number nuclei their enhanced stability. However, for large alkali metal clusters containing more than 1500 atoms the magic numbers are due to closure of atomic shells.[2] Furthermore, experiments show that the clusters exhibiting electronic magic numbers are liquidlike while those exhibiting geometric magic numbers are solidlike.[3] The origin of such behavior and the transition from electronic structure to geometrical structure has recently been explained at the microscopic level.[4,5] It has been shown, in terms of correlation diagram, that at small size range clusters which are bound by long-range forces (such as alkali atoms), the lowest energy structure lie in the liquidlike band since the band is almost continuous in energy. At this size range, in order to have a closed geometrical shell the clusters have to experience excessive strain energy. Therefore, the clusters in these cases instead adopt a structure that removes the strain but gives most favorable electronic structure. However, as the size increases the liquidlike minima have higher energy than the closed shell solidlike structures such as icosahedra, fcc packing and the clusters exhibit geometrical shell structures. The transition from electronic shell closure to atomic shell closure as the dominant mechanism for cluster stability at large sizes has also been shown to be due to the competition of the crystal field effects and the energy gap between the highest occupied and lowest unoccupied molecular orbital.[5] These studies have raised some interesting questions. For example, are the magic numbers in supported clusters same as those in free clusters. If not, what factors are important for understanding their relative stability? This problem is more difficult to answer than the origin of magic numbers in free clusters since in the later case clusters grow without any boundary constraint. For supported clusters one not only has to understand the interaction between the atoms in the cluster but also the interaction of clusters with the substrate. If the cluster-substrate interaction is strong, the clusters would most likely grow in two dimensions as opposed to free clusters which assume three-dimensional structures when clusters contain four or more atoms. Study of the relative stability of supported clusters also provides additional insight. Its understanding can shed light on critical island size enroute to epitaxial growth as well as on the diffusion mechanism.[6]

There have been few studies of mass selected clusters on supports. Recently, Rosenfeld *et al.*[7] have shown that Pt clusters containing seven and nine atoms grown on the Pt(111) substrate exhibit marked stability. Since there are no experiments of mass spectra of free Pt clusters, one cannot determine if and how the relative stabilities of supported clusters differ from that in the gas phase. Theoretical calculations of Li_n and Al_n clusters confined to a two-dimensional structure having the geometry of the (001) and (111) crystal plane showed[8] that the relative stabilities of two-dimensional clusters are indeed different from those grown in the gas phase. However, these calculations did not take into account the interaction of cluster atoms with the infinite substrate nor the effect of surface relaxation. A recent calculation[9] of the stability of the Na_8 cluster on Na and NaCl substrates revealed that while the cluster disintegrated on the Na substrate, it remained stable on the NaCl substrate. The authors did not consider the effect of surface relaxation on cluster stability nor did they investigate the relative stability of clusters as a function of size. Their calculation, however emphasized the strong role the substrate atoms can play on the cluster stability.

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In this paper we report on a theoretical study of the relative stabilities of Ag_n clusters ($n \leqslant 12$) supported on a Ag(001) substrate taking into account the effect of surface relaxation as well as cluster support interaction. The total energies and equilibrium geometries were calculated as a function of cluster size using two complementary methods: The first principles self-consistent Korringa-Kohn-Rostoker (KKR)–Green's function method in the local density approximation and classical molecular-dynamics simulation.

Ab initio calculations of the energetics and equilibrium geometries of supported clusters are difficult not only because clusters destroy the two-dimensional periodicity, but also because surfaces relax due to the adsorption of clusters. The calculations become prohibitively difficult as cluster size increases. It is, therefore, convenient to study these problems using classical molecular-dynamics simulation that employs simple interatomic potential. The difficulty then arises regarding the reliability of such simulation data especially if there are no experiments to compare with. It is because of these difficulties that we have followed a dual procedure. We first calculate the energetics of small ($n \leqslant 4$) supported clusters using the first principles KKR method and compare these results with parallel calculations using the molecular-dynamics simulation. The results are found to be in very good agreement. We then use the molecular-dynamics method to study not only larger ($n \leqslant 12$) clusters but also the effect of relaxation of the substrate.

The study of the energetics of deposited clusters using the KKR method proceeded in several steps. First the Green's function of the bulk crystal is calculated. Using a Dyson equation approach the bulk crystal is split into two half crystals by removing seven layers in such a way that (001) surfaces are generated. The Green's function for the half crystal is now given in a Wannier-Bloch representation. Because the clusters on the surface destroy the remaining transnational symmetry, the Green's function has to be transferred into a local or site representation. By means of the Dyson equation the cluster is included in the system. The cluster atoms are located in the first vacuum layer with respect to the half crystal. In this step the potential perturbations of the clusters and neighboring sites are taken into account. The full charge density is calculated using a multipole expansion. Further details of the method are given in Ref. 10.

