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Density functional investigations for geometric and electronic properties of In_4M and $In_{12}M$ (M = C, Si, In) clusters

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First-principle calculations are performed to study geometric and electronic properties of both neutral and anionic In_4M and $In_{12}M$ (M = C, Si, In) clusters. In_4C and In_4Si are found to be tetrahedral molecules. The icosahedral structure is found to be unfavourable for $In_{12}M$. The most stable structure for $In_{12}C$ is a distorted buckled biplanar structure while for $In_{12}Si$ it is of an In-cage with the Si located in the centre. Charge effect on the structure of $In_{12}M$ is discussed. In_4C has a significantly large binding energy and an energy gap between the highest-occupied molecular-orbital level and the lowest unoccupied molecular-orbital level, a low electron affinity, and a high ionization potential, which are the characters of a magic cluster, enriching the family of doped-group-IIIA metal clusters for cluster-assembled materials.

Keywords: atomic cluster, geometric configuration, electronic properties, stability
PACC: 3640B, 7125W, 7115M

1. Introduction

The structure and the stability of atomic cluster have been important subjects in cluster science. In 1984 the electronic shell structure observed experimentally in alkali metal clusters was successfully explained by using a simple phenomenological model named a spherical jellium model[1] in which valence electrons move freely in an effective electrostatic potential provided by ionic cores and the other valence electrons. Then, the electronic shell was observed in anionic and cationic aluminium clusters.[2−4]

Over the past few years, doped aluminium clusters have received much attention.[5−23] As the pure neutral Al clusters cannot satisfy the closed electron shell, one can dope the pure clusters with a suitable atom, such as doping Al_{12} with a tetravalent atom[5−9] or doping Al_{13} with a monovalent atom[10−15] to obtain a neutral magic cluster, which can serve as building blocks for cluster-assembled materials. Aluminium and indium belong to the same group in the periodic table, and mass spectra of pure or doped clusters of the two elements display many similarities.[24−27] For instance, there is a substantial drop in IP between In_{13} and In_{14}, suggesting the presence of a 40-electron shell closing,[26] just as for aluminium. However, it was shown that inner electronic shell had a significant effect on the structure and other physical properties of clusters.[28] Given the difference in inner electronic configuration between Al and In atoms, it is of interest to investigate the structures, stabilities, and electronic properties of In-doped clusters and to compare the results with those of Al-doped clusters. Moreover, there have been reported few studies about magic indium-doped clusters so far. Thus, this study would also be helpful for developing novel cluster materials. In this work, we perform first-principles calculations on neutral and anionic In_4M and $In_{12}M$ (M = In, C, and Si) clusters to investigate their structures and electronic properties in hopes of exploring the possible magic clusters for cluster-assembled materials.

2. Calculation details

In our calculations, the electron density functional is treated in the generalized gradient approximation (GGA) with an exchange-correlation potential parametrized by Perdew and Wang.[29] The calculations were performed by using the NRLMOL program,[30] which employs a Gaussian basis set. The geometry optimization was carried out by using the

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conjugate-gradient technique. The self-consistent calculation for each structure was performed till the energy difference fell below 1.0×10^{-6} a.u., so as to obtain accurate forces. The force was minimized to a tolerance limit of 0.001 a.u on each atom.

3. Results and discussion

3.1. Atomic structures

The ground-state structures and some metastable isomers for neutral and anionic In_4M and $In_{12}M$ (M = In, C, and Si) clusters are presented in Figs.1 and 2. Similar to the case of Al_4C,[31] the most stable structure for In_4C is of a tetrahedron with the C atom located in the centre. The In–In and In–C distances are 0.378 and 0.231 nm respectively. The In_4Si is also tetrahedral in structure and the In–In and In–Si distances are 0.444 and 0.273 nm respectively. For In_{13}, the lowest energy structure (Fig.1 a) is of a hexagonal closed package (HCP) with a D_{3h} symmetry. An isomer with a D_{5h} symmetry (Fig.1 b) is only 0.01 eV above the most stable one. The icosahedron predicted to be for the ground state structure of Al_{13} is found to be unfavourable for the case of In_{13} cluster. Moreover, there are also found three isomers in Figs.1 c, 1d and 1e to be more stable than the icosahedron. The low-energy isomers such as structures $g-i$ have higher total energies than structure a by ΔE = 0.40, 0.78, 0.84 and 0.92 eV, respectively. For anionic In_{13} clusters, the HCP is also found to be the lowest energy structure.

