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A first-principles study of MgB_2: the effect of pressure and substitution

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Abstract

We performed a first-principles calculation of the electronic band structure of MgB_2, a superconductor discovered recently, by employing a full-potential linear muffin-tin orbital method. In advance, the influences of the lattice parameter on the electronic structure are investigated with different volumes and c/a ratios. The effects of substitution on the electronic structure are discussed in relation to the variation of the lattice parameters and electron filling which is investigated via a Mg pseudo-atom. The variations of the two-dimensional covalent σ-band and three-dimensional metal π-band are investigated in detail at several high-symmetry points of the Brillouin zone (BZ). These results show that the variations of the electronic structure of MgB_2 are mainly determined by the effect of the c/a ratio. Considering the variation of the Fermi surface at the M and Γ points of the BZ, the corresponding electronic topological transition (ETT) induced by the lattice and doping are discussed. The ETT at the M point should be related to the structural phase transition in $Al_xMg_{1-x}B$.

1. Introduction

The recent discovery of superconductivity with $T_c = 39$ K in the binary alloy compound MgB_2 has attracted worldwide attention [1]. Its critical temperature is far from that of traditional superconductors. Compared with the C_{60} series or other high-T_c superconductors, MgB_2 has a simple AlB_2-type crystal structure (space group $P6mmm$). The borons form a primitive honeycomb lattice, consisting of graphite-like sheets with no displacement, and the layers of Mg located in the hexagonal prisms form a hexagonal structure. The B-isotope effects and tunnelling experiments as well as theories indicate that MgB_2 can be an electron–phonon-mediated superconductor [2–7].

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High-pressure experiments as well as theoretical investigations indicate that the MgB_2 crystal is very stable and isotropic [8–16]. Recently, studies of the effects of pressure on superconductivity have shown that anomalies emerge in the $T_c(P)$ dependence [10,11]—which was interpreted as the result of a phonon-assisted Lifshitz electronic topological transition (ETT). Because increasing pressure decreases T_c, it is expected that T_c will be increased by expanding the lattice. However, until now, in the MgB_2 system both electron and hole doping have only been found to decrease T_c [17–21]. In particular, associated with the substitution of about 10–25% Al content, a distinct two-phase coexistence is indicated. This subtle structural transition may also correspond to an ETT, which is associated with special characteristics of the electronic band filling corresponding to slight electron doping [26]. A detailed investigation with the aim of achieving an understanding of the anomaly mentioned above is desirable.

There have been many investigations of the electronic structure of MgB_2. The early works focus on the mechanism of superconductivity. The band structure, bonding, phonon spectra and the related compounds with AlB_2 structure have been investigated *ab initio* [5–7,22–26]. The electronic and structural properties of MgB_2 under hydrostatic and uniaxial compression have been studied using the LAPW method [14–16] and first-principles molecular dynamics (FPMD) [27]. The authors have focused on the pressure dependence of the superconductivity. Suzuki *et al* [28] have calculated the electronic structures of $Mg_{1-x}Al_xB_2$ and $Mg_{1-x}Na_xB_2$ at several points ($x = 0, 1/3, 2/3, 1$) to investigate the influence of σ-holes on the superconductivity.

In order to understand the structure and electronic anomalies mentioned above, it is still necessary to investigate the effects of pressure and substitution on the electronic structure—especially the Fermi surface—in detail. Moreover, there has been no discussion considering the simultaneous effect of the lattice parameters and substitutions.

Substitution changes not only the electron (hole) filling numbers in the unit cell, but also the lattice constant. The compression of the lattice induced by substitution is equivalent to the influence of high pressure. The variations of the electronic structure caused by substitution are very complex. However, considering the similarity of the calculated electronic structures for MgB_2 and AlB_2, the effect of substituting Al for Mg should be treated primarily as a simple filling of available electronic states [17]. We attempt to simulate the effect of substitution of Al by introducing a Mg pseudo-atom with non-integral electronic number. The calculation details are given in section 2. Then, the influences of volume, c/a ratio and various electron numbers on the band structure are investigated. A brief summary is given in the last section.