The binding energy of the supported cluster is defined by,

$$E_b(n) = [E(n) - E(\mathrm{surf})] - n[E(1) - E(\mathrm{surf})]. \tag{1}$$

Here $E(n)$ is the total energy of a cluster consisting of the Ag_n cluster atoms and the corresponding neighbors on the substrate as explained above. $E(1)$ is the energy of a single adatom on the surface. $E(\mathrm{surf})$ is the total energy of the system that excludes the adsorbed Ag_n cluster. Therefore this value is representative of the pure surface. Thus, $E_b(n)$ defines the energy an n-atom cluster would gain if n isolated atoms on the substrate would self-assemble to form a cluster with a particular geometric structure. One has to repeat the calculations for different atomic configurations of the cluster to determine the lowest energy structure. As can be easily seen, this task becomes impossible as cluster size increases. This is why we use the KKR method[10] to calculate the binding energies of all nonequivalent cluster structures of small Ag_n ($n \leqslant 4$) clusters supported on Ag(001) unrelaxed substrate.

We carry out parallel calculations using the molecular-dynamics simulation[11] based on a many-body potential due to Finnis-Sinclair and Sutton-Chen.[12] The interaction between the atoms are described using a many-body potential based on tight binding second moment approximation. The potential has the form

$$V = \sum_{ij} V(r_{ij}) - \sum_{i} \sqrt{\rho_i}, \tag{2}$$

where the first term represents the repulsion between the atomic cores and the second term is the attractive part of the potential obtained from second moment approximation to the electronic density of states.[12,13]

In our molecular-dynamics calculation, we have taken a slab of 972 atoms arranged in six layers. Periodic boundary

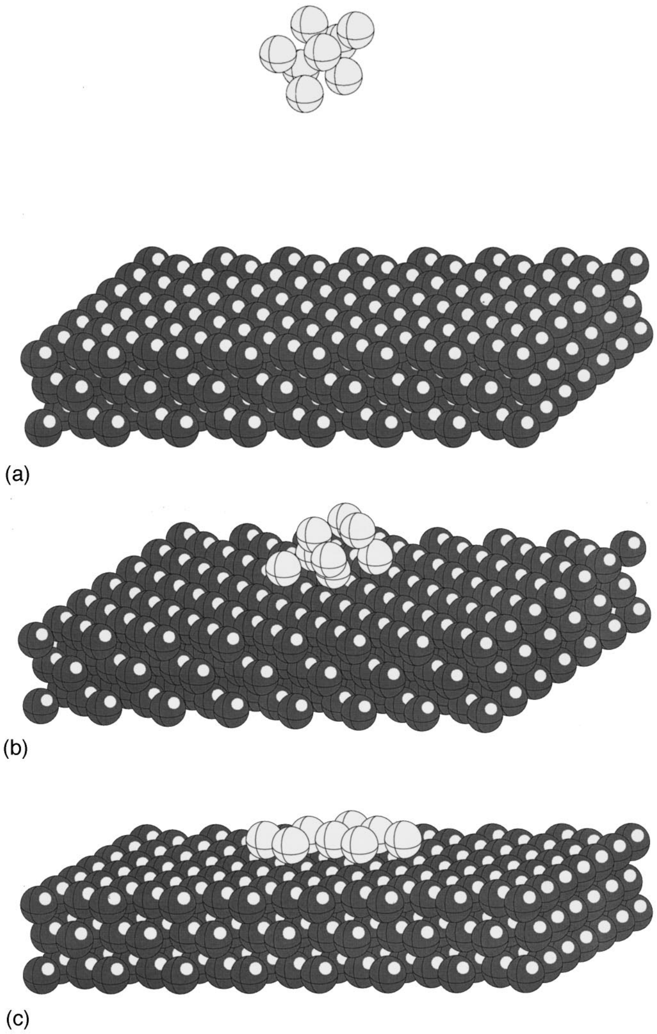

FIG. 1. (a) Structure of Ag_8 cluster in the vicinity of the surface. The substrate atoms are shown as grey circles and the cluster atoms are shown as white circles. (b) Structure of Ag_8 cluster when brought in contact with the surface. The gas-phase equilibrium structure is seen to be modified because of surface-cluster interaction. (c) Equilibrium structure of Ag_8 cluster on Ag(001) surface.

