Electronic structure of B $2p\sigma$ and $p\pi$ states in MgB_2, AlB_2, and ZrB_2 single crystals

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The effect of electron correlation (EC) on the electronic structure in MgB_2, AlB_2, and ZrB_2, is studied by examining the partial density of states (PDOS) of B $2p\sigma$ and $p\pi$ orbitals using the polarization dependence of x-ray emission and absorption spectra. The discrepancies between observed and calculated PDOS's cannot be attributed to EC effects. The present results suggest that the EC effect is less than the experimental error ($\sim$0.2 eV), which indirectly supports a scenario that electron-phonon interaction plays an essential role in the occurrence of superconductivity.

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Since the discovery of superconductivity in MgB_2 with T_c of 39 K,[1] a large number of researches from experimental[2–12] and theoretical[13–19] points of view have been performed on MgB_2 and on a series of isostructural diborides. Most of these studies suggest that MgB_2 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 MgB_2 is an *s*-wave superconductor with a large band gap.[3] On the other hand, high resolution photoemission spectroscopy and specific heat measurement of MgB_2 suggest the two superconducting gaps.[4,5] The tunneling experiment also suggests that two gaps of about 2–3 and 7 meV.[6] A recent Raman study on the single crystalline MgB_2 assigned the two gaps to a large one (6.5 meV) of the σ band and a small one (1.5 meV) of the π bands.[7] These results are in contradiction with a scenario that MgB_2 is a simple *s*-wave superconductor. Theoretical band calculations,[13,14] in the early stage, have suggested that the dimensionless electron-phonon coupling (EPC) constant $\lambda \sim 0.7$, which can give a high T_c of $\sim$40 K if the Coulomb potential μ^*, is very small. On the other hand, two-band mechanisms based on interband electron-correlation (EC) have been proposed.[15–18] In these mechanisms, interband EC (σ and π bands considered by Imada, and bonding and an-

tibonding π bands by Yamaji) enhances T_c from a conventional BCS (EPC based) value, and the mechanisms have a relationship with the experimental results that suggest the two superconducting gaps.[4–7] In order to understand the high T_c of MgB_2, therefore, it is necessary to get information on the EC effects in the superconducting MgB_2 and nonsuperconducting 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 the B *K* edge of polycrystalline MgB_2 and other AlB_2-type compounds, in which the observed PDOS agrees well with the band calculations.[8–10] 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 paraboliclike band is observed around the Γ point, which cannot 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, the dHvA technique is useful to probe the bulk-electronic structure. Yelland *et al.*[21] 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,[23,24] 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 for 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 $Mg_xAl_{1-x}B_2$ 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 $2p\sigma$ and $2p\pi$ by polarization-dependent XES and XAS near the 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 a BN container under high pressure.[22] 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 $2p\sigma$ and $2p\pi$ orbitals are derived from polarization dependence of XES and XAS spectra.[11]

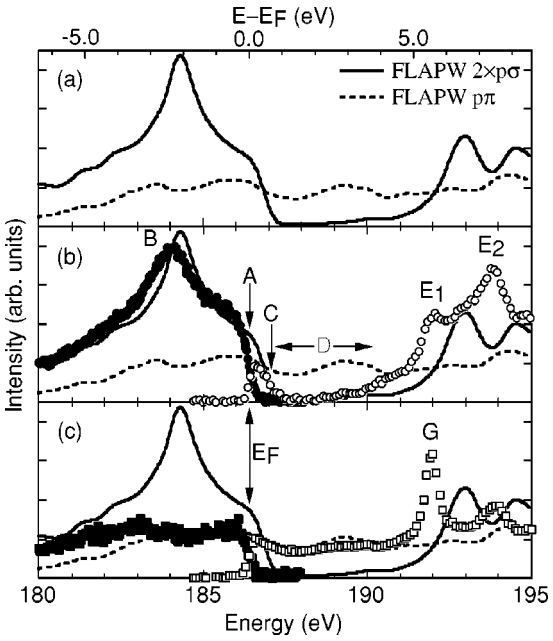

FIG. 1. The partial density of states (PDOS) of $p\sigma$ and $p\pi$ of MgB_2. (a) The theoretical PDOS derived from FLAPW method broadened with experimental resolution. The solid and dotted lines are PDOS's of $2\times p\sigma$ and $p\pi$, respectively. (b) The experimental PDOS of $2\times p\sigma$, 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).