2. Calculation details

We employ a self-consistent full-potential linear muffin-tin orbital method (FP-LMTO) which was developed by Savrasov [30]. For the valence bands, a 3κ–spd LMTO basis is set and the Mg $2p$ semicore states are treated as valence states in a separate energy window. The charge densities and potentials are represented by spherical harmonics with $l \leqslant 6$ inside the non-overlapping MT spheres, and by plane waves with energies $\leqslant$394.15 Ryd in the interstitial region. The Vosko–Wilk–Nusair form of exchange–correlation potential is adopted together with the recently developed generalized-gradient approximation (GGA) of Perdew and Wang [31]. The $\boldsymbol{k}$-space integration over the Brillouin zone (BZ) is performed over a (12, 12, 12) grid by means of the improved tetrahedron method. This corresponds to 212 $\boldsymbol{k}$-points in the irreducible part of the BZ. Muffin-tin-sphere radii of 1.8 and 1.5 au were chosen for the Mg and B atoms, respectively. If the total-energy discrepancy between two subsequent iterations is less than 10^{-6} Ryd, we take it that self-consistency is achieved.

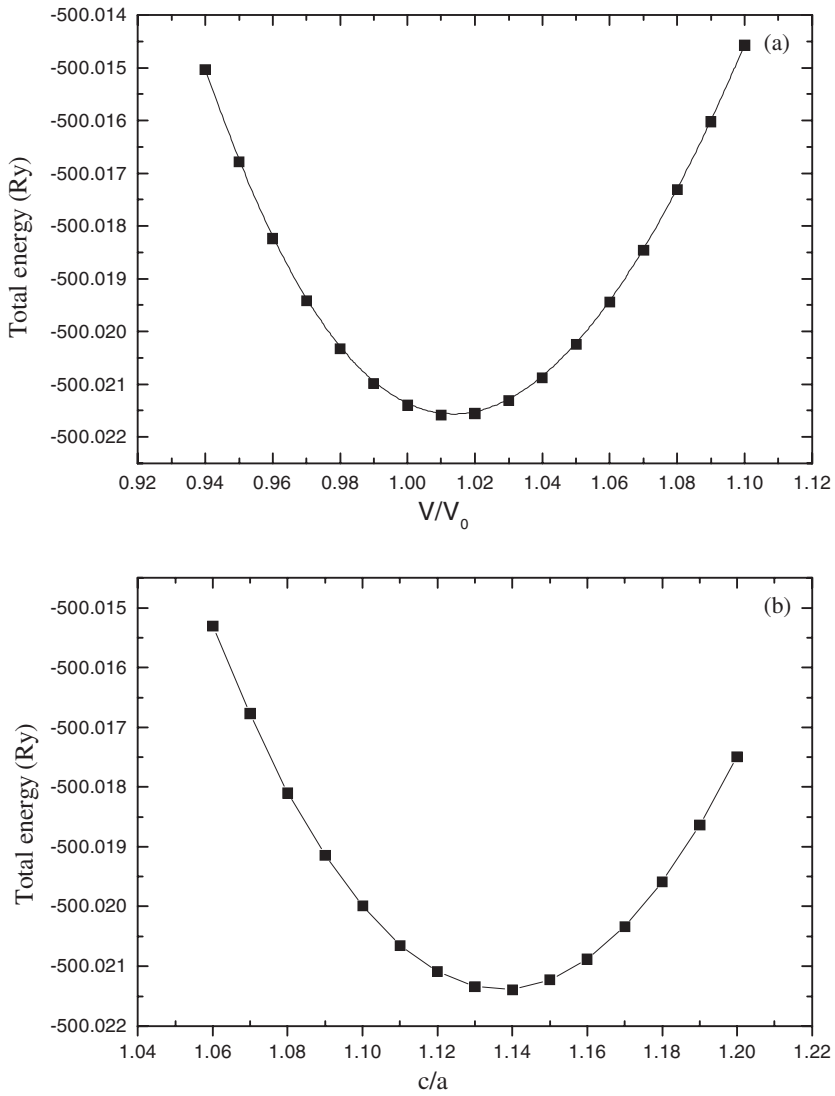

Figure 1. The total energy as a function of (a) the cell volume and (b) the c/a ratio.

