Influence of 4*f* electronic states on the surface states of rare-earth hexaborides

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We study the surface electronic structure of a series of rare-earth hexaborides using state-of-the-art high resolution photoemission spectroscopy. Experimental results reveal a surface state around 1.8 eV binding energy in all the hexaborides indicating its generic nature in this class of compounds. The surface and bulk electronic structures near the Fermi level, ϵ_F are almost similar in each of the compounds. This suggests an interesting possibility of fabricating new materials possessing low work function like LaB_6 where the behavior of mobile electrons can be tuned by rare-earth substitutions. © *2010 American Institute of Physics.* [doi:10.1063/1.3340461]

Technological application of a material relies significantly on its surface properties. It is realized that the surface and bulk electronic structures of a material can be qualitatively different due to lowered symmetry, different surface morphology, surface reconstructions, defects, etc.[1–11] Immense research in this direction during past few decades led to creation of several broad areas of research. For example, the field of nanoparticle magnetism, important for spintronic applications, data storage, etc., has already taken a center stage due to their involved fundamental issues and potential technological applications.[12] Photoemission spectroscopy is an ideal tool to probe the surface states as the mean escape depth of photoelectrons is significantly small. Moreover, one can change the incident photon energy and/or experimental geometry to change its surface sensitivity.[5]

Here, we studied the surface states of rare-earth hexaborides—an important class of materials used extensively in technology. These compounds exhibit diverse physical properties. For example, LaB_6 is a good metal with low work function and is widely used as an efficient thermionic emitter.[13,14] CeB_6 is a dense Kondo system[15] exhibiting complex magnetic phase diagram.[16] PrB_6 and NdB_6 are local moment antiferromagnets.[17] SmB_6 is a Kondo insulator.[18] EuB_6 is a ferromagnetic semiconductor.[19] Such wide varieties of properties appear due to the interaction of 4*f* electrons with the conduction electrons of B $2s2p$ character.[20,21] Earlier photoemission studies of LaB_6 showed a surface feature around 2 eV binding energy due to the dangling B $2p$ orbitals at the surface.[13,22,23] Similar surface feature was also observed in NdB_6.[24] In both these cases, 4*f* bands have negligible contribution around 2 eV. Moreover, the bulk non-4*f* electronic density of states are predicted to be similar across the series.[25] Hence, similar behavior of the surface states of LaB_6 and NdB_6 may be a natural phenomenon. The scenario can be different if 4*f* states appear in the vicinity of surface feature leading to large overlap with these states. In addition, it is important to see how surface effect influences the electronic states near ϵ_F that determines their applications.

In order to address these issues, we have investigated the surface electronic structure of NbB_6, PrB_6, and CeB_6 using high resolution photoemission spectroscopy. Single crystalline samples were prepared at Warwick by the floating zone technique and oriented along the (001) direction for the measurements. The photoemission measurements were performed at 10 K on a cleaved surface using monochromatic Al $K\alpha$($h\nu$=1486.6 eV), He I ($h\nu$=21.2 eV), and He II ($h\nu$=40.8 eV) photon sources, and Gammadata Scienta R4000 analyzer. The energy resolution was set to 2 meV at $h\nu$=21.2 and 40.8 eV, and 300 meV at $h\nu$=1486.6 eV photon energies. The base pressure in the photoemission chamber was 3×10^{-11} Torr. ϵ_F was derived by measuring the Fermi cutoff of the high purity polycrystalline Ag sample mounted on the same sample holder in electrical contact with the samples.

In Fig. 1, we show the He II valence band (VB) spectra of NdB_6. The spectrum from freshly cleaved surface displays a sharp Fermi cutoff and a strong peak at about 1.7 eV as
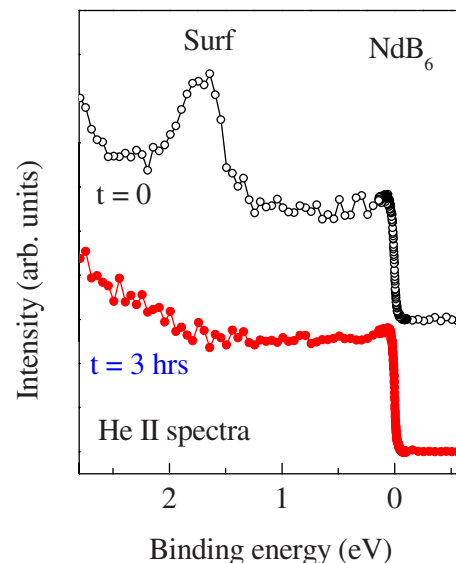

