

Stability and electronic structure of potassium-intercalated hexagonal boron nitride from density functional calculations

Susumu Okada^{1,2} and Minoru Otani^{3,2}¹*Graduate School of Pure and Applied Sciences and Center for Computational Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8571, Japan*²*CREST, Japan Science and Technology Agency, 5 Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan*³*Research Institute for Computational Sciences, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8568, Japan*

(Received 21 December 2009; revised manuscript received 11 March 2010; published 9 June 2010)

By using the local-density approximation in density functional theory, we explore the possibility of a metallic layered compound derived from hexagonal boron nitride (h-BN). We find that the intercalation process of potassium atoms into the interlayer spacing of h-BN is exothermic with a formation energy of approximately 1.6 eV per potassium atom, and that the electronic structure of potassium-intercalated h-BN under equilibrium interlayer distance is metallic, in which electrons are injected into unoccupied, nearly-free-electron states. The calculated Fermi surfaces of the compound exhibit characteristics similar to that of graphite intercalation compounds doped with alkali/alkali-earth metals.

DOI: [10.1103/PhysRevB.81.233401](https://doi.org/10.1103/PhysRevB.81.233401)

PACS number(s): 73.20.At, 73.22.-f, 73.22.Pr, 71.20.Tx

I. INTRODUCTION

Graphite has occupied an important position in low-dimensional sciences and surface sciences for many years because of its layered structure, which comprises perfectly planar hexagonal networks of carbon atoms. This layered structure causes unusual electronic and structural properties in graphite.¹⁻⁵ Graphite is a metal with remarkable electron mobility along the layers but lower conducting properties normal to the layers. From a structural viewpoint, graphite is known to serve as a host material for the intercalation of various atoms and molecules into the two-dimensional interlayer spaces that are several angstrom thick. These complexes are called graphite intercalation compounds (GICs), and some are known to exhibit superconductivity under appropriate conditions.^{1,3} In addition, the large interlayer spacing also induces peculiar electron states whose wave functions are distributed not near atomic sites but in the interlayer region of graphite.^{3,6-9} These states are unoccupied and typically exhibit free-electron character along the layers but they are located below the vacuum level and play decisive roles in the excitation spectrum and even in the ground-state electronic properties upon intercalation of foreign atoms in the interlayer spacing. Indeed, the recent angle-resolved photoemission spectroscopy (ARPES) experiment has shown that this state substantially contributes to the electronic properties near the Fermi level of Ca-GIC.¹⁰ Owing to its distribution, this state is known as the interlayer band or the nearly-free-electron (NFE) state.

Hexagonal boron nitride (h-BN) is another prototypical layered material and possesses a hexagonal network consisting of B and N atoms. Due to the chemical difference between B and N atoms, h-BN is an insulator with a large energy gap.^{11,12} However, the large interlayer spacing caused by its layered structure also leads to the NFE state, as for graphite.¹¹ In this case, the bottom of conduction band at the Γ point also possesses NFE character and is distributed in the interlayer spacing. Although experimental results indicate that some chemical elements are indeed intercalated into

h-BN,¹³⁻¹⁵ the fundamental properties of the compounds remain unclear. Based on the analogy with GICs, the hybrid structure of h-BN and atoms that are intercalated into the interlayer spacing may also exhibit interesting electronic properties because the lower unoccupied electronic structure of h-BN is similar to that of graphite.

In the present study, we explore the possibility of potassium-intercalated h-BN compounds and elucidate its electronic properties. Our first-principles, total-energy calculations of K-intercalated h-BN clarify that the compound is stable in energy and is exothermic upon formation. Furthermore, the electronic structure near the Fermi energy of the compound exhibits characteristics similar to those of GIC. In particular, we find a clear isotropic Fermi surface around the Γ point in K-intercalated h-BN.

