Stable stacked structures built from Ge_{10} subunits

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Abstract:-We have investigated the stacked structures built from a tetracapped octahedron of Ge_{10} cluster by using the full-potential linear muffin-tin orbital molecular-dynamics (FP-LMTO-MD) method. It is found that the stacked structures built from Ge_{10} subunit up to 80 atoms are stable. Of all the stacked structures, Ge_{30} cluster is the most stable. Besides, the compact structure built from four Ge_{10} subunits has also large binding energy. It is more interesting that Ge_{20} cluster including two Ge_{10} subunits has three stable states as the bond length between them increases.

Key-Words:- germanium, clusters, binding energy, structure, subunit

1 Introduction

Semiconductor clusters have been the focus of numerous experimental and theoretical investigations for the potential application in the semiconductor industry. Theoretically, small Ge_n clusters have been investigated considerably due to lesser cost of calculations in comparison with large clusters. Antonio et al. have investigated the ground-state structures and finite temperature properties of the Ge clusters in range n=2-14, using molecular-dynamics simulation along with the method of steepest decent quench, in which the interaction potential is the Stillinger-Weber potential as modified by Ding and Andersen [1-2]. Ogut and co-worker have studied the electronic structures of the neutral and charged Ge_n clusters (n=2-10), using Langevin molecular dynamics coupled to a simulated annealing procedure [3], and explained the substantial differences in the photoemission spectra of some anionic Si and Ge clusters. Shvartsburg and co-workers have performed a systematic ground state geometry search for the neutral Ge_n clusters and their cations in the n≤16 size rang using density functional theory-local density approximation and gradient-corrected method [4]. For the Ge clusters with n=11-25, Wang et al have reported their ground-state structures obtained by using density functional theory (DFT) with a generalized gradient approximation (GGA) [5]. Their results suggest that there are some similarities between the Si and Ge clusters although many differences are presented.

Experimental results show that the mass spectra of Ge_n are nearly the same as that of Si_n, with "magic numbers" for the cations at n=4,6, and 10 [7,8]. But, photoelectron spectra (EPS) for Si^-_{10} and Ge^-_{10} are quite different [3,9]. The global minimum based on LDA is the C_{3v} tetracapped trigonal prism for Si^-_{10} while the C_{4v} bicapped tetragonal antiprism for Ge^-_{10} [3]. The structures of the Ge_n and Si_n clusters for n=13 and n≥15 differ in details [4]. Ion mobility measurements have confirmed the difference [10,11]. Fuke and Yoshida examined the photoionization thresholds of Ge_n (n=2-34) with a wide photon energy (5.0-8.6 eV) using a laser photoionization time-of-flight mass spectrometry [12]. They found a characteristic size dependence of ionization potential (IP) with a maximum at n=10 for the clusters smaller than 22 atoms. The rather high IP of Ge_{10} in comparison with its neighbors is consistent with the results on the photodissociation study of Ge^+_{10}. The experimental results indicate that Ge_{10} is more stable than its neighbors. The Ge^+_{10} cluster is a favored neutral product [12]. Obviously, the Ge cluster with 10 atoms is an important and interesting cluster. We have also investigated some Ge_n (n=3-10, 20-25) clusters by using full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method [6,13-14]. Some new isomers that are lower in energy than any previously reported have been found.

Although the ground state structures of the small Ge_n clusters have been extensively investigated, our knowledge of the Ge_n clusters is still very limited in comparison with semiconductor silicon clusters. Some

results, for example, the ground state structures of the neutral and anionic Ge_{10} clusters, are controversial theoretically. Langevin molecular dynamics method coupled to a simulated annealing procedure suggests that the tetracapped trigonal prism (C_{3v}) and the bicapped tetragonal antiprism (D_{4d}) are the most stable structures of the neutral Ge_{10} and anionic Ge^{-}_{10} clusters, respectively [3]. Their different photoemission spectra are resulted from the structural change upon charging. However, FP-LMTO-MD method produces different results. The tetracapped octahedron with T_d and the tetracapped trigonal prism (C_{3v}) are the ground state structures of the neutral Ge_{10} and anionic Ge^{-}_{10} clusters, respectively [15]. Another distorted tetracapped trigonal prism (C_s) has the same stability as the C_{3v} structure for Ge^{-}_{10}. The C_s structure has a small gap. The photoelectron spectrum of the Ge^{-}_{10} ion observed experimentally can be explained as the mixed results of the two structures.

