

Electronic Structure of B-doped Diamond: A First-principles Study

T. Oguchi¹

*Department of Quantum Matter, ADSM, Hiroshima University, Higashihiroshima
739-8530, Japan*

Abstract

Electronic structure of B-doped diamond is studied based on first-principles calculations with supercell models for substitutional and interstitial doping at 1.5–3.1 at.% B concentrations. Substitutional doping induces holes around the valence-band maximum in a rigid-band fashion. The nearest neighbor C site to B shows a large energy shift of 1s core state, which may explain reasonably experimental features in recent photoemission and x-ray absorption spectra. Doping at interstitial T_d site is found to be unstable compared with that at the substitutional site.

Key words: diamond, boron doping, first-principles calculation, superconductivity, XAS

1 Introduction

Since the discovery of superconductivity in heavily boron doped diamond [1,2], a lot of arguments about its mechanism have been made intensively. One of the

¹ E-mail: oguchi@hiroshima-u.ac.jp

main issues is the B concentration. It is well known that insulator-metal limit is approximately 0.1 at.% of B doping in diamond. All the superconducting samples are in a metallic regime. Bustarret has discussed B-concentration dependence of the superconducting critical temperature (T_c) [3]. Some Hall measurements [4] have been reported in this context. Another important issue is B-doping site, namely substitutional, interstitial or other sites. The observed orientation dependence of T_c in the film samples [5] could be related to the B-doping site.

In theoretical works, the key issue is the electronic nature where the superconductivity takes place, band or impurity states. Several band-theoretical studies have shown moderately strong electron-phonon interaction and similarity to MgB_2 [6–9]. Hole states around the valence-band maximum (VBM) introduced by B doping are strongly coupled with optical bond-stretching modes, assuming B doping at the substitutional site. On the other hand, Baskaran has claimed importance of electron correlation in an impurity band [10,11].

Concerning the electronic structure of B-doped diamond, several experimental measurements have been reported recently. Yokoya *et al.* have reported soft x-ray angle-resolved photoemission spectroscopy (SXARPES) data and concluded that B doping is basically hole doping into host diamond in a rigid-band manner [12]. Additionally important point here is that estimated hole concentration in the band seems to be slightly smaller than values obtained by secondary ion mass spectroscopy (SIMS). This implies that some sort of charge compensation takes place. They have also observed C 1s hard x-ray photoemission spectroscopy (HXPES) spectra for undoped and doped samples [13]. He has found that the heavily doped sample shows asymmetric peak and lower-binding feature simultaneously. Nakamura *et al.* have measured x-

ray emission spectroscopy (XES) and x-ray absorption spectroscopy (XAS) at B and C K -edges [14,15]. B K -edge XES shows hole-doping feature similar to Yokoya's SXARPES. B K -edge XAS reveals in-gap states in addition to the hole states. The in-gap states are prominent in a heavily doped superconducting sample. In C K -edge XAS spectra, there are two structures, "H" and "I", around the VBM. The "H" state depends strongly on doping concentration while the "I" state has less dependence in magnitude and its width is broadened with concentration.

In the present study, by using first-principles approach, we investigate the electronic structure of diamond with B doped at substitutional and interstitial sites for a consistent interpretation of experimental data mentioned above such as SXARPES, XES and XAS at B and C K -edges and C $1s$ HXPES.

2 Methods and models

Our calculations are based on the density functional theory with highly-precise all-electron full-potential linear-augmented-plane-wave method. Exchange and correlation are treated within the local density approximation (LDA) [16] or generalized gradient approximation (GGA). [17] For the present system, LDA and GGA give almost identical electronic band structure and only LDA results are shown below. We adopt several kinds of supercell models $C_{31}B$ (3.1 at.% B) and $C_{63}B$ (1.6 at.% B) for substitutional-site doping and $C_{32}B$ (3.0 at.% B) and $C_{64}B$ (1.5 at.% B) for tetrahedral (T_d) interstitial-site doping. We perform structural optimization with keeping symmetry at the experimental volume (the corresponding lattice constant of host diamond $a = 3.56\text{\AA}$).

