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Theory of the electronic structure of alternating MgB_2 and graphene layered structures

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Structures for realizing hole-doped MgB_2 without appealing to chemical substitutions are proposed. These structures that consist of alternating MgB_2 and graphene layers have small excess energy compared to bulk graphite and MgB_2. Density functional theory based first-principles electronic structure calculations show significant charge transfer from the MgB_2 layer to graphene, resulting in effectively hole-doped MgB_2 and electron-doped graphene. Substantial enhancement in the density of states at the Fermi level and significant in-plane lattice expansion of the proposed structures are predicted. These structures combines three important factors, namely, hole doping, high density of states at the Fermi level, and in-plane lattice expansion, that are favorable for a strong electron-phonon coupling.

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Since the discovery of the unusually high superconducting transition temperature ($T_c = 39$ K) in MgB_2,[1] many attempts have been made to improve its T_c by chemical substitutions without success. Theoretical predictions[2,3] that significantly higher T_c may be achieved in a related compound hole-doped LiBC has not been realized. Recently, an interesting phase of lithium monoboride[4] has generated some renewed interest[5,6] in searching for MgB_2 related high-T_c materials. However, so far, it appears that the only effective and experimentally viable way of improving T_c is by applying tensile strain to the system.[7]

It is now well understood that electron doping through the substitution of Mg with Al or B with C fills the boron $p\sigma$ hole and reduces the electron-phonon (e-ph) coupling strength.[8–17] Surprisingly, hole doping through substituting Mg with Li or B with Be was also found to suppress T_c.[18–20] This is rather unexpected since it would suggest that MgB_2 is naturally optimally doped. In addition to introducing electrons or holes to the system, however, chemical substitution also gives rise to other changes such as impurity scattering[21–23] and pressure effects since the lattice of MgB_2 may shrink upon substitution. Both of these factors are detrimental to superconductivity in MgB_2 and cannot be decoupled easily from the intrinsic doping effects. Furthermore, whereas MgB_2 is readily doped with electrons, hole-doping MgB_2 by substitution of Mg with monovalent ions (e.g., Li or Na) is more difficult,[24,25] and there have been relatively fewer reports on hole-doped MgB_2. A detailed study[26] of the heat of formation suggests that Li or Na substituted systems are indeed unstable or metastable at best. From the viewpoint of the electronic density of states (DOS) at the Fermi level (E_F), hole doping should be more interesting than electron doping since the DOS curve is a sharply decreasing function at E_F in MgB_2.[27] Therefore, realizing ideally hole-doped MgB_2 systems is of great interest for testing theoretical predictions[28,29] as well as achieving potentially higher T_c.

In this Brief Report, we propose structures in which MgB_2 layers are *effectively* hole doped without appealing to chemical substitutions. The proposed structures consist of alternating MgB_2 and graphene layers, as shown in Fig. 1. It is well known that graphite can be doped with electrons by means of metal intercalations.[30,31] Therefore, it is likely that there will be charge transfer from MgB_2 to graphite when they are stacked together, resulting in effectively hole-doped MgB_2 and electron-doped graphene. This charge transfer also gives rise to an enhanced DOS at the Fermi level and expanded in-plane lattice constants of both MgB_2 and graphene subsystems, as will be discussed later. Therefore, these structures combine *three favorable factors*, namely, effective hole doping,[29] enhanced DOS at the Fermi level, and expanded in-plane lattice constants,[7] which are expected to contribute to an enhanced T_c. Such structures may be realizable using modern deposition techniques. For example, a heteroepitaxial double-layer system consisting of a monolayer of boron nitride on Ni(111) and a graphene overlayer has been reported.[32] Ultrathin graphite (or few-layer graphite) have been the subject of tremendous recent research interest, ranging from a fundamental understanding[33,34] of the behavior of two dimensional electrons with a linear dispersion (Dirac fermions) to graphite-based electronics.[35] This recent interest should motivate the development of new techniques to control the growth of graphene and related layered systems.

