



## Original article

Density functional theory calculations of lithium alloying with Ge<sub>10</sub>H<sub>16</sub> atomic cluster

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## ABSTRACT

We exploited a hydrogen-passivated germanium atomic cluster (Ge<sub>10</sub>H<sub>16</sub>) as a model to study the mechanism of lithium alloying with germanium. Based on the density functional theory, the electronic and crystal structures of lithium-alloyed Ge<sub>10</sub>H<sub>16</sub> were investigated. The theoretical results indicate that the alloying of lithium with Ge<sub>10</sub>H<sub>16</sub> will weaken the germanium-hydrogen bond and repel the closest germanium atom away from the alloyed lithium atom. Based on the maps of the electron density distribution, the nature of the lithium-germanium chemical bond was analyzed. Moreover, the diffusion process of the lithium on the Ge<sub>10</sub>H<sub>16</sub> cluster was detected, which suggested that there is a close relationship between the diffusion barriers and the coordination number around the lithium atom.

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## 1. Introduction

An atomic cluster consisting of three to a few tens of atoms is an intermediate state of matter. The novelty of an atomic cluster mostly arises from the fact that its physical and chemical properties usually explain the transition from a single atom to the solid-state, which has been proved and studied by modern experimental techniques [1]. The science of clusters is a highly interdisciplinary field concerning astrophysicists, atomic physicists/chemists, solid-state physicists, nuclear physicists and as well as plasma physicists. Because of the strong dependence of its electronic properties on its size and crystal structure, atomic clusters provide exciting prospects for designing new materials. It may also serve as a model to elucidate the chemically reactive sites on the surface. Studies of the chemistry and physics that occurs on the surface of the atomic cluster provide a new way to investigate surface reaction processes. This research may generate further insight into the fundamental steps that make up the complicated chemical processes taking place on the solid surface.

Silicon (Si) atomic clusters (Si<sub>n</sub> with  $n < 12$ ) have been extensively investigated owing to their wide applications in nanoelectronic devices [2,3] and as anode materials for lithium-ion batteries (LIBs) [4]. Previous results demonstrated that Si<sub>6</sub> and Si<sub>10</sub> clusters are energetically stable [5–9]. In contrast, as a congener,

the investigation of electronic properties of germanium (Ge) atomic clusters was rarely reported. Ge is one of the most important alternatives to Si applied either in semiconducting electronic devices or LIBs, since it has superior electron/hole and lithium (Li) ion mobility at room temperature than Si because of its lower band gap [10–12].

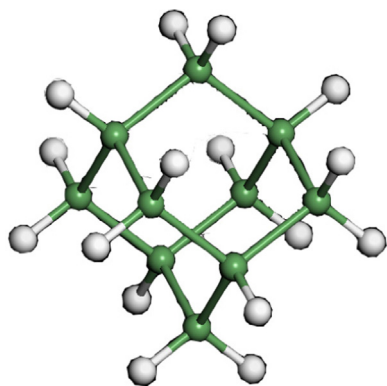
Owing to its high theoretical capacity (1623 mA h/g) by formation of Li<sub>4.4</sub>Ge with Li and high volumetric capacity of 7366 A h/L, Ge has been widely utilized as the anode electrode for LIBs [13,14]. However, the dynamic process and electronic interaction between Li and Ge atoms still remain unknown. An understanding of the structure and electronic properties of Li-alloyed Ge atomic cluster is thus helpful to explain the phenomena such as surface chemistry and reaction processes during Li alloying with Ge electrode, since in the atomic cluster most of the atoms can be regarded as sitting at the surface. The aim of this article is to study the effects of surface alloying of the Li atom on the crystal structure and the electronic properties of the Ge<sub>10</sub>H<sub>16</sub> cluster. This knowledge can be very useful in understanding the chemical reactions of Li with Ge when Ge is applied as an anode material for LIBs.

## 2. Model and calculation method

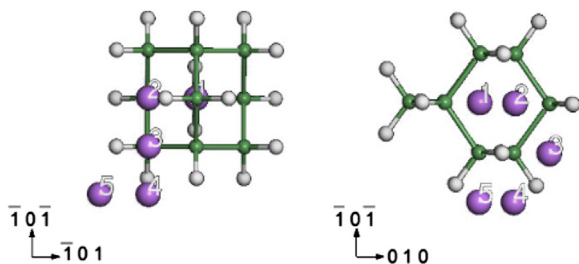
The atomic structure of the Ge<sub>10</sub>H<sub>16</sub> cluster is shown in Fig. 1, which was then placed in a cubic cell with periodic boundary situations to investigate the influence of Li alloying on its electronic and crystal structures. The Li atom was located firstly

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**Fig. 1.** Atomic structure of the  $\text{Ge}_{10}\text{H}_{16}$  cluster, Ge and H atoms are represented with green and white balls, respectively.



**Fig. 2.** Five different  $T_d$  sites for the Li atom (labeled as 1, 2, 3, 4 and 5) in the  $\text{Ge}_{10}\text{H}_{16}$  cluster. The left is a cross view and right is side view of Fig. 1. The Ge, H, and Li atoms are indicated with green, white, and purple balls, respectively.

at the tetrahedral ( $T_d$ ) sites of the cluster due to energetical priority. Then, we calculated five different  $T_d$  sites for the locations of Li atom as shown in Fig. 2. We discussed the Mulliken populations including the atomic populations and band populations, calculated the density of states (DOS), partial DOS (PDOS), and difference in charge density. Finally, we employed complete linear synchronous transit (LST)/quadratic synchronous transit (QST) calculations with convergence thresholds to study the root mean square (RMS) forces on the atoms lower than  $0.05 \text{ eV/\AA}$ .