3. Results and discussion

The variation of the crystal structure of MgB_2 can be simply described in terms of the volume of the unit cell and ratio c/a. The effects of the two factors on the electronic structure can be investigated separately. With a fixed ratio of $c/a = 1.14$, the effect of various volumes on the electronic structure was investigated, from $0.9V_0$ to $1.1V_0$ with a step of 0.01, where V_0 and $c/a = 1.14$ correspond to the experimental lattice parameters $a = 3.085$ Å, $c = 3.521$ Å. With a fixed volume of V_0, the effect of the ratio c/a was investigated, from 1.06 to 1.20 with a step of 0.01.

The calculated total energy as a function of the volume and c/a ratio is shown in figure 1. In advance, with different c/a ratios (volumes), the total-energy variation with volume (c/a ratio)

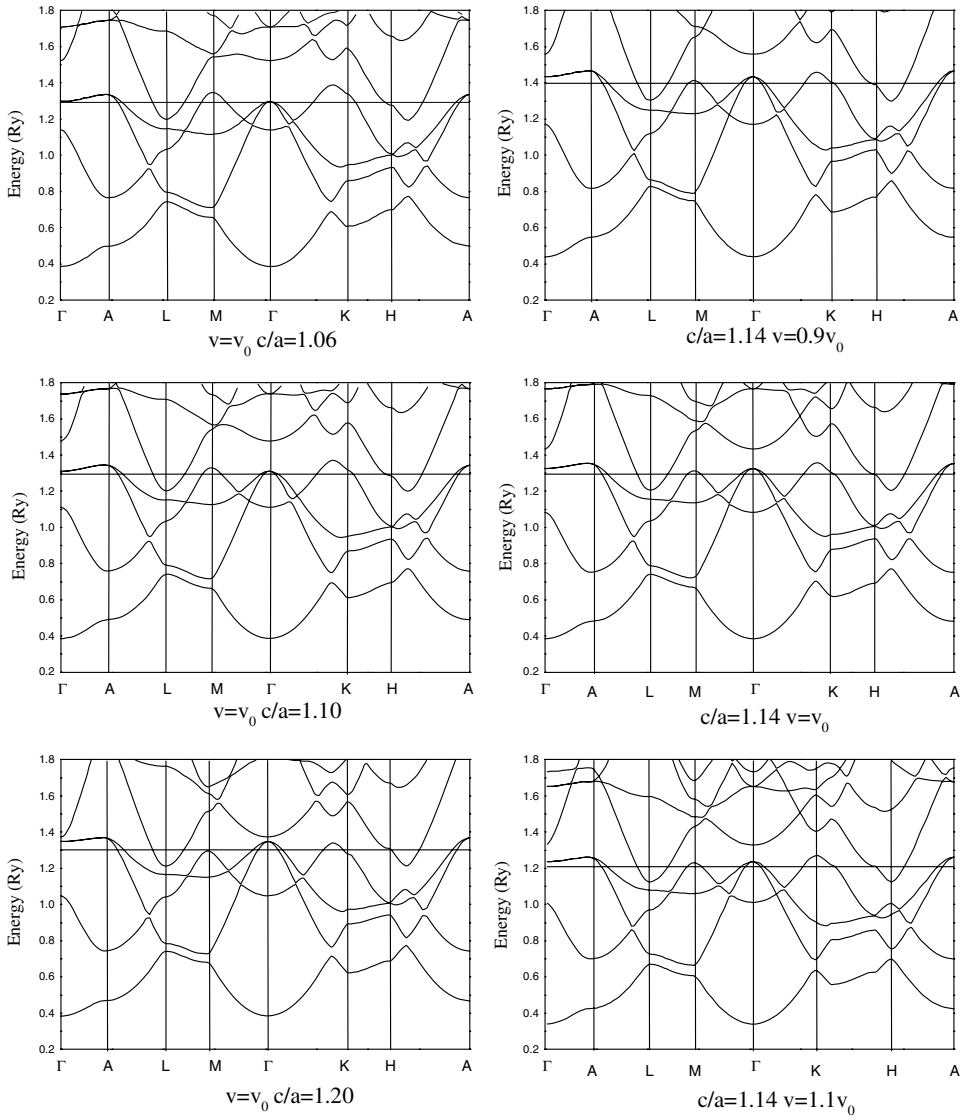

Figure 2. The band structure along high-symmetry directions at different cell volumes and c/a ratios.