Recently, Greytak and co-workers have studied that growth and transport properties of complementary germanium nanowire field-effect transistors (FET) experimentally [16]. n-and p-type Ge nanowires were synthesized by a multistep process. Complementary FETs made from these nanowires show high transconductances and excellent ohmic contacts. C, Si and Ge belong to the group IV in the period table. Both chains, fullerene cages and nanotubes for carbon, and nanowires for silicon and germanium exhibit novel physical and chemical properties. Using the FP-LMTO-MD method, we found that tricapped tetragonal prism (TTP) subunits can stack thin and short stable silicon structures [17]. Motivated by these results, we would investigate stacked structures for Ge in this letter theoretically. It is found that the ground state tetracapped octahedron subunit of the neutral Ge_{10} cluster can form a thin-stacked stable structure, whereas the structure is unstable for Si. The investigation helps us understand the growth mechanism and fragment pattern of the Ge clusters.

2 Method

The FP-LMTO method is a self-consistent implementation of the Kohn-Sham equations in the local-density approximation [18-20]. During the molecular-dynamics calculations, space is divided into two parts: non-overlapping muffin-tin (MT) spheres centered at the nuclei, and the remaining interstitial region. LMTOs are augmented Hankel functions inside the MT spheres, but not in the interstitial region [20-23]. Self-consistent filed calculations are carried out with a convergence criteria of 10^{-5} a.u. on the total energy and 10^{-3} a.u. on the force. In the local density approximation, the calculated bond lengths can be expected to be reliable to within 1-2%. The details of how the molecular dynamics method can be performed are described in references [20-23].

3 Results and discussion

An adamantine cage with T_d symmetry is a piece of the bulk diamond structure. We can obtain a much more stable structure though distorting the cage by elongating it along its fourfold vertices so that its twofold vertices could begin to participate in more than two bonds. The distorted structure is just the tetracapped octahedron (T_d symmetry), which is regarded as the ground state structure of the neutral Ge_{10} cluster, shown as 10A in Fig.1. Its binding energy per atom is 3.625 eV.

By using the T_d structure as stack subunit, we can obtain a series of stable stacked structures. The structures are shown as 20A-80A in Fig.1. Their common structural characteristic is that only one bond ties two neighbor subunits. The ground state structure of Ge_{20} cluster is just built from two such subunits [14]. Further calculations suggest that its symmetry, the bond length between two subunits, and its total binding energy are D_{2d}, 3.12 A° and 72.91 eV, respectively. Besides, the binding energy between the upper subunit and the lower subunit is only 0.30 eV. The result suggests that the two subunits are bound loosely, and the bond between them is easy to break. It is more interesting that 20A has other two energy minimums as the bond length between two subunits changes. The two stable positions correspond to 2.82 A° and 4.21 A°, respectively. Their corresponding binding energies are 72.88 eV and 72.83 eV, respectively.

On the other hand, if the upper subunit in 20A rotates 90° in relation to the lower subunit, the stacked structure is meta-stable. It is easy to transfer into 20A because the potential barrier height between them is only 0.03 eV. Why is there such a small interaction between the two subunits? In fact, the subunit (T_d) is a compact structure, in which there is a cumulative atomic dipole moment at the atom connected into another subunit [24]. The orientation of the atomic dipole moment refers to an axis through the center of

mass of the subunit and the atom connected. The two subunits are bound loosely through atomic dipole moments.

