



Unusual line shape of B 1s core level spectra in rare earth hexaborides

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ABSTRACT

We investigate the B 1s core level spectra of hexaborides, RB_6 ($R = \text{La, Ce, Pr, Nd}$), using high resolution X-ray photoemission spectroscopy. While all the B sites are identical, the experimental spectra exhibit a signature of multiple features manifested as an unusual asymmetry in the lower binding energy side. The analysis of the spectra reveals that the surface and bulk photoemission signals are different. In addition, the peak position shifts towards lower binding energies with the increase in 4f binding energy of the rare earth elements that can be attributed to the chemical potential shift due to lower degree of 4f–conduction electron hybridization. Decrease in temperature leads to a narrowing of the linewidth in every case. The Kondo systems exhibit more prominent narrowing of the B 1s linewidth.

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Hexaborides (RB_6), in general, have attracted a great deal of attention recently due to the observation of varied physical properties highly interesting for studies in fundamental physics and potential technological applications. For example, LaB_6 is a well-known thermionic emitter with a very low work function that shows a pseudogap at low temperatures [1,2], CeB_6 is a dense Kondo system ($T_K \sim 2 \text{ K}$) [3], PrB_6 and NdB_6 are local moment antiferromagnets [4], SmB_6 is a Kondo insulator [5], EuB_6 is a ferromagnetic semiconductor [6], CaB_6 is a high temperature ferromagnet [7], etc. The crystal structure of these compounds is cubic, where B_6 octahedra occupy the cube corners and R cations occupy the body centered position. The valence band of this class of compounds is primarily derived by the B 2s2p electronic states. These non-4f valence states are known to possess similar electronic structures [8] across the family of RB_6 . Early electronic structure calculations suggested that the B_6 octahedron requires two electrons to complete its inert shell configuration [9] and hence divalent alkaline earth hexaborides are small gap semiconductors. In RB_6 , the rare earth atom forms a trivalent configuration donating an additional electron to the boron-derived valence band making the system metallic. Clearly, the wide variation in electronic properties observed in these systems is derived by the coupling of 4f electrons with the conduction electrons having B 2s2p character.

While the electronic states in the valence band determine the electronic properties, the influence of various electronic interaction parameters can efficiently be probed by studying the core level spectra which are often difficult to access using valence band spectroscopy [10]. In order to probe the influence of rare-

earths on the B-sublattice, we probe the B 1s core levels using high resolution X-ray photoemission spectroscopy (XPS). The core level spectra as a function of rare earth and temperature exhibit an interesting evolution.

The well characterized single crystalline samples of RB_6 ($R = \text{La, Ce, Pr and Nd}$) were prepared by the floating zone technique using a four mirror Xe arc lamp image furnace [11]. The photoemission measurements were performed using a monochromatic Al $K\alpha$ X-ray source ($h\nu = 1486.6 \text{ eV}$) and a Gamdata Scienta SES2002 analyzer at an energy resolution of 0.3 eV. The temperature variation of the sample was achieved by using an open cycle He cryostat from Advanced Research Systems, USA. The base pressure during the measurements was maintained at $3 \times 10^{-11} \text{ Torr}$. The sample surface was prepared by both scraping and cleaving *in situ*—the spectra look identical in both the cases.

In Fig. 1, we show the B 1s core level spectra collected at 10 K for all the samples. All the spectra exhibit a sharp peak around 188 eV (feature A in the figure) with an unusual lineshape possessing an asymmetry towards lower binding energies. In normal cases, low energy excitations across the Fermi level in metallic systems lead to asymmetry towards higher binding energies [12]. A comparison of the spectra from different samples indicates enhancement in intensity around the binding energies shown by vertical lines B and C. We have superimposed the LaB_6 spectrum (lines in the figure) over the other ones to visualize the changes. The energy region near the feature A is expanded in Fig. 1(b) to bring out clarity. There are two changes observed. (i) The feature A becomes broader and shifts slightly towards lower binding energies as the rare earth's atomic number is increased. (ii) The intensity of the features B and C appears to increase. Increase in atomic number of the rare earth enhances both the 4f occupation and 4f binding energy. The