has been calculated in detail. The minimum of the total energy is at $1.01V_0$ and $c/a = 1.138$, corresponding to the equilibrium lattice, which is in agreement with the experimental values [1]. Both curves are very smooth, which indicates that there is no anomaly induced by the variation of the lattice parameters.

Figure 2 shows band structures with different volumes and c/a ratios. The variations of the volume and c/a ratio do not change the essential band characters which have been described elsewhere [26]. The weak dispersion of the σ-bands along the Γ–A line reflects the particular quasi-two-dimensional character of the σ-band. The Fermi surface consists of four disjoint sheets: two hexagonal heavy- and light-hole tubes ($p_{xy}(\sigma)$) around the Γ–A line, a light-hole tube ($p_z(\pi)$) and one electron-like $p_z(\pi)$ sheet.

Now, we compare the different effects of the volume and c/a ratio on the particular structures of two-dimensional (2D) σ-bands and three-dimensional (3D) π-bands. The compression of the volume affects the shape of the bands less than the c/a ratio does—which obviously widens the band. Furthermore, 20% variation of volume shifts the Fermi energy up by about 0.2 Ryd, whereas compression of the c/a ratio has little influence on the width of the band and the Fermi energy, which obviously changes the gap, the fillings of the σ- and π-bands, and the formation of the Fermi surface.

Figure 2 shows that uniform compression of the volume increases the occupations of electrons in bonding and antibonding π-bands and decreases those in σ-bands. The compression of the c/a ratio increases the B–B in-plane distance, which decreases the overlap of the $p_{x,y}$ and weakens the σ-bonding. Considering that the σ-bonding is stronger than the π-bonding, it seems to be more reasonable that uniform compression should increase the occupations of the σ-band. In contrast, due to the 3D character of π, compression of the c/a ratio should increase the strength of the π-bonding, with enhancement of the inter-plane interaction.

Such a phenomenon is explained in terms of the interactions between the strongly covalent bonding of B sheets and delocalized, 'metallic-type' bonding between these sheets [22]. Because the s electrons of the Mg atom and its p electrons do not interact with B atoms, it is nearly completely ionized and can be treated as a positive-isotropy ion. The B anion shows anisotropy due to its two kinds of p orbital. It is noted that both the compression of the volume and that of the c/a ratio decrease the Mg–B distance. Despite the different space distributions of p_z and $p_{x,y}$, uniform compression of the volume increases the interaction between the Mg and two kinds of p orbit of B simultaneously. However, because of the 3D character of π, the π-electrons feel the attraction of Mg ions more strongly than the 2D σ-electrons do; this causes lowering of the π-bands and leads to charge transfer from σ to π. Upon compression of the c/a ratio, the separation of the Mg–B sheets is decreased and the in-plane B–B distance is increased. The interaction between the Mg cations and $p_{x,y}$ of B—which is indicated in figure 2 by the additional dispersion of Γ–A with increasing compression of the c/a ratio—is greater than that between the Mg cations and p_z. The interaction between Mg and p_z of B, as well as the B–B interaction, decreased. The Mg–B($p_{x,y}$) interaction plays a more important role; this led to carrier transfer from π to σ. For the electron-like antibonding π, which reflects the inter-plane interaction, there is only little enhancement with compression of the c-axis.