We first study two structures (Fig. 1) in which (a) Mg atoms distribute evenly in the B-C interfaces and (b) Mg atoms intercalate into one of the two B-C interfaces. Higher-stage intercalation structures, such as those shown in Fig. 1(c), may also be possible. All calculations are done using the *ab initio* pseudopotential plane wave method,[36] unless indicated otherwise. The energy cutoff for the plane wave

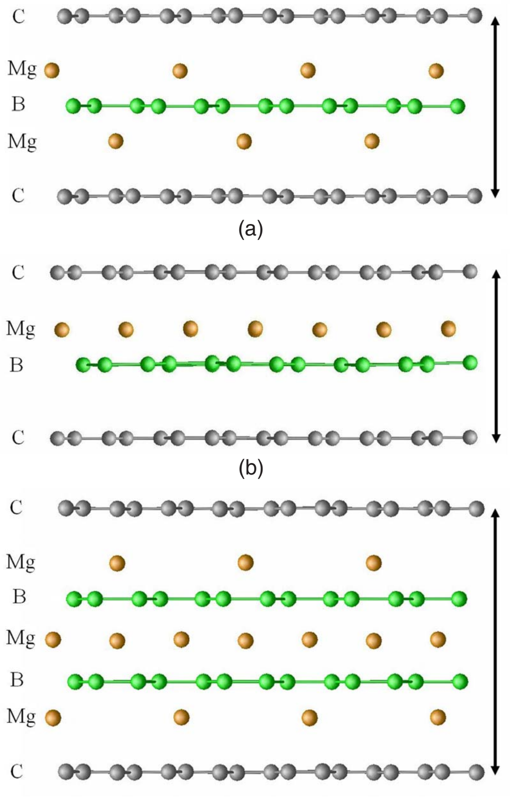

FIG. 1. (Color online) Proposed composite MgB_2/graphite structures. Higher-stage intercalation structures are also possible.

expansion is set at 60 Ry to ensure the convergence of the calculations since we use norm-conserving pseudopotentials.[37] The Brillouin zone is sampled by using a uniform k grid with a density equivalent to $24\times24\times18$ for a primitive MgB_2 cell.

Structural properties. The calculated in-plane lattice constant a is 2.448 Å for graphite and 3.033 Å for MgB_2. It is interesting to note that the ratio of the in-plane lattice constants $a(MgB_2)/a(\text{graphite}) \approx 5/4$. Therefore, we use a supercell containing 4×4 MgB_2 and 5×5 graphene units in our calculations. We note that lattice mismatch is not an issue here since interlayer coupling is rather weak in these layered structures. All structures studied are fully relaxed within the local density approximation. The average distortion of boron atoms from their ideal positions after relaxation is about 1.2×10^{-3} a.u., indicating that the underlying hexagonal boron network is minimally perturbed. The separation between the boron and the carbon layers in structure A is 3.42 Å, whereas those in structure B are 3.05 and 3.79 Å. The excess energy of structure A is 0.25 eV/interfacial atom compared to bulk graphite and MgB_2. Structure B is about 30 meV/atom higher in energy than structure A. The stage-2 structure shown in Fig. 1(c) also has a small excess energy of 0.22 eV/interfacial atom. These small excess energies indicate the relative stability of the proposed structure. In comparison, the curvature energy of a (10,0) nanotube is about 0.15 eV/atom.[38] The cohesive energy of C60 is about 0.4 eV/atom,[39] smaller than that of graphite. Therefore, with advances in deposition techniques, growing such metastable structures may be possible.

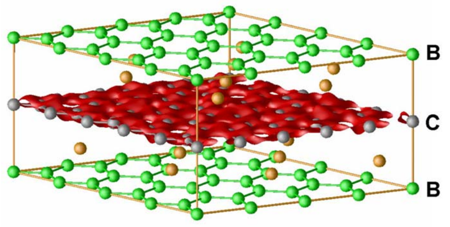

FIG. 2. (Color online) Isosurface plot of the charge density difference $\Delta\rho$ defined in the text ($\Delta\rho = 1.5\times10^{-3}$ e/a.u.^{3}). Electron transfer from MgB_2 to graphene in the proposed structure A results in a charge density enhancement near the graphene (C) plane.

One of the important results of our study is that the in-plane lattice constants of the proposed structures (both the graphene and MgB_2 layers) expand substantially, 0.9% for structure A and 1.1% for structure B. These lattice expansions are significantly greater than those achieved in MgB_2 films grown on a SiC substrate ($\sim$0.55%);[7] an observed 5% T_c enhancement was attributed to the tensile strain induced softening of the E_{2g} phonon.[7] Although we have not done detailed phonon calculations, we expect that similar phonon softening exists in the proposed systems, potentially leading to a higher T_c.