3 Results and discussions

Let us first discuss results of the substitutionally doped case. Bond distance between B and the nearest neighbor C (called C1) is slightly elongated by 0.02\AA and the other relaxation is negligibly small for both supercell models $C_{31}B$ (3.1at.% B) and $C_{63}B$ (1.6 at.% B) . Figure 1 shows the partial density of states projected on the s and p orbitals at each site, B, the first to fifth neighbor C sites (C1-C5) for $C_{63}B$ model. Substitutional B doping introduces holes into the states around the VBM, which are composed mostly of p orbital. One can see in Fig. 1 large hybridization between B and C1 p orbitals in the hole-doping region, being consistent with SXARPES and XES experimental results.

In case of the interstitial T_d site, there are four first neighbor C1 sites and six second neighbor C2 sites. Atomic relaxation is sizable about 0.11\AA for the C2 sites and those for C1 and C3 are marginal ($\leq 0.02\text{\AA}$) for both models $C_{32}B$ (3.0 at.% B) and $C_{64}B$ (1.5 at.% B). Interstitial B doping leads to in-gap states just below the conduction-band minimum lightly hybridized with C1, C2 and C4, as shown in Fig. 2. Quite few B states in the valence-band region suggests that the interstitial B tends to be a positively charged state in a p -type sample. This means that some charged state can be seen as an in-gap state.

Since our theoretical approach is based on an all-electron scheme, we can estimate the relative core-level positions for the different C sites. In the substitutional case, the C1 site shows a significant core shift by 1.3eV to shallower binding energy, which is consistent with lower-binding feature observed in the

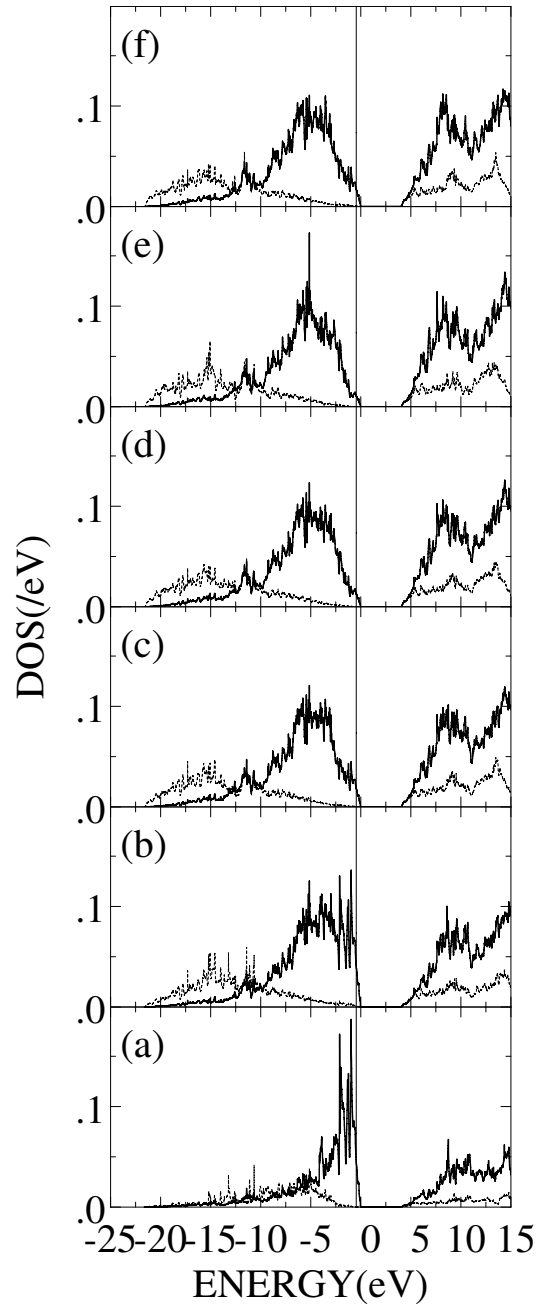


Fig. 1. Calculated partial density of s (broken lines) and p (solid lines) states projected on the (a) B, (b) first neighbor C (C1), (c) second neighbor C (C2), (d) third neighbor C (C3), (e) fourth neighbor C (C4) and (f) fifth neighbor C (C5) sites of diamond with B at the substitutional site ($C_{63}B$ supercell model). The top of the valence band is taken at the origin. A vertical line denotes the Fermi energy.