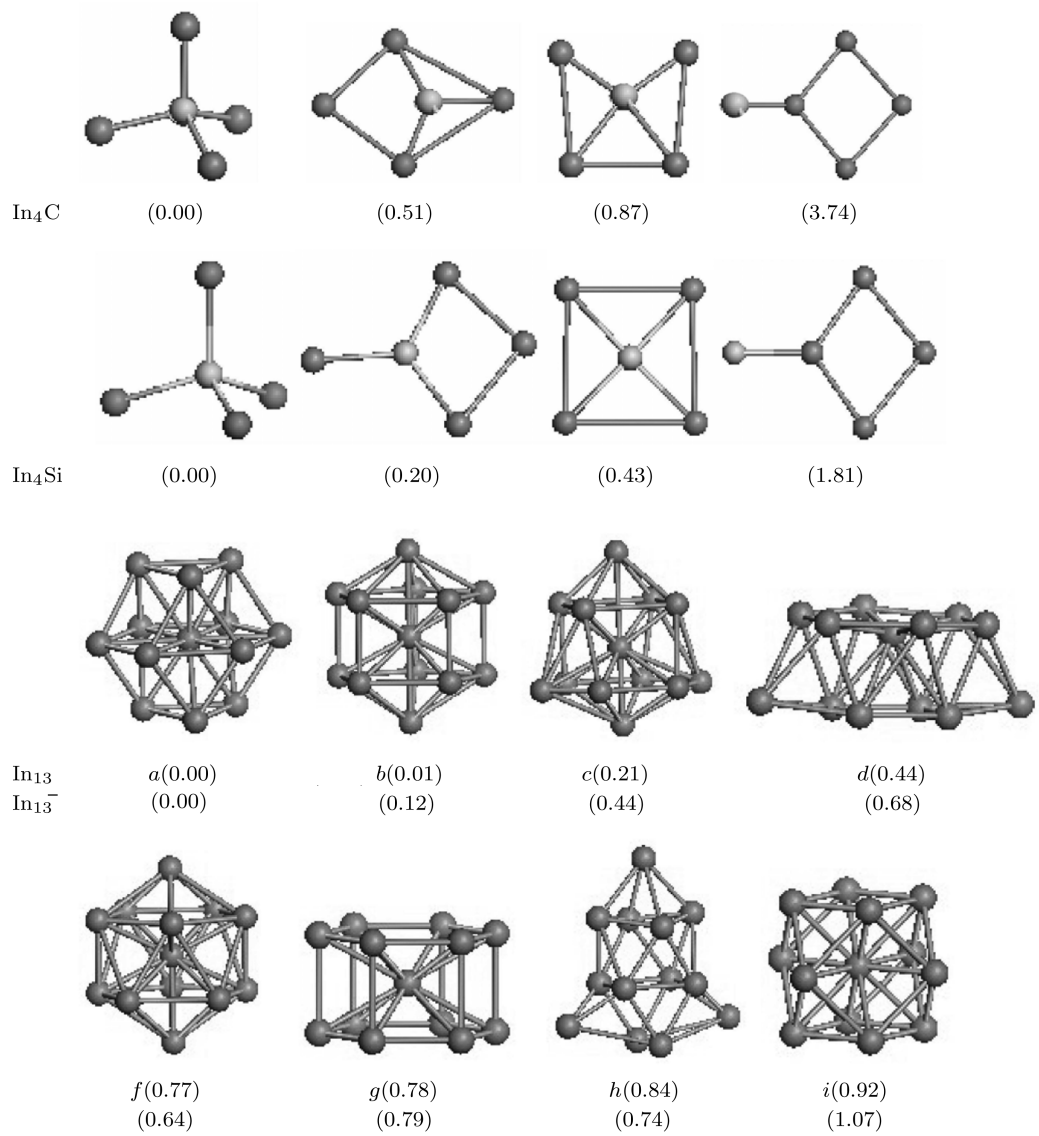


Fig.1. Schematic drawing of structures for In_4C, In_4Si, neutral and anionic In_{13} clusters. The differences in total energy (in eV) between an isomer and the most favourable isomer are given below the structure.