TABLE I. Comparison of binding energies (eV/atom) between first principle KKR and molecular-dynamics (MD) simulations.

Cluster size	KKR	MD
2	0.16	0.12
3 (chain)	0.18	0.16
3 (island)	0.18	0.17
4 (chain)	0.19	0.18
4 (island)	0.31	0.25

conditions are imposed only along the directions parallel to the surface. In order to minimize the interaction between the deposited cluster on the Ag(001) surface and periodic images of the substrate atoms we have considered fairly extended (001) planes. The interaction between the adsorbed cluster and the bottom and edge layers of the surface is seen to be negligible. Since our interest is to study the relative stabilities of free and supported clusters, we first systematically studied the energetics and ground-state geometries of the free clusters. The details of these calculations will be discussed elsewhere. For studying energetics and geometries of the deposited clusters, free clusters with geometries corresponding to their respective ground-state geometry are brought in the vicinity of the surface. The clusters are then allowed to interact with the surface atoms. As an example, we show in Fig. 1 snapshots of a Ag_8 cluster approaching the Ag(001) substrate. Figure 1(a) shows a free cluster well above the substrate. Figure 1(b) is a snapshot of the Ag_8 cluster as it is deposited on the substrate and Fig. 1(c) shows the equilibrium geometry of Ag_8 after all the relaxations within the cluster are complete. In the first step, we do not allow the substrate to relax as clusters are deposited. The equilibrium geometry of the deposited cluster was determined by minimizing the total energy of the system. We achieved this by using the steepest descent method in which the atoms are moved in the direction of the forces until the forces between the atoms are negligible. During the process, the cluster morphology is seen to be modified substantially. We see that the three-dimensional structure of Ag_8 is completely destroyed and the cluster spreads on the surface. With the further minimization of energy, the cluster assumes a complete two-dimensional (2D) structure as shown in Fig. 1(c). To make sure this is the ground state of the supported Ag_8 on Ag(001) substrate, we repeat the calculation by heating both the top

