Observation of Kondo resonance in rare-earth hexaborides using high resolution photoemission spectroscopy

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Abstract.
We studied the electronic structure of rare earth hexaborides, CeB$_6$, PrB$_6$ and NdB$_6$ using state-of-the-art high resolution photoemission spectroscopy. CeB$_6$ is a dense Kondo system. PrB$_6$ and NdB$_6$ are antiferromagnetic (Neel temperature $\sim 7$ K), known to be stable moment systems and do not exhibit Kondo effect. Photoemission spectra exhibit distinct signature of surface and bulk electronic structures of these compounds. The energy position of the surface feature is not influenced by the 4$f$ density of states. High resolution spectra of CeB$_6$ reveal multiple Kondo resonance features in the bulk spectra due to various photoemission final states. Interestingly, high resolution photoemission spectra of antiferromagnetic PrB$_6$ also exhibit a sharp feature at the Fermi level that shows temperature dependence similar to the Kondo resonance features.

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Magnetic impurity in a metal often leads to a logarithmic enhancement in resistivity at lower temperatures, which is known as Kondo effect. At very low temperatures, the conduction electrons couples to the impurity moment antiferromagnetically forming a singlet state (non-magnetic state), termed as Kondo singlet. Such electronic states manifest as a sharp feature in the spectral density of states at the Fermi level, $\epsilon_F$ called Kondo resonance feature (KRF), which depends on the proximity of the impurity band to $\epsilon_F$ and the hybridization of the impurity states with the conduction electronic states. Numerous efforts are put forward during past several decades in identifying KRF in the electronic spectra using various forms of experimental techniques [1, 2]. However, experimental identification of KRF delineated from the uncompensated moment contributions is still a puzzle. Hexaborides are an important class of materials used extensively in technology and possess plethora of interesting properties making them well suited to address the issue. For example, LaB$_6$ is a good metal [3], CeB$_6$ is a dense Kondo system [4], PrB$_6$ & NdB$_6$ are local moment antiferromagnets [5], SmB$_6$ is a Kondo insulator [6], EuB$_6$ is a ferromagnetic semiconductor [7].

Such wide varieties of properties appear due to the interaction of 4$f$ electrons with the conduction electrons of B 2s2p character [8, 9]. It is predicted that the bulk non-4$f$ electronic density of states are very similar across the series[10]. Thus, by changing rare-earth element, one can tune the 4$f$ binding energy, $\epsilon_{4f}$ and hence the coupling of 4$f$ moment with the conduction electrons. Here, we studied the electronic structure of RB$_6$ ($R$ = Ce, Pr and Nd) employing high resolution photoemission spectroscopy that revealed distinct features corresponding to surface and bulk electronic structure. CeB$_6$ spectra exhibit multiple Kondo resonance features. Interestingly, the signature of Kondo resonance feature could also be observed in the photoemission spectra of PrB$_6$.

Large single crystals of all the compounds were produced at Warwick by the floating zone technique using a four mirror Xe arc lamp image furnace. The growths were carried out in a flow of argon gas and growth speeds of 10-18 mm/hr. Cylindrical boules of ~6 mm diameter and ~50 - 60 mm length were obtained by this technique [11]. Photoemission measurements were performed using monochromatic He i ($h\nu = 21.2$ eV) and He ii ($h\nu = 40.8$ eV) photons, and Gammadata Scienta SES2002 analyzer operating at an energy resolution of 2 meV. The sample surfaces were prepared by cleaving the single crystals in situ. It was noticed that the angle integrated spectra from cleaved surface and scraped surface using a diamond file are identical.