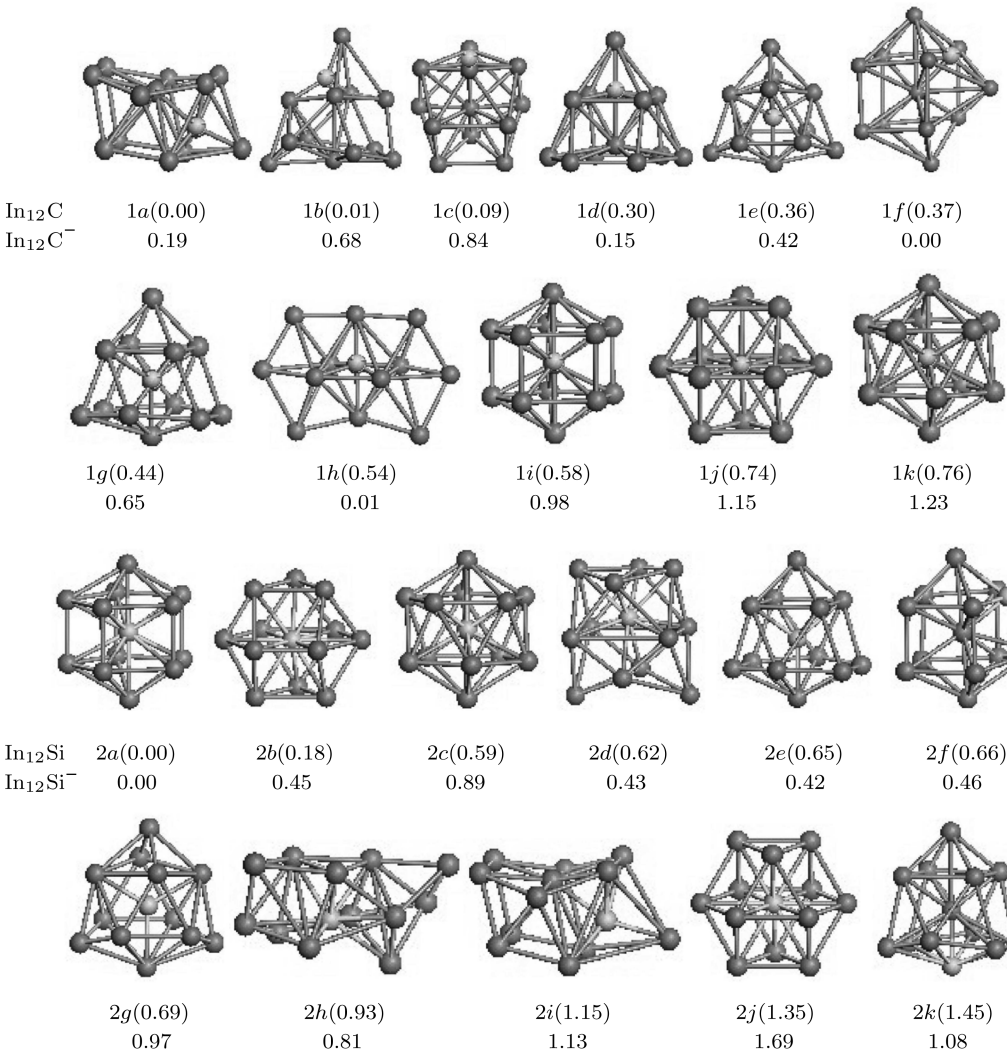


Fig.2. Schematic drawing of structures for $In_{12}M$ and $In_{12}M^-$ (M = C and Si) clusters, in which the brown spheres represent In atoms and the differences in total binding energy (in eV) between an isomer and the most favourable isomer are given below the structure.

