How "Magic" is a Magic Metal Cluster?

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(Received 18 December 1995)

The stability of a closed-shell metal cluster, Na_8, is studied in a variety of surroundings using *ab initio* molecular dynamics. On the insulating NaCl(001) surface, Na_8 is magic; even at 600 K it retains its intrinsic structure. On the Na(110) surface it spontaneously collapses, forming an epitaxial adlayer. In the vacuum, interaction with another Na_8 cluster destroys its shell structure and a deformed Na_{16} is formed. The results are discussed in a context relevant to cluster-assembled structures.

Physics of small simple metal clusters is governed by the shell structure of the valence electrons, as shown by their size-evolutionary properties, including, e.g., the abundance in the mass spectra, ionization potential, optical absorption spectra, and reactivity [1]. Clusters with a closed major electronic shell are called "magic"; they are characterized by an exceptional stability in the mass spectra, high ionization potential, nearly spherical shape, and reduced reactivity. Because of these properties, closed-shell clusters have been suggested [2–4] as promising building blocks of a new class of materials, where the intracluster interactions overcome the intercluster interactions such as in fullerene materials, in analogy to solids formed by closed-shell rare-gas atoms. Recently, there has been a growing interest also in nanostructured coating of surfaces by cluster deposition [5]. Closed-shell clusters could play a role here by making it possible to use highly size-selective cluster beams for a better control of the coating pattern.

In this Letter we readdress the concept of a "magic cluster" in a context relevant to cluster-assembled structures. We use a molecular dynamics approach based on an *ab initio* description of the electronic structure. We chose Na_8 cluster for the probe to explore the behavior of a magic metal cluster in various environments. Na_8 is ideal for this purpose, since its properties are both experimentally and theoretically well established [1,6–9].

Our results show that the magic nature of the cluster greatly varies with the environment to which it is exposed; an insulating surface [NaCl(001)] induces only minor changes to the electronic structure and the geometry, whereas a metallic surface [Na(110)] or another metal cluster completely destroys the electronic structure, as well as the geometric identity.

The calculations are done using the BO-LSD-MD (Born-Oppenheimer local-spin-density molecular dynamics) method, described in detail by Barnett and Landman [10]. For the simulations which include a semi-infinite substrate, we use a modified version [11] of the method which incorporates the standard supercell technique in the electronic structure calculation. The key ingredients of our calculations are summarized as follows. For the

electronic structure, we treat explicitly the chlorine $3s^2 3p^5$ and sodium $3s^1$ electrons with norm-conserving nonlocal pseudopotentials [12], and the electronic wave functions are expanded on a plane-wave basis with a kinetic energy cutoff ranging from 5.8 to 9.9 Ry, depending on the system. The higher cutoff is used when chlorine is present in the simulation [13]. The Wosko-Vilks-Nusair [14] LSD parametrization for the exchange and correlation energy is used. At each molecular dynamics step, the Kohn-Sham one-particle equations are solved self-consistently using an iterative matrix diagonalization scheme. From the converged solution, the Hellman-Feynman forces to ions are determined, and these forces added to the interionic Coulomb repulsion are used for advancing the ions on the BO potential energy surface with a time step of 3–5 fs. In the MD runs only the cluster atoms are dynamical.

Let us first briefly recall those properties of the Na_8 cluster which are relevant to our study [6–9]. From the few low-energy structure isomers calculated for this cluster, we have chosen the one with a symmetry of a dodecahedron (D_{2d}). Its electronic structure represents a typical magic cluster with a HOMO-LUMO (high occupied molecular orbital–low unoccupied molecular orbital) gap of about 1 eV (1.1 eV with the pseudopotential used in this study [9]); see Fig. 1(a). The gap has been shown to persist at temperatures above 500 K. The electronic structure is rather "rigid," i.e., insensitive to the variations in the ionic configurations, and previous *ab initio* studies seem to indicate that above room temperature the cluster is able to sample various low-lying structure isomers in a typical time scale (≈ 10 ps) of the molecular dynamics simulation. Each of the four occupied states shows an easily identifiable primary angular momentum component, as marked in Fig. 1(a).

In what follows we discuss the stability and the electronic structure of Na_8 in view of results from molecular dynamics runs performed in various surroundings having different electronic properties: an insulating NaCl(001) surface, a metallic Na(110) surface, and a reaction with another magic Na_8 cluster in vacuum.

