Topological Phase and Strong Correlation in Rare-Earth Hexaborides XB$_6$ ($X =$ La, Ce, Pr, Nd, Pm, Sm, Eu)

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Abstract: The rare-earth hexaboride SmB$_6$, known as the topological Kondo insulator, has attracted tremendous attention in recent years. It was revealed that the topological phase of SmB$_6$ is insensitive to the value of on-site Coulomb interactions (Hubbard U), indicating that the topological phase in SmB$_6$ is robust against strong correlations. On the contrary, the isostructural YbB$_6$ displays a sensitivity to the Hubbard U value. As U increases, YbB$_6$ transforms from topological Kondo insulator to trivial insulator, showing the weak robustness of the topological phase of YbB$_6$ against U. Consequently, the dependence of the topological phase on Hubbard U is a crucial issue in the rare-earth hexaboride family. In this work, we investigate the structural and electronic properties of rare-earth hexaboride compounds through first-principles calculations based on density functional theory. By taking the strong correlations into consideration using a wide range of on-site U values, we study the evolution of the topological phases in rare-earth hexaboride (XB$_6$, $X =$ La, Ce, Pr, Nd, Pm, Sm, Eu). Unlike YbB$_6$, the topological trends in all the examples of XB$_6$ studied in this work are insensitive to the U values. We conclude that in addition to the well-known SmB$_6$, PmB$_6$, NdB$_6$ and EuB$_6$ are also topologically nontrivial compounds, whereas LaB$_6$, CeB$_6$ and PrB$_6$ are topologically trivial metal.

Keywords: topological phase; strong correlation; Hexaboride; first-principles calculations; electronic structures

1. Introduction

The discovery of the topological phase in condensed matter paved the way to classify electronic states [1,2]. Topological insulators have been attracting world-wide extensive attention in recent research [3–6]. Three dimensional materials with time reversal symmetry and inversion symmetry may harbor a topologically nontrivial phase if a band gap and band inversion emerge owing to spin–orbit interaction (SOI) [7].

The rare earth hexaboride XB$_6$ crystallizes in the CaB$_6$-structure, as shown in Figure 1. Its lattice structure is similar to a body-centered cubic such as the CsCl-type lattice with Cs replaced by rare earth ions, and with Cl substituted by B$_6$ octahedra. The variety of the physical properties observed in these compounds is intriguing. For example, the application of LaB$_6$ has been paid attention due to its low work function, which is suitable for thermionic emission. LaB$_6$ is metallic and becomes superconducting at $T_C = 0.45$ K [8]. CeB$_6$ is considered as a Kondo system. CeB$_6$ presents an antiferro-quadrupolar ordering in the paramagnetic phase between $T_Q = 3.3$ K (quadrupolar ordering temperature) and $T_N = 2.4$ K (Neel’s Temperature) [9,10]. PrB$_6$ has been confirmed that negative quadrupolar pair interactions exist in the paramagnetic phase ($T_N = 6.9$ K) [11]. NdB$_6$ is a localized 4f
system that orders ferro-magnetically at low temperatures [12]. SmB$_6$ is a well-known topological Kondo insulator [1,13,14]. EuB$_6$ orders ferro-magnetically below 15.1 K with a huge decrease of resistivity and a significant blue shift of the reflectivity plasma edge [15–17]. At 12.7 K, another phase transition takes place, which is observed as a broad peak in the specific heat or an anomaly in the resistivity [18]. GdB$_6$ is a localized 4f system with a ferromagnetic order at low temperatures [19]. YbB$_6$ is a topology Kondo insulator at low temperatures, and is a classical mixed valence narrow band gap semiconductor [1,20,21]. Structural studies are also presented in Ref. [22,23]. As reported in Ref. [1], the topological phase of YbB$_6$ is sensitive to the Hubbard U value. As U increases, YbB$_6$ transforms from topology Kondo insulator to trivial insulator, showing the weak robustness of the topological phase of YbB$_6$ against U.

![Image](a) Side view. (b) Oblique view. (c) Brillouin Zone and high symmetry k-points.

In this study, the lattice structures of rare-earth hexaboride (XB$_6$, X = La, Ce, Pr, Nd, Pm, Sm, Eu) are fully optimized through first-principles calculations. We then perform self-consistent field electronic structure calculations with and without SOI. To reveal the topological phases, we analyze if SOI would open up a continuous energy gap at the Fermi level with band inversion around the energy gap. To examine the robustness of the topological phase upon the strong correlation in XB$_6$, we trace the evolution of its electronic structure by tuning the on-site U of the f electrons. We demonstrate that besides SmB$_6$, PmB$_6$, NdB$_6$ and EuB$_6$ are also topologically nontrivial compounds, while the others are topologically trivial normal metals.

2. Computational Details

First-principles calculations were performed using the Vienna Ab initio Simulation Package (VASP) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional used in the generalized gradient approximation (GGA) as well as the GGA plus Hubbard U (GGA + U) schemes [24–27] based on density functional theory (DFT). The cut-off energy of 500 eV was adopted for the plane-wave basis. A Γ-centered 15 × 15 × 15 k-mesh was used in geometry optimization and self-consistent field calculations. The geometry optimization converged until all residual forces remained below 0.01 eV/Å. Table 1 compares the experimental lattice parameters of rare-earth hexaboride with our geometrically optimized ones. Good agreement between experimental and theoretical results can be found with deviations, in general, of less than 1%.
Table 1. Experimental (exp) and theoretical (the) lattice parameters. The rare-earth hexaboride crystallizes in a bcc-like structure with space group of Pm3m (No. 221), in which metal ions are located at the Wyckoff position 1a(0,0,0) and octahedral B6 at the Wyckoff position 6f (1/2,1/2,1/2). The subscripts “exp” and “the” indicate experimental and theoretical results, respectively.