II. CALCULATION METHODS

We perform a total-energy electronic-structure calculation in the framework of the density functional theory (DFT).^{16,17} The exchange-correlation energy of interacting electrons is treated in terms of the local-density approximation with a functional form fitted to the Ceperley-Alder result.^{18,19} Norm-conserving pseudopotentials generated by using the Troullier-Martins scheme²⁰ with the Kleinman-Bylander approximation²¹ are adopted to describe the electron-ion interaction. The valence wave functions are expanded in a plane-wave basis set with a cutoff energy of 50 Ry, which achieves sufficient convergence for the relative total energies of h-BN.^{22,23} We adopt the conjugate-gradient minimization scheme for both the electronic-structure calculation and for geometry optimization.²⁴ Structural optimizations are performed iteratively until the remaining force acting on each atom is less than 5 mRy/Å. Integration over the Brillouin zone is performed using equidistant k -point sampling in which 64 k points ($=4 \times 4 \times 4$) were taken. All calculations were performed by using a program package PSPW.²⁴

To investigate the possibility of K atoms to intercalate into the interlayer spacing of h-BN and to elucidate the elec-

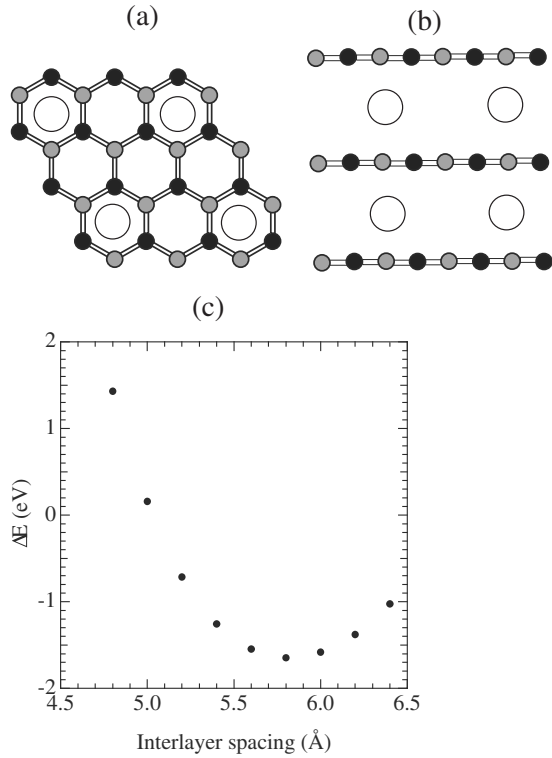


FIG. 1. Schematic (a) top and (b) side views of K-intercalated h-BN compound. White, pale shaded, dark shaded circles denote K, B, and N atoms, respectively. (c) The formation energy of K-intercalated h-BN as a function of interlayer spacing of h-BN per unit cell $[\text{K}(\text{BN})_4]$.

tronic structure of the resulting intercalation compound, we consider the structural model shown in Figs. 1(a) and 1(b). In this model, we assume the pseudostage-one structure in which each interlayer spacing is occupied by a K atomic layer. The intercalated K atoms are located on the hollow site of one of four hexagonal rings of h-BN. Thus, the stoichiometry of the compound is $\text{K}(\text{BN})_4$. In the model, each h-BN layer is stacked in the AA arrangement as for stage-one GIC. Because of the model considered here, the lateral periodicity of the compound is twice that of conventional h-BN whereas the vertical periodicity is half that of h-BN.