Electronic properties. It is now well understood that the C-C bonds in metal intercalated graphite elongate monotonically with increasing charge transfer.[30,31] Similarly, doping MgB_2 with holes weakens the boron network and may also lead to lattice expansion. Therefore, the expanded in-plane lattice constant of the alternating MgB_2/C structures suggests that there is significant charge transfer from MgB_2 to graphite. To verify this observation, we have carried out a calculation using a local basis set as implemented in the SIESTA code.[40] A standard Mulliken charge analysis shows that the charge (electron) transfer from MgB_2 to graphite is about 0.037 e/C atom or 0.125 e/MgB_2. The charge transfer effect can also be visualized by plotting the charge density difference between the proposed composite structures (cs) and the isolated graphite (g) and MgB_2 (mb) layers defined by $\Delta\rho(\mathbf{r}) = \rho^{cs}(\mathbf{r}) - [\rho^{g}(\mathbf{r}) + \rho^{mb}(\mathbf{r})]$. Figure 2 shows the isosurface plot for $\Delta\rho(\mathbf{r}) = 1.5\times10^{-3}$ e/a.u.^{3}. It is clear that the charge (electron) density enhancement in the composite structures is strongly localized near the carbon plane. This further confirms the charge transfer from MgB_2 to graphene, resulting in effectively hole-doped MgB_2.

To illustrate better the charge transfer effect on the electronic structure, we compare the DOS for bulk graphite and MgB_2 [Fig. 3(a)] with that of the proposed structure A [Fig. 3(b)]. The DOS of structure B is similar to that of structure A and is not shown. Note that the DOS of graphite is rescaled to that of a two-atom cell; the DOS of the proposed structures is scaled to that of the corresponding supercells. Since the DOS of graphite rises sharply away from the E_F, within the rigid-band approximation, we expect a significant increase in the DOS at E_F if electrons are transferred to the graphene layer. Similarly, hole-doping MgB_2 will result in an increase in the DOS at E_F. Indeed, the calculated DOS at E_F of the proposed structure A is greatly enhanced compared to

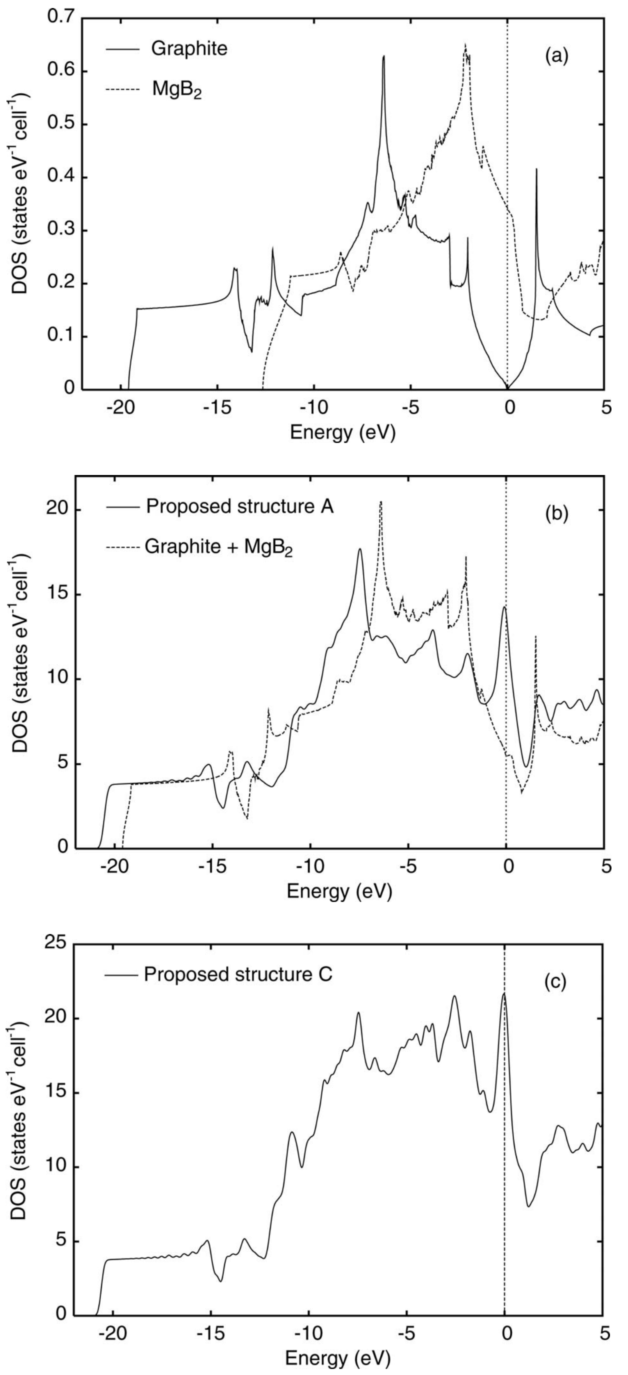

FIG. 3. Comparison between the density of states of the proposed structures and those of bulk graphite and MgB$_2$. The Fermi level E_F is fixed at zero. The significant enhancement in the density of states at the Fermi level of the proposed structures is largely due to charge transfer effects, as explained in the text.