Na_8 on NaCl(001).—The supercell for the NaCl(100) surface consists of a one-layer slab in the x-y plane with
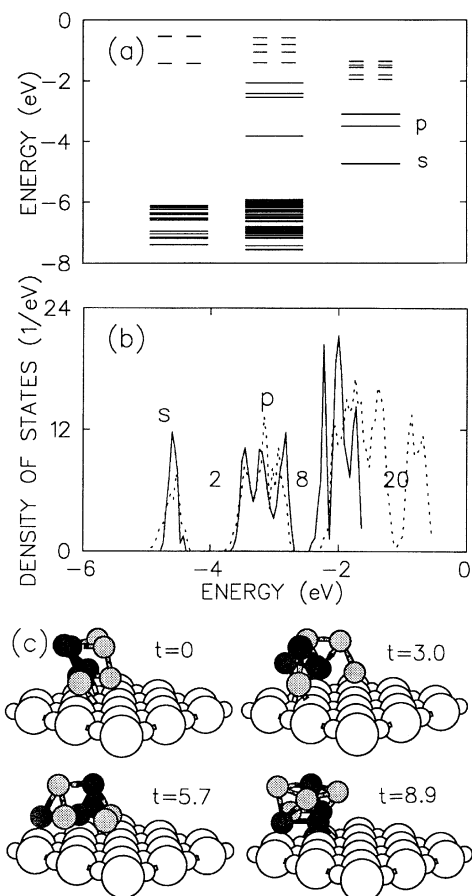
FIG. 1. (a) Kohn-Sham eigenvalues for the NaCl(001) substrate (left), for the relaxed Na_8/NaCl(001) system (middle), and for the free Na_8 cluster (right). The broken lines for energies close to zero correspond to empty levels. The HOMO of the free Na_8 has a twofold degeneracy. (b) The time-averaged distribution $g(\epsilon)$ of KS states for the adsorbed cluster at 350 K (solid curve), and the corresponding distribution for a free Na_8 at 550 K (dotted curve, taken from Ref. [9]). $\int g(\epsilon)d\epsilon$ gives the indicated numbers of electrons for the closings of the major shells. The two curves are shifted for comparison such that the s peaks approximately coincide. (c) Selected snapshots at 600 K. The cluster atoms are shown in black and grey in order to visualize the diffusion process. The unit for time is ps.

(6×6) lattice sites for ions of alternating charge. In the surface plane the nearest-neighbor distance between the unlike ions is 2.82 Å [15]. The supercell dimension in the z direction (thickness of the vacuum region) is 13.2 Å. We initialize the molecular dynamics by relaxing the cluster, brought in the vicinity of the surface, into a local minimum by a quenching molecular dynamics run where the excess heat generated in the relaxation process is taken away by exponential cooling. Only minor changes in the electronic structure are seen in the relaxation process [Fig. 1(a)]; the HOMO-LUMO gap reduces to 0.7 eV, and the two uppermost p states split off due to a slight deformation away from the initial shape of the cluster. An important feature in Fig. 1(a) is that the s state of

the cluster is separated from the "band" formed by the chlorine $3p$ electrons by 2.1 eV. By calculating the local density of states separately for the cluster and the substrate atoms, we see that there is no significant spatial overlap between the cluster and substrate states, and the nature of the adsorption can be characterized as physisorption. The calculated adsorption energy per atom is about 0.4 eV [16].

We have followed the dynamics of the cluster in three microcanonical runs, where the temperature [17] sets at about 350, 600, and 1100 K, with a duration of 9.5, 9.8, and 6.0 ps, respectively. Figure 1(b) compares the distribution of Kohn-Sham (KS) levels associated to the cluster, time averaged over the run at 350 K, to those obtained for a free cluster at 550 K [9]. Noting the difference in the cluster temperature, *the thermally averaged structure of the occupied states of the adsorbed cluster is virtually identical to that of the free cluster.* A similar agreement of the distributions is seen also in the run at 600 K. Figure 1(c) shows selected snapshots at 600 K, and visualizes the atomic diffusion processes taking place. The analysis of the dynamical properties of the adsorbed cluster, such as diffusion constant and the Fourier spectrum of the velocity autocorrelation function, provides further support [16] to the conclusion that the adsorbed Na_8 on NaCl(001) behaves at these temperatures very much like a free cluster. The underlying reason for this is the weakness of the electronic interaction between the cluster and the substrate which manifests itself by the large gap between the corresponding KS states, as discussed above.