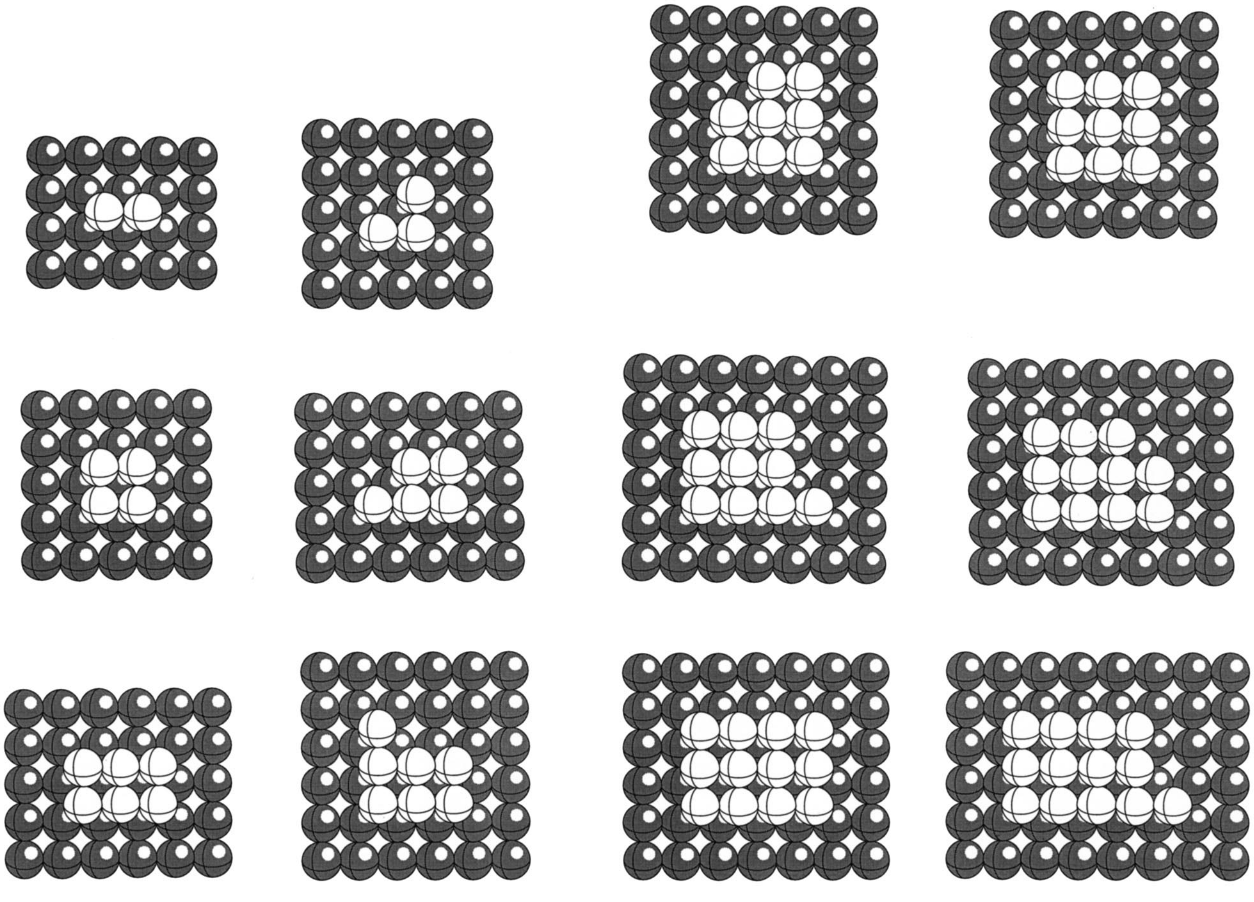

FIG. 2. Schematic diagram of equilibrium geometries of supported Ag clusters. The color code is the same as in Fig. 1.

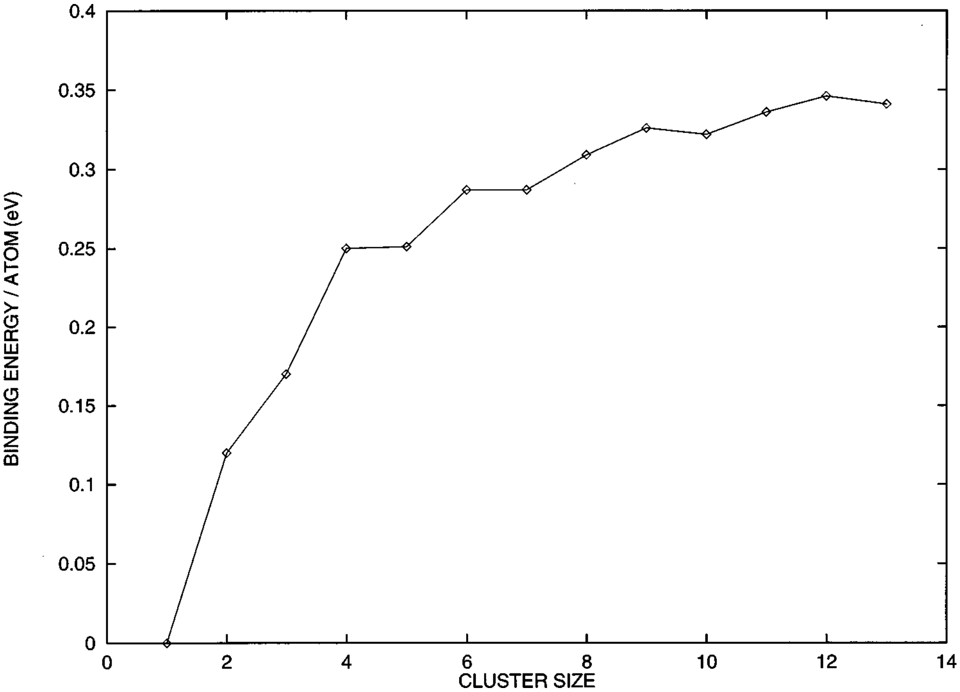

FIG. 3. Plot of binding energy (eV)/atom of supported Ag clusters as a function of size.

layers of the substrate and the clusters to a higher temperature followed by annealing the system back to 0 K. The temperature of the system is increased by rescaling the velocities of the atoms of the cluster and the surface atoms of the top layers. The effect of surface relaxation is studied as described below. This process is carried out for all the clusters.

