

Electronic structure of C₆₀ semiconductors under controlled doping with B, N, and Co atoms

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Abstract

We present our recent studies of *ab initio* density functional theory (DFT) calculations of the electronic structures of several selected n- and p-type doped C₆₀ semiconductors. A super-cell approach was used. We performed a series of *ab initio* density functional computations to systematically study the changes of the electronic structure of C₆₀ semiconductors doped with boron, nitrogen and cobalt atoms. We found that boron and cobalt doped, face-centered cubic (FCC) C₆₀ solids have the electronic structures of n-type semiconductors. Nitrogen doped FCC C₆₀ solid has an electronic structure similar to those of a p-type semiconductor, with shallow impurity energy levels near the top of the valence bands of the host material.

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1. Introduction

The unique properties of C₆₀ materials present some new opportunities for technology applications [1,2]. Especially, the very low Debye temperature ($\Theta_D=70$ K) and the low thermal conductivity of C₆₀ bulk semiconductors present an opportunity for constructing new thermoelectric materials with a high *figure-of-merit* ZT, [3] where $ZT = \frac{S^2\sigma T}{\kappa}$; S is the thermoelectric power (or Seebeck coefficient); σ is the electrical conductivity; T is the temperature; and κ is the thermal conductivity. Controlled doping of C₆₀ semiconductors presents an effective method to tune the electronic properties of the material. However, to identify suitable doping elements and doping concentrations in C₆₀ bulk semiconductors, for achieving a high thermoelectric *figure-of-merit*, is a challenging task in the exploration of the new C₆₀ fullerene based thermoelectric materials. Understanding the electronic structure of the doped materials is another major task in the research. On the other hand, *ab initio* density functional calculations are effective

methods to reveal the electronic structure of the materials under controlled doping. In this work, we performed the *ab initio* density functional calculations to study the electronic structure of C₆₀ semiconductors doped with B, N, and Co atoms in the interstitial sites of the parent material in FCC lattice. Miyamoto et al. [4] studied the B-doped C₆₀ (BC₅₉) with one carbon atom substituted by a boron atom. Ching et al. calculated the electronic energy bands, the density of states (DOS), and the optical properties of C₆₀, K₃C₆₀, and K₆C₆₀ solids in FCC lattice [5–7]. For more than a decade, most of the research on the interstitially doped C₆₀ solids focused on high doping concentrations and for the superconducting properties. Gu et al. performed AC susceptibility measurements of Sn doped C₆₀ superconductor [8]. Saito and Oshiyama [9] calculated electronic structures of Ca₃C₆₀ and Ca₅C₆₀ solids and Kortan et al. [10] found by measurements that the high concentration Ca doped C₆₀ solid experienced FCC → BCC (body-centered cubic) → SC (simple cubic) phase transformations for the Ca concentration from Ca₃C₆₀ → Ca₄C₆₀ → Ca₅C₆₀. By doping Rb and Tl alloy to C₆₀ solids, Iqbal et al. [11] increased the T_c to 45 °K. Umemoto and Saito [12] calculated body-centered-orthorhombic fulleride

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Ba₄C₆₀ using local density approximation(LDA), they explained the observed lattice-constant differences, $a > b > c$. Korenivski and Rao [13] evaluated the BCC phase Ba₆C₆₀ using SQUID measurements and found the upper critical field H_{c2} to be approximately 2 T. Alkali metal-doped C₆₀ solids at high concentrations (with the alkali atoms in the interstitial sites of bulk C₆₀ solids) have been intensively investigated (see Ref. [14–22] and Ref. [23] for a review). We are aware of no detailed report of experiment or theoretical work on the electronic properties of C₆₀ semiconductors with low B, N and Co doping concentrations. In this brief report, we present the results of utilizing an *ab initio* plane-wave pseudopotential method to calculate the changes of the electronic structure of the above three doped C₆₀ semiconductors.

2. Computation methods

We implemented the first-principle density functional calculations using the projector augmented wave (PAW) method, taking the relativistic effects into account [24,25]. The exchange-correlation interaction was described by the generalized gradient approximation (GGA). The Vienna *ab initio* simulation package (VASP) [26–29] was used in these calculations. The 2s and 2p electron states of C, B and N atoms were described as valence states, whereas for Co atom, the 3d and 4s states were treated as valences. The core electron states were treated as those of free atoms in a frozen core approximation. We used a super-cell approach that includes 60 carbon atoms and one doping atom (1:60 doping concentration) as well as 240 carbon atoms and one doping atom (1:240 doping concentration) in the comparative calculations. All the atomic coordinates and unit-cell volumes were relaxed in the *ab initio* DFT calculations. We implemented spin-polarized electron density calculations. With the plane-wave energy cutoff at 450 eV, the calculated total energies converged to the order of about 0.01 meV. The residue forces on atoms were less than 10 meV/Å. In the super-cell method, we used a $4 \times 4 \times 4$ and $1 \times 1 \times 1$ Monkhost grids in the k space sampling for the 1:60 and 1:240 doping concentrations, respectively. The Bader charge [30] was calculated for both the dopant atoms and the host C₆₀ atoms.

