Electronic Structure of B-2p State in AlB₂ Single Crystal: Direct Observation of $p\sigma$ and $p\pi$ Density of States

Jin Nakamura*, Masamitsu Watanabe¹, Tamio Oguchi², Shin-ya Nasubida, Eiki Kabasawa, Nobuyoshi Yamada, Kazuhiko Kuroki, Hisashi Yamazaki, Shik Shin³, Yuji Umeda³, Shin Minakawa⁴, Noriaki Kimura⁴ and Haruyoshi Aoki⁴

Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182-8585
¹RIKEN/Spring-8, Kouto 1-1-1, Mikazuki, Sayo, Hyogo 679-5148
²Department of Quantum Matter, ADSM, Hiroshima University, Higashihiroshima, Hiroshima 739-8530
³The Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581
⁴Center for Low Temperature Science, Tohoku University, Sendai 980-8578

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X-ray emission (XES) and absorption (XAS) spectra near the B-K edge were measured on single-crystalline AlB₂ compound which is an isostructural diboride of superconducting MgB₂. The partial density of states (PDOS) of B-2s and s-p orbitals were derived from the polarization dependence of XES and XAS spectra. There are considerable amounts of PDOS near the Fermi energy in AlB₂ similarly to that in MgB₂, but there are almost no PDOS in $p\sigma$ orbitals of AlB₂ near the Fermi energy, i.e., a pseudo-gap in $p\sigma$ state and a broad metallic state in $p\pi$ state are observed. The present result indirectly supports scenarios that the $p\sigma$ holes play an important role in the occurrence of superconductivity in MgB₂. The overall features of PDOS were found to be in good agreement with the result of band calculation of AlB₂, but a small discrepancy in the Fermi energy is observed, which is attributed to the Al vacancy in the compounds, i.e., the estimated concentration is Al$_{0.95}$B$_2$.

KEYWORDS: MgB₂, AlB₂, single crystal, partial density of state, $p\sigma$ and $p\pi$ orbitals, X-ray emission and absorption spectroscopy

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Since the discovery of superconductivity in MgB₂ with a transition temperature, $T_c$, of 39 K by Nagamatsu et al.,¹¹ a large number of research studies from experimental²⁻⁴ and theoretical⁵⁻¹⁴ points of view have been performed on this compound and on a series of isostructural diborides. In a previous paper,⁴¹ we reported a large partial density of states (PDOS) of B-2$p\sigma$ and $p\pi$ orbitals were derived from the polarization dependence of XES and XAS spectra. There are considerable amounts of PDOS near the Fermi energy in AlB₂ similarly to that in MgB₂, but there are almost no PDOS in $p\sigma$ orbitals of AlB₂ near the Fermi energy, i.e., a pseudo-gap in $p\sigma$ state and a broad metallic state in $p\pi$ state are observed. The present result indirectly supports scenarios that the $p\sigma$ holes play an important role in the occurrence of superconductivity in MgB₂. Although there are many experimental results that suggest MgB₂ is considered as an s-type superconductor with a strong electron-phonon coupling, the reason for the high value of $T_c$ as a conventional BCS-type superconductor is not clear. An efficient step towards understanding the mechanism of superconductivity in MgB₂ is to clarify the difference between this material and other materials which have the same crystal structure but are not superconductors. An example of such materials is AlB₂. From a theoretical point of view, first principles band calculations reveal that a large difference between MgB₂ and AlB₂ is that the Fermi level intersects the 2$p\sigma$ band in the former, while it does not in the latter, suggesting that the $p\sigma$ band plays an important role in the occurrence of superconductivity in MgB₂.⁹,¹⁵ However, until now, a direct experimental confirmation that such band-calculation predictions are indeed correct has not yet been reported.