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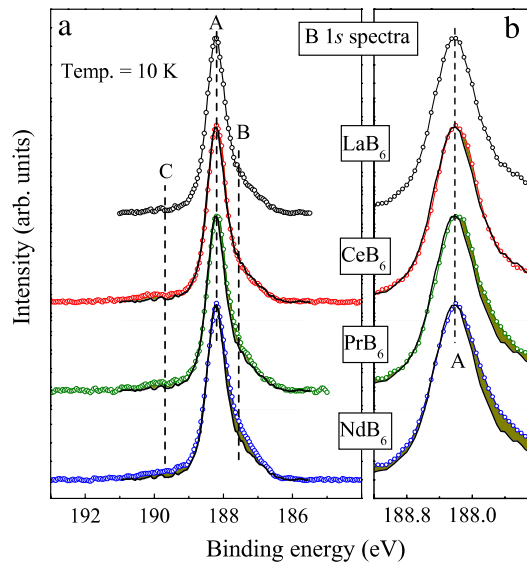


Fig. 1. (Color online) (a) B 1s core level spectra LaB_6 , CeB_6 , PrB_6 and NdB_6 at 10 K exhibiting multiple features. (b) The same B 1s spectra are shown in an expanded scale. The lines superimposed on the raw data (symbols) represent the B 1s spectrum of LaB_6 .

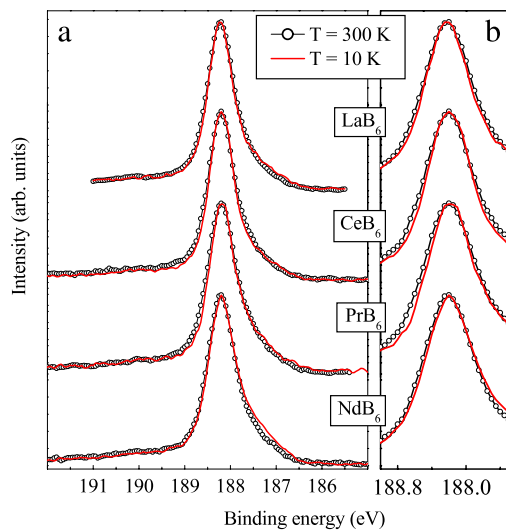


Fig. 2. (Color online) (a) B 1s spectra at room temperature (symbols) and 10 K (lines) exhibiting a broadening of the linewidth with increase in temperature. (b) Near peak region shown in an expanded scale.

hybridization of 4f states with the conduction electronic states will gradually reduce as the 4f band moves away from the Fermi level leading to a smaller degree of electron transfer. Thus, the chemical potential, highly sensitive to the B 2s2p electron counts, will have a tendency to shift towards lower energies leading to a decrease in core level binding energies. The change in intensities will be discussed below.

Change in temperature also has a significant influence on the spectral lineshape. We show the room temperature spectra (symbols) and 10 K spectra (lines) in Fig. 2. In LaB_6 , the feature A becomes slightly broader at 300 K and the intensity of the feature B reduces by a small amount. The broadening of the feature A becomes more prominent in CeB_6 . The scenario in PrB_6 remains almost similar to that in CeB_6 . Interestingly, the change in broadening parameters becomes less prominent in NdB_6 .

In order to estimate the evolution of the lineshape as a function of temperature and rare earth element, we have fitted the spectra using three asymmetric peaks (Pearson's IV type as used in

