Stability, structural transformation, and reactivity of Ga_{13} clusters

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First-principles pseudopotential calculations were performed to investigate the atomic structure, structural transformation, and reactivity of Ga_{13} clusters. Ga_{13} energetically favors a distorted decahedron. The decahedron is more stable than a relaxed icosahedron and a relaxed cuboctahedron by 0.22 and 0.67 eV, respectively. Structural transformations from the cuboctahedron and the icosahedron to the lowest-energy structure need to overcome barrier heights of less than 0.55 and 0.05 eV, respectively. Small activation energies are responsible for the flexibility and floppiness of Ga_{13} clusters. Reactions of the decahedral Ga_{13} cluster with Ga and As atoms induce structural changes of the substrate and produce cohesive-energy gains of 3.65 and 4.71 eV, respectively. Migrations of the Ga and As adatoms on the surface of the Ga_{13} cluster need to go over activation barriers with heights of less than 0.30 and 0.34 eV, respectively.

Clusters are free from the translation symmetry constraints and have unique atomic and electronic properties depending on a type of constituent atoms and a size of clusters.[1] The unique properties might be useful in developing new electronic devices. Clusters usually retain a large fraction of surface atoms, resulting in a large reactivity. This is the reason that a transition-metal cluster acts as a good catalysis. The information on the atomic structure of clusters is essential to understanding the growth mechanism of bulk materials. However, measurable structural properties of small clusters are limited and indirect measurements such as relative abundance, cluster reactivity, ionization potential, and electron affinity are available.[2–4] Therefore, the information on the structure and dynamics of small clusters can only be obtained using indirect measurements and comparison to theoretical results.

Small simple-metal clusters usually favor polyhedral structures. For 13-atom clusters, high-symmetric structures such as cuboctahedrons, icosahedrons, and decahedrons are energetically preferred. Many studies have shown that the icosahedron is generally favored for metal clusters.[5–7] The high stability of decahedrons in Al_{13} clusters was very recently reported.[8] Even though the structure of small clusters has been well studied, their dynamical properties have not been acknowledged yet. Interest in structural transformation, melting, and reactivity increased recently with the development of experimental techniques and the improvement of computational methods. Studies on those properties of small metal clusters have been limited in spite of their importance. One of the processes of particular interest, practical as well as theoretical, is sintering. This is a process in which small particles fuse together under the influence of surface tension forces. The information on structural and dynamical properties of clusters is essential to understanding the process.

In this work, an extensive *ab initio* study of Ga_{13} clusters was carried out to investigate the lowest-energy structure, structural transformation, and reactivity with Ga and As atoms. Since various structures with high symmetry are available for 13-atom clusters, Ga_{13} is considered as a paradigm of clusters with well-defined structures. The results applicable to other metal clusters show how a large fraction of surface atoms and the lack of structural constraints lead to the energetically nearly degenerate structures and structural flexibility. They are responsible for the structural distortion, large reactivity, and floppiness at relatively low temperatures.

Calculations were performed employing Car-Parrinello method based on the pseudopotential method and the local-density-functional formalism.[9] The clusters were placed in the center of supercells large enough for the interaction with images to be weak. Pseudopotentials were generated using Bachelet's code modified by Stumpf *et al.*[10] The Kleinman-Bylander procedure was used to treat the *s* and *p* nonlocal pseudopotentials.[11] Plane waves with less than the cutoff energy of 14 Ry were included in the calculation of kinetic energies. The exchange and correlation contributions to total energy were calculated using Ceperley-Alder exchange-correlation potentials.[12] Geometry optimizations were carried out with the use of both the dynamic relaxation method and the simulated annealing method.[13]

Three competing and high-symmetric structures of the Ga_{13} cluster are the decahedron, icosahedron, and cuboctahedron. Figure 1 shows the optimized structures obtained through total-energy calculations. Distortions from ideal structures are mainly due to a large fraction of surface atoms and electronic effects such as the Jahn-Teller effect. The lowest-energy structure is shown in Fig. 1(a). This structure is substantially distorted but is assumed to be a decahedron rather than an icosahedron. Its total energy is smaller than those of the relaxed icosahedron and cuboctahedron by 0.22 eV (0.0017 eV per atom) and 0.67 eV (0.051 eV per atom). The decahedron and icosahedron are nearly degenerate in total energy. This result agrees with the recent study on Al clusters.[8] In order to evaluate ionization potentials (IP) and electron affinities (EA) of the decahedron and icosahedron, total energies of charged states were calculated using the isolated cluster method.[7] Both structures produce similar IP's and EA's as listed in Table I. It is very difficult to distinguish the decahedron from the icosahedron with experimental data about IP and EA. The calculated IP of the Ga_{13} cluster agrees well with the available experimental result.[14] The IP and EA

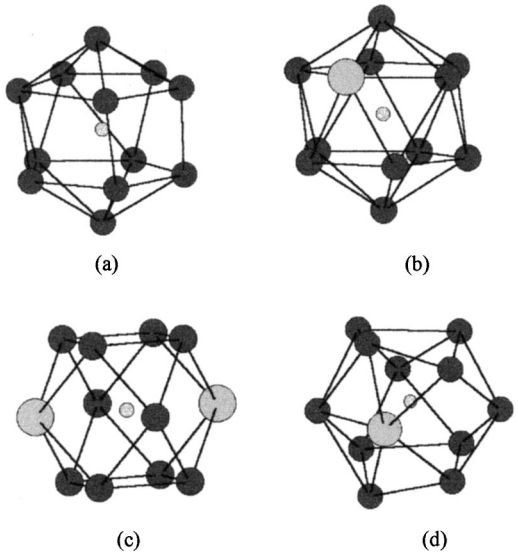

FIG. 1. Atomic structures of (a) the decahedral Ga_{13}, (b) the relaxed icosahedral Ga_{13}, (c) the relaxed cuboctahedral Ga_{13}, and (d) Ga_{13} at the saddle point of the structural transformation from the cuboctahedron to the decahedron. The smallest and largest circles represent the Ga atom located at the center of clusters and the atom forced to move along the chosen direction during barrier height calculations.

