Is $\Delta_\pi$-gap-only superconductivity possible in Mg$_{1-x}$Al$_x$B$_2$ and Mg(B$_{1-y}$C$_y$)$_2$ alloys?

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Abstract

Using density-functional-based method, we study the $k$-resolved $\sigma$- and $\pi$-band holes in Mg$_{1-x}$Al$_x$B$_2$ and Mg(B$_{1-y}$C$_y$)$_2$ alloys. We find that the calculated profiles of the loss of $\sigma$- and $\pi$-band holes in these two systems as a function of impurity concentration are in qualitative agreement with experiments, as expected. We also describe its implications vis-a-vis superconductivity in Mg$_{1-x}$Al$_x$B$_2$ and Mg(B$_{1-y}$C$_y$)$_2$. Based on our results, a $\Delta_\sigma$-gap-only superconductivity seems unlikely in Mg$_{1-x}$Al$_x$B$_2$ alloys.

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1. Introduction

The surprising discovery of superconductivity at 40 K in a simple metal MgB$_2$ [1] a few years ago continues to test the details of the microscopic picture offered by Bardeen–Cooper–Schrieffer theory of superconductivity and its extensions thereof. Generally, it is agreed that in MgB$_2$: (i) there are two superconducting gaps [2–8] $\Delta_\sigma$ and $\Delta_\pi$ of 7 MeV and 2 MeV, respectively, (ii) the two gaps arise from the holes in the B $p_\sigma$ and $p_\pi$ bands [8–14], (iii) the holes in the B $p_\sigma$ and $p_\pi$ bands couple strongly to the in-plane $E_{2g}$ phonon mode [14–17], and (iv) the coupling is particularly strong along $\Gamma$–$A$ direction and around $M$ point in the hexagonal Brillouin zone [18].

To gain further insight into the role played by the holes of the B $p_\sigma$ and $p_\pi$ bands in deciding the superconducting properties as well as the relative strengths of the two gaps $\Delta_\sigma$ and $\Delta_\pi$ in MgB$_2$, recently, there has been a concerted effort to examine the various superconducting properties of doped MgB$_2$. In particular, the Al doping at the Mg site and the C doping at the B site in MgB$_2$[19–29] are expected to fill up the holes in the B $p_\sigma$ and $p_\pi$ bands which, in turn, would affect the two gaps $\Delta_\sigma$ and $\Delta_\pi$. Understanding the changes in the superconducting properties of Mg$_{1-x}$Al$_x$B$_2$ as a function of Al concentration $x$ and of Mg(B$_{1-y}$C$_y$)$_2$ as a function of C concentration $y$ would provide a more detailed information about the electron–phonon and the electron–electron interactions in these alloys.

Experimentally, in Mg$_{1-x}$Al$_x$B$_2$ the superconducting transition temperature $T_c$ as well as the gap $\Delta_\sigma$ are found to decrease with increasing Al concentration [19,22,31,30,21]. The change in the gap $\Delta_\pi$ is relatively small up to $x = 0.7$ at which the superconductivity vanishes in Mg$_{1-x}$Al$_x$B$_2$. However, in Mg(B$_{1-y}$C$_y$)$_2$ the $T_c$ [34,32,27,35,33,36,40,39,38,37] and the $\Delta_\sigma$ decrease rapidly as a function of C concentration with superconductivity vanishing at around $y = 0.15$. The change in $\Delta_\pi$, once again, is found to be minimal in Mg(B$_{1-y}$C$_y$)$_2$ [42,28,40,41,38].

Most of the previous theoretical studies [43–52] of Mg$_{1-x}$Al$_x$B$_2$ and Mg(B$_{1-y}$C$_y$)$_2$ used virtual-crystal approximation [44,48,49,51,52] or supercell approach [43,47], having limited predictive capability, to describe the chemical
disorder in the Mg sub-lattice and the B sub-lattice, respectively. An accurate and reliable description of chemical disorder, provided by coherent-potential approximation, has been used previously in the study of Mg$_{1-x}$Al$_x$B$_2$ and Mg$_{1-x}$C$_{2y}$ [45,46,50] but these studies provided either k-integrated information or were inconclusive.