the simple addition of the DOSs of the bulk graphite and MgB$_2$ (without shifting the Fermi levels), as shown in Fig. 3(b). In addition, there is a large downshift ($\sim$1.15 eV) of the bottom of the valence band with respect to the Fermi level in the alternating MgB$_2$/C structure. Since the bottom of the valence band is primarily of carbon 2s character, the downshift of these states with respect to the Fermi level is a result of occupying originally empty $p\pi^*$ states. If we simply integrate the DOS of graphite from its Fermi level E_F to E_F+1.15 eV, we obtain a charge transfer of 0.039 e/C atom in the rigid-band approximation. This is in excellent agreement with the Mulliken charge analysis. Higher-stage structures have a similar enhancement in the DOS at the Fermi level. For example, Fig. 3(c) shows the DOS of the proposed structure C [Fig. 1(c)], and such an enhancement is evident. It should be pointed out that having a Fermi level located near the peak position of the DOS curve, although often viewed as a signature of structural or magnetic instability, does not necessarily lead to structural instability in three dimensions. Such electronic degeneracy, however, is well known to result in structural distortion in zero dimensionla (Jahn-Teller instability) and one dimensional (Peierls instability) systems at low enough temperatures. In fact, some silicon clathrates[41,42] are known to have a Fermi level located near the peak position of the DOS.

It is expected that the e-ph coupling strength should increase moderately in the ideally hole-doped MgB$_2$, at least for low doping levels.[29] However, a detailed theoretical understanding of the hole-doped system is still lacking. On the experimental side, although there have been reports[18–20] that T_c drops in the hole-doped systems, it is too early to conclude that MgB$_2$ is naturally optimally doped. Difficulties in synthesizing high quality hole-doped MgB$_2$ through chemical substitution as well as impurity scattering effects may offset the intrinsic doping effects. In fact, even the published results[18,19] cannot be easily reproduced.[25] Therefore, the proposed structures, if successfully synthesized, are ideal for studying the ultimate e-ph coupling strength in hole-doped MgB$_2$. As discussed above, these structures combine three favorable factors, namely, effective hole doping, higher DOS at the Fermi level, and in-plane lattice expansion, which may lead to a higher T_c.

In summary, structures for realizing hole-doped MgB$_2$ without chemical substitution are proposed. These structures consist of alternating MgB$_2$ and graphene layers and have small excess energy compared to bulk graphite and MgB$_2$. Detailed density-functional-theory-based electronic structure calculations indicate that there is a sizeable charge transfer from MgB$_2$ to graphene layers, resulting in hole-doped MgB$_2$ and electron-doped graphene. This charge transfer also results in a significant enhancement in the DOS at the Fermi level and expanded in-plane lattice constants.

