Electronic Structure of B-2pσ and pπ States in MgB₂, AlB₂ and ZrB₂ Single Crystals

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The effect of electron correlation (EC) on the electronic structure in MgB₂, AlB₂ and ZrB₂, is studied by examining the partial density of states (PDOS) of B-2pσ and pπ orbitals using the polarization dependence of x-ray emission and absorption spectra. The discrepancies between observed and calculated PDOSs cannot be attributed to EC effects. The present results suggest that the EC effect is less than the experimental error (∼ 0.2 eV), which indirectly supports a scenario that electron-phonon interaction plays an essential role in the occurrence of superconductivity.

74.70.Ad, 74.25.Jb, 78.70.Dm, 78.70.En

Since the discovery of superconductivity in MgB₂ with \( T_c \) of 39 K [1], a large number of researches from experimental [2–12] and theoretical [13–19] point of view have been performed on MgB₂ and on a series of isostructural diborides. Most of these studies suggest that MgB₂ is a phonon-mediated BCS type superconductor. Bud’ko et al. reported a boron isotope effect with \( \alpha = 0.26 \). [2] The temperature dependence of \( ^{11}\)B-nuclear spin relaxation rate, \( 1/T_1 \), shows an exponential decay in the superconducting state revealing a tiny coherence peak just below \( T_c \), which means that MgB₂ is an s-wave superconductor with a large band gap. [3] On the other hand, high resolution photoemission spectroscopy and specific heat measurement of MgB₂ suggest the two superconducting gaps. [4,5] The tunneling experiment also suggest that two gaps of about 2-3 and 7 meV. [6] Recent Raman study on the single crystalline MgB₂ assigned the two gaps to a large one (6.5 meV) of the \( \sigma \) band and a small one (1.5 meV) of the \( \pi \) bands. [7] These results are in contradiction with a scenario that MgB₂ is a simple s-wave
In the early stage, high $T_c$ was suggested. Theoretical band calculations [13,14] have been proposed. In these mechanisms, band calculations (σ and π bands considered by Imada, and bonding and antibonding π-bands by Yamaji) enhance $T_c$ from a conventional BCS (EPC based) value, and the mechanisms have relationship with the experimental results that suggest the two superconducting gaps [4–7]. In order to understand the high $T_c$ of MgB$_2$, it is necessary to get information on the EC effects in the superconducting MgB$_2$ and non-superconducting other diborides. The density of state gives important information on the EC effects. The partial density of states (PDOS) of boron have been measured by x-ray absorption (XAS) and x-ray emission (XES) spectroscopy near B-K edge of polycrystalline MgB$_2$ and other AlB$_2$-type compounds, in which the observed PDOS agrees well with the band calculations. Furthermore, angle resolved photoemission spectroscopic (ARPES) [20] and de Haas van Alphen (dHvA) effect [21] studies were performed on the single crystalline MgB$_2$ sample [22]. The ARPES spectra along the Γ-K and Γ-M directions show three dispersive curves that can be assigned to theoretically predicted σ and π bands. However, some predicted bands were not observed. In addition, a small parabolic-like band is observed around the Γ point, which can not be explained by band calculations. Because this technique is quite surface sensitive, the results may not represent the bulk-electronic structure. On the other hand, dHvA technique is useful to probe the bulk-electronic structure. Yelland et al. reported that only three dHvA frequencies were resolved among four Fermi surfaces predicted theoretically. The derived three dHvA frequencies and the large effective mass are, however, explained by precise band calculation. The calculation insists that the bands near $E_F$ should shift with decreasing number of holes near $E_F$. They pointed out that the discrepancies between the experimental results and the band calculations may be caused by EC effects or beyond-LDA effect. Furthermore, several authors have proposed a model based on a weak electron-phonon coupling [25] that is consistent with the optical conductivity and DC resistivity studies of c-axis oriented MgB$_2$ films [26]. Thus, it is necessary to investigate the significance of the EC effects, which can play an important role on the appearance of high $T_c$ in MgB$_2$. XAS and XES measurements of single crystal are quiet useful for this purpose because these techniques give PDOS which can reflect the existence of strong EC. XAS and XES of single crystalline AlB$_2$ and XAS of single crystalline Mg$_2$Al$_{1-x}$B$_2$ were already performed, [11,12] in which a good agreement between the observation and the band calculation was reported. 