Since many of the superconducting properties of MgB$_2$ and its alloys Mg$_{1-x}$Al$_x$B$_2$ and Mg$_{1-x}$C$_{2y}$ are crucially dependent on their normal state electronic structure [15,17,54,8,53,55], especially along Γ–A direction and M point of the hexagonal Brillouin zone (BZ), we study the changes in Mg$_{1-x}$Al$_x$B$_2$ and Mg$_{1-x}$C$_{2y}$ alloys as a function of Al and C concentrations respectively, using k-resolved Bloch spectral function $A(k,E)$ [56,57] and B and C p$_{\sigma\nu}$ and p$_{\pi}$ densities of states. It is expected that with increasing Al and C concentrations the holes in the respective alloys would get gradually filled up. However, not surprisingly, the way the holes are filled up in Mg$_{1-x}$Al$_x$B$_2$ and Mg$_{1-x}$C$_{2y}$ alloys make the two systems quite different from each other as detailed below.

In this work we show that in Mg$_{1-x}$Al$_x$B$_2$: (i) the σ-band holes along Γ–A get annihilated by x = 0.8 with the holes at Γ vanishing first at x = 0.5, and (ii) the π holes at M vanish by x = 0.7. However, in Mg$_{1-x}$C$_{2y}$: (i) the σ-band holes along Γ–A deplete rapidly and vanish beyond $y \sim 0.25$ with the holes at A vanishing first, and (ii) the π-band holes at M as well as σ-band holes at A reduce substantially beyond $y \sim 0.1$. Before we discuss our results, we briefly describe the details of our calculations.

2. Computational details

The normal metal electronic structure of the disordered alloys Mg$_{1-x}$Al$_x$B$_2$ and Mg$_{1-x}$C$_{2y}$ are calculated using the Korringa–Kohn–Rostoker (KKR) Green’s function method formulated in the atomic sphere approximation (ASA) [58,59], which has been corrected by the use of both the muffin-tin correction for the Madelung energy, needed for obtaining an accurate description of ground state properties in the ASA [60], and the multipole moment correction to the Madelung potential and energy which significantly improves the accuracy by taking into consideration the non-spherical part of polarization effects [61]. Chemical disorder was taken into account by means of coherent-potential approximation (CPA) [62]. The exchange and correlation were included within the local-density approximation (LDA) using the Perdew–Wang parameterization of the many-body calculations of Ceperley and Alder [63]. During the self-consistent procedure the reciprocal space integrals were calculated by means of 2299 k-points in the irreducible part of the hexagonal BZ, while the energy integrals were evaluated on a semicircular contour in the complex energy plane using 24 energy points distributed in such a way that the sampling near the Fermi energy was increased. When calculating the density of states the number of k-points were increased to 6075. The atomic sphere radii of Mg and B were kept as 1.294 and 0.747, respectively, of the Wigner–Seitz radius. The sphere radii of the substituted Al and C were kept the same as that of Mg and B, respectively. The overlap volume resulting from the blow up of the muffin-tin spheres was approximately 10%, which is reasonable within the accuracy of the approximation [64]. The charge self-consistency iterations were accelerated using the Broyden’s mixing scheme [65], the CPA self-consistency was accelerated using the prescription of Abrikosov et al. [66]. The calculations for Mg$_{1-x}$Al$_x$B$_2$ for 0 ≤ x ≤ 1 and Mg$_{1-x}$C$_{2y}$ for 0 ≤ y ≤ 0.3 were carried out at experimentally obtained lattice parameters of these alloys [67,68], assuming a rigid underlying lattice. The effects of local lattice-relaxation as well as any possible short-range ordering effects are not considered. Our results for Mg$_{1-x}$Al$_x$B$_2$ and Mg$_{1-x}$C$_{2y}$ are analyzed in terms of Bloch spectral density, $A(k,E)$ [56] and the B and C p densities of states. A k-resolved understanding of how the addition of Al and C in Mg$_{1-x}$Al$_x$B$_2$ and Mg$_{1-x}$C$_{2y}$ alloys affect the hole states, which are responsible for superconductivity in these alloys, over the entire BZ is essential. Such changes in the states are reliably described by the Bloch spectral density.