To clarify this point, here we directly observe the PDOS of B-2$p\sigma$ and 2$p\pi$ bands in AlB₂ by performing polarization-dependent XES and XAS on a single crystalline compound. The single-crystalline AlB₂ samples were prepared by the Al-flux method. Mixtures of Al (purity, 4N) and B (purity, 4N) powders were placed in an Al₂O₃ crucible and heated in an Ar gas atmosphere up to 1000°C, and then cooled slowly to 660°C. The synthesized AlB₂ single crystals were separated from the solidified melts by dissolving the Al flux with sodium hydroxide solution. The obtained crystals resemble a hexagonal plate with the edge length (in ab-plane) of about 1–2 mm and with the thickness of about 10 µm along the c-axis. Before XES and XAS measurements, the crystal was polished in order to remove Al-flux on the surface of the specimen and mounted on a Au plate with Ag paste. The XES measurements were performed at the undulator beamline BL-2C in KEK-PF.¹⁶ The incident photon energy is about 400 eV. Emitted photons were detected using the MCP detector combined with the 1200 lines/mm grating. The energy resolution of the spectrometer with the slit width of 20 µm was estimated as about $\Delta E \sim 0.2$ eV at the energy of $E = 200$ eV.¹⁷ Polarization dependence of emission spectra on the angle between the c-axis and the detector-direction $\theta$ was measured at room temperature (Fig. 1). The XAS measurements were performed at BL-19B in KEK-PF by the total fluorescence yield (TFY) method. The energy resolution of the incident photon was about 0.2 eV. The geometry of XAS measurement was the same as that of the XES measurement.

In our experimental geometry, the fluorescence intensity with the incidence angle $\theta$, $I^{\text{fluo}}(\theta)$, is expressed using PDOS components parallel to the $p\sigma$ and $p\pi$ orbitals, $I^{\sigma\sigma}_{\text{fluo}}$ and $I^{\pi\pi}_{\text{fluo}}$. 

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*E-mail: jin@pc.uec.ac.jp
Fig. 2. Theoretical partial density of states of MgB$_2$.

Because of the dipole transition (radiation) from B-2$p$ to 1$s$ states,

$$I_{\text{fluo}}(\theta) = [1 + \cos^2(\theta)]I_{p\sigma} + \sin^2(\theta)I_{p\pi}.$$  (1)

Therefore, an ideal XES spectrum $I_{\text{fluo}}(0^\circ)$ contains only the $p\sigma$ component, and $I_{\text{fluo}}(90^\circ)$ contains both the $p\sigma$ and $p\pi$ components with equal weight.

We first show the theoretical PDOS of $p\sigma$ and $p\pi$ orbitals of MgB$_2$ and AlB$_2$ derived from band calculation (Fig. 2). It is found that the overall feature of PDOS of MgB$_2$ is almost the same as that of AlB$_2$, i.e., the rigid band model roughly represents these materials. This is consistent with the previous XAS and XES results for the polycrystalline samples. To be more precise, the detailed form of PDOS of MgB$_2$ is sharp in comparison with that of AlB$_2$, i.e., the peak of the $p\sigma$ band of MgB$_2$ at $E = -2$ eV is relatively sharp compared with that of AlB$_2$ at $E = -4.5$ eV. This is due to a reduction of two-dimensionality of B-$p$ bands in AlB$_2$, which is consistent with the decrease of the lattice-constant ratio from MgB$_2$ ($c/a = 1.14$) to AlB$_2$ ($c/a = 1.08$). As mentioned in the introduction, an important difference between MgB$_2$ and AlB$_2$ predicted theoretically is that the Fermi energy lies within the $p\sigma$ band in the former, but not in the latter.

We now move on to the experimental results. Figure 3 shows the partial density of states (PDOS) of B-2$p\sigma$ and 2$p\pi$, $I_{\text{fluo}}$ and $I_{\text{abs}}$, derived from observed $I_{\text{abs}}(20^\circ)$ and $I_{\text{abs}}(45^\circ)$. A self-absorption correction was applied to the observed XES spectra before the derivation of $I_{\text{fluo}}$ and $I_{\text{abs}}$. The area intensities of $I_{\text{fluo}}$ and $I_{\text{abs}}$ are normalized to unity in the energy region below 188 eV, and the 2$p\sigma$ and 2$p\pi$ are shown in the figure. The value of $E_F$ is about 187.5 eV which is about 1.5 eV higher than the value of MgB$_2$ (186.5 eV), which is in good agreement with the previous report for the polycrystalline AlB$_2$ sample. It is clearly seen that there is almost no PDOS in $p\sigma$ orbitals of AlB$_2$ near $E_F$. Furthermore, there is a considerable amount of PDOS in $p\pi$ orbitals of AlB$_2$ around $E_F$.

