# Soft x-ray spectroscopy experiments on the near *K*-edge of B in $MB_2$ ($M$=Mg, Al, Ta, and Nb)

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Soft x-ray-absorption and emission measurements are performed for the *K*-edge of B in $MB_2$ ($M$=Mg, Al, Ta, and Nb). Unique feature of $MgB_2$ with a high density of the B $2p_{xy}(\sigma)$ state below and above the Fermi edge, which extends to 1 eV above the edge, is confirmed. In contrast, the B $2p$ density of states in $AlB_2$ and $TaB_2$, both of occupied and unoccupied states, decreased linearly towards the Fermi energy and showed a dip at the Fermi energy. Furthermore, there is a broadening of the peaks with $p\sigma$ character in x-ray emission spectra and x-ray-absorption sepctra of $AlB_2$, which is due to the increase of three dimensionality in the $p\sigma$ band in $AlB_2$. The density of states (DOS) of $NbB_2$ has a dip just below the Fermi energy. The present results indicate that the large DOS of B-$2p\sigma$ states near the Fermi energy are crucial for the superconductivity of $MgB_2$.

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Since the discovery of superconductivity in $MgB_2$ with a transition temperature $T_c$ of 39 K by Nagamatsu *et al.*,[1] a large number of researches from experimental[2,3] and theoretical points[4] of view have been performed, to explain the superconducting properties and mechanism of this new high-$T_c$ superconductor. The observed $T_c$ of ~40 K seems to exceed the upper bound of the transition temperature (~30 K) estimated for conventional BCS-type superconductors. Hence it is very important to clarify whether its superconducting mechanism is conventional or not. In this context, Bud'ko *et al.* reported a boron isotope effect of $\alpha = 0.26$, which suggests that phonons are playing an important role in the occurrence of superconductivity in this compound.[5] Tunneling results indicate an *s*-wave nature of superconductivity.[6] Theoretically, band calculations have suggested strong electron-phonon coupling.[7–13] All this evidence supports the conventional BCS-type superconductivity in $MgB_2$. However, a detailed analysis of the specific heat and recent high-resolution XPS experiment indicate that the superconducting gap must be anisotropic or two-band like.[14,15]

In order to clarify the mechanism of high-$T_c$ superconductivity in $MgB_2$, it is important to investigate the difference in the electronic states between $MgB_2$ and other related compounds: $MB_2$ ($M$=Al, Ta, and Nb). $MgB_2$ is a superconductor with $T_c$=39 K as mentioned, while $AlB_2$ has been reported to be a nonsuperconductor.[16] $TaB_2$ has been reported as a superconductor of 9.5 K by Kaczorowski *et al.*,[17] while it has recently been reported to be a nonsuperconductor by Gasparov *et al.*[18] $T_c$ of $NbB_2$ is also controversial: $T_c$=6 K by Cooper *et al.*,[19] 5.2 K by Akimitsu *et al.*,[20] and 0.62 K by Leyarovskaya and Leyarovski,[21] while Gasparov reported it as a nonsuperconductor.[18]

In the present study, we present x-ray emission (XES) and absorption spectra (XAS) near the boron (B) *K*-edge in $MB_2$ ($M$=Mg, Al, Ta, and Nb). XAS was measured by both the total fluorescence yield (TFY) and the total electron yield (TEY) measurements at the same time. XES and XAS studies are powerful tools to probe the filled and empty electronic states of a specific orbital. The reason we choose boron is because the band calculations for $MgB_2$ indicate that the bands near the Fermi energy are mainly composed from boron $2p$ orbitals. By measuring the dipole transition between $2p$ states and $1s$ core level of boron, we can specifically probe the partial density of states (PDOS) of B $2p$ states. Furthermore, XES and XAS by TFY are not surface sensitive in contrast to photoelectron spectroscopy.

The commercial specimens from Rare-Metallic Co. were used as samples of $MB_2$ ($M$=Mg, Al, Ta, and Nb). The specimens were examined by powder x-ray-diffraction (XRD) measurements.

XRD measurements showed a single phase $MgB_2$-type pattern for all specimens. The dc magnetizations were measured with a superconducting quantum interference device (SQUID) magnetometer in the temperature range from 1.8 to 100 K. The temperature dependencies of the susceptibility indicate that the superconducting transition temperature of about 38 K for $MgB_2$, and no superconducting transition for $TaB_2$, $NbB_2$, and $AlB_2$ above 1.8 K.