3. Results and discussion

In general, electron doping of MgB$_2$ by substituting Al at the Mg sub-lattice or C at the B sub-lattice can have three important effects: (i) the outward movement of the Fermi energy due to addition of electrons, (ii) disorder-induced broadening of peaks in $A(k,E)$, and (iii) redistribution of states due to hybridization. If the disorder and hybridization-related effects are negligible then electron doping can be well described by a rigid-band-like picture, where $E_F$ is shifted up using MgB$_2$ densities of states until the added electrons are accommodated. In such a case, the σ- and π-band holes would gradually get filled up as a function of electron doping. Thus, in the rigid-band picture the σ- and π-band-hole-dependent superconducting properties of MgB$_2$ alloys would be similar as a function of electron doping. However, if the disorder and the hybridization lead to significant modifications of the σ- and π-band holes then the electronic properties of both the normal and the superconducting states of MgB$_2$ alloys would depend on the details of electron doping rather than just the electron count. Experimentally, as outlined in earlier paragraphs, the σ- and π-band-hole-dependent properties of the two alloys, Mg$_{1-x}$Al$_x$B$_2$ and Mg$_{1-x}$C$_{2y}$, are found to differ significantly from each other as a function of Al and C concentrations, underscoring the importance of disorder and hybridization effects in these alloys, in particular on σ- and π-band holes. Therefore, in the following, we primarily focus on the changes in the states close to $E_F$, which happen to be the p$_\sigma$ states at Γ and A points and p$_\pi$ state at M point of the hexagonal BZ.

The most important result of the present work for Mg$_{1-x}$Al$_x$B$_2$ alloys is shown in Fig. 1, where we show the Bloch spectral function $A(k,E)$ as a function of x for
$0 \leq x \leq 1$ at $\Gamma$, $A$ and $M$ points of the hexagonal BZ in a limited energy window ($\pm 0.1$ Ry) around Fermi energy $E_F$. Along $\Gamma-A$, the doubly degenerate $p_\sigma$ states in Mg$_{1-x}$Al$_x$B$_2$ alloys move closer to $E_F$ with increasing Al concentration from $x = 0.1$ to $x = 0.70$, indicating a decrease in $\sigma$-band holes and subsequently, weakening of electron–phonon coupling along this direction. We also find that for $x \approx 0.5$, the peak in $A(k, E)$ is at $E_F$ indicating some topological changes in the Fermi surface of the alloy. By $x = 0.90$, the $p_\sigma$ states at $A$ are well inside $E_F$, resulting in the annihilation of all the $p_\sigma$ hole states along $\Gamma-A$. Thus, we should not expect $\sigma$-band-hole-based superconductivity beyond $x = 0.80$. The present result should be compared with the supercell-based results of Ref. [43], which predict annihilation of $\sigma$-band holes by $x = 0.6$.

We also find that the Mg-derived antibonding s-state ($\Gamma_\delta$) moves closer to the $p_\sigma$ state for intermediate concentrations but separates out for $x = 1.0$.

The $B$ $p_\pi$ hole states at $M$ in Mg$_{1-x}$Al$_x$B$_2$ alloys get gradually annihilated with increasing Al concentration from $x = 0.1$ to $x = 0.50$. We find that the $A(k, E)$ peak corresponding to $p_\sigma$ states crosses $E_F$ at a lower $x$ than the $p_\sigma$ states at $A$ point. As the contribution to the electron–phonon coupling responsible for $\pi$-band superconductivity comes from $M$ and other similar points in the BZ, a $\Delta_\pi$ gap-only superconductivity seems unlikely in Mg$_{1-x}$Al$_x$B$_2$ alloys. However, it does not preclude a crossover from a $\sigma$ to $\pi$ dominated superconductivity [52].

