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First principles study of structural, electronic and vibrational properties of heavily boron-doped diamond

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ABSTRACT

The structural, electronic and vibrational properties of a series of heavily B-doped diamond models have been investigated using the density functional theory within a local density approximation. The doped models $C_{64-n}B_n$ ($n = 1$–3) were constructed using supercell techniques. The structural and electronic calculations confirmed that the B dimers are always energetically stable and electrical inactive. The superconducting transition temperature T_C is not only decided by the B concentration, but also by the lattice configurations of boron atoms. The vibrational frequencies and eigenmodes were determined using the linear response approach, while Raman intensities were obtained by the second response method. The Raman analysis in terms of atomic vibrations found that the "500 cm^{-1}" and "1230 cm^{-1}" bands are both superposed bands including not only C vibrations but also B–B vibrations and B–C vibrations, respectively. The calculated Raman spectra with isotopic substitutions are in excellent agreement with corresponding experimental results. The reasonable explanation was provided for no obvious Raman shift of main bands from $^{10}B^{12}C$ to $^{11}B^{12}C$ model.

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1. Introduction

Since the experimental discovery of superconductivity in heavily boron-doped diamond (HBDD, the B concentration $N_B \sim 5 \times 10^{21}\ \text{cm}^{-3}$, 2.8 ± 0.5 at%) films synthesized at high pressure and high temperature [1], various experimental [2–6] and theoretical [7–13] studies have been performed to confirm and understand the observed superconducting transition. Most results favor the standard Bardeen–Cooper–Schrieffer (BCS) theory of superconductivity involving the electron–phonon coupling (EPC) mechanism and the type of metal-to-superconductor transition in HBDD as the temperature drops to the superconducting transition temperature T_C. However, the effect of B content on the T_C is controversial. The experimental T_C was found to depend on the impurity concentration [3,4]. Umezawa's experiment suggested that the dependence of T_C on N_B has also depended on the growth direction [5]. The difficulties in relating the observed T_C with boron content may result from variations in the doping efficiency of boron atoms [6]. By first-principles density-functional calculations employing the supercell approach, Bourgeois et al. [12] suggested that boron dimers are always energetically stable in HBDD and that they cannot enhance the T_C because of their electrical and vibrational inactivity. In contrast, the calculations of Long et al. [13] suggested that B dimers are not energetically favorable in higher B-doped diamond (achieving 4.69%) and the T_C increases with B concentration in a certain range.

In addition, the origin of two new Raman broad bands centered at approximately 500 and 1230 cm^{-1} are still uncertain [14–19]. These bands were attributed to the vibrational density of states (VDOS) of diamond in some papers [14–16]. There is also evidence [5,12,17] that the 500 cm^{-1} band may be associated with local vibrational modes of boron dimers in which boron would preferentially aggregate at high concentrations. The result of Ref. [19] suggested that these broad bands originate from the electronic scattering of the boron acceptor. Recently [20], the isotopic substitution with ^{13}C and ^{10}B allowed to assign the "500 cm^{-1}" and "1230 cm^{-1}" vibration modes of HBDD to only the motion of carbon atoms.

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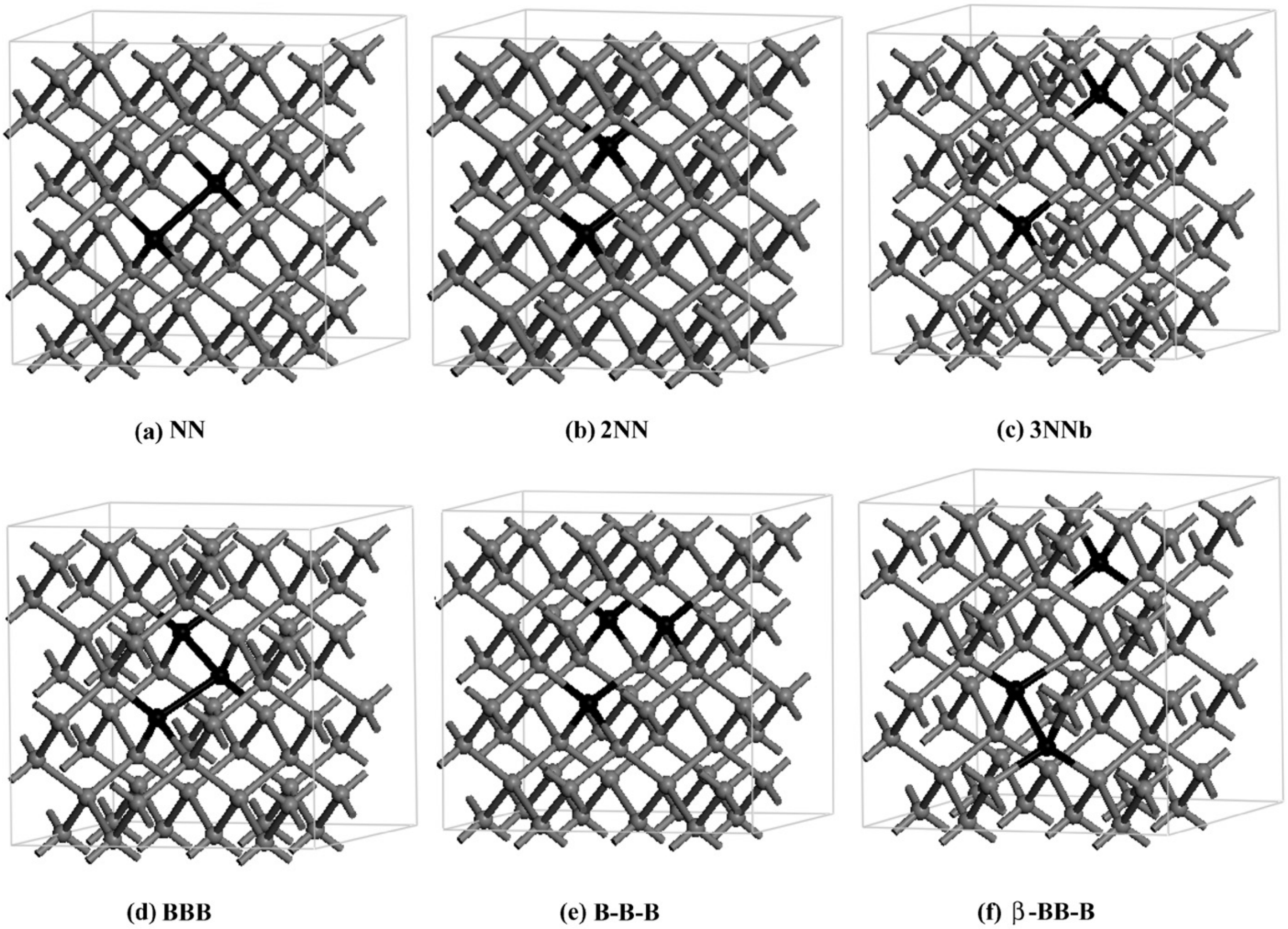