FIG. 1. (Color online) He II VB spectra of NdB_6. The open and closed circles represent the spectra collected from a surface freshly cleaved and 3 h after cleaving, respectively.

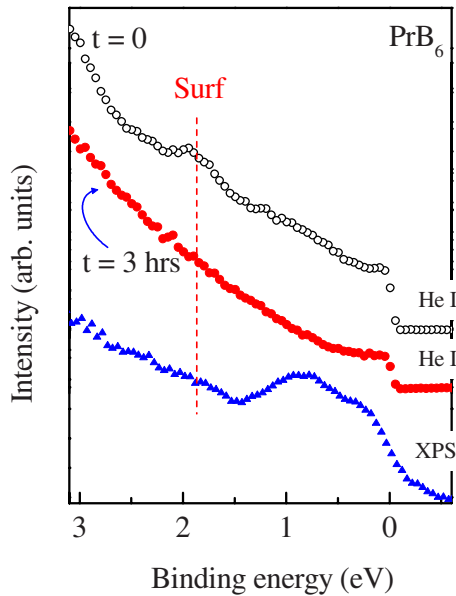a)Author to whom correspondence should be addressed. Electronic mail: kbmaiti@tifr.res.in.

FIG. 2. (Color online) He I (circles) and Al $K\alpha$ (triangles) VB spectra of PrB_6. The open and closed circles represent the spectra collected from a surface freshly cleaved and 3 h after cleaving, respectively. The XP spectrum do not exhibit significant change with time.

FIG. 3. (Color online) He II (circles) and Al $K\alpha$ (triangles) VB spectra of CeB_6. The open and closed circles represent the spectra collected from a surface freshly cleaved and 2.5 h after cleaving, respectively. The XP spectrum do not exhibit significant change with time.

also observed earlier on (110) surface.[24] This feature gradually weakens in intensity with time delay although the base pressure in the chamber remained 3×10^{-11} torr during the whole measurement time. The change can be attributed to the adsorption of foreign gas molecules on the sample surface that destroys the surface states. The feature vanished completely in about 3 h after cleaving as shown in the figure. However, the spectral line shape near ϵ_F remained almost unchanged.

The He I spectrum from freshly cleaved surface of PrB_6 also exhibit a distinct feature around 1.8 eV that disappears in about 3 h after cleaving (see Fig. 2) indicating its surface character. Evidently, the smaller $4f$ binding energy in PrB_6 than that in NdB_6 does not have significant influence on the binding energy of the surface feature. The surface sensitivity is significantly reduced in the x-ray photoemission (XP) spectroscopy that provides a good representation of the bulk features.[2,5] This is manifested by the absence of the surface feature in the XP spectrum shown in Fig. 2. The XP spectral line shape near ϵ_F is significantly different from that of He I spectra. The Pr $4f$ photoemission cross section[26] is about three orders of magnitude larger than that for B $2p$ states at 1486.6 eV photon energy. In contrast, B $2p$ cross section is larger than that of Pr $4f$ states in ultraviolet energies. Thus, the enhancement in intensity of the features near ϵ_F in XP spectrum indicates large Pr $4f$ contribution in this energy range. These features correspond to the well screened $4f^2$ electronic configuration in the final state, where one of the conduction electron screens the $4f$ hole created by the photoemission. In this energy range, the spectral line shape of both XP and He I spectra was found to remain unchanged with time.