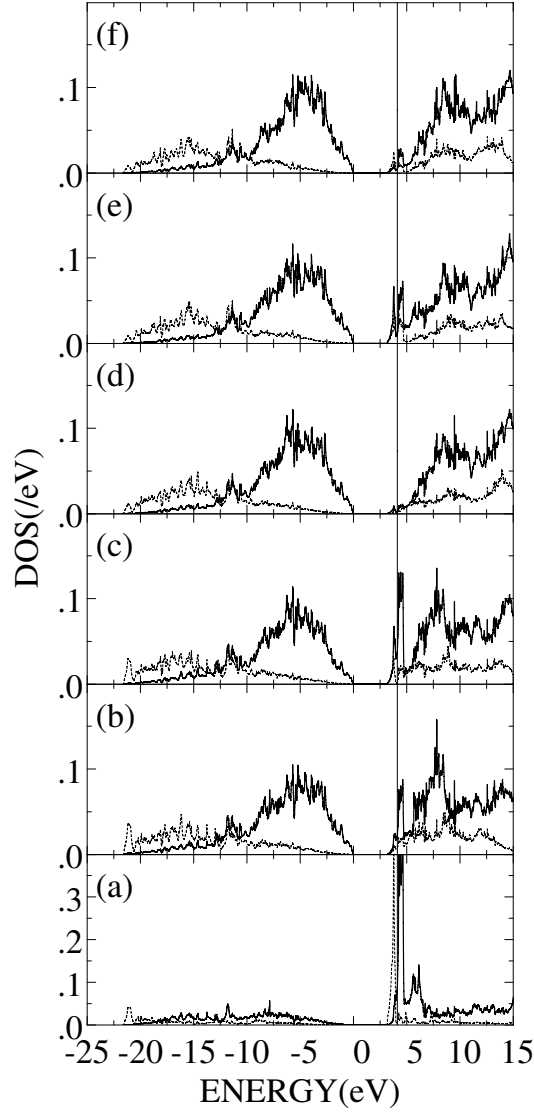


Fig. 2. Calculated partial density of s (broken lines) and p (solid lines) states projected on the (a) B, (b) first neighbor C (C1), (c) second neighbor C (C2), (d) third neighbor C (C3), (e) fourth neighbor C (C4) and (f) fifth neighbor C (C5) sites of diamond with B at the interstitial T_d site ($C_{64}B$ supercell model). The top of the valence band is taken at the origin. A vertical line denotes the Fermi energy.

photoemission spectra [13]. On the other hand, C1 and C2 $1s$ core levels become deeper by 0.8eV in the interstitial case, which may possibly explain asymmetric peak in the spectra. Mechanism of the core shift is quite simple. By substitutional B doping, potential at the C1 site goes up because B has

shallower potential than C and by B insertion at the interstitial site, potential at the C1 and C2 sites surrounding B goes down. This core shift may be a clue to understand the observed XAS spectra at the C K -edge.

XAS transition probability is given by the Fermi golden rule as

$$W(\omega) = \frac{2\pi}{\hbar} \sum_f |\langle f|\hat{F}|i\rangle|^2 \delta(\varepsilon_f - \varepsilon_i - \hbar\omega), \quad (1)$$

where $|f\rangle$ ($|i\rangle$) is the final (initial) state of the transition and ε_f (ε_i) is the corresponding eigen energy. Electric dipole transition is usually dominant and the matrix element $\langle f|\hat{F}|i\rangle$ is expressed in terms of electric-field vector of photon \mathbf{E} and electron coordinate \mathbf{r} as $\langle f|\hat{F}|i\rangle = e\langle f|\mathbf{E} \cdot \mathbf{r}|i\rangle$. So, parity of the initial and final states should be different and one can see transitions from $1s$ to $2p$ states for C and B at the K edge.