Figure 4 shows the PDOS of B-2$p\sigma$ and $p\pi$, 2$x_l$ $I_{\text{abs}}$ and $I_{\text{abs}}$, derived from observed absorption spectra $I_{\text{abs}}(20^\circ)$ and $I_{\text{abs}}(70^\circ)$. Similarly to the XES spectra, the self absorption correction was applied before their derivation, and the normalized absorption intensity $I_{\text{abs}}(\theta)$ is expressed as follows:

$$I_{\text{abs}}(\theta) = \sin^2(\theta)I_{\text{abs}} + \cos^2(\theta)I_{\text{abs}}.$$  (2)

In PDOS of $p\pi$ [Fig. 4(a)], there is large absorption at about 194 eV in contrast to no sharp absorption in $p\sigma$-PDOS, which is assigned to the $p\pi$ resonance state on the sample.
resonance state (a) Overall feature of PDOS and (b) comparison with the band calculation results. Dotted and solid lines are the theoretical PDOS of $p_\sigma + p_\pi (= 2 \times p\pi)$ and $p_\pi (= p\pi)$ orbitals derived from band calculation (FLAPW) for AlB.

Fig. 4. Partial density of states (PDOS) of B-2p\sigma and p\pi, 2\times F^{\text{abs}}_{\text{py}} (\odot) and F^{\text{expt}}_p (\bullet), derived from observed absorption spectra $F^{\text{abs}}_{\text{py}}(20^\circ)$ and $F^{\text{expt}}_p(70^\circ)$.

In both figures (Figs. 3 and 4), the theoretical PDOS of AlB$_2$ are shown again by the dotted line (p\sigma) and the solid line (p\pi). It is found that the theoretical PDOS reproduces the observed PDOS well, for both the empty and occupied states. We have clearly observed a pseudo-gap of about 3 eV around 187–190 eV in the B-2p\sigma orbital in sharp contrast to the broad metallic state of the B-2p\pi orbital. The pseudo-gap is attributed to the bonding and anti-bonding state separation due to the strong covalent nature of p\sigma orbitals. However, there is a small difference in the value of $E_F$ between the experimental and theoretical PDOS. The band calculation predicts the energy of p\sigma–shoulder at about $-1.8$ eV below the Fermi level. However, the observed energy of the shoulder (186.3 eV) locates $-1.2$ eV below the Fermi level (187.5 eV), i.e., the observed Fermi energy $E_F$ is 0.6 eV lower than the theoretical prediction. The reason for this difference is considered to be the lack of Al atoms from the stoichiometry. The observed pseudo-gap in p\sigma–PDOS at around the Fermi energy suggests the strong covalent bonding feature of boron forming the 2D honeycomb plane as reported by maximum entropy method (MEM)/Rietveld analysis. We considered that the layered B-honeycomb plane is the fundamental structure of AlB$_2$. There is a small difference in electronegativity between Al and B atoms, so electrons transfer from Al to B atoms in AlB$_2$ compound. Vacancies of Al atoms in AlB$_2$ reduce the number of electrons of B-2p orbitals, thus the Fermi levels shift down. If we assume that the decrease of the states below $E_F$ is due to an Al vacancy, the vacancy concentration $x$ of Al$_{1-x}$B$_2$ is estimated to be about 0.07. The theoretical band calculation suggests that the heat of formation of AlB$_2$ is lower than that of MgB$_2$, which suggests the compound which has a lower number of electrons of the cation than the stoichiometric AlB$_2$ is more stable. The present result is consistent with this prediction.

To summarize, we have performed direct measurement of partial density of states (PDOS) of B-2p\sigma bands in single-crystalline AlB$_2$ using polarization-dependent XES and XAS. We have clearly observed a pseudo-gap of about 3 eV in the B-2p\sigma orbital in sharp contrast to the broad metallic state of the B-2p\pi orbital. Although the experimentally observed PDOS is in excellent agreement with the band calculation results, the Fermi level in the former is found to be lower by about 0.6 eV than in the latter. Nevertheless, the Fermi level still lies well above the p\sigma band, providing a direct confirmation that there are no p\sigma holes in AlB$_2$. Conversely, considering the fact that AlB$_2$ is not superconducting, our result indirectly supports scenarios that the p\sigma holes play an important role in the occurrence of superconductivity in MgB$_2$.

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