The calculations were performed using the Vienna Ab initio simulation Package (VASP) based on the density functional theory (DFT) with generalized gradient approximation (GGA) [15]. The  $k$ -point mesh of  $1 \times 1 \times 1$  (Gamma) was generated by the Monkhorst–Pack sampling scheme. To eliminate the interactions, the space between the cluster and its replica was beyond  $17 \text{ \AA}$ . Ultrasoft pseudopotential with a plane wave cutoff energy of  $330 \text{ eV}$  was applied to model the interactions between core electrons and ions. Valence state electrons studied in this work include Ge  $4s^2 4p^2$ , H  $1s^1$ , and Li  $1s^2 2s^1$ . The Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm is utilized for relaxing the internal coordinates with the convergence criterion for force less than  $0.01 \text{ eV/\AA}$  and the energy change  $5 \times 10^{-6} \text{ eV}$ . During geometric optimization, the stress was less than  $0.02 \text{ GPa}$  and the maximum displacement was  $0.0005 \text{ \AA}$ .

### 3. Results and discussion

The full geometric optimization of the atomic cluster results in a tetrahedral structure as shown in Fig. 1, in which the Ge–Ge bond length is  $2.44 \text{ \AA}$ , a value close to the experimental Ge–Ge bond length found in amorphous Ge nanoparticles ( $2.46 \text{ \AA}$ ) [16]. The distances of Ge–H bonds are  $1.551 \text{ \AA}$  for  $\text{Ge}_3\text{–Ge–H}$  and  $1.546 \text{ \AA}$  for  $\text{Ge}_2\text{–Ge–H}_2$ . Then we calculated the Mulliken charge, bond population, and band structure of the  $\text{Ge}_{10}\text{H}_{16}$  cluster, as provided in Table 1. The Mulliken charge suggests the degree of charge

**Table 1**

Mulliken charge, bond population, total energies ( $E_{\text{tot}}$ ) and band gap of the  $\text{Ge}_{10}\text{H}_{16}$  cluster.

Charge (e)		Bond population		$E_{\text{tot}}$ (eV)	Band gap (eV)
Ge	H	Ge–H	Ge–Ge		
0.12, 0.2	−0.10, −0.09	0.78, 0.68	0.62	−1325.26	3.67

transfer between Ge and H atoms, which obviously indicates that the charge density transfer from the Ge atoms to the H atoms. This is due to the electronegativity of H (2.20) which is higher than that of Ge (2.01), and draws the Ge electrons to the lower energy level. Bond population is an accepted method to investigate the bonding properties between a pair of atoms. The results reported in Table 1 show that the bonding characteristics of both Ge–H and Ge–Ge are covalent. The system total energy ( $E_{\text{tot}}$ ) and band gap are calculated to be  $-1325.26$  and  $3.67 \text{ eV}$ , which are very close to those of the  $\text{Si}_{10}\text{H}_{16}$  cluster [4]. The energy gap is fundamentally important for the physical and chemical properties of a solid on which most behaviors of material depend, such as intrinsic conductivity, electronic transitions, and optical transitions. One may note that the band gap of the atomic cluster is much larger than the Ge crystal that is about  $0.67 \text{ eV}$ . This occurs when the size of a solid is reduced to the nanometer or atomic length scale. Energy gap values more than triple the size of crystalline Si have been reported for nanoscale Si particles [17,18]. Calculations for the small Si quantum dots and Si nanostructures have predicted a considerable opening of the band gap up to an energy of  $4 \text{ eV}$  [19], in addition, when the size of a solid decreases to an atomic scale, the effects such as structural change, lattice contraction, atomic relaxation, surface reconstruction, or surface passivation will greatly alter its energy gap. For example, calculation of the Ge clusters with different numbers of atoms give band gap values of  $1.35 \text{ eV}$  for  $\text{Ge}_{10}$ ,  $1.84 \text{ eV}$  for  $\text{Ge}_9$ , and  $2.64 \text{ eV}$  for  $\text{Ge}_8$  [20]. In our calculations, due to the surface passivation of H, the energy gap is much wider than  $2.64 \text{ eV}$ , which indicates that the observed photoluminescence radiation is not only due to the size dependent quantum confinement, but also to the surface state transitions.

We then studied all the  $T_d$  positions (labeled with 1–5) for the locations of the Li atom as indicated in Fig. 2. The binding energy ( $E_b$ ) is defined as,

$$E_b = E_{\text{Ge}} + E_{\text{Li}} - E_{\text{tot}} \quad (1)$$

where  $E_{\text{Ge}}$  is the energy of pristine  $\text{Ge}_{10}\text{H}_{16}$  cluster,  $E_{\text{Li}}$  is the energy of the isolated Li atom, and  $E_{\text{tot}}$  is the energy of Li-alloyed  $\text{Ge}_{10}\text{H}_{16}$  cluster. By this definition, the higher value of  $E_b$  suggests the stronger binding of Li to the cluster. It is easy to determine from Table 2 that the  $E_b$  is highest when the Li atom is located at the site 3 and the lowest at site 1. The coordinate number is also provided in Table 2 in which we found that the number of neighboring Ge atoms may have a strong effect on the Li interstitial space. The  $E_b$  is the highest when the Li coordinate Ge number is three, while when the Li is located at site 1 with four coordinate Ge atoms, the  $E_b$  is lowest, which means it is energetically unstable. This could be a result of the large radius of the Li atom, which is bigger than the

**Table 2**

The record of the calculated binding energies ( $E_b$ ) and corresponding coordinate number when the Li atom locates at the five various  $T_d$  sites in Fig. 2.

Site	$E_b$ (eV)	Coordinate number
1	0.018008	4
2	0.667678	3
3	0.744799	3
4	0.402058	2
5	0.262325	1

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