Figure 3 shows calculated XAS spectra for C at the K edge in $C_{63}B$ model. Due to core shift to smaller binding energy at the C1 site, hole-doping states at the C1 site is shifted from those at the others. This calculated feature is in good agreement with the "H" and "I" structures in the experimental XAS spectra by Nakamura [15]. As the B concentration increases (from $C_{63}B$ to $C_{31}B$), XAS spectrum at the hole states is amplified while the energy difference between the two structures is unchanged. As expected from the partial density of B p states in Fig. 1, XAS spectrum for B at the K edge shows hole-doping states around the VBM and nothing in the energy-gap region. Thus, the in-gap states seen in experiment [15] may be attributed to impurity states of charged B at the interstitial site or other B-related impurity states.

In order to investigate the relative stability of the impurity sites, we have

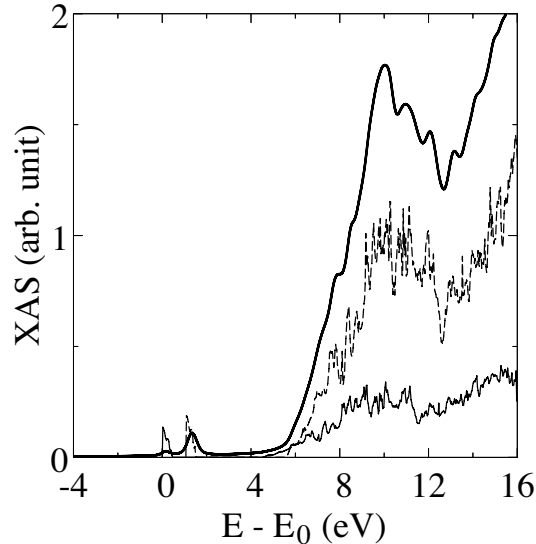


Fig. 3. Calculated XAS spectrum for C at the K edge in $C_{63}B$ model (thick solid line). Thin solid and broken lines denote its contributions from the C1 and C2 sites, respectively. The Fermi energy is taken at the absorption threshold E_0 . estimated formation energy as follows,

$$E_{tot}[C_{63}B] + \mu_C - E_{tot}[C_{64}B] = -17.1\text{eV} \quad (2)$$

$$E_{tot}[C_{31}B] + \mu_C - E_{tot}[C_{32}B] = -16.9\text{eV}, \quad (3)$$

where $E_{tot}[A]$ is the calculated total energy for model A and μ_C is the chemical potential of C. This result shows that B doping at the substitutional site is definitely favored compared with that at the interstitial T_d site. Even if possible charged states are considered, it is unlikely that B impurities are doped at the interstitial T_d site in diamond. It is, therefore, reasonable to conclude that the in-gap states in the observed B K -edge XAS spectra might be assigned to a B-related impurity state other than of the interstitial-B origin. Since a large amount of hydrogen is co-doped in B-doped diamond, a B-H impurity complex might be a candidate for the in-gap states. It has been reported [18] that the B^-H^+ complex is stabilized in diamond, forming such in-gap impurity states.

4 Summary

In summary, we have performed first-principles calculations for B-doped diamond with different doping sites, substitutional and interstitial. In the substitutional B case, a hole-doping situation in a rigid-band picture takes place like observation in SXARPES and XES. It is found that core shift at C1 may explain the "H" and "I" structures in the C K -edge XAS. The interstitial B forms possibly charged states in the energy gap in a p -type sample, as seen in the B K -edge XAS. However, calculated formation energy denies the possible existence of the interstitial B. For a consistent explanation for the observed results, another B impurity state should be considered in addition to the substitutional B.

Acknowledgements

This work is supported by a Grant-in-Aid for Scientific Research in Priority Area (No.16076212) and COE Research (No.13CE2002) of the Ministry of Education, Culture, Sports, Science and Technology of Japan. We thank N. Yamada, J. Nakamura and T. Yokoya for invaluable discussions.