Furthermore, if more subunits are stacked along z-axis, longer stacked structures up to 8 subunits can be obtained. We do not investigate the stacked structures with more than 8 subunits because of too much time-consuming calculation. But, their basic structural property is similar. Our calculations show that the thin-stacked structures are stable. For Ge_{30} cluster, its binding energy per atom is 3.645 eV, which is largest among the thin-stacked structures. It is found from observing 30A in Fig.1 that the bond length (3.09 A°) between the top subunit and the mid subunit is not equal to the bond length (3.15 A°) between the bottom subunit and the mid subunit. The asymmetry can be also found in all the other thin-stacked structures. 40A, 50A, 60A, 70A and 80A in Fig.1 are the stacked structures of Ge_{40}, Ge_{50}, Ge_{60}, Ge_{70} and Ge_{80}, respectively. The bond lengths between any two neighboring subunits are also shown in Fig.1. There are three such single bonds among four subunits in 40A. The middle bond length is 3.24 A°, which is larger than the other two bond lengths. It is interesting that all the longest bonds are located in their middle position in every stacked structure of 50A, 60A, 70A and 80A. The longest bond ties two parts. One part consists of three subunits; the remainder subunits build another part. This maybe relate to the larger binding energy of the thin-stacked structure of Ge_{30}. Besides, all the bond lengths between the subunits are larger than the bond lengths in the subunit 10A. For Ge_n (n=30-80), the shortest bond length tied two neighbor subunits is 2.96 A° (their average value is 3.08 A°), whereas the average bond length in any subunit is only 2.66 A°. This suggests that the thin-stacked structures are easy to fragment into Ge_{10} subunit. According to the discussions above, the stacked structures firstly fragment into two parts. One part of which is the stacked structure of Ge_{30}. Because of its asymmetry, Ge_{30} would fragment into Ge_{20} and Ge_{10} again. Finally, Ge_{20} fragments into two Ge_{10} subunits.

Zhang and co-workers have investigated photodissociation of semiconductor positive cluster ions [25]. The larger Ge_n^+ species show a fragmentation corresponding to loss of Ge_{10} and to some extent Ge_7. Ge_{30}^+ fragments at low fluence to produce almost exclusively Ge_{20}^+ presumably by loss of neutral Ge_{10}. At higher fluence, Ge_{10}^+ appears presumably by stepwise loss of Ge_{10} from Ge_{20}^+. Obviously, we can explain the experimental results by using the stacked structures.

In order to investigate the stability of the stacked structures, we search for the ground state structure of Ge_{30} cluster. It is found that 30B, which is 1.26 eV more stable than 30A, is the most stable structure of Ge_{30} cluster. It also consists of three such subunits. But it undergoes obvious structural distortion. 40B in Fig.2 consists of four subunits, forming a ring. Its binding energy per atom is up to 3.653 eV, which is larger than 3.641 eV of 40A in Fig.1. The subunits in 40B undergo slight structural distortion compared with 10A. 40C is a prolate structure. It is also not so stable as 40B.42A and 48A are obtained by adding some Ge atoms on the top and bottom positions of the hollow site in 40B. The subunits in 42A and 48A have significant structural distortion. But, their stability decreases. 60B is obtained by adding two subunits on the top and bottom positions of the hollow site in 40B. 60B is 5.88 eV less stable than 60A.

The ground state structures of the neutral Ge_{20} and Ge_{30} clusters are stacked from the ground state structure of the Ge_{10} cluster. The thin-stacked structure of the Ge_{40} cluster is not the most stable. But, the ring structure built from the Ge_{10} subunit has also larger binding energy. Calculations show that the ring stacked structures for Ge_{50} and Ge_{60} clusters are not stable. Besides, it is found that the stability of the thin-stacked structures decreases as the number of the stacked subunits increases. Therefore, the ground state structures of Ge_n clusters adopt other geometrical configurations. For Si_n clusters, similar properties have been found [17]. The tricapped trigonal prisms (TTP subunit) can build the thin-stacked structures for the Si_n clusters. They include five TTP subunits at most. For the Ge clusters, they can include eight tetracapped octahedron subunits at least. But, more subunits also destabilize the stacked structures.

By using the FP-LMTO-MD method, we have investigated the structural characteristics of anionic Si_n clusters as the atomic number increases. We found a structural transition to more compact geometries at n=27 for anionic Si_n clusters [26]. The conclusion is verified by experiment this year [27]. The transition begins at n~65 for Ge_n clusters [28-29]. The transition at different size makes them have different stacked

length.

4 Conclusions

The stacked structures built from the ground state structure of the Ge_{10} cluster have been investigated. It is found that the thin-stacked structures are stable up to eight subunits. The stacked structures with two and three subunits are the most stable structures, respectively. The ring structure with four subunits exhibits high stability. But, the longer stacked structures are not the lowest energy structures. On the other hand, they are easy to break two parts because they are not symmetry structures. Our calculations show that the Ge_{20} cluster consisting of two subunits has three stable structures as the bond length between them changes.

Acknowledgments

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Fig.1: The ground state structure of the Ge_{10} cluster and its thin stable stacked structures up to 8 subunits. The numbers between two neighboring subunits presents their bond lengths (in A°).