In Fig. 2 we show the Bloch spectral function $A(k, E)$ of Mg(B$_{1-x}$C$_x$)$_2$ as a function of $y$ for $0 \leq y \leq 0.3$ at $\Gamma$, $A$ and $M$ points around Fermi energy. We find that with increasing C concentration from $y = 0.05$ to $y = 0.2$ the $p_\sigma$ states along $\Gamma-A$ move towards $E_F$ as well as get redistributed on the energy scale due to disorder and hybridization. In fact, in the range $y = 0.1 - 0.15$, we find substantial reduction in $p_\sigma$ states around $A$ point. Since the electron–phonon coupling is stronger near $A$ point, the loss of $p_\sigma$ states should dramatically affect the $\sigma$-band superconductivity. Similar to the reduction of $p_\sigma$ states along $\Gamma-A$, the $p_\pi$ hole states at $M$ point in Mg(B$_{1-x}$C$_x$)$_2$ alloys are drastically reduced by $y = 0.1$. Here, it must be noted that the reduction in $\sigma$– $\pi$-band holes in Mg$_{1-x}$Al$_x$B$_2$ with increasing Al concentration is mostly due to the upward movement of the Fermi energy. In contrast, disorder and hybridization play a dominant role in reducing the $\sigma$- and $\pi$-band holes in Mg(B$_{1-x}$C$_x$)$_2$ alloys.

The changes in the $B$ $p_\sigma$ and $p_\pi$ hole states in Mg$_{1-x}$Al$_x$B$_2$ as a function of Al concentration and in Mg(B$_{1-x}$C$_x$)$_2$ as a function of C concentration can be seen more clearly in their respective partial densities of states as shown in Fig. 3. In Mg$_{1-x}$Al$_x$B$_2$ alloys the $B$ $p_{x(y)}$ hole states decrease steadily as a function of $x$, vanishing for
\( x \sim 0.8 \) as shown in Fig. 3. Thus, as stated earlier in the context of \( A(k, E) \), we should not expect \( \sigma \)-band-hole-based superconductivity beyond \( x = 0.80 \text{Mg}_1-x\text{Al}_x\text{B}_2 \). However, the decrease in \( B \) \( p_\sigma \) hole states with increasing \( x \) is not as much. Even for \( x = 1.0 \), there are \( B \) \( p_\sigma \) hole states available in \( \text{Mg}_1-x\text{Al}_x\text{B}_2 \) as shown in Fig. 3 but it does not sustain \( A_\sigma \)-gap-only superconductivity.

For \( \text{Mg}(\text{B}_{1-y}\text{C}_y)_2 \) alloys, our results show that \( p_\sigma(y) \) and \( p_\pi \) densities of states of both \( B \) and \( C \) behave similarly with increasing \( C \) concentration, as can be seen from Fig. 3. By \( y < 0.25 \), most of the \( p_\sigma(y) \) hole states of \( B \) and \( C \) have moved inside \( E_F \). As pointed out above, in \( \text{Mg}(\text{B}_{1-y}\text{C}_y)_2 \) alloys with the addition of \( C \) those \( \sigma \)-band holes are lost first which couple to the phonons more strongly which may lead to a loss of superconductivity in spite of having some \( p_\sigma(y) \) hole states of \( B \) and \( C \). The changes in the \( p_\sigma \) hole states are minimal in \( \text{Mg}(\text{B}_{1-y}\text{C}_y)_2 \) alloys for \( y \sim 0.2 \) because for these concentrations we have used the lattice constants corresponding to \( y = 0.15 \). However, our results for \( \text{MgB}_2 \) and \( \text{AlB}_2 \) are consistent with the more accurate, full-potential approximation is known to describe the effects of disorder reliably, we expect our intermediate-concentration-results to be robust and qualitatively correct.

4. Conclusions

In conclusion, we have studied the \( k \)-resolved \( \sigma \)- and \( \pi \)-band holes in \( \text{Mg}_1-x\text{Al}_x\text{B}_2 \) and \( \text{Mg}(\text{B}_{1-y}\text{C}_y)_2 \) alloys. The calculated profiles of the loss of \( \sigma \) - and \( \pi \)-band holes in these two systems as a function of impurity concentration are expected to be in qualitative agreement with the experiments. We have also described its implications \( \text{vis-a-vis} \) superconductivity in \( \text{Mg}_1-x\text{Al}_x\text{B}_2 \) and \( \text{Mg}(\text{B}_{1-y}\text{C}_y)_2 \) alloys. In particular, we have shown that a \( A_\pi \)-gap-only superconductivity was unlikely in \( \text{Mg}_1-x\text{Al}_x\text{B}_2 \) alloys.

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References


