The band structure of MgB$_2$ with different lattice constants

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Abstract

We report a detailed study of the electronic structure of the MgB$_2$ with different lattice constants by using the full-potential linearized augmented plane wave (FPLAPW) method. It is found that the lattice parameters have great effect on the $\sigma$ band of Boron. Our results indicate that increasing the lattice constant along the $c$ axis will increase the density of states (DOS) at the Fermi level, shift the $\sigma$ band upward, and increase the hole number in the $\sigma$ band. So, the superconducting transition temperature $T_c$ will be raised correspondingly. Changing the lattice constant along $a$ axis has the opposite effect to that of the $c$ axis. Our result is in agreement with experiment. A possible way of searching for higher $T_c$ superconductor has been indicated, i.e., making MgB$_2$ to have longer $c$ axis and shorter $a$, $b$ axis by doping.

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The discovery of superconductivity in magnesium diboride (MgB$_2$) [1,2] has stimulated worldwide excitement. The superconducting transition temperature for MgB$_2$ ($T_c \approx 39$ K) exceeds by almost two times the record values of $T_C$ for conventional $B_1$- and $A_{15}$-type intermetallic superconductors (SC) [3], which is by far the highest if we exclude copper oxides and $C_{60}$ based materials. As distinct from the high-temperature superconductor, MgB$_2$ has an exclusively simple composition and crystal structure [4]. The B isotope shift of $T_c$ reported by Bud’ko [5] and most other early experimental data[6] suggests conventional BCS strong-coupling s-wave electron-phonon (EP) pairing.

Band structure calculations show that the compound is not only quite ionic with a reasonable DOS, but also has strong covalent B-B bonding (the bonding-antibonding splitting due to in-plane B-B hopping is about 6 eV) and thus exhibits strong electron-phonon interactions[7, 8, 9]. Mg s-states are pushed up by the B $p_z$ orbitals and fully donate their electrons to the boron-derived conduction bands. Hirsch used a hole-superconductivity model to explain the high temperature superconductivity in MgB$_2$ as driven by undressing of hole carriers in the planar boron $p_{x,y}$ orbitals in the negatively charged B$^-$ planes [10]. The model by Hirsch predicts a positive pressure effect on $T_c$. However, high pressure studies show negative pressure coefficient of $T_c$[11, 12]. Based on an estimate of phonon frequencies and band structure calculations, Kortus et al[8] explain the superconductivity in MgB$_2$ as a result of strong electron-phonon coupling and An and Pickett[7] attributed it to the behavior of $p_{x,y}$-band holes in negatively charged boron planes. Many authors[7-9] emphasize the significant role of metallic B states in the appearance of superconductivity. According to the McMillan formula for $T_C$[13], the high transition temperature is probably due to a high density of states at the Fermi level, $N(E_F)$, high averaged electron-ion matrix elements, as well as high phonon frequencies, which increase for light elements and depend on $B-B$ and $M-B$ bonding.

Past experience said that $T_c$ should be strongly affected by doping or changing the lattice constants. Some experiments concerning substitutions on the Mg site have been done[14, 15]. Substitution of Al leads, apart from doping with electrons, to a compression of the structure
due to the difference in ionic radius between Al and Mg. The compression is anisotropic
and an Al content of x=0.1 leads to a structural instability. The rate of compression along
the c axis is about twice as much as along the a axis[14]. Both hole doping by substitution
of Li$^+$[15], and electron doping by substitution of Al$^{3+}$[14] for Mg$^{2+}$ led to a decrease of
$T_c$. In fact, Al doping will destroy bulk superconductivity when the Al content x is larger
than 0.3[14]. There are also many experiments concerning Boron sublattice doping[16].
The lattice parameter $a$ decreases almost linearly with increasing carbon content x, while
the c parameter remains unchanged, indicating that carbon is exclusively substituted in
the Boron honeycomb layer without affecting the interlayer interactions. $T_c$ also decreases
about linearly as a function of the carbon concentration. A recent experiment had also
found BiB$_2$ not to be a superconductor[17]. BiB$_2$ and MgB$_2$ are isostructural, and their
valence electron number is the same. So, the basic change is due to structural factors, i.e.
lattice parameter, $a$, and interatomic distance, $c/a$. Recently, high pressure studies show
that $T_c$ will decrease with increasing pressure[11, 12]. Compression will decrease both lattice
constant $a$ and $c$, but it is not yet know which one of them is responsible for decreasing $T_c$.
So, it is very interesting to investigate the Boron band structure, especially the $\pi$ and $\sigma$
band, as a function of lattice constants $a$ and $c$.