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[1] J. Nagamastsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature (London) **410**, 63 (2001).
[2] H. Rosner, A. Kitaigorodsky, and W. E. Pickett, Phys. Rev. Lett. **88**, 127001 (2002).
[3] J. K. Dewhurst, S. Sharma, C. Ambrosch-Draxl, and B. Johansson, Phys. Rev. B **68**, 020504(R) (2003).
[4] A. N. Kolmogorov and S. Curtarolo, Phys. Rev. B **74**, 224507 (2006).
[5] A. Y. Liu and I. I. Marzin, Phys. Rev. B **75**, 064510 (2007).
[6] M. Calandra, A. N. Kolmogorov, and S. Curtarolo, Phys. Rev. B **75**, 144506 (2007).
[7] A. V. Pogrebhyakov, J. M. Redwing, S. Raghavan, V. Vaithyanathan, D. G. Schlom, S. Y. Xu, Qi Li, D. A. Tenne, A. Soukiassian, X. X. Xi, M. D. Johannes, D. Kasinathan, W. E. Pickett, J. S. Wu, and J. C. H. Spence, Phys. Rev. Lett. **93**, 147006 (2004).
[8] T. Takenobu, T. Ito, Dam Hieu Chi, K. Prassides, and Y. Iwasa, Phys. Rev. B **64**, 134513 (2001).
[9] P. Postorino, A. Congeduti, P. Dore, A. Nucara, A. Bianconi, D. Di Castro, S. De Negri, and A. Saccone, Phys. Rev. B **65**, 020507 (2002).
[10] J. S. Slusky, N. Rogado, K. A. Regan, M. A. Hayward, P. Khalifah, T. He, K. Inumaru, S. M. Loureiro, M. K. Haas, H. W. Zandbergen, and R. J. Cava, Nature (London) **410**, 343 (2001).
[11] J. Q. Li, L. Li, F. M. Liu, C. Dong, J. Y. Xiang, and Z. X. Zhao, Phys. Rev. B **65**, 132505 (2002).
[12] O. de la Peña, A. Aguayo, and R. de Coss, Phys. Rev. B **66**, 012511 (2002).
[13] A. Bianconi, S. Agrestini, D. Di Castro, G. Campi, G. Zangari, N. L. Saini, A. Saccone, S. De Negri, M. Giovannini, G. Profeta, A. Continenza, G. Satta, S. Massidda, A. Cassetta, A. Pifferi, and M. Colapietro, Phys. Rev. B **65**, 174515 (2002).
[14] W. Mickelson, J. Cumings, W. Han, and A. Zettl, Phys. Rev. B **65**, 052505 (2002).
[15] M. Putti, M. Affronte, P. Manfrinetti, and A. Palenzona, Phys. Rev. B **68**, 094514 (2003).
[16] R. H. T. Whilke, S. L. Bud'ko, P. C. Canfield, D. K. Finnemore, R. J. Suplinskas, and S. T. Hannahs, Phys. Rev. Lett. **92**, 217003 (2004).
[17] P. Zhang, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **94**, 225502 (2005).
[18] Y. G. Zhao, X. P. Zhang, P. T. Qiao, H. T. Zhang, S. L. Jia, B. S. Cao, M. H. Zhu, Z. H. Han, X. L. Wang, and B. L. Gu, Physica C **361**, 91 (2001).
[19] S. Y. Li, Y. M. Xiong, W. Q. Mo, R. Fan, C. H. Wang, X. G. Luo, Z. Sun, H. T. Zhang, L. Li, L. Z. Cao, and X. H. Chen, Physica C **363**, 219 (2001).
[20] J. S. Ahn, Y.-J. Kim, M.-S. Kim, S.-I. Lee, and J. Choi, Phys. Rev. B **65**, 172503 (2002).
[21] J. Kortus, O. V. Dolgov, and R. K. Kremer, Phys. Rev. Lett. **94**, 027002 (2005).
[22] A. V. Sologubenko, N. D. Zhigadlo, S. M. Kazakov, J. Karpinski, and H. R. Ott, Phys. Rev. B **71**, 020501 (2005).
[23] A. V. Sologubenko, N. D. Zhigadlo, J. Karpinski, and H. R. Ott, Phys. Rev. B **74**, 184523 (2006).
[24] R. J. Cava, H. Z. Zandbergen, and K. Inumaru, Physica C **385**, 8 (2003).
[25] J. S. Schilling (private communication).
[26] X. S. Wu and J. Gao, Physica C **418**, 151 (2005).
[27] J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, and L. L. Boyer, Phys. Rev. Lett. **86**, 4656 (2001).
[28] N. I. Medvedeva, A. L. Ivanovskii, J. E. Medvedeva, and A. J. Freeman, Phys. Rev. B **64**, 020502 (2001).
[29] H. J. Choi (private communication). T_c is predicted to increase slightly with hole doping by solving a fully anisopropic Eliashberg equation.
[30] L. Pietronero and S. Strässler, Phys. Rev. Lett. **47**, 593 (1981).
[31] C. T. Chan, W. A. Kamitakahara, K. M. Ho, and P. C. Eklund, Phys. Rev. Lett. **58**, 1528 (1987).
[32] A. Nagashima, Y. Gamou, M. Terai, M. Wakabayashi, and C. Oshima, Phys. Rev. B **54**, 13491 (1996).
[33] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, Nature (London) **438**, 197 (2005).
[34] Y. B. Zhang, Y. W. Tan, H. L. Stormer, and P. Kim, Nature (London) **438**, 201 (2005).
[35] C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, Science **312**, 1191 (2005).
[36] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).
[37] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[38] D. Sánche-Portal, E. Artacho, J. M. Soler, A. Rubio, and P. Ordejón, Phys. Rev. B **59**, 12678 (1999).
[39] S. Okada and Susumu Saito, Phys. Rev. B **59**, 1930 (1999).
[40] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002).
[41] S. Saito and A. Oshiyama, Phys. Rev. B **51**, 2628(R) (1995).
[42] K. Moriguchi, M. Yonemura, and A. Shintani, Phys. Rev. B **61**, 9859 (2000).