In this paper, we report a direct observation of PDOS of B-2pσ and 2pπ by polarization dependent XES and XAS near B-K edge using single crystalline MgB$_2$, AlB$_2$ and ZrB$_2$ samples. Comparing the observed PDOS with the first principle band calculation results [27], we examine the significance of EC effects in MgB$_2$.

The single crystalline MgB$_2$ samples were grown in BN container under high pressure. AlB$_2$ and ZrB$_2$ crystals were prepared by Al-flux [11] and FZ methods [28], respectively. The XES measurement was performed at BL-2C in KEK-PF, in which the energy of the incident photons is about 400 eV. The energy resolution of XES spectrometer is about 0.2 eV. The XAS spectra were measured at BL-8.0.1 of Advanced Light Source (ALS) in LBNL by the partial fluorescence yield (PFY) method. The energy resolution of the incident photons is about 0.1 eV. PDOSs of each B-2pσ and 2pπ orbitals are derived from polarization dependence of XES and XAS spectra. [11]

Figure 1 shows the observed partial density of states (PDOS) of B-2pσ [Fig. 1(b)] and pπ states [Fig. 1(c)] from observed polarization-dependent XES and XAS spectra with the results of band calculation. Solid and dotted lines in Fig.1 are the results of the first principle band calculations (FLAPW method) by Oguchi [27], which are convoluted by gaussian function with FWHM of the experimental resolution. Solid and open circles (or squares) represent occupied and empty states of pσ (or pπ), respectively. It is clearly seen that the Fermi energy $E_F$ [A in Figs. 1(b) and (c)] measured from B-1s core level of MgB$_2$ is 186.4 eV, which agrees well with the previous reports. [9] In the Figs. 1(b) and (c), the theoretical $E_F$ value is set to the experimental $E_F$ value, 186.4 eV. A sharp peak B in XES spectrum [Fig.1(b)] is observed at around $E-E_F=-2.4$ eV. Observed PDOS of pσ in XES spectrum steeply decreases at $E_F$ and a considerable amount of PDOS just above $E_F$ is observed in XAS spectrum. The pσ-PDOS near $E_F$ disappears above 0.6 eV (C), and there is almost no pσ-PDOS in the energy region D (0.6 eV<$E-E_F<$3.6 eV). Figure 1(c) shows XES (◼) and XAS (○) of B-2pπ of MgB$_2$. Observed PDOS of pπ shows a broad metallic state except a large sharp peak G at 5.6 eV. The overall features of observed XES near $E_F$ and XAS are well reproduced by the band calculation. However, in whole energy region, some discrepancies are observed as follows. Observed peak B is lower than the theoretical prediction by 0.3 eV. The value of observed pseudo-gap is about 3 eV in contrast to the prediction of about 4 eV. Peaks, $E_1$ and $E_2$ in pσ-XAS and G in pπ-XAS, are not reproduced by the band calculation. Before going into detailed comparison between the theory and the experiment, let us show the results AlB$_2$.

Figure 2 shows PDOS of AlB$_2$ with the same symbols of MgB$_2$ in Fig.1. The observed $E_F$ is estimated to be 187.5 eV which agrees well with the previous report. [9,11] The value of $E_F$ is slightly lower than the theoretical prediction by 0.6 eV, but the small shift is explained by the lack of Al atoms by 0.07 from the stoichiometric AlB$_2$. [11] As in MgB$_2$, overall shapes of experimental
$p\sigma$- and $p\pi$-PDOS are in good agreement with the band calculation results. Especially, in AlB$_2$, it is found that a detailed shape of PDOS including a pseudo-gap in the empty state is in good agreement with the theoretical prediction within the experimental resolution. This is in contrast with the case of MgB$_2$.