III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show energy diagrams of a h-BN monolayer and of graphene, respectively. Because h-BN is an insulator with a 4.67 eV energy gap at the K point, the top of the valence band and the bottom of the conduction band are located at a lower energy and at a higher energy, respectively, compared with the Fermi energy of graphene. More specifically, the valence-band top and the conduction-band bottom of h-BN are located at 6.20 eV and 1.53 eV below the vacuum level, respectively, whereas the Fermi level of graphene is at 4.57 eV below the vacuum level. In sharp contrast, the eigenvalues of the NFE state for both h-BN and graphite are almost equal; 1.26 eV and 1.10 eV below the vacuum level for h-BN and graphene, respectively. This result raises the possibility of electron injection into the NFE

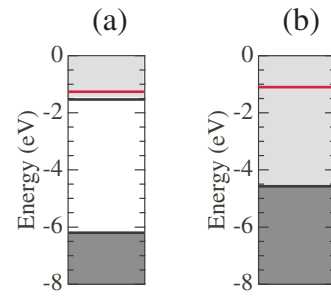


FIG. 2. (Color online) Energy diagrams of (a) h-BN monolayer and (b) graphene. The dark and pale shaded areas denote the valence and conduction bands, respectively. A red (pale) line denotes the energy position of the bottom of the nearly-free-electron state. Energies are measured from that of the vacuum level. The vacuum level is evaluated by the energy level at the region far from the layers where the local potential is almost constant.

state of h-BN by interaction of atoms or molecules in the interlayer spacing because the NFE state of graphite is essential to the metallic nature of GICs. Furthermore, h-BN is expected to be applicable for *n*-type semiconducting devices by tuning its lower unoccupied states.

Figure 1(c) shows the formation energy of the K-intercalated h-BN compound as a function of interlayer spacing. The energy is evaluated by taking the difference between the total energy of K-intercalated h-BN and the sum of the total energies of pristine h-BN and the solid phase of potassium. The intercalation is exothermic and the resultant intercalation compound is energetically stable. The calculated formation energy of the compound under equilibrium interlayer distance is 1.6 eV per K atom. Furthermore, the equilibrium interlayer spacing is about 5.8 Å, which is close to that of KC_8 . This result clearly indicates that the intercalation of K atoms into h-BN should occur from the viewpoint of the energetics. We note that the formation energy calculated here is slightly underestimated or overestimated compared with that obtained under a realistic stacking arrangement because the model used in this work is not a real stage-one structure but a pseudostage-one structure. Furthermore, the formation energy is also underestimated or overestimated due to the calculation methods used in this work.

We find that the K-intercalated h-BN compound is a metal in which the metallic nature is due to a parabolic energy band around the Γ point, as shown in Fig. 3(a). The Fermi level clearly crosses the energy band at the Brillouin-zone boundaries. A detailed analysis of this energy band clarifies its unusual character compared with the other electronic energy bands. Indeed, the wave function of this energy band is distributed not only on the atomic layer but also in the spacious region between the layers, where the B and N atoms are absent. The distribution of the wave function clearly indicates its NFE nature as the case of the pristine h-BN.¹¹ The distribution is completely different from the wave function associated with the remaining states. For example, the top of the valence band possesses a bonding π character [Fig. 3(c)]. This result indicates that the electronic system around the Fermi level of the compound is qualitatively identical to that of alkali- or alkali-earth-metal-doped GICs.⁷ Thus,

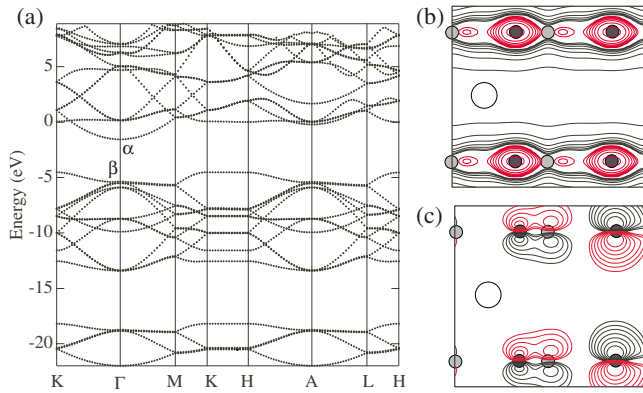


FIG. 3. (Color online) (a) Electronic energy band of K-intercalated h-BN compound. Energy is measured from that of the Fermi level. Distribution of wave function of (b) the nearly-free-electron state denoted by α and of (c) the electronic energy band denoted by β (the top of valence band and a nondegenerate state) at the Γ point, respectively. Black and red contours characterize the sign of the wave functions. Each contour represents twice (or half) the density of the adjacent contour lines.

potassium-intercalated h-BN compounds are expected to be candidates for metallic layered materials that exhibit unusual physical properties such as superconductivity and magnetism as is the case of GICs.