The notable thermal stability of the adsorbed cluster in its initial three-dimensional (3D) geometry, obviously related to the 3D closed-shell electronic structure, raises an interesting question about the temperature range in which and the mechanism by which a dynamic transition into a 2D adsorbed structure would take place. Such a transition is made possible by the fact that a 2D structure is necessarily more open, causing the vibrational spectrum to shift into lower frequencies, which lowers the vibrational contribution of the total free energy [18]. The central question is then what is the net result of the competition between the lost intracluster potential energy and the energy gained from the increased interactions to the surface, and how the energy associated to the change in the electronic structure relates to those energies. We immediately see the complex nature of the problem, and obtaining the solution is not possible without a simplified model on the energetics. However, with a direct approach of doing simulations at yet higher temperatures where the transition is directly seen, one can get an estimate of the (upper bound of the) relevant temperature range. Indeed, we have been able to see the transition in a simulation performed at 1100 K, and we have confirmed that the changes in the dimensionality of the geometry and the electronic structure take place simultaneously. For the electronic structure, this requires the closing

of the HOMO-LUMO gap for the 3D shell structure, subsequently, the gap opens again when the 2D shell structure is established [16].

Na$_8$ on Na(110).—The bcc Na(110) surface is modeled with a supercell having a two-layer slab, with (3 × 4) unit cells in the ⟨110⟩ and ⟨100⟩ directions, respectively, with a lattice parameter of 4.23 Å [15] and a vacuum region of 17.2 Å in thickness. The total number of substrate atoms in the supercell is 48. To start the calculations we bring the cluster in the vicinity of the surface such that the closest distance from a cluster atom to the surface plane is 3.5 Å; see Fig. 2. The electronic structure of this geometry is now profoundly different from the case of Na$_8$ on NaCl(001); the cluster states fall within the band formed by the substrate 3s electrons. This is of course what is expected, since the cluster and the substrate are of the same material. Analysis of the local density of states suggests that the cluster and the substrate states are largely overlapping in space, which indicates that drastically different dynamical behavior for the cluster could be expected. In fact, during a similar quenching run, which produced an adsorbed 3D structure on the NaCl(001) surface, the cluster collapses into an epitaxially ordered adatom layer (Fig. 2) without any apparent activation barrier.

Two Na$_8$ clusters in vacuum.—For the final case, we study the reaction between two free Na$_8$ clusters in vacuum. This kind of situation is relevant, for instance, for considerations whether the magic clusters produced in the cluster source remain magic also when interacting with the other clusters in the cluster beam. Here we show that this is not the case, but reactions which result in
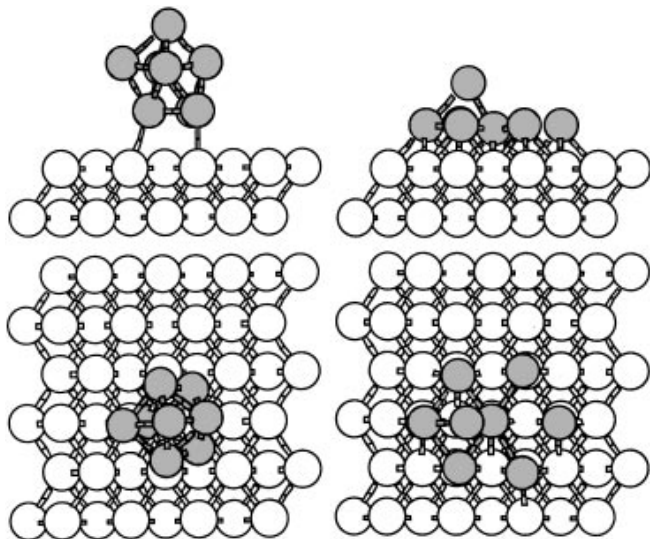
nonmagic deformed clusters are possible within a short time scale.

