Physica B 437 (2014) 47–52

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Theoretical investigation of endohedral complexes of Si and Ge with C_{60} molecule

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ARTICLE INFO

Article history:
Received 19 November 2013
Received in revised form
20 December 2013
Accepted 25 December 2013
Available online 3 January 2014

Keywords:
Fullerene
Ab initio calculations
Endohedral doping
Electronic structure
Magnetic moment
Binding energy

ABSTRACT

The electronic and magnetic properties of Si and Ge doped C_{60} fullerene are investigated with ab initio density functional theory calculations. In endohedral Si_n (n=1–10) and Ge_n (1–9) doped C_{60} complexes we have seen that Si and Ge doped complexes are stable up to 9 and 4 atoms, respectively. We have also investigated binding energy and ionization potential of the endohedral fullerene C_{60}. Endohedral fullerenes have been found to be more chemically reactive. Mullikan charge analysis shows the presence of the magnetic moment in these systems.

1. Introduction

Encapsulating atoms or molecules [1–3] inside a C_{60} has attracted attention for its scientific interest and practical application in diverse areas including physical and biological sciences [4]. C_{60} is most suited for doping as it is most stable among fullerenes and has also been extensively doped to tailor electronic properties of fullerenes [5,6]. Doping of C_{60} with impurity atoms can drastically change the electronic structure of the pristine C_{60}. These are grouped as endohedral, substitutional and exohedral doping. In the case of endohedral doping, a dopant is encapsulated inside the fullerene shell. In substitutional doping the dopant atoms replace carbon atoms on the fullerene shell. Whereas, in case of exohedral doping, the dopant is outside or between fullerene shells [7]. These doping configurations can be achieved depending on the dopant species and the production technique [8,9]. Endohedral doping with metal atoms is a primarily used to study stabilization of C_{60} molecule. Si as dopant atom is important since there is a large family of compounds which originate from it. Few examples are porous Si, Si as semiconductor, doped Si cages as clatherate compounds etc. All these compounds have a wonderful and a variety of properties to offer. The exceptional elastic, thermoelectric, optoelectronic and superconducting properties of these porous crystals [10–14] have already demonstrated their unique potential for tailoring novel materials made of Si-based subunits. Apart from this, Si and Ge are nearest neighbors of carbon in group IV, and, therefore, suitable candidates for designing novel nanostructures out of carbon [15–19]. On one hand, SiC compounds and alloys exhibit outstanding properties such as polymorphism, extraordinary hardness, variable band gaps etc. On the other hand, the hollow-cage structure of fullerenes offers a unique frame-work for developing new SiC compounds. Although, silicon is isoelectronic with carbon it exhibits quite different physical and chemical properties, e.g., it does not develop sp^2 networks. Substitutional doping of C_{60} with Si, Ge, and Al results in change in electrical and magnetic properties [20].

One interesting aspect of fullerene cages is the existence of a cavity large enough to contain an atom or a small molecule. In the recent years, an increasing variety of species have been encapsulated in fullerenes [21]. The magnetic susceptibility of C_{60} as well as the magnetic field due to π-electron ring in the carbon spheroid are also of interest. During endohedral doping, the fullerene plays the role of a protective screen and the properties of the dopant remain intact, for example, Gd@C_{60} and Gd3N@C_{80} [22,23], which are recently considered as a new generation of magnetic resonance imaging contrast agents due to the high spin ground state of Gd while its toxicity is shielded by the fullerene.