Fig.2: The other stable structures for the Ge_{42}, Ge_{48} and Ge_{60} clusters built from the Ge_{10} subunit.

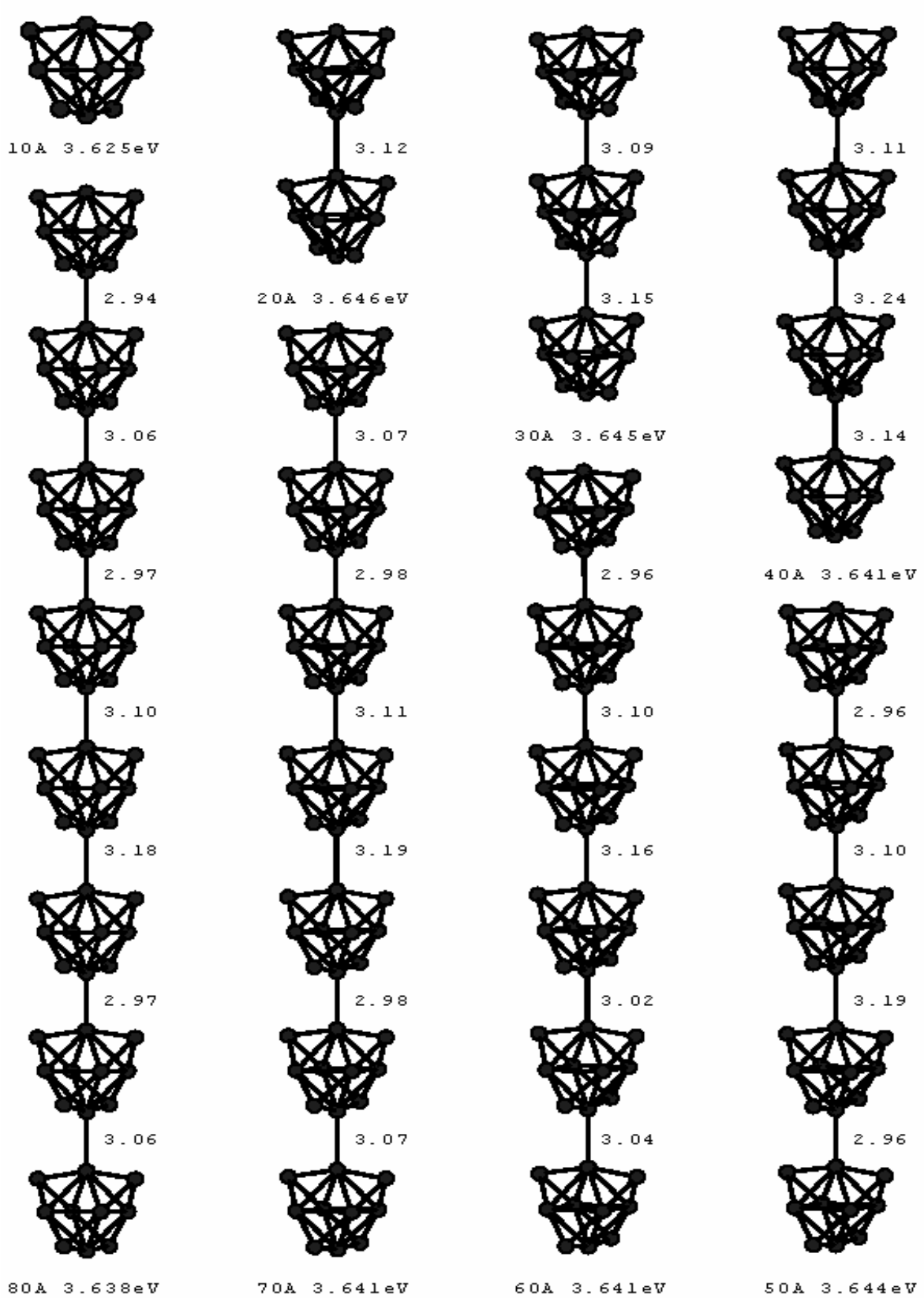
10A 3.625eV
2.94
3.06
2.97
3.10
3.18
2.97
3.06
80A 3.638eV
3.12
20A 3.646eV
3.07
2.98
3.11
3.19
2.98
3.07
70A 3.641eV
3.09
3.15
30A 3.645eV
2.96
3.10
3.16
3.02
3.04
60A 3.641eV
3.11
3.24
3.14
40A 3.641eV
2.96
3.10
3.19
2.96
50A 3.644eV