References

- [1] E. A. Ekimov, V. A. Sidorov, E. D. Bauer, N. N. Mel'nik, N. J. Curro, J. D. Thomson, S. M. Stishov, Superconductivity in diamond, *Nature* 428 (2004) 542-545.
- [2] Y. Takano, M. Nagao, I. Sakaguchi, M. Tachiki, T. Hatano, K. Kobayashi, H.

Umezawa, H. Kawarada, Superconductivity in diamond thin films well above liquid helium temperature, *Appl. Phys. Lett.* 85 (2004) 2851-2853 .

- [3] E. Bustarret, J. Kacmarcik, C. Marcenat, E. Gheeraert, C. Cytermann, J. Marcus, T. Klein, Dependence of the superconducting transition temperature on the doping level in single-crystalline diamond films, *Phys. Rev. Lett.* 93 (2004) 237005 (4 pages).
- [4] V. A. Sidorov, E. A. Ekimov, S. M. Stishov, E. D. Bauer, J. D. Thomson, Superconducting and normal-state properties of heavily hole-doped diamond, *Phys. Rev. B* 71 (2005) 060502(R) (4 pages).
- [5] H. Umezawa, T. Takenouchi, Y. Takano, K. Kobayashi, M. Nagao, I. Sakaguchi, M. Tachiki, T. Hatano, G. Zhong, M. Tachiki, H. Kawarada, *cond-mat/0503303*.
- [6] L. Boeri, J. Kortus, O. K. Andersen, Three-dimensional MgB₂ superconductivity in hole-doped diamond, *Phys. Rev. Lett.* 93 (2004) 237002 (4 pages).
- [7] K.-W. Lee, W. E. Pickett, Superconductivity in boron-doped diamond, *Phys. Rev. Lett.* 93 (2004) 237003 (4 pages).
- [8] X. Blase, Ch. Adessi, W. E. Connétable, Role of the dopant in the superconductivity of diamond, *Phys. Rev. Lett.* 93 (2004) 237004 (4 pages).
- [9] H. J. Xiang, Z. Li, J. Yang, J. G. Hou, Q. Zhu, Electron-phonon coupling in a boron-doped diamond superconductor, *Phys. Rev. B* 70 (2004) 212504 (4 pages).
- [10] G. Baskaran, Resonating valence bond mechanism of impurity band superconductivity in diamond, *cond-mat/0404286*.
- [11] G. Baskaran, Strongly correlated impurity band superconductivity in diamond: x-ray spectroscopic evidence for upper Hubbard and mid-gap bands, *cond-mat/0410296*.

- [12] T. Yokoya, T. Nakamura, T. Matsushita, T. Muro, Y. Takano, M. Nagao, T. Takenouchi, H. Kawarada, T. Oguchi, Origin of the metallic properties of heavily boron-doped superconducting diamond, *Nature* 438 (2005) 647-650.
- [13] T. Yokoya, private communication.
- [14] J. Nakamura, E. Kabasawa, N. Yamada, Y. Einaga, D. Saito, H. Isshiki, S. Yugo, R. C. C. Perera, Electronic structures of B $2p$ and C $2p$ levels in boron-doped diamond films studied using soft x-ray absorption and emission spectroscopy, *Phys. Rev. B* 70 (2004) 245111(6 pages).
- [15] J. Nakamura, T. Oguchi, N. Yamada, K. Kuroki, K. Okada, Y. Takano, M. Nagao, I. Sakaguchi, H. Kawarada, R. C. C. Perera, D. L. Ederer, Holes in the valence band of superconducting boron-doped diamond film studied by soft x-ray absorption and emission spectroscopy, *cond-mat/0410144*.
- [16] J. F. Janak, V. L. Moruzzi and A. R. Williams, Ground-state thermomechanical properties of some cubic elements in the local-density formalism, *Phys. Rev. B* 12 (1975) 1257-1261.
- [17] J. P. Perdew, K. Burke and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* 77 (1996) 3865-3868.
- [18] H. Katayama-Yoshida, private communication.