For $In_{12}C$, the most stable structure (Fig.2 1*a*) can be derived from the buckled biplanar structure with a C_{2v} symmetry of the In_{13} (Fig.1 *d*) by moving one of In atoms out of the bottom and then doping a carbon atom, which, thus, is in a cage formed by several In atoms. Two isomers (Figs.2 1*b* and 1*c*) each with a C atom staying in the surface of the cluster are in competition with the ground-state geometry, and the relative energies are merely 0.01 and 0.09 eV respectively. Others isomers each with a C atom located in the In-cage (Figs.2 1*d*, 1*e* and 1*g*–1*k*) are metastable, for which the relative energies are in a range from 0.3 to 0.76 eV. For a neutral $In_{12}Si$, its structure is different from that of $In_{12}C$. The distorted buckled biplanar structure (Fig.2 2*i*) and HCP (Fig.2 2*b*), which are the most stable structures of $In_{12}C$ and In_{13}, respectively, are found to be unfavourable for $In_{12}Si$. The most stable structure for $In_{12}Si$ is an In-cage structure with a D_{5h} symmetry and a Si atom located in the centre.

The structural characteristics of $In_{12}C$ and $In_{12}Si$ clusters may be related to binding of their corresponding dimers, In_2, InC, and InSi. As shown in Table 1, the calculated binding energies of heteronuclear dimers, E_b(In–C) (3.16 eV) and E_b(In–Si) (2.32 eV) are large than that of $E_b(In_2)$ (1.31 eV). Moreover, the bond lengths for all heteronuclear dimers are shorter than that for In_2. Therefore, the doping of C or Si gives rise to a more compact structure with a lower energy. One can find that the distance between impurity and indium atoms in $In_{12}M$ cluster is shorter than that of corresponding bond length of the In_{13} cluster. Thus, the inside site for impurity is favourable for stabling the clusters indeed.

Table 1. The average binding energy, vertical ionization potential (IP), vertical electron affinity (EA) per atom (E_b), and the HOMO-LUMO gap (E_{gap}) of In_4M and $In_{12}M$ clusters in eV. R (nm) is the distance between the impurity atom and its neighbours. The letters a, b, c, etc indicate the structures of $In_{12}M$ shown in Figs.1 and 2.

Clusters		R/nm	E_b/eV	EA/eV	IP/eV	E_{gap}/eV
In_2		0.315	1.31			
InC		0.224	3.16			
InSi		0.269	2.32			
Al_4C		0.203	2.72	0.72	6.63	1.75
In_4C		0.231	2.15	0.50	6.11	1.71
In_4Si		0.273	1.71	0.61	5.69	1.41
	a	1.2×0.327	1.58	2.33	5.31	0.15
In_{13}	b	1.2×0.321				
	f	0.2×0.322 1.0×0.327				
	1a	0.237 0.2×0.236 0.2×0.268 0.244	1.82	1.71	5.23	0.68
$In_{12}C$	1b	1.2×0.301				
	1c	0.2×0.301 1.0×0.308				
	2a	0.275 0.2×0.297 0.2×0.277 0.278				
$In_{12}Si$	2b	1.2×0.312				
	2f	0.2×0.312 1.0×0.318	1.78	1.74	5.50	0.93

The previous studies indicate that introducing an extra electron into the $Al_{12}C$ cluster drives the carbon atom from the cluster centre to the surface.[32] To investigate the charge effect on the structure of $In_{12}C$ cluster, we optimize the structures of $In_{12}C^-$ with many different initial configurations, including all the geometric structures of the neutral $In_{12}C$ cluster. Noticeably, the relative stability of the structures for the $In_{12}C^-$ is quite different from that of $In_{12}C$. Although the buckled biplanar structure, which is of the most stable neutral cluster, is still an isomer, a few other structures with much lower symmetries are found to have larger binding energies. The lowest energy structure for $In_{12}C^-$ can be obtained by substituting one of indium atoms in the D_{5h} structure of In_{13}, in which the C atom stays in the surface of cluster. There is a structure shown in Fig.2 1h, for which the total energy is quite close to that for the ground state structure, only with a small difference of 0.01 eV in between. In contrast to the $In_{12}C$, the D_{5h} structure, which is the ground state structure of neutral $In_{12}Si$, is still the lowest energy structure due to the introduction of a negative charge.