We have used the highly accurate all-electron full-potential linear augmented plane
wave method[18, 19]. The standard local density approximation to the electron exchange-
correlation potential was used together with the generalized gradient corrections of
Perdew[20]. The muffin-tin sphere radii (R) of 2.00 a.u. and 1.50 a.u. were chosen for
the Mg and B atoms, respectively, with a cutoff $R_{K_{\text{max}}}=8.0$.

MgB$_2$ is isomorphous with AlB$_2$[4]; the lattice constants of the hexagonal unit cell are
$a_0=3.0834$ and $c_0=3.5213$ Å. From the existing experiments we can see that high hydrostatic
pressure has an anisotropic influence along $a$ and $c$. The compression along the $c$ axis is 64%
stronger than along the $a$ axis, which is in line with the weaker Mg-B bond[21]. Thermal
compression along the $c$ axis is about twice the one along the $a$ axis. So, we fix $a=3.0834\,\text{Å}$,
and vary lattice constant $c$. The total energy-vs-c relation is shown in Fig.1. It can be seen

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that $c = c_0 = 3.5213 \, \text{Å}$ with the lowest total energy agrees with the experimental result.

The band structure of MgB$_2$ is shown in Fig. 2. For convenience, we set $E_f = 0$. From it we can see that there are two kinds of bands: the $\sigma$ and $\pi$ band. Both of them are contributed by Boron. The $\sigma$ band along $\Gamma$-A is double degenerate. Change of lattice constant will not change the symmetry, and so will not change its character. We found when $c = 1.4c_0$, the $\sigma$ band has a very small dispersion along $\Gamma$-A. But it will increase with decreasing $c$. Thus increasing $c$ will strengthen the 2D character of the $\sigma$ band, and if $c$ approaches $\infty$, MgB$_2$ becomes an ideal 2D B$_2$ layer. Another evident change is that the $\sigma$ band will shift upward with respect to the $E_f$ when we increase $c$. For $c = 0.8c_0$, the $\sigma$ band is below the Fermi energy, and the $\sigma$ bonding state would be completely filled. For $c = 0.9c_0$, the $\sigma$ band will cross the Fermi energy at the $\Gamma$ point. With increasing $c$, the $\sigma$ band will shift upward, and so will have more holes. On the other hand, increasing $c$ will decrease the hopping coefficient $t_{p\sigma}$ in Kortus’s TB model [8] for the $\pi$ band, and will cause the $\pi$ band dispersion along $\Gamma$-A decrease. Comparing with $E_f$, increasing $c$ will decrease the position of bonding $\pi$ band at $M$ and $\Gamma$ point, and will raise the position of bonding $\pi$ band at $A$ and $L$ point.

We have also studied the effect of lattice constant $a$ on the electronic structure, and found it to be opposite to $c$. With decreasing $a$, both bonding and antibonding $\sigma$ band will move upward with respect to $E_f$, and the splitting between bonding and antibonding $\sigma$ band will increase. When $c = 0.8c_0$ and $a = a_0$, the bonding $\sigma$ band is below the Fermi energy. Fixing $c$ and decreasing the $a$, the bonding $\sigma$ band will move upward. From Fig. 2(d), we can see that, when $c = 0.8c_0$ and $a = 0.9a_0$, its $\sigma$ band lies higher than it in Fig. 2(a), and there are holes in the bonding $\sigma$ band. The increase of splitting between bonding and antibonding $\sigma$ band is due to increase of the hopping coefficient with decreasing $a$. The possible reason why $\sigma$ band moves upward is electrostatic effect. Being different from $\sigma$ band, the bonding $\pi$ band will move downward with respect to the $E_f$ when $a$ decreases. Compression will decrease both the $a$ and $c$. But $\sigma$ bond of B-B is much stronger than the Mg-B bond, so, it is natural to expect that compression will mainly cause the decrease of $c$ [21]. Thus, we
can conclude that compression will shift the $\sigma$ band downward and decrease the number of holes in the $\sigma$ band.