Figure 1 shows the observed partial density of states (PDOS) of B $2p\sigma$ [Fig. 1(b)] and $p\pi$ 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 $p\sigma$ (or $p\pi$), respectively. It is clearly seen that the Fermi energy E_F [*A* in Figs. 1(b) and (c)] measured from B 1*s* core level of MgB_2 is 186.4 eV, which agrees well with the previous reports.[9] In the Figs. 1(b) and 1(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 $p\sigma$ in XES spectrum steeply decreases at E_F and a considerable amount of PDOS just above E_F is observed in XAS spectrum. The $p\sigma$ PDOS near E_F disappears above 0.6 eV (C), and there is almost no $p\sigma$ PDOS in the energy region D ($0.6\ \text{eV}<E-E_F<3.6\ \text{eV}$). Figure 1(c) shows XES (■) and XAS (□) of B $2p\pi$ of MgB_2. Observed PDOS of $p\pi$ shows a broad metallic state except a large sharp peak G at 5.6 eV. The overall features of observed XAS near E_F and XES are well reproduced by the band calculation. However, in whole energy region, some discrepancies are observed as

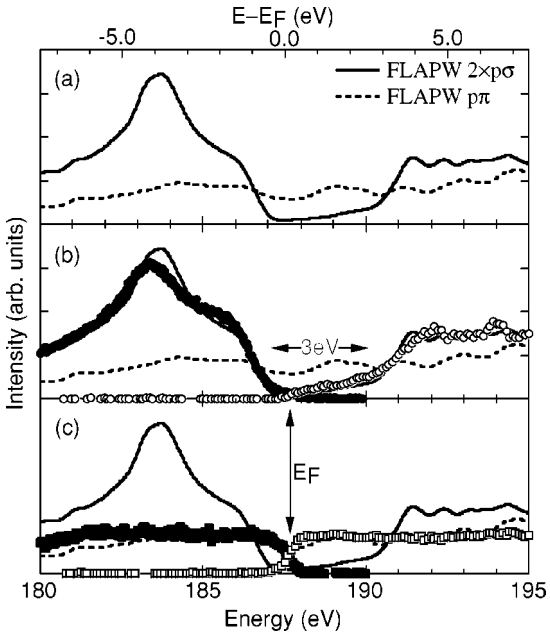

FIG. 2. The partial density of states (PDOS) of $p\sigma$ and $p\pi$ of AlB_2. (a) The theoretical PDOS derived from FLAPW method broadened with experimental resolution. The solid and dotted lines are PDOS's of $2\times p\sigma$ and $p\pi$, respectively. (b) The experimental PDOS of $2\times p\sigma$, 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).

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 $p\sigma$ XAS and G in $p\pi$ 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 as 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 pseudogap 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 $p\sigma(\bigcirc)$ and $p\pi(\bullet)$ PDOS of ZrB_2 derived from XES spectra.[29] In sharp contrast to the PDOS's of MgB_2 and AlB_2, the $p\pi$ PDOS of ZrB_2 shows two clearly resolved 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 PDOS's decrease with increasing energy, but the small Fermi edge is observed in both PDOS's. 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 PDOS's of ZrB_2 are well reproduced by the first principle band calculation. The detailed comparison between observed PDOS and theoretical ones is as follows.

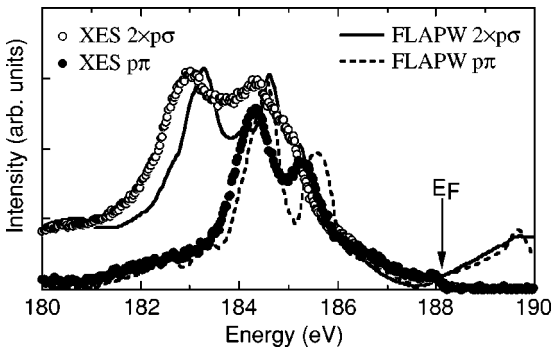

FIG. 3. The partial density of states (PDOS) of $2\times p\sigma(\bigcirc)$ and $p\pi(\bullet)$ of ZrB_2. The solid and dotted lines are theoretical PDOS's of $2\times p\sigma$ and $p\pi$, respectively, which are broadened with experimental resolution.

As mentioned before, overall shapes of the observed PDOS's 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 the 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 that E_F shifts.[11] However, in MgB_2, observed antibonding $p\sigma^*$ PDOS's E_1 and E_2 are higher than the theoretical ones F_1 and F_2. This means the observed pseudogap 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's around the pseudogap of about 3 eV. The values of observed pseudogap 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 the $p\pi^*$ 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 a 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 PDOS's 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 PDOS's of both compounds do not deny the rigid band picture, but suggest a small discrepancy between both compounds, i.e., antibonding $p\sigma^*$ 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 $4d_{yz,zx}$ 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 interband 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 ($\sim$0.2 eV) in MgB_2, AlB_2, and ZrB_2 compounds. The interband EC has a possibility to enhance the phonon-mediated T_c.[15,18] If a small interband EC effect that cannot 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 PDOS's and theoretical ones, the first principle band calculation reproduces well the overall features of observed $p\sigma$ and $p\pi$ PDOS's. In superconducting MgB_2, a considerable amounts of $p\sigma$ hole state near the Fermi energy is clearly observed. The pseudogap 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 PDOS's 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 ($\sim$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, the possibility of a small interband electron-correlation effect that supports the phonon-mediated superconductivity still remains.

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[30] 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. Second, 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 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.