 

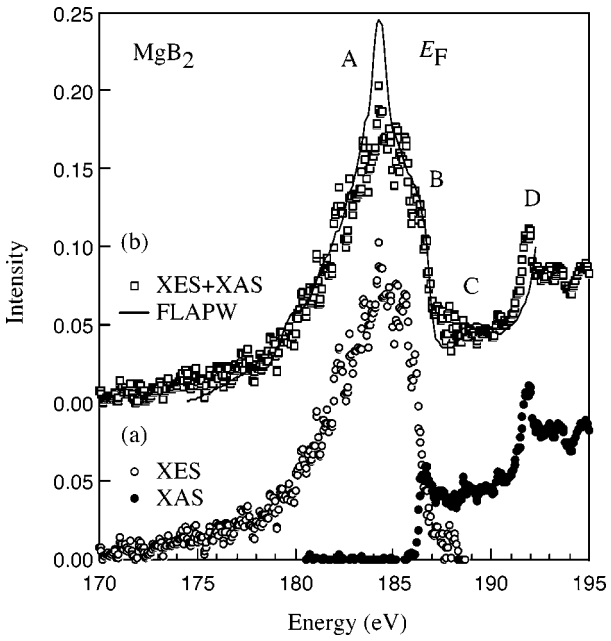


FIG. 1. (a) The observed XES (○) and XAS (●) spectra of $MgB_2$. (b) The sum of XES and XAS (□) and the theoretical PDOS (solid line) derived from FLAPW method broadened with experimental resolution.

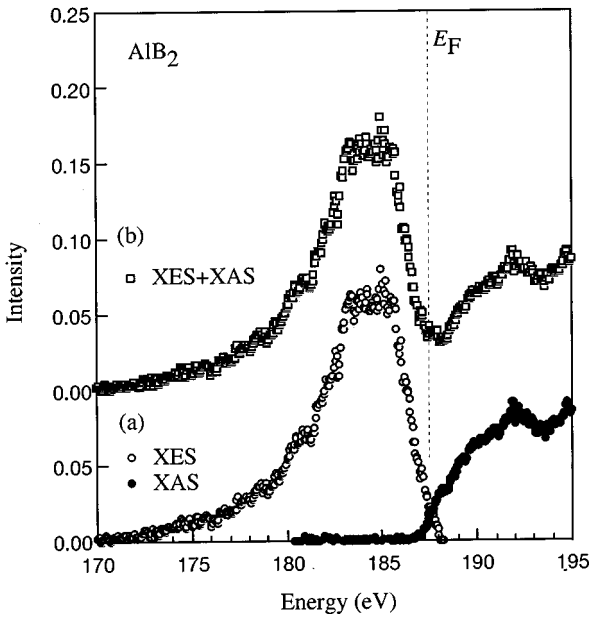


FIG. 2. (a) The observed XES (○) and XAS (●) spectra of $AlB_2$. (b) The sum of XES and XAS (□).

The soft x-ray emission and absorption spectroscopies were performed at BL-8.0.1 of Advanced Light Source (ALS) in LBNL. The resolutions of emission and absorption spectra are 0.3 and 0.1 eV, respectively. In order to calibrate energy, XAS by TEY were also measured at the well calibrated beam line BL-6.3.2 of the ALS. The XAS for all $MB_2$ compounds obtained by TEY shows a sharp peak at about 193.8 eV, which is attributed to boron oxides,[22] while the XAS obtained by TFY shows no detectable peak at about 194 eV. These results indicate that there is a small amount of boron oxide only on the surface, but not inside the bulk. Here, we present the XAS obtained by TFY, so the presented results are free from the influence of boron oxides.

Figure 1(a) shows XES (○) and XAS (●) of $MgB_2$. The sharp decrease of XES and XAS at about 186.3 eV is attributed to the Fermi energy measured from the $1s$ core level. The solid line in Fig. 1(b) is the boron PDOS obtained from a band-structure calculation,[9] where we have taken into account the effect of the instrumental resolution by Gaussian broadening. The intensities of experimental XES and XAS in Fig. 1(a) are scaled to the theoretical PDOS in the energy region $E \leqslant 182$ eV for XES and 187 eV$\leqslant E \leqslant$191 eV for XAS. The sum of the experimental XES and XAS are also plotted in Fig. 1(b). It can be seen that the overall feature of both XES and XAS, including the existence of a large PDOS around the Fermi energy, are remarkably well reproduced by the band-structure calculation, enabling us to attribute each observed structure to $p\pi$ and/or $p\sigma$ states. Namely, the existence of peaks A and B, which is consistent with recent studies,[2,3] are characteristic of bonding $p\sigma$ states.[9,11] The region C in the energy range from 187 to 191 eV is attributed to the $p\pi$ states. A sharp peak D at about 192 eV in XAS is reported to be a resonance peak of $p\pi^*$ state,[3] and also corresponds to antibonding $p\sigma^*$ state predicted by a band calculation. Thus peak D contains both the $p\sigma^*$ and resonance state of $p\pi^*$ states.

Figure 2(a) shows XES and XAS of $AlB_2$. The intensity of XES is normalized so that the area intensity coincides with that for $MgB_2$ below $E_F$, while the intensity of XAS is scaled so that the intensity in the high-energy region, $E \geqslant 198$ eV, coincides with that for $MgB_2$. In the high-energy region, XAS shows no strong characteristic peaks. A broad tail of XES below 183 eV is similar to that of $MgB_2$, but the value of $E_F$ shifts to be 187.5 eV. The form of XES of $AlB_2$ is broad compared to that of $MgB_2$. Figure 2(b) shows experimental PDOS derived from the sum of XES and XAS. A dip is observed at about 188 eV near the Fermi energy, indicating that the B $2p$ PDOS around the Fermi energy is drastically reduced compared to that in $MgB_2$. This is the major difference between $MgB_2$ and $AlB_2$.