In the literature various modeling techniques have been used to understand the physical properties of fullerenes and their derivatives. Ab initio calculations have been used to investigate the structural and

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http://dx.doi.org/10.1016/j.physb.2013.12.039

electronic properties of small silicon clusters as well as endohedral metallofullerenes [24–25]. Semi-empirical and density functional theory (DFT) studies on the structures and stabilities of $C_{60}CH_2$ isomers have also been reported [26]. In addition, ab initio calculations on stability of MC_{60} (M=Sc, Y, and K) and Si atom doped endohedral C_{60} has been reported in the literature as well [20,27–29]. In another theoretical study, Si-doped carbon fullerenes exhibit profound changes in their electronic spectrum and have important implications in the conducting character, chemical reactivity and stability of the molecules. In all cases charge transfer has been observed from Si to C [30]. Semi-empirical calculations of C_{60} were also proposed to study the structure and vibrational properties of C_{60}, C_{80} and their epoxides [28]. On the basis of energy considerations, Ge atom appears to be quite potential candidate for doping in order to stabilize C_{80} skeleton in the form of $M@C_{80}$ type structure [7].

We can expect that nanoscale carbon–silicon composite structures may exhibit novel properties due to the large surface area and quantum size effect. Recently, research interest in carbon–silicon composite nanostructures [31] has arisen due to their applications in quantum dots, quantum wires, nonlinear electronic components and memory devices. The large cavity of the fullerene molecule may be used as storage materials with high capacity and stability. Therefore, it becomes pertinent to study the properties of endohedral fullerenes by doping with different number of atoms of Si and Ge.

In the present work we have studied the stability, geometries, binding energies per atom and Fermi energies of Si and Ge doped C_{60} fullerene by optimizing the atomic geometries.

2. Computational approach

The calculations have been performed by the SIESTA program [32–34], which allows standard calculation with density function theory (DFT) [35] for systems with large number of atoms. Ab initio electronic structure calculations based on the Kohn–Sham (DFT) have been enormously successful using generalized gradient approximation (GGA) [36]. The pseudopotentials are constructed using a Trouiller–Martins scheme [37] to describe the interaction of valence electrons with the atomic cores. The nonlocal components of pseudopotential were expressed in the fully separable form of Kleiman and Bylander [38,39]. The Perdew–Burkle–Ernzerhof (PBE) form generalized gradient approximation (GGA) corrections are adopted for the exchange-correlation potential. [40]. The atomic orbital set employed throughout, in the present work, is was a double-plus polarization DZP function, which has been was generated using the scheme proposed by Junquera et al. [41]. Since it variationally optimized the basis quality and maintained the strict localization of the orbital′s while ensuring the continuity of the basis-function derivatives at the cutoff radius. The numerical integrals are performed and projected on a real space grid with an equivalent cutoff of 250 Ry for calculating the self-consistent Hamiltonian matrix elements. For carbon, the DZP basis set was described with cutoff radii of 5.43 Bohr for the 2s orbitals, 6.83 Bohr for the 2p orbitals, and 5.05 Bohr for the d polarizing orbital. For silicon, the basic functions were strictly localized within radii that correspond to confinement energy of 0.01 Ry, with exception of the polarization function where a fixed cutoff radius of 6.0 Bohr was specified. In the calculations of cohesive energies, we considered that the ground states of an isolated carbon and silicon atoms are in the triplet states.

3. Results and discussion

We have performed test calculations on C_{60} and Si_2 molecule. In C_{60} we found that calculated bond lengths C–C bonds are 1.41 Å and 1.46 Å which is in good agreement with the reported values 1.40 Å and 1.46 Å [42], for double and single bonds, respectively. The calculated values of ionization potential (IP) and the electron affinity (EA) were 7.099 eV and 2.326 eV, respectively. These values are in agreement with the experimental values of IP and EA 7.5 eV and 2.689 eV, respectively [20]. For the Si_2 molecule the calculated values of Si–Si bond length, ionization potential and electron affinity are 2.23 Å, 7.55 eV and 2.29 eV. These values agree well with the reported values 2.23 Å, 7.86 eV and 2.2 eV of corresponding parameters [43–46].