In Table I we compare the binding energies/atom of small supported Ag_n $(n \leqslant 4)$ clusters obtained using both the molecular-dynamics and KKR methods. For the trimers and tetramers we have tried both the chain and island configuration. Note that the results using the two methods agree very well with each other. In addition, the binding energy/atom for the trimer is not sensitive to the cluster geometry while the tetramer clearly favors a two-dimensional structure. This can be understood qualitatively by counting the average number of first and second near-neighbor atoms for each of the clusters. For the trimer in the chain configuration there are 4 first near-neighbor and 12 second near-neighbor atoms. For the island structures these numbers are respectively 4 and 14. Thus, the binding energies/atom vary little with geometry. For the tetramer, however, the average number of first and second near-neighbor atoms are 6 and 16 for the chain structures and 8 and 20 for the island structure, respectively. Consequently, the increased amount of bonding makes the island structure energetically more preferable over the chain structure. The second important point to note is that the stability of the trimer is essentially the same as that of the dimer—in sharp contrast to the gas-phase clusters where Ag_2 is far more stable than Ag_3. The good agreement between the KKR and molecular-dynamics results in Table I is proof that our molecular-dynamics simulation can provide quantitative results on the relative stabilities of supported clusters. Thus, we have used molecular dynamics method to study the energetics and equilibrium structure of larger Ag_n $(n \leqslant 12)$ clusters systematically.

The *equilibrium* geometries of these supported Ag_n clusters are shown in Fig. 2. We note that none of these clusters form three-dimensional structures. Instead, all clusters have compact two-dimensional geometries. In the gas phase, Ag_n clusters containing four or more atoms have three-dimensional structures. The binding energies/atom of supported clusters as a function of size are shown in Fig. 3. Note that the energies are not a smooth function of size. To better describe the relative stabilities, we plot in Fig. 4 the second difference of the energies shown in Fig. 3. The maxima in this plot indicates enhanced stability while the minima indicates reduced stability. We see that for $n \leqslant 7$, the supported clusters exhibit odd-even alternation in stability just as they do in the gas phase, but for larger clusters the behavior is entirely different. Of particular interest is Ag_8 and Ag_9 clusters. In the gas phase Ag_8 is far more stable than Ag_9 (Ref. 14) due to electronic shell closure effect. The opposite is true for supported clusters. This is due to the interaction of the cluster with the substrate. We will show in the following that the equilibrium geometries of the supported clusters can be used to explain their diffusion behavior.

The structures of Ag clusters on Ag(001) agree with those inferred from an experimental study of Rh_n on Rh(001).[16] The structures of Rh clusters containing 4, 6, 9, and 12 atoms were found to be compact and less mobile. This indicates that the closed packed structures are extra stable. On the other hand, clusters with atoms at the periphery such as 7, 8, 10, 11 (see Figs. 2 and 4) were found to be less stable. Insight into the origin of the relative stabilities of closed packed structures can be obtained by simple bond-counting arguments. For example, let us consider clusters of 5, 7, and 9 atoms. The energy needed to dissociate a 5 atom cluster into a 4 atom cluster and an adatom is equal to the energy required to break one nearest and one next nearest bond. Similar is the case for clusters of 7 and 9 atoms. In contrast, in order to dissociate a 4 atom cluster one has to break two nearest neighbors and one next nearest neighbor bond. Simi-