Figure 3 shows $p\sigma($•$)$- and $p\pi($○$)$-PDOS of ZrB$_2$ derived from XES spectra. [29] In sharp contrast to the PDOSs of MgB$_2$ and AlB$_2$, the $p\pi$-PDOS of ZrB$_2$ shows clearly-resolved two-large peaks at about 184.3 eV and 185.4 eV, respectively. The $p\sigma$-PDOS also shows two peaks at about 183.0 eV and 184.3 eV. Both PDOSs decrease with increasing energy, but the small Fermi edge is observed in both PDOSs. The $E_F$ is estimated to be 188.1 eV. The solid and dotted lines are the theoretical ones with the experimental $E_F$ value. As in MgB$_2$ and AlB$_2$, even though the PDOS shapes are different, the observed PDOSs of ZrB$_2$ are well reproduced by the first principle band calculation. The detailed comparison between observed PDOS and theoretical ones is as follows.

As mentioned before, overall shapes of the observed PDOSs of these compounds are roughly reproduced by the band calculations, but some discrepancies are pointed out in MgB$_2$ and AlB$_2$. A sharp peak B in MgB$_2$, which is due to van Hove singularity (VHS) of $p\sigma$ band at M- and L-points, slightly shifts from the theoretical prediction by about $-0.3$ eV. An energy, measured from $E_F$, of bonding $p\sigma$-top at Γ-point [C in Fig. 1(b)] is about 0.6 eV in MgB$_2$ and $-1.0$ eV in AlB$_2$, respectively. It agrees with the theoretical prediction in MgB$_2$, and agrees with the prediction in AlB$_2$ assuming the $E_F$ shifting. [11] However, in MgB$_2$, observed anti-bonding $p\sigma^*$ PDOSs $E_1$ and $E_2$ are higher than the theoretical ones $F_1$ and $F_2$. This means the observed pseudo-gap located at region D is smaller than the theoretical prediction in MgB$_2$ by about 1 eV. On the other hand, in AlB$_2$, one can see an excellent agreement between observed and theoretical PDOS around the pseudo-gap of about 3 eV. The values of observed pseudo-gap of both compounds are the same (3 eV). In AlB$_2$, there is no characteristic structure in PDOS above $E_F+5$ eV. Therefore, it seems that there is no discrepancy between experimental and theoretical PDOS in AlB$_2$ compound even in the high energy region.

The large sharp peak G is due to $p\pi^*$ resonant state of the sample surface or of some oxides of the surface. [8] And it does not appear in a polished-large single-crystal of AlB$_2$. For AlB$_2$ single crystal, in order to remove the Al-flux on the surface, the crystals were polished. [11] Therefore the fluorescence spectrum will be free from the surface oxidation. But the size of MgB$_2$ single crystals is too small to remove surface oxides by polishing. Then the small amount of oxides leads to the resonant peak G in MgB$_2$ spectrum. The present observation of PDOS of $p\pi$ band also agrees with the theoretical one except for the surface states mentioned above. The present results indicate that the experimental PDOSs are reproduced by the band calculation in the energy region of $E < E_F+5$ eV in both diborides.

One might consider that the discrepancy between experiment and the theory in the XAS regime of MgB$_2$ may be due to EC effects that is not properly taken into account in LDA band calculations. However, the EC effects generally tend to widen the gap, while in the present case, the experimental band gap is narrower than the theoretical one. Then, this discrepancy between the experiment and the theory may be attributed to the fact that the band calculation deals with the ground state of the system. A possible reason for the gap narrowing might be due to an excitonic effect [30] that arises in the excited states of the XAS process, which is not taken into account in the band calculation.