We further performed calculations which involve doping of Si and Ge atoms inside C_{60}. Parameters of calculations are same as that of test calculations. First we have considered various isomers of $(Si)_n$ cluster having almost known bond length between nearest neighbors. In the next step we have considered an endohedral system by taking into account the coordinates already obtained for C_{60} and $(Si)_n$ cluster. This configuration has been allowed to relax till tolerance of the maximum forces reached 0.04 eV/Å. We have calculated B.E/Si (binding energy per Si atom) and B.E/Ge (binding energy per Ge atom) atom using the formula

$$U_M = [E_{Mn@C_{60}} - E_{C_{60}} - nE_M]/n \quad (1)$$

where M=Si or Ge as the case may be, U_M denotes the binding energy per M atom of the $Mn@C_{60}$ complex, $E_{Mn@C_{60}}$ is the total energy of the endohedral fullerenes C_{60} doped with n the number of M atoms. $E_{C_{60}}$ is the total energy of pure C_{60} and E_M is the energy of one dopant (Si or Ge) atom.

Same procedure has been repeated for other isomers and the one with minimum energy is reported as the $Si_n@C_{60}$ molecule. The lowest energy structures of $Si_n@C_{60}$ and $Ge_n@C_{60}$ are shown in (Figs. 1 and 2) respectively. Initially we calculate C_{60} doped single Si and Ge atom. These atoms were placed at different positions inside C_{60}. We found that Si and Ge atoms at the centre give rise to most stable structure. Doping of C_{60} with single atom of Si and Ge did not deform the cage as confirmed by the calculated value of the diameter of $Si_n@C_{60}$ and $Ge_n@C_{60}$. Calculated diameter had a maximum value of the diameter of cage 7.16 Å, minimum 7.00 Å and average 7.08 Å in both the cases. These values are same as that of undoped C_{60}. The C=C and C–C bond distances were found to be 1.41 Å and 1.46 Å respectively in both the cases. In $Si_1@C_{60}$ and $Ge@C_{60}$ the B.E./Si was found to be −0.3194 eV and −0.0047 eV, respectively. These values indicate that $Si_1@C_{60}$ is more stable than $Ge_1@C_{60}$ (Fig. 3). Doping with two atoms of Si and Ge resulted in $Si_2@C_{60}$ and $Ge_2@C_{60}$, structures. B.E/Si atom was −1.1743 eV and in case of Ge it is −0.0189 eV. Again we found that $Si_2@C_{60}$ is more stable than $Ge_2@C_{60}$. Calculated Si–Si interatomic distance in the optimized structure was 2.24 Å (approximately 0.01 Å more than in bare diatomic Si–Si) and Ge–Ge interatomic distance was found to be 2.37 Å (approximately 0.03 Å more than in bare diatomic Ge–Ge). In the case of $Si_3@C_{60}$, Si_3 formed a triangular structure with bond lengths 2.21 Å as compared to bond lengths of 2.17 Å in bare structure as shown in (Fig. 1). Si atoms also formed bonds with C atoms of C_{60} (Fig. 1). In case of $Ge_3@C_{60}$, Ge_3 also formed triangular structure and Ge atoms formed bond with C atoms similar to $Si_3@C_{60}$ as shown in Fig. 2. The Ge–Ge bond length of the structure was 2.42 Å in comparison with 2.4 Å in bare Ge_3. Calculated B.E/Si atom was −1.5213 eV and B.E/Ge atom was −0.0253 eV. In $Si_4@C_{60}$, Si_4 has a tetrahedron with optimized structure having distorted interior with Si–Si bond length 2.32 Å compared to 2.31 Å of bare Si_4. Si atoms formed bonds with C atoms as shown in Fig. 1. In case of $Ge_4@C_{60}$, Ge_4 has tetrahedron structure having Ge–Ge bond length 2.45 Å with respect to bond length values of 2.46 Å in bare tetrahedron. Similar to $Ge_3@C_{60}$, Ge also formed bond with C atoms. Minor distortion has also been observed in both the cases. B.E/Si and B.E/Ge atom has been calculated as −1.5508 and −0.0042 eVrespectively, which suggests that $Si_4@C_{60}$ is more