Soft X-ray emission spectroscopy study of the valence electron states of α-rhombohedral boron

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Abstract. High energy-resolution boron K-emission spectra of single-crystalline α-rhombohedral-boron (α-r-B) were measured with a newly developed soft X-ray emission spectroscopy (SXES) instrument attached to a conventional transmission electron microscope. The intensity profiles of the spectra, which correspond to the density of states of the valence bands with p-symmetry, were compared with those of amorphous boron (am-B), single-crystalline β-rhombohedral-boron (β-r-B) and B₄C. A characteristic shoulder structure appears in the spectrum of α-r-B but not of am-B, β-r-B or B₄C. This structure should be due to the inter-cluster three-center bonding states among B₁₂ clusters in α-r-B.

1. Introduction

Boron forms four allotropes: α-rhombohedral boron (α-r-B), α-tetragonal boron, β-rhombohedral boron (β-r-B) and β-tetragonal boron. Those allotropes and amorphous boron (am-B) are constructed by B₁₂ icosahedral clusters [1-3]. The crystal structure of α-r-B is the simplest among them, in which B₁₂ clusters are placed at the corners of the rhombohedral unit cell [4,5]. Each B₁₂ cluster in α-r-B is covalently bonded to twelve nearest-neighbor B₁₂ clusters. The B₁₂ clusters in the (111) plane are connected by the three-center bonding and those between two (111) planes by the two-center bonding.

Horn measured the band gap energy of α-r-B single crystals as about 2eV from optical absorption experiments [6]. Theoretical calculations of the electronic structure indicate that α-r-B is a semiconductor with an indirect energy gap [7-9]. A theoretical calculation reported peaks in the density of states (DOS) of α-r-B near the Fermi level [10]. The peaks originate from small deviation of α-r-B from an ideal B₁₂ cluster with icosahedral symmetry. The peak structures of the DOS of the conduction band (CB) were confirmed by a high energy-resolution electron energy loss spectroscopy (EELS) of single-crystalline α-r-B [11]. After that, metal-doped α-r-B and β-r-B have been investigated by high energy-resolution EELS based on transmission electron microscopy [12-14].

Domashevskaya et al investigated the DOS of the valence band (VB) of α-r-B, β-r-B and am-B
using X-ray emission spectroscopy, but could not find a significant difference among them [15]. It may be due to insufficient energy resolution and specimen quality. Fujimori et al derived the spatial distribution of valence electrons of α-r-B from powder X-ray diffraction experiment using maximum-entropy analysis combined with Rietveld structure refinement [16]. They visualized the spatial distribution of the three-centered bonding of intra- and inter-clusters. The inter-cluster three-centered bonding is unique for α-r-B. To detect the electronic state of the inter-cluster three-center bonding, high energy-resolution measurements are required on high-quality single crystalline α-r-B.

In this report, high energy-resolution soft X-ray emission spectroscopy measurements are reported on single-crystalline α-r-B and compared with those of am-B, β-r-B and B$_4$C. From the comparison of boron K-emission spectra, the characteristic structure in the DOS of VB of α-r-B is ascribed to the inter-cluster three-center bonding states of the crystal.

2. Experimental details
Specimens of α-r-B were prepared by annealing am-B powder, which was deposited by electron-beam evaporation, at 1200 °C for 10 h in a BN crucible. The crucible was held in an Ar-sealed quartz tube, in which tantalum foil was placed to prevent oxidation of the specimen. After annealing, the specimens were composed of small single crystals of α-r-B (20-40 µm) and β-r-B (50-100 µm). The crystals were crushed in a crucible and put on a grid for transmission electron microscopy experiments. Electron diffraction patterns showed that the specimens were high quality single crystals of α-r-B and β-r-B.

Figure 1 shows a soft X-ray emission spectroscopy (SXES) instrument, which is attached to a conventional transmission electron microscope JEM2010 [17]. Soft X-ray emission was induced by 100 kV electrons. It was dispersed by a grating and detected by a charge-coupled-device (CCD) camera. We used a Ni-coated varied-line spaced grating with an average groove density of 1600 lines/mm and a CCD camera without an anti-reflection coating. The calculated energy-dispersion of the grating for boron K-emission energy of 180 eV was about 0.07 eV/channel (1 channel: 13.5 µm) on the CCD surface. Probe current, probe diameter and acquisition time were 5-10 nA, 500 nm and 30-60 min, respectively.