We have also studied the relationship between the density of states at the Fermi level ($N_f$) and the lattice constants, which is shown in Fig.3. It is found that $N_f$ will increase with increasing of the lattice constant $c$, which is in agreement with other theoretical results[22, 23]. Many theories and experiments show that the MgB$_2$ is a BCS-like superconductor. So the electron-phonon coupling constant $\lambda$, which enters the BCS equation, is very important[13], and is proportional to $N_f$. Since $N_f$ will decrease for smaller $c$, $T_c$ will be decreased, which is in agreement with experiments[11, 12]. The states at the Fermi level, responsible for superconductivity, show two different orbital characters: $p-\sigma$ bonding (column-like FS around $\Gamma-A$) and $p_z$, which has $\pi$-bonding and antibonding characters on the basal and on the top ($k_z = \pi/c$) planes, respectively. Which one of them is the most important for the superconductivity is not yet known. In order to answer this question, we calculate the partial DOS of $\pi$ and $\sigma$ band of MgB$_2$ with different lattice constants $c$. We find that with a larger $c$, $N_f(\sigma)$ will increase, whereas $N_f(\pi)$ will decrease. Here, the $N_f(\sigma)$ ($N_f(\pi)$) means the density of $\sigma$ ($\pi$) state at Fermi energy. So, we can say that the $\sigma$ band of Boron plays a more important role for superconductivity than the $\pi$ band. The $p_\sigma$ and $p_\pi$ bands move with respect to each other with increasing $c$, thus inducing charge transfer between these two bands. It is the reason why the $N_f(\sigma)$ has an opposite trend to $N_f(\pi)$. Our result is in agreement with Goncharov and Bud’ko et al.,’s result[24].

In summary, we calculated the electronic structure of MgB$_2$ for different lattice constants. Our results show that increasing lattice constant $c$ will increase the DOS at the Fermi level, shift the $\sigma$ band upward, and thus increase the hole number in the $\sigma$ band. Decreasing $c$ will lower the $T_c$. The effect of changing $a$ is opposite to $c$. For constant $c$, a shorter $a$ will raise $T_c$. The main influence of compression is to decrease $c$, and thus will decrease the $T_c$, which is in agreement with the experiments[11, 12]. A search for a higher $T_c$ superconductor by doping MgB$_2$, would require a longer lattice constant $c$ and shorter $a$, $b$. A possible way would be a suitable substrate, which forces MgB$_2$ film to have longer $c$ but shorter $a$, $b$. 5
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REFERENCES

[1] R. J. Cava; Nature 410, 23 (2001).

[2] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani and J. Akimitsu; Nature 410, 63 (2001).

[3] S. V. Vonsovsky, Y. A. Izumov, and E. Z. Kurmaev; Superconductivity of Transition Metals, Alloys and Compounds, Springer, Berlin, (1982).

[4] M. E. Jones and R. E. Marsh; J. Am. Chem. Soc. 76, 1434 (1954).

[5] S. L. Bud’ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Canfield, Phys. Rev. Lett. 86, 1877 (2001).

[6] D. K. Finnemore, J. E. Ostenson, S. L. Bud’ko, G. Lapertot, and P. C. Canfield, Phys. Rev. Lett. 86, 2420 (2001); G. Rubio-Bollinger, H. Suderow, and S. Vieira, Phys. Rev. Lett. 86, 5582 (2001); B. Lorenz, R. L. Meng, C. W. Chu, P. C. Canfield, D. K. Finnemore, S. L. Bud’ko, J. E. Ostenson, G. Lapertot, C. E. Cunningham, and C. Petrovic, Phys. Rev. Lett. 86, 2423 (2001); A. Sharoni, I. Felner, and O. Millo Phys. Rev. B 63, 220508R (2001); H. Kotegawa, K. Ishida, Y. Kitaoka, T. Muranaka, J. Akimitsu, cond-mat/0102334.