In a previous paper [9], we insisted that a rigid band picture is valid for the relation between MgB$_2$ and AlB$_2$. The present detailed PDOSs of both compounds do not deny the rigid band picture, but suggest a small discrepancy between both compounds, i.e., anti-bonding $p\sigma^*$ states is lower than the theoretical prediction in MgB$_2$ but that in AlB$_2$ is in agreement with the theoretical one. In ZrB$_2$, the observed $p\pi$-PDOS structure is similar to the theoretical PDOS of Zr-4d. [29] The high energy peak at 184.3 eV of $p\sigma$-PDOS is also similar to the Zr-4d$_{yz,zz}$ PDOS, but the low energy PDOS at 183.0 eV is considered to be based on the covalent character of B-B bonding in basal plane. As mentioned in the introductory part, there are two types of theoretical two-bands model based on electron-phonon [14] and inter-band EC mechanisms [15,18] in MgB$_2$ superconductivity. The present result indicates that the EC is smaller than the value of the present energy resolution (~0.2 eV) in MgB$_2$, AlB$_2$ and ZrB$_2$ compounds. The inter-band EC has a possibility to enhance the phonon-mediated $T_c$. [15,18] If a small inter-band EC effect that can not be detected in our experiment enhances the high $T_c$, the present result does not contradict with these propositions.

To summarize, in order to examine the electron correlation (EC) effect in the diborides, we have performed direct measurement of PDOS of B-2p in single-crystalline MgB$_2$, AlB$_2$ and ZrB$_2$ using polarization-dependent XES and XAS measurements. Although there are some discrepancies between observed PDOSs and theoretical ones, the first principle band calculation reproduces well the overall features of observed $p\sigma$- and $p\pi$-PDOSs. In superconducting MgB$_2$, a considerable amounts of $p\sigma$-hole state near the Fermi energy is clearly observed. The pseudo-gap of $p\sigma$ band is observed in MgB$_2$ and AlB$_2$ compounds in sharp contrast to the broad metallic state of the B-2p $\pi$ bands. The observed gap values of about 3 eV are same in both compounds, which is smaller than the theoretically predicted value for MgB$_2$ and is consistent with it for AlB$_2$. Because the band calculation describes the ground state, it may be plausible that the calculation reproduces the experimental PDOS only for $E < E_F+5$ eV in both compounds. In ZrB$_2$, the observed PDOSs reproduced well by the calculation, suggest strong hybridization between B-2p and Zr-4d orbitals. The observed discrepancies are contrary to the
EC effects. The present results suggest that the EC effect is less than the experimental error (∼0.2 eV), which indirectly supports a scenario that electron-phonon interaction plays an essential role in the occurrence of superconductivity in MgB$_2$. However, a possibility of a small inter-band electron-correlation effect which supports the phonon mediated superconductivity, still remains.

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FIG. 1. The partial density of states (PDOS) of $p\sigma$ and $p\pi$ of MgB$_2$. (a) The theoretical PDOS derived from FLAPW method broadened with experimental resolution. The solid and dotted lines are PDOS’s of $2 \times p\sigma$ and $p\pi$, respectively. (b) The experimental PDOS of $2 \times p\sigma$, occupied one (solid circle) and empty one (open circle). (c) The experimental PDOS of $p\pi$, occupied one (solid square) and empty one (open square).

FIG. 2. The partial density of states (PDOS) of $p\sigma$ and $p\pi$ of AlB$_2$. (a) The theoretical PDOS derived from FLAPW method broadened with experimental resolution. The solid and dotted lines are PDOS’s of $2 \times p\sigma$ and $p\pi$, respectively. (b) The experimental PDOS of $2 \times p\sigma$, occupied one (solid circle) and empty one (open circle). (c) The experimental PDOS of $p\pi$, occupied one (solid square) and empty one (open square).

FIG. 3. The partial density of states (PDOS) of $2 \times p\sigma(\bullet)$ and $p\pi(\bigcirc)$ of ZrB$_2$. The solid and dotted lines are theoretical PDOSs of $2 \times p\sigma$ and $p\pi$, respectively, which are broadened with experimental resolution.

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Two points should be mentioned here. First, although the excitonic effect is a Coulombic effect, it is not essentially an EC effect. Namely, the excitonic shift of the energy can essentially be evaluated within a mean field scheme if we take into account the excited states of the system. Secondly, one may consider that excitonic effects may not be so large in metallic systems, where the screening of the Coulomb potential is prominent. If that is indeed the case, a clearcut reason for the discrepancy between theory and the experiment remains to be an open question. However, since EC effects generally tend to widen the gap, we believe our scenario that the EC effects is not so large in MgB$_2$ remains unchanged in any case.
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