3. Results and discussions

The calculated results of B, N, and Co-doped C₆₀ semiconductors with 1:60 concentration are summarized in Table 1. The calculated total and partial electron density of states (DOS)

Table 1
Summary results of B, N, and Co-doped (1:60 concentration) C60 semiconductors

Dopant	Dopant site	Type	$\Delta V/V$	$M_B(\mu_B)$	ΔQ (e)
B	Tetra	n	+0.27%	0.0	+0.29
N	Tetra	p	+0.27%	0.0	-0.26
Co	Tetra	n	+0.415%	3.0	+0.415

The positive and negative signs of ΔQ mean losing and gaining electrons in |e|. The positive and negative signs of $\Delta V/V$ denote expansion and contraction of unit-cell volume, respectively. M_B is the magnetic moment of the system in μ_B .

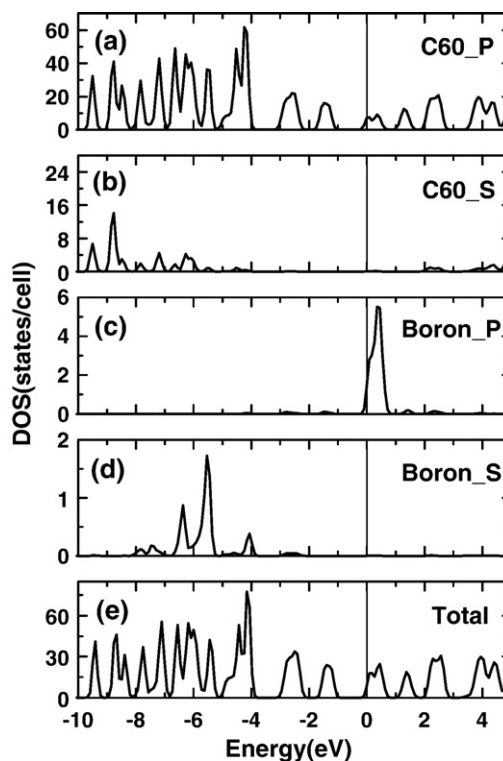


Fig. 1. The partial and total densities of states of B-doped C₆₀ solid. The Fermi energy is set at 0.0 eV.

are presented in Figs. 1–3, where the Fermi level (E_F) was set at 0.0 eV. As can be seen from Table 1 and Figs. 1–3, nitrogen doped C₆₀ solid is a p-type semiconductor, while boron and cobalt doped C₆₀ solids are n-type semiconductors. There are small expansions of +0.27 % (for B and N) and +0.415% (for Co) of the unit-cell volumes in the three doping cases at the tetrahedral site of FCC C₆₀ solids. The boron and nitrogen doped C₆₀ have no net magnetic moment. Interestingly, the net magnetic moment of cobalt doped C₆₀ solid is 3 μ_B , which is nearly the same as that of a free cobalt atom.

There is a small charge transfer of about +0.29|e| from the dopant B atom to the carbon atoms of C₆₀. Similarly, the charge transfer from the dopant Co atom to the carbon atoms of C₆₀ is about +0.415|e|. The charge transfer from the dopant N atom to the carbon atoms of C₆₀ is negative, i.e. -0.26|e|, which is consistent with the character of p-type doped semiconductors. Different from the substitutional doping in n- or p-type silicon semiconductors, the dopants in C₆₀ solids occupy interstitial sites of the FCC lattice because of the high stability of the C₆₀ fullerene structure and a weak interaction between them. The charge transfer properties can be understood from the relative weak electron affinities of B atom (at 0.28 eV) and Co atom (at 0.66 eV) in comparison with that of carbon atom (at 1.26 eV) [31]. The charge transfers also agree qualitatively with the octet rule which suggest carbon losing electrons to nitrogen but not to boron and cobalt. The results are also consistent with the partial DOS of B and N-doped C₆₀ solid in Figs. 1 and 2. The boron p-states form the impurity electron states that merge with the electron states of the conduction band edge of host C₆₀ material

around the Fermi level, as in Fig. 1. Miyamoto et al. [4] calculated the substitutionally doped BC_{59} using a local density approximation (LDA). From the calculated results of DOS, they found that the BC_{59} is a hole doped fullerene. The DOS of dopant boron is situated about 0.2 eV above the valence band of C_{59} . The results reported here for C_{60} solids interstitially doped with B are different from those of Miyamoto et al. We find the DOS of the dopant boron to be close to the bottom of the conduction band of the system and the doped material is an n-type semiconductor.