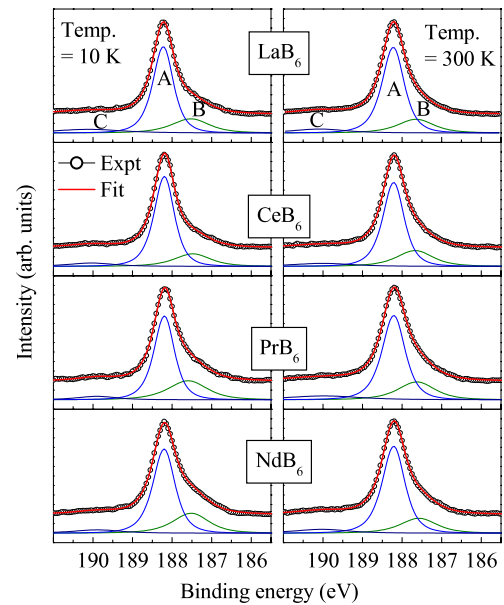


Fig. 3. (Color online) Simulated B 1s spectra at different temperatures.

various other cases [13]) representing the features A, B and C. The fits are shown in Fig. 3. The simulated spectra provide a good representation of the experimental spectra. The intensity of the feature C seems to be significantly small. The intensity ratio of the feature B to feature A is about 0.27 ± 0.03 and remains very similar across the series and at all the temperatures studied. It is already observed [14] that the effective escape depth of photoelectrons is about 20 Å at 1480 eV (valence electrons in Al K α spectra), the escape depth of B 1s electrons will be about 18.7 Å. Assuming a surface depth of about 4–5 Å (in rare earth systems, layers below the top two layers possess electronic structure similar to the bulk) the surface and bulk contributions will be about 19%–23% and 81%–77%, respectively. The surface to bulk intensity ratio becomes 0.23–0.3, which matches excellently well with the values estimated in the present case.

The above observations suggest that the feature B appearing around 187.5 eV corresponds to the surface feature and the feature A at 188.2 eV is the bulk feature. Valence band photoemission studies of these compounds showed a surface feature around 2 eV binding energy due to the dangling B 2p orbitals at the surface [1,15]. The Madelung potential of these surface borons will be much smaller compared to the bulk borons as the positive lattice sites above the surface layers are vacant—half of the nearest cation neighbors are absent. Thus, photoemission of electrons from surface boron requires less energy compared to that from the bulk borons and explains the appearance of the surface feature at lower binding energy. At the cation site, this effect will be reversed as the absence of negative ions above the surface layer makes the electrons bind more strongly to the cation site.

We now discuss the temperature induced effects on the lineshape. The temperature induced effects have been studied using neutron/Raman scattering experiments that help to determine the effect of the crystal field on the Ce 4f levels, etc. [16–20]. The Raman scattering measurements on CeB_6 reveal splitting of the ground state quartet (crystallographic ground state of 4f¹ configuration in a perfectly cubic crystal field) into two doublets ~ 30 K apart; the origin of which was attributed to the departure from perfectly cubic structure either due to static or dynamic distortions [16]. The energy scale of this change is significantly small compared to the linewidth (\sim eV) of the core level peaks. The small increase in linewidth at higher temperatures in the LaB_6 spectrum may be attributed to various thermal effects such as crystallographic

change discussed above, phonon induced effects, etc. The increase in linewidth seems to be stronger in CeB₆ and PrB₆—such differences cannot be accounted for by the thermal effects as they are expected to be similar in all the cases. The linewidth and asymmetry strongly depend on the low energy excitations of the electrons across the Fermi level. The formation of Kondo resonance features (sharp features at the Fermi level) will lead to significant reduction in linewidth at low temperatures. Thus, the more prominent effects observed in CeB₆ and PrB₆ may be related to the Kondo resonance formation at low temperatures.

In summary, we have studied the B 1s core level spectra using high resolution X-ray photoemission spectroscopy. All the spectra exhibit multiple features that could be attributed to the different photoemission signals from surface and bulk borons. The spectral lineshape is found to be sensitive to the change in rare earth element and temperature. Increase in 4f binding energy in the rare earth elements leads to a reduction of the B 1s binding energy (~20 meV) indicating a small chemical potential shift—a reflection of lower electron transfer due to the weaker 4f–conduction electron hybridization. B 1s features become narrower with the decrease in temperature—the Kondo systems exhibit more prominent narrowing of the B 1s linewidth.

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