This difference can be understood from results of the band calculation for $AlB_2$.[12] Namely, there are several factors that make the boron $2p$ PDOS around the Fermi level in $AlB_2$ much smaller than in $MgB_2$. First of all, the bonding $\sigma$ bands, whose tops are located above the Fermi level in $MgB_2$, are fully filled in $AlB_2$. Second, the Fermi level is located at a point where the top of the bonding and bottom of the antibonding $\pi$ bands touch with each other at the $K$ point. If the system were purely two dimensional, this would be a point where the DOS vanishes linearly as a function of energy. Although the $\pi$ band is three dimensional, the above two-dimensional property remains because the system is anisotropic.

The difference between $MgB_2$ and $AlB_2$ can qualitatively be understood within a simple rigid-band model, namely by simply shifting the Fermi energy as mentioned above. To be more precise, there are some quantitative differences, whose origin seems to lie beyond a rigid band picture. Namely, in

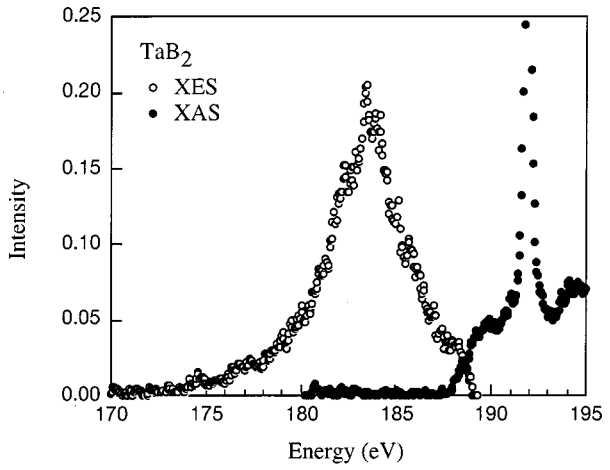


FIG. 3. The observed XES (○) and XAS (●) spectra of $TaB_2$.

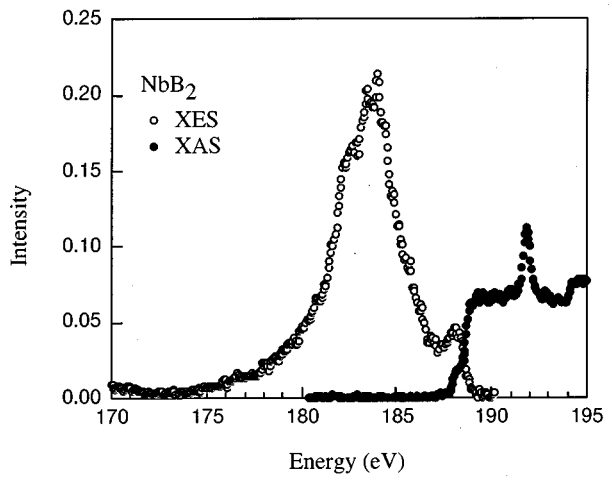


FIG. 4. The observed XES (○) and XAS (●) spectra of $NbB_2$.

$AlB_2$, the intensity of XAS just above the dip is larger than that in $MgB_2$, while the intensity of peaks A and D is suppressed. Looking again into the band calculation results, these features may be attributed to the increase of three dimensionality in $AlB_2$.

The XES and XAS of $TaB_2$ are similar to those for $AlB_2$ except for a shift in the Fermi energy (Fig. 3) up to 188.6 eV, owing to a larger band filling compared with $AlB_2$. The B $2p$ PDOS at the Fermi energy is similar to that for $AlB_2$, so if $TaB_2$ is indeed superconducting, the difference between these two compounds should lie elsewhere.

Figure 4 shows XES and XAS of $NbB_2$. The Fermi energy is almost the same as that of $TaB_2$, but a considerable amount of DOS below the Fermi energy is observed. A dip is also observed at $\sim 187$ eV and is lower than the Fermi energy. The form of the XAS indicates a flat PDOS above 189 eV and shows a small peak D. The PDOS around the Fermi energy is not so small. The character of the states near the Fermi energy cannot be identified from the present results.

To summarize, the most characteristic feature in $MgB_2$ as compared to other related materials is the large B $2p$ PDOS around the Fermi level. Since this is partially attributed to the existence of the $p\sigma$ bonding band at the Fermi level, one may be tempted to consider that the $p\sigma$ band plays a crucial role in the occurrence of superconductivity in $MgB_2$.[4] This is indeed probable, but is not necessarily the case because the $p\pi$ band filling is also different between $MgB_2$ and other materials as mentioned above, which should result in a large difference in the shape of the $p\pi$ band Fermi surfaces. Let us note that the shape of the Fermi surfaces can play an essential role in the occurrence of superconductivity. For example, in those mechanisms that exploit nesting between the Fermi surfaces of bonding and antibonding $\pi$ bands,[23–25] the shape of the Fermi surfaces (namely the $\pi$-band filling) is crucial. We believe that further studies are necessary to clarify this point.

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