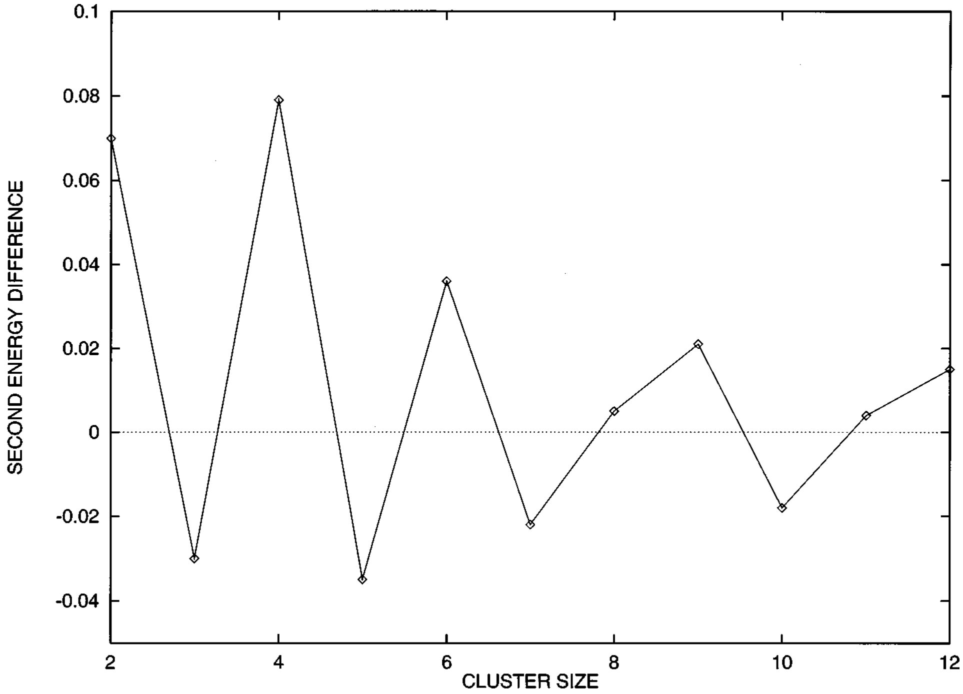

FIG. 4. Plot showing the second-order energy difference in eV of the binding energy $\Delta' E$ as a function of cluster size. The substrate was not allowed to relax.

lar is the case for clusters of 6 and 9 atoms. This illustrates why the compact structures are more stable.

We have also considered the effect of substrate relaxation on cluster geometry and stability. To study the effect of relaxation, atoms in the bottom two layers were fixed at their respective unperturbed bulk positions. The atoms in the top layers as well as those in the cluster were allowed to move. Our dynamical simulation reveals that the top layer of the bare surface (without the adsorbed cluster) contracted by 0.5%. The corresponding experimental value is 1%.[15] We find that the equilibrium geometries of the adsorbed cluster remain unchanged due to substrate relaxation. To examine the influence of substrate relaxation quantitatively, we have recomputed the second energy difference. The results are plotted in Fig. 5. These results agree very well with those in Fig. 4 confirming the weak role of substrate relaxation on relative stability of deposited clusters.

In summary, we have systematically studied the structures and energetics of Ag_n clusters on the Ag(001) surface using a first principle KKR technique and the molecular-dynamics method. Our results show that unlike in free clusters, the relative stabilities of supported clusters are governed by the

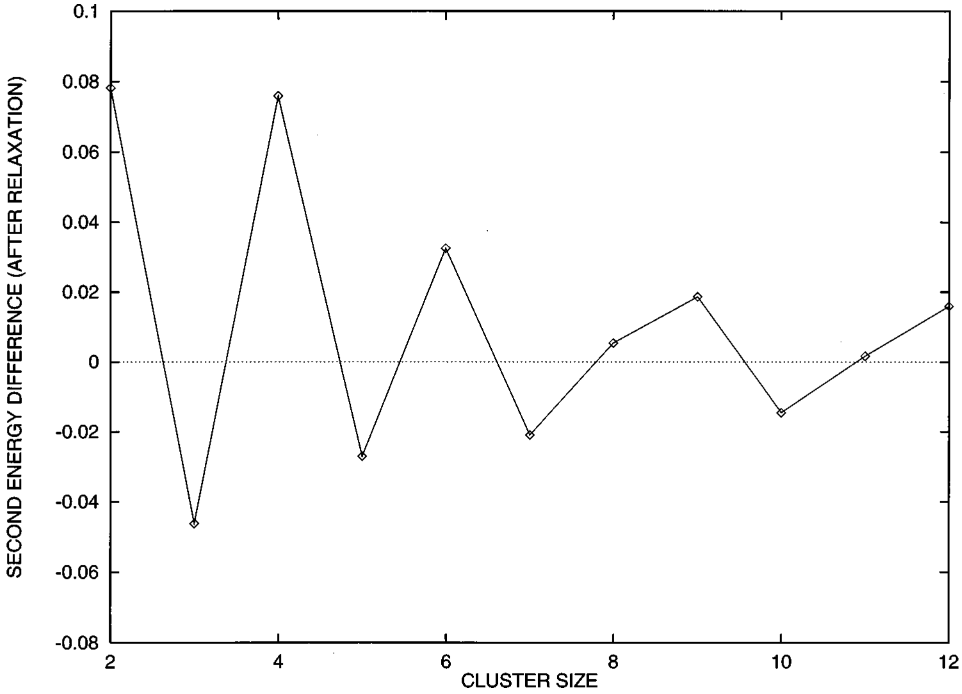

FIG. 5. Plot of second-order difference of the binding energy in eV as a function of cluster size where the substrate was allowed to relax.

underlying substrate structure. This leads to magic numbers for supported clusters that are different from those in the gas phase. We have studied the structures and energies by allowing both the clusters and the substrate to relax and found that the relaxation has no effect on the relative stabilities of supported clusters. The clusters are seen to grow as 2D islands on the surface as opposed to 3D structures in free space. It will be interesting to study the critical size of supported clusters at which the transition from two-dimensional to three-dimensional structures occurs.

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