3. Results and discussions
Figure 2 shows boron K-emission spectrum of α-r-B obtained from a single-crystalline area of about 500 nm in diameter. K-emission spectra of β-r-B and am-B are also shown for comparison. The energy scale was determined by the energy dispersion of the grating, and the origin was taken
arbitrarily. The spectra are due to electronic transitions from the VB states to a K-shell core-hole state created by electron-beam illumination. A dipole transition is associated with soft-X-ray emission. Therefore, the intensity distribution of each spectrum corresponds to the partial DOS of the VB with $p$-symmetry for each material. The intensity maximum of each spectrum, indicated by a dotted vertical line, occurs at almost the same energy. The top (the dotted vertical line on the right-hand side) and the bottom (the dotted vertical line on the left-hand side) of the VB are also almost the same for all materials. This may be due to that all those materials have common structural unit of B$_{12}$ cluster. It should be noted that a circled area of $\alpha$-r-B shows a characteristic additional shoulder structure compared with those of $\beta$-r-B and am-B. Furthermore, the intensity profile of the top part of the main peak of $\beta$-r-B is the sharpest among the three spectra. Those differences in the DOS of the VB of the three boron allotropes were successfully identified for the first time using a developed SXES-TEM instrument [17].

Figure 3 shows the DOS with $p$-symmetry of the VB calculated for $\alpha$-r-B using the Wien2k code. A characteristic DOS peak is indicated by an arrow. The DOS is attributed to boron atoms, which form three-centered bonding between B$_{12}$ clusters. Three-centered bonding state between B$_{12}$ clusters is known as a characteristic of the crystalline $\alpha$-r-B. The energy position of the peak is about 2 eV lower than the top of the DOS peak. The energy difference between the experimentally observed
shoulder structure and the DOS peak in figure 2 is almost the same with this calculated result. Thus, the shoulder structure observed in figure 2 can be due to the three-centered bonding state. To confirm this, more detailed DOS calculations for \( \beta \)-r-B and am-B are desired, but have not performed those due to the structural complexity of the materials.

When the shoulder structure of \( \alpha \)-r-B is due to the three-centered bonding, anisotropic X-ray emission intensity is expected due to the anisotropic distribution of the three-centered bonding. Figure 4 shows boron K-emission from crystalline \( \alpha \)-r-B, measured with a different crystal orientation from that of figure 2. The spectra of \( \beta \)-r-B and am-B are also obtained from different specimens. The shoulder structure of \( \alpha \)-r-B is also seen as indicated by a vertical line. However the intensity distribution is different from that in figure 2. This different intensity distribution for different crystal settings can be due to the anisotropic distribution of the three-centered bonding.

The structure of \( B_4C\) is similar to that of \( \alpha \)-r-B except that carbon atoms are placed on the body diagonal line, [111]. Although the stoichiometry of this system is not well defined and is considered
between $\text{B}_1\text{C}_2$ and $\text{B}_4\text{C}$, this material may not have the inter-cluster three-center bonding between $\text{B}_{12}$ clusters as in $\alpha$-r-B \cite{18,19}. Figure 5 shows a boron K-emission spectrum of a single-crystalline $\text{B}_4\text{C}$. The $\alpha$-r-B spectrum of figure 2 is also shown for comparison. Contrary to $\alpha$-r-B, the spectrum of $\text{B}_4\text{C}$ does not show a shoulder structure. This again suggests that that the origin of the shoulder structure of the DOS of $\alpha$-r-B is mainly due to the inter-cluster three-center bonding, which is a characteristic electronic state of $\alpha$-r-B.

4. Concluding remarks

Newly developed SXES instrument based on transmission electron microscope has been applied for measuring boron K-emission spectra from identified single-crystalline areas of $\alpha$-r-B, $\beta$-r-B and $\text{B}_4\text{C}$ and also from amorphous boron. It is clearly revealed that the DOS of $\alpha$-r-B has a characteristic shoulder structure, which may be due to the inter-cluster three-center bonding. For discussing the DOS in terms of the inter-cluster three-center bonding and for comparison with the result of MEM/Rietveld analysis \cite{16} on the three-centered bonding in real space, an angle-resolved SXES measurement is necessary on single-crystalline $\alpha$-r-B by changing the take-off angle of X-ray emission.

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