Special attention is focused on the Γ and M points in the BZ, where the variations of bands are dominantly expressed. The Γ point is near to the cylindrical Fermi surface, which reflects the character of the $p_{xy}(\sigma)$ band. M is near the tubular Fermi surface, which presents the character of a hole-like p_z-band (bonding π-band). The variation of the electron-like p_z-band (antibonding π-band) is not shown, because there is only slight enhancement when either the volume or the c/a ratio is compressed. The variations of the bands at the Γ and M points are described by the difference between E_{top} and E_F, where E_{top} is the energy of valence band top at the high-symmetry points and E_F is the Fermi energy, which is defined as zero here. In figure 3, the dependence on the volume and c/a ratio of E_{top} is shown. In figure 3(a), as the volume changes from $1.1V_0$ to $0.9V_0$, E_{top} increases by 0.01 Ryd at the Γ point and decreases by 0.006 Ryd at the M point. In figure 3(b), as the c/a ratio changes from 1.2 to 1.06, E_{top} decreases by 0.04 Ryd at the Γ point and increases by 0.07 Ryd at the M point. When the c/a ratio is equal to 1.18 and 1.06, the σ-band and π-band are nearly totally occupied at the Γ and M points, respectively. All of the above indicates that the compression of the volume and that of the c/a ratio have opposite influences.

Experimentally, with the pressure increasing from 0 to 12 GPa, the volume and c/a ratio decrease by 6.5 and 1.6% respectively [9]. As mentioned above, there is competition between the effects of the changes of the volume and the c/a ratio. Figures 3(a) and 3(b) show that

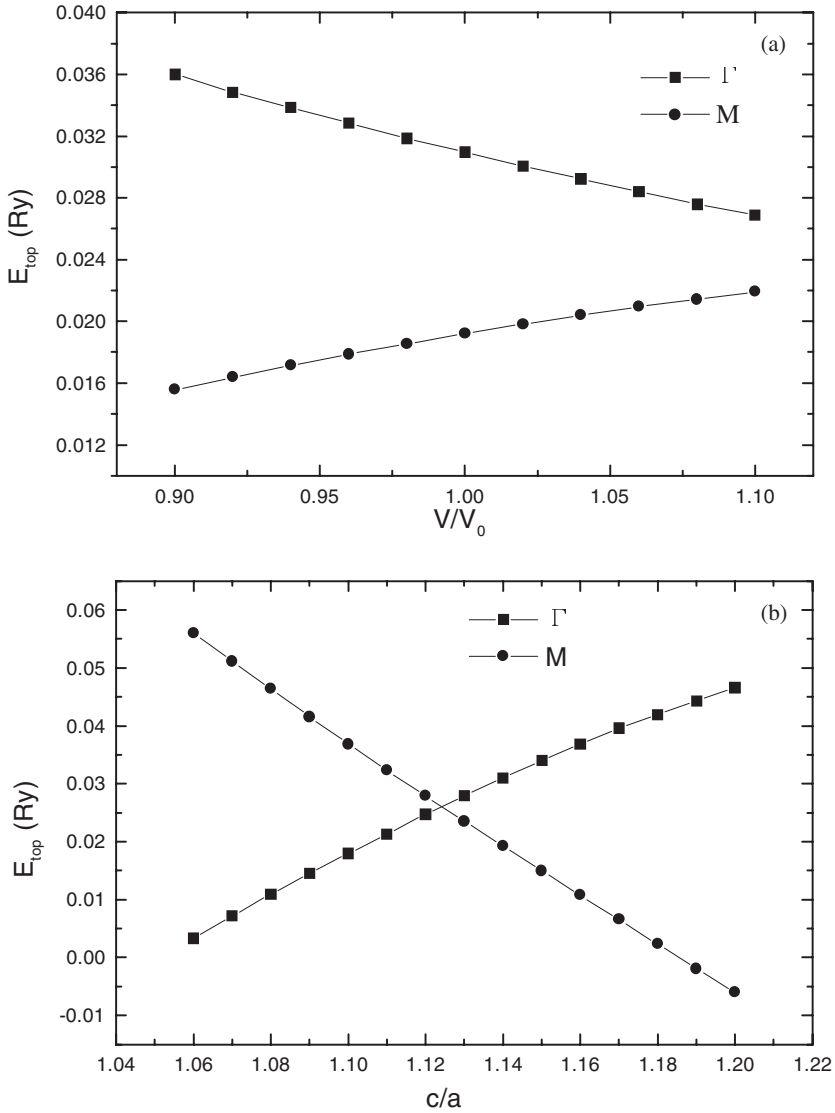

Figure 3. The variation of $E_{\text{top}} - E_F$ with volume and c/a ratio at the Γ and M points.