[7] J. M. An and W. E. Pickett; Phys. Rev. Lett. 86, 4366 (2001).

[8] J. Kortus, I. I. Mazin, K. D. Belashenko, V. P. Antropov and L. L. Boyer, Phys. Rev. Lett. 86, 4656 (2001).

[9] K. D. Belashenko, M. van Schilfgaarde and V. P. Antropov, cond-mat/0102290 (2001); T. Yildirim, O. Gulseren, J. W. Lynn, C. M. Brown, T. J. Udovic, H. Z. Qing, N. Rogado, K.A. Regan, M.A. Hayward, J.S. Slusky, T. He, M.K. Haas, P. Khalifah, K. Inumaru, R.J. Cava, Phys. Rev. Lett. 87, 037001 (2001).

[10] J. E. Hirsch, Phys. Lett. A 282, 392 (2001).
[11] B. Lorenz, R. L. Meng and C. W. Chu; Phys. Rev. B 64, 012507 (2001).

[12] M. Monteverde, M. Nunez-Regueiro, N. Rogado, K. A. Regan, M. A. Hayward, T. He, S. M. Loureiro, and R. J. Cava, Science 292, 75 (2001).

[13] W. L. McMillan, Phys. Rev. 167, 331 (1968).

[14] J. S. Slusky, N. Rogado, K. A. Regan, M. A. Hayward, P. Khalifah, T. He, Nature 410, 343 (2001).

[15] 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, B. L. Gu, cond-mat/0103077 (2001).

[16] S. Zhang, J. Zhang, T. Zhao, C. Rong, B. Shen, Z. Cheng, cond-mat/0103203; T. Takenobu, T. Ito, Dan H. Chi, K. Prassides, Y. Iwasa, cond-mat/0103241; J. S. Ahn, and E. J. Choi, cond-mat/0103169 (2001).

[17] I. Felner, cond-mat/0102508 (2001).

[18] D. J. Singh, Planewaves, Pseudopotentials, and the LAPW Method (Kluwer Academic, Boston, 1994).

[19] P. Blaha, K. Schwarz, and J. Luitz, WIEN97, Vienna University of Technology, 1997; P. Blaha, K. Schwarz, P. Sorantin, and S. B. Trickey, Comput. Phys. Commun. 59, 399 (1990).

[20] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais , Phys. Rev. B 46, 6671 (1992); J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

[21] J. D. Jorgensen, D. G. Hinks, and S. Short, Phys. Rev. B 63, 224522 (2001).

[22] I. Loa and K. Syassen, Solid State Commun. 118, 279 (2001).

[23] J. B. Neaton and A. Perali, cond-mat/0104098 (2001).
[24] A. F. Goncharov et al., cond-mat/0106258 (2001).
Figure Captions

Figure 1 The total energy of MgB$_2$ as a function of lattice parameter $c/c_0$. $c_0 = 3.5213\text{Å}$.

Figure 2 The band structure of MgB$_2$ with different lattice constants. The circles represent the Boron $\sigma$ band. $a_0 = 3.0834\text{Å}$, $c_0 = 3.5213\text{Å}$. (a) $a=a_0$, $c=0.8c_0$; (b) $a=a_0$, $c=c_0$; (c) $a=a_0$, $c=1.4c_0$; (d) $a=0.9a_0$, $c=0.8c_0$.

Figure 3 Density of states near $E_f$ for MgB$_2$ with different lattice constants, $c/c_0 = 0.8$, 1.0 and 1.4. Fermi level is set at the zero.
Fig1
Fig2a

Energy (eV)
Fig 2b
Fig 2c

Energy (eV)

M Γ Δ A L

-8.0 -7.0 -6.0 -5.0 -4.0 -3.0 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0

E_F
Fig 2d

Energy (eV)