Fig.1

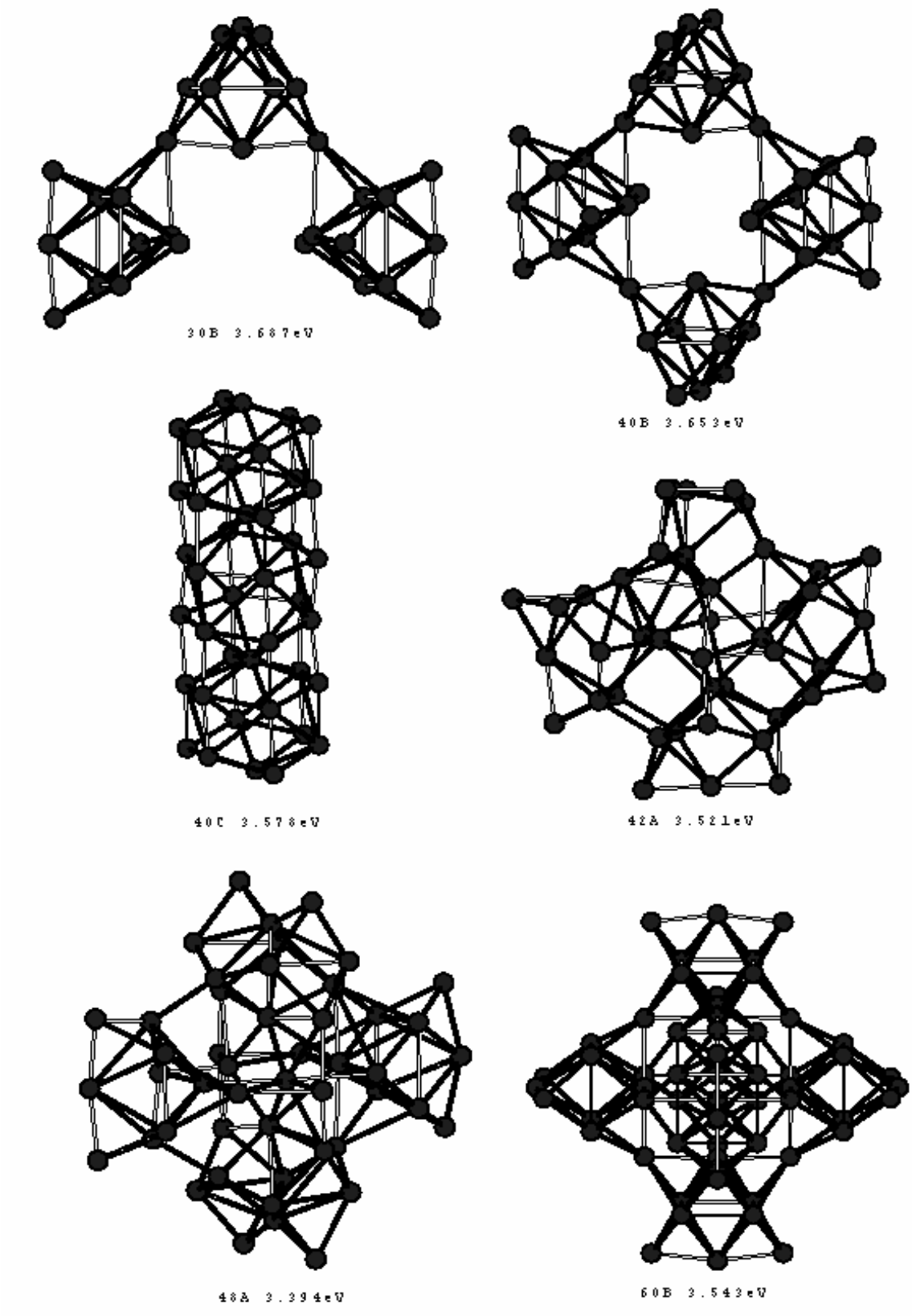
30B 3.687eV
40B 3.653eV
40C 3.578eV
42A 3.521eV
48A 3.394eV
60B 3.543eV

Fig. 2