Hole doping MgB$_2$ without chemical substitution

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Abstract

Structures for realizing hole-doped MgB$_2$ without appealing to chemical substitutions are proposed. These structures which 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$_2$. Substantial enhancement in the density of states at the Fermi level of the proposed structure is predicted.
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. It is now well understood that electron doping through substitution of Mg with Al or B with C fills the boron $p\sigma$ hole and reduces the electron-phonon (e-ph) coupling strength [2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. Surprisingly, hole doping through substituting Mg with Li or B with Be was also found to suppress the $T_c$ [12, 13, 14]. 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 [15, 16, 17] 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 [18, 19], and there have been relatively fewer reports on hole-doped MgB$_2$. Detailed study [20] 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 ($E_F$), another important parameter to raise $T_c$, hole doping should be more interesting than electron doping since the DOS curve is a sharply decreasing function at $E_F$ in MgB$_2$ as will be shown later. Therefore, realizing ideally hole-doped MgB$_2$ systems is of great interest for testing theoretical predictions [21, 22] as well as achieving potentially higher $T_c$.

In this paper, we propose novel 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. 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 [23]. The recent interest in graphite electronics [24] and the quantum Hall Effect in graphene [25, 26] should motivate the development of novel techniques to control the growth of graphene and related layered systems.

It is well-known that graphite can be doped with electrons by means of metal intercalations. 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$_2$. 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 shown in Fig. 1(C) may also be possible. All calculations are done using the \textit{ab initio} pseudopotential plane wave method [27] unless indicated otherwise. The energy cut-off for the plane waves expansion is set at 60 Ry to ensure the convergence of the calculations since we use norm-conserving pseudopotentials [28]. The Brillouin zone is sampled with a uniform $k$-grid with a density equivalent to $24 \times 24 \times 18$ for a primitive MgB$_2$ cell. 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 $\frac{a(\text{MgB}_2)}{a(\text{graphite})} \approx 5/4$. Therefore, we use a supercell containing $4 \times 4 \text{MgB}_2$ and $5 \times 5$ graphene units in our calculations.

All structures studied are fully relaxed within the local density approximation (LDA). The average distortion of boron atoms from their ideal positions after relaxation is about $1.2 \times$
FIG. 2: Charge density enhancement of the proposed structure B. The extra charges are mostly localized near the graphene plane.

$10^{-3}$ 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 cohesive energy of structure A is only 0.25 eV/atom higher compared to those of 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) has an even smaller excess energy of 0.15 eV/atom. These small excess energies indicate the relative stability of the proposed structure. With advances in deposition techniques, growing such metastable structures, especially higher-stage structures, may be possible.

One of the important results of our study is that the in-plane lattice constants of the proposed structures expand substantially, 0.9% for structure A and 1.1% for structure B. It is now well-understood that the C-C bonds in metal intercalated graphite elongate monotonically with increasing charge transfer \[29, 30\]. 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 also carried out a calculation using local basis-set as implemented in the Siesta code \[31\]. 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 $\Delta \rho (\mathbf{r}) = 2.5 \times 10^{-3}$ e/a.u.$^3$. It is clear that the charge density enhancement in the composite structures is localized near the carbon plane.

To better illustrate the charge transfer effect on the electronic structure, we compare the
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. 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.
DOS for bulk graphite and MgB$_2$ [Fig. 3 (a)], and that of proposed structure A [Fig. 3 (b)]. The DOS of structure B is similar to that of structure A; therefore it is not shown. Note that the DOS of graphite is rescaled to that of a 2-atom cell. 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 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 down-shift ($\sim 1.15$ 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 2$s$ character, the down-shift of these states with respect to the Fermi level is a result of occupying originally empty $p\sigma^*$ states. If we simply integrate the DOS of graphite from its Fermi level $E_F$ to $E_F + 1.15eV$, 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 similar enhancement in the DOS at the Fermi level. For example, figure 3 (c) shows the DOS of the proposed structure C [Fig. 1 (C)] and such an enhancement is evident.

It is widely expected that the e-ph coupling strength should increase moderately in the ideally hole-doped MgB$_2$, at least for low doping levels. However, a detailed theoretical understanding of the hole-doped system is still lacking. On the experimental side, although there have been reports [12, 13, 14] that the $T_c$ 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 [12, 13] can not be easily reproduced [19]. Therefore, the proposed structures, if successfully synthesized, are ideal for studying the ultimate e-ph coupling strength in MgB$_2$ and related systems. The significant enhancement in the DOS of these systems is beneficial for a stronger e-ph coupling and potentially for 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. Detailed DFT-based electronic structure calculations indicate that there is a sizeable charge transfer from the MgB$_2$ to graphene layers. In addition, significant enhancement in the DOS of these
structures suggests a stronger e-ph coupling beyond that of ideally hole-doped MgB$_2$.

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