It is important to depict the Fermi surfaces of K-intercalated h-BN to discuss the similarity of the electronic structure near the Fermi level between K-doped h-BN and alkali/alkali-earth-metal-doped GICs. Figures 4(a)–4(c) show the Fermi surfaces (lines) of h-BN in the k_x - k_y , k_x - k_z , and k_y - k_z planes of the Brillouin zone, respectively. The Fermi surface in the k_x - k_y plane is found to be isotropic, forming a perfect closed circle [Fig. 4(a)]. The diameter of the circle in the k_x - k_y plane is about $0.51(2\pi/a)$, where a is the lattice constant of the compound corresponding to twice the conventional lateral lattice parameter of h-BN. The circular shape of the Fermi surface is the same as that of the alkali/alkali-earth-metal-doped GICs. The recent ARPES experiment has clearly indicated the circular Fermi surface on k_x - k_y plane.¹⁰ The insulating character of h-BN also leads to larger-diameter Fermi surfaces than those of GICs. In addition, along the k_z direction, the squeezed shape of the Fermi surfaces for h-BN is also qualitatively identical to that for GICs. Thus, these results suggest that K-intercalated h-BN is a metal possessing characteristics similar to alkali/alkali-earth-metal-intercalated graphite compounds around the Γ point. On the other hand, there are small but substantial discrepancies between the Fermi surfaces in the k_x - k_y plane of h-BN and GICs. In sharp contrast to the Fermi surfaces of GICs, the Fermi surfaces around the six corners of the hexagonal Brillouin zone (K points) are absent in h-BN. These surfaces are ascribed to the Dirac cone of the unoccupied π band of graphite, which is partially filled by electrons injected from the alkali/alkali-earth metals. Pristine h-BN is an insulator with a large energy gap so that the Fermi surfaces around the K point of the K-intercalated h-BN are absent.

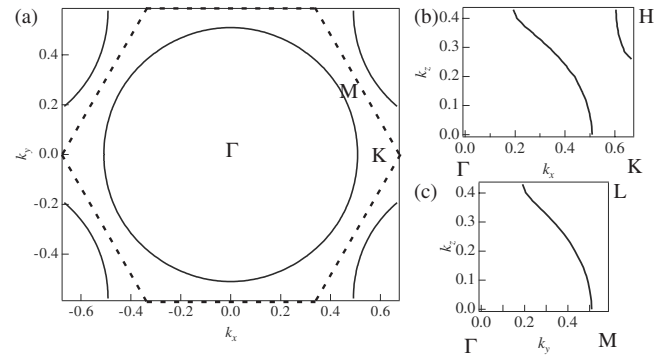


FIG. 4. The Fermi surfaces of K-intercalated h-BN compound on (a) k_x - k_y , (b) k_x - k_z , and (c) k_y - k_z planes in the Brillouin zone. Dotted line in (a) denotes the zone boundary of the hexagonal Brillouin zone.

IV. SUMMARY

We present a study of the energetics and electronic structure of the potassium-intercalated h-BN compound that uses first-principle total-energy calculations based on density functional theory. We show that K-intercalated h-BN is energetically stable with an interlayer distance of approximately 5.8 Å, as is the case of the K-doped graphite intercalated compound with a stage-one structure. The formation energy of K-intercalated h-BN is calculated to be approximately 1.6 eV per K atom. The large formation energy is ascribed to Coulomb interaction caused by the electron transfer from the K atom to the h-BN layer.