Initially, we place the two clusters in a rectangular calculational cell with dimensions of 17.2 × 17.2 × 31.0 Å^3 such that their center-of-mass (c.m.) coordinates are separated by 9.5 Å [Fig. 3(a)] [19]. The line joining the c.m. coordinates is close to, but not exactly, the D_{2d} symmetry axis. In this configuration, the closest intercluster atomic distance is 6.5 Å, which is about twice the shortest bond length within the clusters. The separation is large enough for the clusters to retain their magic nature, as confirmed by the calculated electronic structure, which shows simply a doubled closed-shell picture with the degeneracy of every occupied level broken by 0.06 eV at maximum. When the dynamics is turned on (with zero velocities initially), the c.m. distance starts to decrease steadily, followed by a rapid intercluster bonding between 1 and 1.5 ps. At the same time, the electronic structure
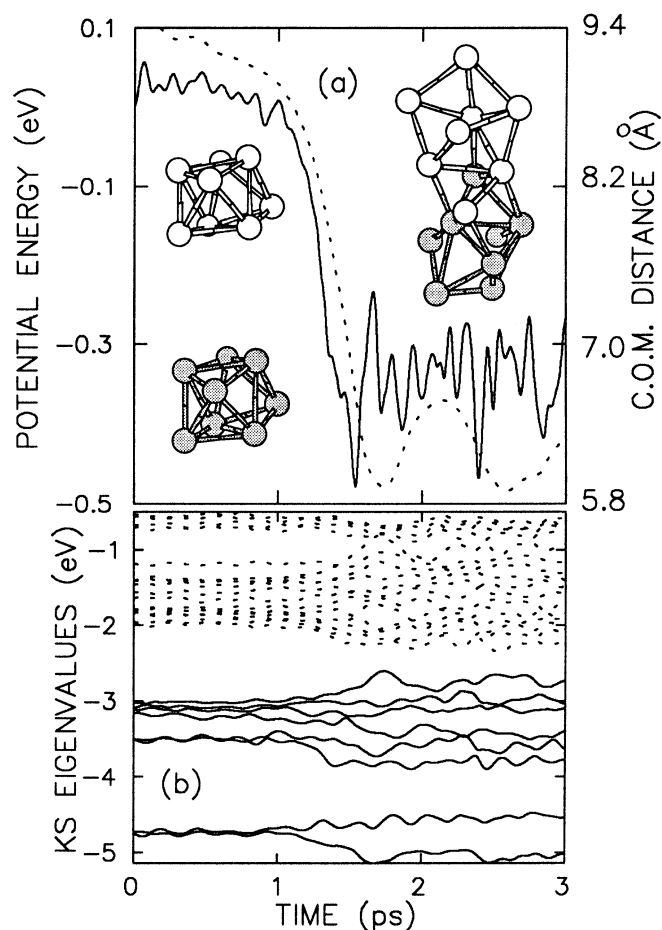

FIG. 2. The initial (left) and the final (right) configuration of the collapse of Na$_8$ on Na(100). Note the epitaxial arrangement of the adatoms at the end of the run (at 2.8 ps). Both side and top views of the two configurations are shown.

FIG. 3. Reaction between two Na$_8$ clusters in vacuum. (a) Time evolution of the total potential energy, relative to its value in the initial configuration (solid curve, scale on the left), and the center-of-mass distance of the two clusters (dotted curve, scale on the right). The two snapshots indicate the initial configuration (left) and the configuration at 2.6 ps (right). (b) Time evolution of the KS eigenvalues. The dotted curves indicate empty states.

changes dramatically [Fig. 3(b)]; one of the nearly degenerate *s* states of the initially separated clusters becomes the *s* state of the resulting Na_{16} cluster, whereas the other one deforms to a *p*-like state along the long axis of the prolate Na_{16}. The gain in the potential energy during the process is about 0.36 eV, which transforms into a vibrational temperature of about 200 K, at which the resulting cluster appears to be stable up to the end of the run. Our result is in agreement with previous tight-binding molecular dynamics studies of cluster-cluster collisions [20].

Previous studies with simple model potentials and the jellium approach suggest [3] that cluster materials could be formed by assembling closed-shell metal clusters in a close-packed lattice like fcc. The results obtained in the present study are at variance with previous conjectures. The formation of stable cluster materials requires basic cluster units that have *both* inert electronic properties *and* a high degree of rigidity in their intrinsic structural degrees of freedom. The first property produces the intercluster *repulsion* at short distances (analogously to the rapidly rising core repulsion between, say, two rare-gas atoms), and the second property is needed in order to retain the identity of the individual cluster units. Obviously, a purely metallic bond is far too flexible and allows a large reorganization of the intracluster bonds [21]. A considerable degree of directional bonding is needed for a cluster to be a successful candidate for a basic unit to form cluster-assembled structures. Nature provides many examples of stable "clusters" by covalently bonded molecules (such as methane or molecular hydrogen), which naturally form condensed phases.

On the other hand, we have obtained a strong indication that a closed-shell metal cluster could be thermally considerably stable when deposited on a substrate which is electronically inert, such as an insulating surface. This indicates that studies of well-defined substrate-supported metal clusters are feasible with a proper selection of the substrate material. In such studies, however, the concentration of the clusters cannot be too high, since reactions which lead to the coalescence to larger adsorbed islands cannot be avoided even for the closed-shell clusters.

In conclusion, our *ab initio* molecular dynamics study shows that the concept of a magic cluster is not meaningful without reference to the the electronic environment to which the cluster is exposed. Closed-shell clusters having purely metallic intracluster bonding are too reactive to form cluster-assembled structures. A clear gap between the electronic states of a cluster and a substrate is required for the deposited cluster to retain its intrinsic structure.

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