3.2. Electronic properties

The average binding energy per atom (E_b), the vertical ionization potential (IP), the vertical electron affinity (EA), and the HOMO–LUMO gap (E_{gap}) calculated for In_4M and $In_{12}M$ are given in Table 1. To facilitate a comparison, we also optimize the structure of Al_4C. The most stable structure for Al_4C that accords with the previous result is of a tetrahedron.[31] The 0.72 eV of vertical electron affinity for Al_4C is comparable with 0.93 eV obtained by Li *et al.*[31] The 1.75 eV of gap for Al_4C, which is in good agreement with the previous result[18] exhibits its chemical inertness. For In_4C, the 0.50 eV of EA is slightly smaller than that of Al_4C and the 1.75 eV of gap is comparable with that of Al_4C. When the C is substituted with a silicon atom, the E_b slightly decreases. This may be attributed to the fact that the InSi dimer has a smaller binding energy than InC. The EA and the IP of In_4Si are close to those of In_4C, and the about 1.50 eV of gap also indicates its high stability. Contrary to the large gaps of neutral In_4M, the calculated gaps for anionic In_4C^- and In_4Si^- clusters are significantly small, and they are 0.37 and 0.18 eV, respectively, which implies that there is a closure of electronic shell in the neutral In_4M.

From Table 1, one can find a noticeable characteristic that the calculated values of EA for all $In_{12}M$ are much larger than those for In_4M. The gap for a neutral In_{13} is only 0.15 eV, however, it increases to 0.8 eV due to the introduction of an negative charge into it. The $In_{12}C$ has a larger binding energy, a lower EA, a slightly smaller IP and a much larger gap than In_{13}. The $In_{12}Si$ also shows a similar trend to that for $In_{12}C$,

except for its higher IP. These characteristics show the enhanced stabilities of $In_{12}C$ and $In_{12}Si$ clusters. It is known that Group IIIA elements are characterized by the s^2p^1 configuration and the energy separation between s and p orbitals for heavier elements (3.6 eV for Al and 4.3 eV for In). Therefore, the group IIIA metal clusters of the heavier elements should be characterized by the p electrons for small values of n, where the composed atoms are monovalent.[33] As cluster size increases, the s-band hybridizes with p band, and the atoms in the clusters become trivalent. The large difference in EA between In_4M and $In_{12}M$ implies that the s- and the p-bands may not hybridize in In_4M but overlap in $In_{12}M$ cluster. Thus, In_4M would have 8 valance electrons while $In_{12}M$ contains 40 ones. Within a simple jellium picture, clusters containing 2, 8, 18, 20, 34, 40 - electrons, which are in closed electronic shells, are particularly stable. Accordingly, the enhanced stabilities of In_4M and $In_{12}M$ clusters may be rationalized with the help of the spherical jellium model.

4. Summary

A systematic theoretical study on the structures and the stabilities of In_4M and $In_{12}M$ (M = In, C and Si) clusters has been performed by treating the density functional in the GGA. For In_{13}, the lowest energy structure is a hexagonally closed package with a D_{3h} symmetry, differing from that of Al_{13}. For $In_{12}C$, the ground state structure is a distorted buckled biplanar structure, in which C atom prefers to stay inside the cluster. For $In_{12}Si$, the lowest energy structure is of an In-cage with a Si atom located in the centre. Introduction of an electron substantially changes the ground state structure of $In_{12}C$, but it does not significantly change the structure of $In_{12}Si$. $In_{12}C$ and $In_{12}Si$ show higher stabilities than In_{13} cluster. The In_4C cluster is found to be particularly stable with a higher binding energy and a larger electronic gap, showing its magic behaviour. We hope that our results would help experiments look for these clusters.

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