In Fig. 1(a), we show the He ii spectra of NdB$_6$ and CeB$_6$ collected at 10 K from freshly cleaved samples. The NdB$_6$ spectrum exhibit a sharp feature at about 1.7 eV binding energy as observed earlier [12]. This feature gradually weakens in intensity with time delay and vanished completely in about 3 hours after cleaving. Since the surface electronic structure is associated to only top few layers [13], the vanishing of the peak with time characterizes it to be a surface feature and can be attributed to dangling B 2s2p states. Earlier studies of LaB$_6$ also showed such a surface feature [3, 14]. In both, NdB$_6$ and LaB$_6$, the binding energy of 4$f$ band is different from 2 eV and hence may have small influence on surface states.
In order to probe the influence of $4f$ states on the surface feature, we study the He II spectrum of CeB$_6$ in the same figure, where $4f$ signal appear close to $\epsilon_F$. Ultra high resolution employed in the He II spectroscopy helped to reveal four distinct features at 2.1 eV, 1.7 eV, 0.28 eV 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 again indicates the surface character of this feature.

The identical energy position in both the cases establish that the surface feature in hexaborides are not influenced by the $4f$ electronic states. Evidently, the other features can be attributed to the bulk electronic structure.

The feature around 2.1 eV corresponds to the unscreened final state having $f^0$ electronic configuration [15]. The well screened features having $f^1$ electronic configuration appear near $\epsilon_F$ and represent the signature of Kondo resonance feature [2]. In order to reveal the details of these features, we show the He II spectrum at 10 K and 300 K in an expanded scale in Fig. 1(b). There are three distinct features marked S, C and K could be viewed in the spectrum at 10 K and can be attributed to the photoemission final states, $|f_{7/2}\uparrow\Uparrow\rangle$, $|f_{5/2}(\Gamma_7)^{1}\downarrow\rangle$ and $|f_{5/2}(\Gamma_8)^{1}\downarrow\rangle$, respectively ($\Uparrow$ represents a hole in the conduction band). These features almost vanished in the 300 K spectrum characterizing them as the signature of Kondo resonance features.

In Fig. 2(a), we compare the He $i$ and He II spectra of PrB$_6$ at 10 K. While the line shape of the features look very similar in the whole energy range shown, a small mismatch is observed near $\epsilon_F$. In order to bring this out clearly, we show the subtracted (He II - He $i$) spectrum in Fig. 2(c). Such subtraction provides the Pr $4f$ contributions as the relative photoemission cross section of $4f$ states increases significantly in He II energy compared to that in He $i$ energy. Thus, the sharp feature visible at $\epsilon_F$ in the figure possess $4f$ character. Interestingly, the intensity of this feature vanishes at 104
Figure 2. (a) He I (line) and He II (open circles) spectra of PrB$_6$ at 10 K. (b) He II (open circles) spectrum is compared with the corresponding Fermi-Dirac (FD) distribution function (line) at 10 K. (c) (He II - He I) and (d) He II/FD spectra at 10 K and 104 K.

K.

Spectral density of states (SDOS) can directly be obtained by dividing the resolution broadened Fermi-Dirac (FD) distribution function. Thus obtained SDOS exhibit a feature similar to that in Fig. 2(c) that vanishes at 104 K - the comparison of the raw data and the FD function is shown in Fig. 2(b). Sharp peaks near $\epsilon_F$ can appear from bare band structure and photoemission cross section effects and/or photoemission final state effects. Therefore, the identification of Kondo resonance feature has been a long standing issue since the birth of Kondo physics. The key difference appears in the temperature evolution - in all the above cases, the feature remains unchanged with temperature while the Kondo peak vanishes at higher temperature. The observation of vanishing of the feature at 104 K in Figs. 2(c) and 2(d), thus, attribute it to be a Kondo resonance feature. This is not unusual as the Pr 4$f$ levels are significantly hybridized with the conduction electrons. The absence of such effect in the bulk measurements may be related to the dominance of other bulk effects.

In summary, we investigated the evolution of the electronic structure in RB$_6$ (R = Ce, Pr and Nd) using high resolution photoemission spectroscopy and good quality single crystals. We observe that the surface states in these compounds are generic and are not influenced by the 4$f$ electronic states. High resolution spectra exhibit Kondo resonance feature in CeB$_6$ - a dense Kondo system. Interestingly, high resolution spectra of PrB$_6$ at 10 K also show a sharp feature at the Fermi level that vanishes at higher temperature indicating it to be signature of Kondo resonance in this compound.
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