the relative variation of E_{top} is about 0.005 Ryd between the Γ and M points as the volume decreases by 6.5%, whereas the relative variation of E_{top} is about -0.02 Ryd as the c/a ratio decreases by 1.6%. As a whole, the variation of the electronic structure of MgB_2 under pressure is mainly determined by the c/a ratio, which will raise the π-band and lower the σ-band. With increasing pressure, the carriers of the heavy-hole-like p_{xy} σ-band transfer to the light-hole-like p_z π-band. Thus, the light-hole-like and electron-like carriers of the p_z π-band play a more important role in the conductivity properties under compression.

The anomalies of the pressure dependence of T_c correspond to c/a ratios of about 1.13 and 1.12 [10, 11]. Analysing the band structures, we do not find the opening or closing of a Fermi surface, which indicates that there is no ETT taking place in the range of our calculations (c/a ratio from 1.2 to 1.06 and volume from $0.9V_0$ to $1.1V_0$). In order to understand the anomalies,

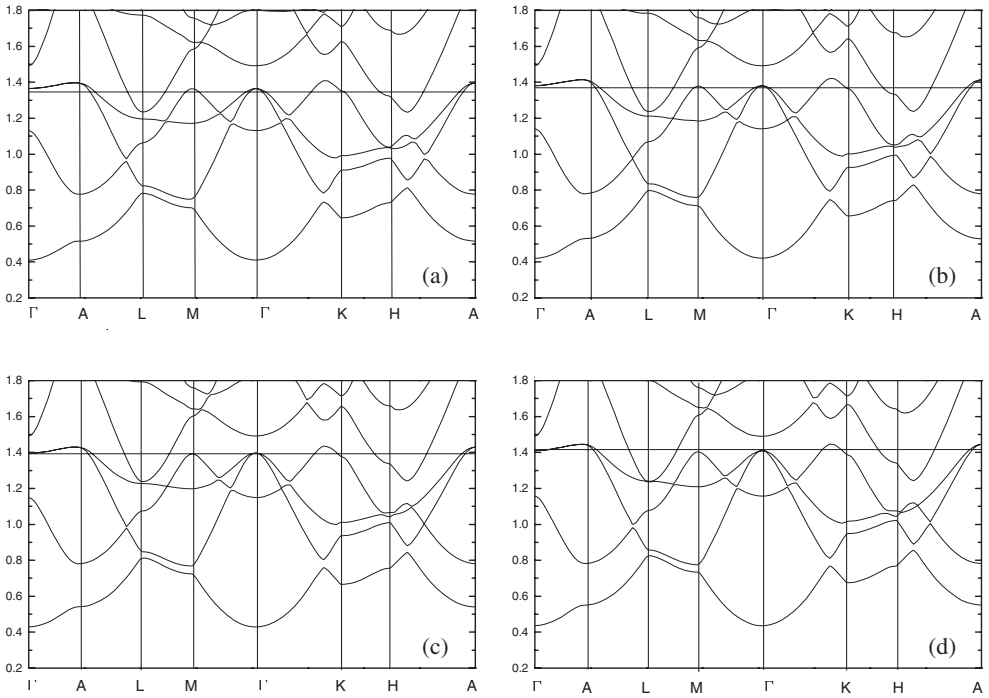

Figure 4. The band structure calculated by the Mg-pseudo-atom method for phases corresponding to the following valence electron numbers: (a) 2.1e; (b) 2.2e; (c) 2.3e; (d) 2.4e. The experimental volume and c/a ratio are adopted.

the effect of phonons should be taken into account. In fact, the relation between the 2D σ-band and the E_{2g} phonon mode was noticed previously [10, 11]. However, a detailed description of the band was lacking, but is now furnished by our results.