Under the equilibrium interlayer spacing, we show that K-intercalated h-BN is a metal, in sharp contrast to insulating character of pristine h-BN. Potassium intercalation leads to carrier injection into the nearly-free-electron states of h-BN. The characteristics of the carrier distribution of K-intercalated h-BN are almost equivalent to the electron system of alkali/alkali-earth-metal-doped GICs. Indeed, the Fermi surfaces are found to possess qualitatively similar characteristics to that of alkali/alkali-earth-metal-doped GICs; which is to say that they exhibit a circular and isotropic surface in the k_x - k_y plane of the Brillouin zone whereas they are squashed along the k_z direction. However, due to the insulating character of pristine h-BN, the area around the Γ point, which is surrounded by the Fermi surfaces, is wider than that of the alkali/alkali-earth-metal-doped GICs.

ACKNOWLEDGMENTS

We thank A. Oshiyama for providing the DFT program used in this study. This work was partly supported by CREST, Japan Science and Technology Agency, and a Grant-in-Aid for scientific research from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Computations were performed on an NEC SX-8/4B at the University of Tsukuba, on an NEC SX-8 at the Yukawa Institute of Theoretical Physics, Kyoto University, and on an NEC SX-9 at the Information Synergy Center, Tohoku University.

- ¹M. S. Dresselhaus and G. Dresselhaus, *Adv. Phys.* **30**, 139 (1981).
- ²A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, *Rev. Mod. Phys.* **81**, 109 (2009).
- ³H. Kamimura, *Phys. Today* **40**(12), 64 (1987).
- ⁴N. A. W. Holzwarth, S. G. Louie, and S. Rabii, *Phys. Rev. B* **26**, 5382 (1982).
- ⁵J.-C. Charlier, J.-P. Michenaud, X. Gonze, and J. P. Vigneron, *Phys. Rev. B* **44**, 13237 (1991).
- ⁶M. Posternak, A. Baldereschi, A. J. Freeman, E. Wimmer, and M. Weinert, *Phys. Rev. Lett.* **50**, 761 (1983).
- ⁷M. Posternak, A. Baldereschi, A. J. Freeman, and E. Wimmer, *Phys. Rev. Lett.* **52**, 863 (1984).
- ⁸Y. Miyamoto, A. Rubio, X. Blase, M. L. Cohen, and S. G. Louie, *Phys. Rev. Lett.* **74**, 2993 (1995).
- ⁹S. Okada, A. Oshiyama, and S. Saito, *Phys. Rev. B* **62**, 7634 (2000).
- ¹⁰K. Sugawara, T. Sato, and T. Takahashi, *Nat. Phys.* **5**, 40 (2009).
- ¹¹A. Catellani, M. Posternak, A. Baldereschi, and A. J. Freeman, *Phys. Rev. B* **36**, 6105 (1987).
- ¹²S. Okada, *Phys. Rev. B* **80**, 161404(R) (2009).
- ¹³C. Shen, S. G. Mayora, R. Biagioni, C. Piskoti, M. Ishigami, A. Zettl, and N. Bartlett, *J. Solid State Chem.* **147**, 74 (1999).
- ¹⁴E. Budak and C. Bozkurt, *J. Solid State Chem.* **177**, 1768 (2004).
- ¹⁵M. Hubáček, T. Sato, and M. Ueki, *J. Mater. Res.* **12**, 113 (1997).
- ¹⁶P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- ¹⁷W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ¹⁸J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ¹⁹D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- ²⁰N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- ²¹L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).
- ²²S. Okada and A. Oshiyama, *Phys. Rev. Lett.* **87**, 146803 (2001).
- ²³S. Okada, S. Saito, and A. Oshiyama, *Phys. Rev. B* **65**, 165410 (2002).
- ²⁴O. Sugino and A. Oshiyama, *Phys. Rev. Lett.* **68**, 1858 (1992).