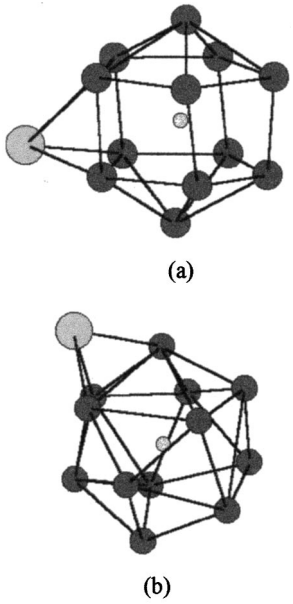

FIG. 2. Atomic structures of (a) the Ga-adsorbed Ga_{13} and (b) the As-adsorbed Ga_{13}. The large circle denotes the adsorbed atom.

of Ga_{13} cluster are smaller than those of the Al_{13} cluster by 0.8 and 0.21 eV, respectively.[7]

Barrier height calculations provide some useful information on the structural transformation, melting, migration of surface atoms, etc. Barrier heights for the structural transformations from the isomer states to the lowest-energy state were investigated using the trajectory calculation method.[15] In the calculations a chosen atom was forced to move along a designed direction, and then the total energies along trajectory were calculated. During calculations, the magnitude of the velocity of the atom along the direction was fixed at 0.25×10^{-4} atomic units and the others were adjusted using *ab initio* forces. Then structural transformations can occur along the lowest-energy trajectory.

This method may overestimate barrier heights, but the small fixed velocity guarantees the accurate calculation. The structural transformation from the relaxed icosahedron to the lowest-energy structure needs to overcome the negligible barrier height of less than 0.05 eV, indicating that the transition can occur at very low temperatures. These two structures can coexist at room temperature because both the difference of total energy between these structures and the barrier height are very small.

The structural transformation from the relaxed cuboctahedron to the lowest-energy structure needs to go over the potential barrier with height of 0.55 eV. The height is relatively small and the transformation can occur at relatively low temperatures. Figure 1(d) shows the atomic structure at the saddle point. Small barrier heights indicate that structural transformations and deformations of the Ga_{13} cluster can occur at relatively low temperatures, and its melting point might be much lower than room temperature. Other paths for structural transformation were investigated. But much higher activation energies were required for structural transformation along those paths. For example, a path where two atoms are simultaneously forced to move along designed directions needs to go over much larger barrier height of 1.76 eV during the structural transformation from the cuboctahedron to the decahedron.

TABLE I. Ionization potentials and electron affinities of decahedral and icosahedral Ga_3.

	Ionization potential (eV)	Electron affinity (eV)
Decahedron	6.35	3.60
Icosahedron	6.37	3.57

The reactivity of the Ga_{13} cluster with Ga and As atoms was investigated. A single Ga atom is adsorbed on the center of the square of the distorted decahedron. The adsorption produces a heat of 3.65 eV and results in a structural change of the substrate Ga_{13} from the distorted decahedron to more ideal-like decahedron as shown in Fig. 2(a). In contrast to the Ga adsorption, a single As atom favors the center of the triangle as shown in Fig. 2(b) and the adsorption induces a structural change of the substrate from the distorted decahedron to a distorted icosahedron. The adsorption produces a cohesive energy gain of 4.71 eV. The exchange of As and substrate Ga atoms is energetically prohibited. The As adsorption favors a low-coordinated site compared to the Ga adsorption. Same trend was observed in the study of small GaAs clusters. Ga atoms intend to aggregate together in the center of clusters and As atoms try to locate at the surface of clusters in small compound GaAs clusters.[16] The energy difference between the most stable adsorbed structure and an exchanged structure was found to be less than 0.33 eV. Surface migrations of the adatoms were investigated through the trajectory calculation. The barrier heights of surface migrations of the Ga and As adatoms are less than 0.30 and 0.34

eV, respectively. Surface diffusions of Ga and As atoms can easily occur at relatively low temperatures.

In summary, structural and dynamical properties of Ga_{13} clusters were investigated as a paradigmatic study. There are two nearly degenerate structures, the decahedron and icosahedron, in total energy. Barrier height calculations on the structural transformation between high-symmetric structures show that Ga_{13} cluster is very flexible and the structural transformation can easily occur in relatively low temperatures. The adsorption of Ga and As atoms on the distorted decahedral Ga_{13} cluster results in the structural change of the substrate Ga_{13} from the distorted decahedron to structures closer to the more ideal-like decahedron and the distorted icosahedron, respectively. The adsorbed Ga and As atoms can diffuse on the surface with relatively low barrier heights

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