We discuss the effect of electron doping below. When the Al content is less than 0.1 in $Mg_{1-x}Al_xB_2$, the substitution has little effect on the crystal lattice. The structural instability arose upon substitution of a low Al content ($0.1 < x < 0.25$). The a-axis lattice parameter remains almost constant but the c/a ratios are about 1.14 (phase I) and 1.12 (phase II) [17]. Using the Mg-pseudo-atom method, we calculate the electronic structure of $Mg_{1-x}Al_xB_2$ ($0 < x < 0.4$). Except that the Fermi level is shifted up, the results show that the band structures are almost unchanged. Comparing the variations of the band between phases I and II, we see that the effect of the c/a ratio overwhelms that of the volume. In phase I ($c/a = 1.14$), E_{top} is lower at M than at the Γ point; however, in phase II ($c/a = 1.12$), E_{top} is same at Γ as at the M point.

For phase I, nearly 0.2 of an additional valence electron is required for the top of the π-band to touch the Fermi surface at the M point. Furthermore, 0.4 of an electron is needed for fill the σ-band at Γ. The previous calculation indicates that doping with about 0.25 of an electron can lead to the top of the valence σ-band coinciding with E_F [7]; this is slightly different from our results. Figure 4 shows the calculated band structures of phase II with different numbers of valence electrons. The results show that nearly 0.3 of an additional valence electron fills the holes of the π- and σ-bands for phase II.

With increasing electron doping, there are two possible ETT. One happens at the Γ point, where the doubly degenerate cylindrical Fermi surface shrinks to two packets. Another appears

at the M point, where the cylindrical Fermi surface closes. This result indicates that replacing 0.1 Mg by Al is not enough to change the topology of the Fermi surface. In order to understand the structural instability, it is necessary to take into account the strong electron–phonon coupling correlating with the π-band in MgB_2. Comparing the variations of the σ-band with pressure, we see that the effects of additional electron doping are similar at the Γ point, because both effects raise the Fermi level. Similarly, the phonon-assisted Lifshitz ETT happens at the Γ point; it should not induce a structural transition, but should influence the superconductivity. The ETT at the M point should correspond to a structural transition. The experimental and theoretical studies have confirmed that there is strong coupling between the σ-band and the E_{2g} phonon mode. Although the electron–phonon coupling correlating with the π-band is weaker [23], it is possible that a vertical phonon mode like A_{1g} could induce structural instability.

In figure 4(c), for electron doping exceeding 0.3, both Fermi surfaces closed at the Γ and M points also close simultaneously for phase II ($c/a = 1.12$). The disappearance of holes in the σ- and π-bands results in the destruction of the superconductivity and the vanishing of the coexistence of phases in $Mg_{1-x}Al_xB_2$.

Many substitution experiments have been reported [18–21], but no similar structural transition was found in them. As mentioned above, electron doping favours such a transition. For a hole-substituted system like Li, there will be an increase in the c/a ratio and a drop in the Fermi level. This does not favour structural instability. Other electron-substituting elements, unlike Al, will make the band structure close to the Fermi level become complex and will affect the electron–phonon interaction. This will reduce the possibility of an ETT. On the other hand, further experiments are needed to clarify whether a structural transition happens in other systems besides the $Al_xMg_{1-x}B$ system.

4. Conclusions

In summary, we have employed a FP-LMTO method to calculate the electronic structure of MgB_2. The different effects of pressure and substitution on the electronic structure are discussed in detail. It is shown that the variation of the volume has little effect on the shape of band, but the c/a ratio has an opposite effect. Considering the competition between the effects of the volume and c/a ratio, we find that the c/a ratio plays a more important role under pressure.

At the Γ and M points, the variations of the Fermi surface with the lattice and substitution, as well as the corresponding ETT, are considered in detail. It is indicated that the electron–phonon coupling should be taken into account to explain the anomalies of the pressure dependence of T_c. Furthermore, it is indicated that the structural transition happening in $Mg_{1-x}Al_xB_2$ ($x = 0.1$) corresponds to a phonon-assisted ETT at the M point. In our calculations, it is shown that when the Al substitution exceeds 0.3, the cylindrical Fermi surfaces at the Γ and M points will shrink to a point and disappear together, which results in the two-phase coexistence and superconductivity disappearing simultaneously.

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