Fig. 1. The microstructure for the (a) $C_{62}B_2$–NN, (b) $C_{62}B_2$–2NN, (c) $C_{62}B_2$–3NNb, (d) $C_{61}B_3$–BBB, (e) $C_{61}B_3$–B–B–B, and (f) β–$C_{61}B_3$–BB–B. Black and gray denote boron and carbon atoms, respectively.

Therefore, further work is necessary to investigate the origin of the Raman broad bands and the effect of boron concentrations on the T_C of HBDD. In this Letter, the first-principles studies of the equilibrium geometries, stability, energy band structures, the electronic density of states (eDOS), the VDOS, and Raman spectra are performed using the density functional theory (DFT) within a local density approximation. To our knowledge, no theoretical calculations of Raman spectra for HBDD are available. The rest of the Letter is organized as follows. In Section 2, we briefly described the computational methods used in this work. Results and discussions of the structural, electronic and vibrational properties will be presented in Section 3. Finally, conclusions are given in Section 4.

2. Computational methods

We considered a 64-atom supercell built as a 2 × 2 × 2 repetition of the conventional simple cubic 8-atom cell. The equilibrium lattice parameter was determined by minimizing the crystal total energy calculated for different values of the lattice parameter. The resultant energies were fitted to the Murnaghan equation of state [21] in order to obtain the lattice constant. The calculated lattice constant is 3.546 Å, which is in good agreement with experimental 3.567 Å [22]. One to three carbon atoms were substituted by boron leading to a series of B-doped systems. Geometry optimization, electronic properties and vibrational properties were calculated using first-principles methods, as provided in the QUANTUM-ESPRESSO package [23]. The exchange-correlation energy was accounted for through local density approximation (LDA), while core valence interactions were described by norm-conserving pseudopotentials for C and B [24]. The plane-wave cutoff energy is taken as 55 Ry and a 2 × 2 × 2 Monkhorst–Pack k-point [25] sampling is used for integration of the Brillouin zone (BZ), and a finer 4 × 4 × 4 mesh is used in the electronic structure and total energy calculations. The phonon modes were obtained through the linear-response approach [26]. Because of the computational cost, phonons were calculated at the sole Γ point of the BZ. This is equivalent to a 2 × 2 × 2 sampling of the undoped diamond BZ of simple cubic 8-atom cell. The Raman intensities were calculated by the second response method of DFT [27]. Taking into account the experimental width of the Raman lines and the finite size of the model, the final spectra were broadened by a Gaussian function.

3. Results and discussion

3.1. Structure and stability

To study structural stability, we considered a series of B-doped models with one to three B atoms substituting for C atoms $C_{64-n}B_n$ ($n = 1$–3), corresponding to B concentration about 1.56 at% ($\sim 2.8 \times 10^{21}$ cm^{-3}), 3.13 at% ($\sim 5.6 \times 10^{21}$ cm^{-3}) and 4.69 at% ($\sim 8.4 \times 10^{21}$ cm^{-3}), respectively. Fig. 1 shows the ball-and-stick models of six relaxed B-doped structures in a simple cubic supercell. An isolated B replacing for one C model represents as $C_{63}B_1$

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