In Fig. 3, we show the He II and XP spectra of CeB_6, where $4f$ band appears close to ϵ_F leading to strong Kondo effect. Ultrahigh resolution employed in the He II spectroscopy helped to reveal four distinct features at 2.1, 1.7, 0.28, and 0.05 eV binding energies. The feature around 1.7 eV disappears gradually with the increase in delay time and
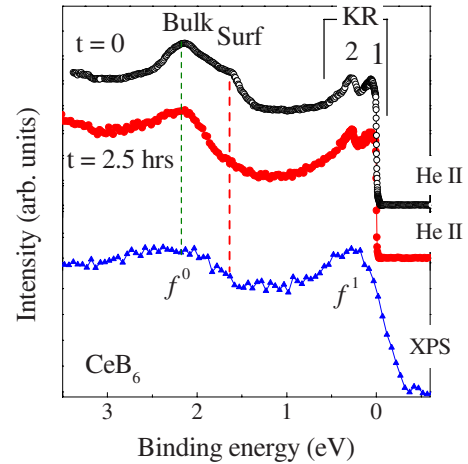
completely vanishes in about 2.5 hours after cleaving. This indicates the surface character of this feature. The feature around 2.1 eV corresponds to the unscreened final state having f^0 electronic configuration as also observed in other Ce-compounds.[27] The feature in the vicinity of ϵ_F is the well screened feature having f^1 electronic configuration and represents the signature of Kondo resonance feature (KR).[28] In the He II spectrum, the KR feature splits into two distinct features; the spin-orbit split components are marked by 1 and 2 in the figure. These features remain almost unchanged with time.

These experimental observations suggest that the appearance of surface state at about 1.7–1.8 eV binding energy is a generic phenomena in hexaborides. This eigenenergy of the surface state is not influenced by the presence/absence of $4f$ bands. We observed that the intensity of the surface feature is clearly visible only in He I and He II spectra. The intensity in that energy region of XP spectra is almost nonobservable. A change in photoemission angle, thereby enhancing the surface sensitivity of the XP spectroscopy also shows similar trend. This suggests B $2p$ character of the surface feature as the photoemission cross section of these states are significantly enhanced in the He I and He II photon energies—dangling B $2p$ electronic states presumably form the surface state at 1.8 eV in all these compounds.[24,29]

CeB_6 is known to be a Kondo lattice system, where the Ce $4f$ electronic states couples strongly with the conduction electrons (*Kondo coupling*). The Kondo coupling strength becomes weaker as the $4f$ band moves to higher binding energies. Consequently, Kondo behavior is not observed in the physical properties of PrB_6 and NdB_6. In this study, we observe that the surface feature binding energy is insensitive to the presence of $4f$ levels in its proximity and/or near ϵ_F—hybridization of the $4f$ states with the conduction electrons does not influence the surface state at 1.8 eV.

The electronic states in the vicinity of ϵ_F are found to be unchanged although the surface feature at 1.8 eV disappears. If the 1.8 eV feature is the only signature of surface states, the electronic structure at the surface is highly insulating with a band gap ≥ 2 eV. However, no signature of such insulating surface is observed in various other physical properties measurements carried out so far. Thus, the surface and

bulk electronic structures near ϵ_F are presumably very similar. This suggests an attracting possibility in the field of technological applications—one can tune the local character of the conduction electrons, thereby, the properties of these compounds via substitution of suitable rare earth elements keeping work function low as in LaB_6. Similar substitutions have already been carried out in some cases leading to interesting properties. For example, Y-substitution for La in LaB_6 gives rise to superconductivity,[30] Ca-substitution for La in LaB_6 gives rise to ferromagnetism with very high Curie temperature,[31] and hence are potential candidates for spintronic applications, field sensors, switches, etc.

In summary, we have studied the evolution of surface electronic structure of a series of rare earth hexaborides as a function of $4f$ energies using state-of-the-art high resolution photoemission spectroscopy. The experimental observations on CeB_6, PrB_6, and NdB_6 reveal the signature of a surface feature at about 1.8 eV in all the compounds indicating its generic nature in this class of compounds. The binding energy of the surface feature is found to be insensitive to the energy of the $4f$ band and therefore, independent of the hybridization of the highly localized $4f$ electrons with the conduction electrons. Electronic states close to the Fermi level remain unchanged even if the surface sensitivity of the technique and/or time delay is changed suggesting similar surface and bulk electronic structures in this energy range.

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