The nitrogen p-states form a distinct peak structure that is located above the top of the valence band of host C_{60} solid, as in Fig. 2. Therefore, for interstitial doping, nitrogen doped FCC C_{60} solid has an electronic structure similar to that of a p-type semiconductor, with shallow impurity energy levels near the top of the valence bands of the host material.

In all of the three doped C_{60} semiconductors considered, the total energy is lower for the dopants at the tetrahedral site than for other sites such as the octahedral sites. Consequently, in this article, we report the results of the dopant B, N, and Co atoms at the tetrahedral site of C_{60} host material. From the partial DOS in Figs. 1 and 2, we can see that C_{60} also has a contribution to the DOS near the Fermi level. This is due to the hybridization of the C 2p state with states of the corresponding dopant atoms. Fig. 3 shows the spin-polarized electron density of states for Co-doped C_{60} semiconductors. The spin up and down DOS of Co-doped C_{60} solid have noticeably different structures near the Fermi level. For the cases of lower doping concentrations at 1:240, we only observed that the density of states due to the dopant atoms

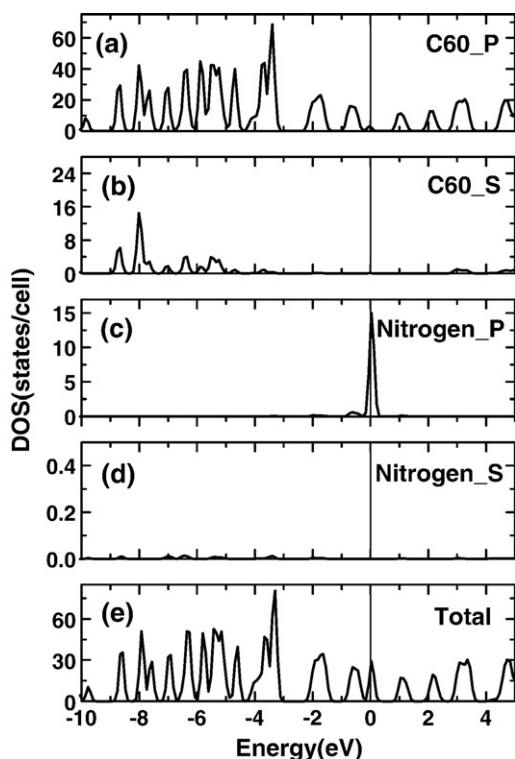


Fig. 2. The partial and total densities of states of N-doped C_{60} . The Fermi level is at 0.0 eV.

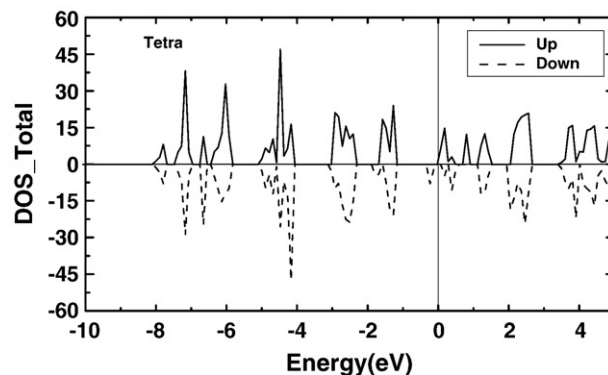


Fig. 3. The spin up and down density of states of Co-doped C_{60} solid. The Fermi energy is at 0.0 eV.

(B, N, or Co) decreased while the general structure of the DOS remained nearly the same.

4. Conclusions

In summary, we utilized the *ab initio* DFT method to calculate the electronic structures of B, N, and Co-doped C_{60} semiconductors. Both the B and Co-doped C_{60} solids are n-type semiconductors. The N-doped C_{60} solid is a p-type semiconductor. The calculated electronic properties of B, N, and Co-doped C_{60} semiconductors will facilitate the exploration of the new materials for the near future applications.

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