| Material | a_{exp} (Å) | a_{the} (Å) | Error of a | B(z)_{exp} | B(z)_{the} | B–B Bond Length_{exp} (Å) | B–B Bond Length_{the} (Å) |
|----------|-------------|-------------|------------|-------------|------------|--------------------------|--------------------------|
| LaB6 [15]  | 4.1527      | 4.1553      | 0.06%      | 0.1993      | 0.1997     | 1.7660                  | 1.7647                 |
| CeB6 [16]  | 4.14        | 4.1130      | −0.65%     | 0.1992      | 0.1984     | 1.7611                  | 1.7543                 |
| PrB6 [22]  | 4.13        | 4.1024      | −0.67%     | 0.2         | 0.1984     | 1.7522                  | 1.7498                 |
| NdB6 [16]  | 4.127       | 4.1007      | −0.64%     | 0.1989      | 0.1987     | 1.7574                  | 1.7473                 |
| SmB6 [23]  | 4.128       | 4.1131      | −0.36%     | 0.2         | 0.1990     | 1.7514                  | 1.7508                 |
| EuB6 [29]  | 4.1346      | 4.1087      | −0.63%     | 0.2018      | 0.1993     | 1.7436                  | 1.7474                 |
| YbB6 [29]  | 4.1489      | 4.1325      | −1.25%     | 0.2027      | 0.1999     | 1.7595                  | 1.7539                 |

3. Results and Discussion

3.1. Topologically Trivial Normal Metal LaB6, CeB6, and PrB6

Figure 2a,b show the PBE band structures of LaB6 without and with SOI, respectively. The atom-orbital decomposition demonstrates that the valence bands below −1.5 eV are mainly composed of B-p orbital, while the conduction La-f bands (blue curves) are located mainly from 0.5 eV to 2.5 eV above the Fermi level (E_F). In between, there is a dispersive band composed of La-d orbital connecting the valence and conduction bands, resulting in an overall semimetal character. This in-gap La-d band also gives an electron pocket at E_F along ΓM. A comparison of band structures without SOI (a) and with SOI (b) shows that the SOI in LaB6 is weak and has no significant effect on band structure. Consequently, the semimetal character remains as SOI is included. Without any continuous gap, LaB6 is therefore a topologically trivial normal metal. On the other hand, the band structures remain more or less the same when the on-site Coulomb repulsion U is taken into account for the strong correlation in f orbitals, as can be seen in Figure 3. This constitutes preassembly, owing to the empty f states that have no effect near E_F.

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Figure 2. Atom-orbital decomposed band structure of LaB6 calculated using Perdew–Burke–Ernzerhof (PBE) functional without spin–orbit interaction (SOI) (a) and with SOI (b). The size of blue, green and yellow circles indicates components from La-f, La-d and B-p orbitals, respectively.
Figure 3. Atom-orbital decomposed band structures of LaB$_6$ with on-site $U = 2$ eV (a,b), 4 eV (c,d), 6 eV (e,f), and 8 eV (g,h).
With one more electron than La, the Fermi level of CeB\(_6\) is thus raised up to the bottom of Ce-f bands, as shown in Figure 4. The flat Ce-f conduction bands are located around \(E_f\) from 0.6 eV below to 1.2 eV above \(E_f\). As shown in Figure 5, for all the four cases with \(U = 2, 4, 6, 8\) eV studied, there are no significant changes in band structures. Similar to LaB\(_6\), CeB\(_6\) is also insensitive to the on-site U values. Although the SOI is included in the calculations and the degeneracy at M is lifted by SOI, there is no continuous gap in all cases, leading to topologically trivial normal metal ground state for CeB\(_6\).

**Figure 3.** Atom-orbital decomposed band structures of LaB\(_6\) with on-site U = 2 eV (a,b), 4 eV (c,d), 6 eV (e,f), and 8 eV (g,h).

**Figure 4.** Band structure of CeB\(_6\) without (a) and with (b) spin–orbit interaction.

**Figure 5.** (a–d) CeB\(_6\) band structures given from PBE + SOI + U with \(U = 2, 4, 6, 8\) eV, respectively. The sizes of blue, green and yellow circles indicate components from Ce-f, Ce-d and B-p orbitals, respectively.
Elementary Pr has three electrons occupying the f-orbitals in the ground state. Therefore, in PrB$_6$, the Pr-f conduction band is occupied by one more f electron than CeB$_6$, through the rigid-band shift, as shown in Figure 6. The band dispersions remain similar with different on-site U values. However, because the Fermi level is raised to the middle of the Pr-f conduction band, on-site U affects the bandwidth more significantly than that in the previous two species. With U = 8.0 eV, the f bandwidth is enhanced by about 0.5 eV. On the other hand, gapless ground state remains in PrB$_6$ even when the SOI is taken into consideration. Consequently, the same as LaB$_6$ and CeB$_6$, PrB$_6$ is also a topologically trivial normal metal.

**Figure 6.** PrB$_6$ band structure without (a) and with (b) spin–orbit interaction (noted in the figures), and with spin–orbit interaction plus on-site U = 2, 4, 6, 8 eV (c–f, respectively) as noted in the figures.
3.2. Topologically Nontrivial Kondo Insulator SmB$_6$, PmB$_6$, NdB$_6$ and EuB$_6$

Figure 7 shows our calculated band structures of the well-known topological Kondo insulator. The relatively flat La-f bands locate around $E_f$, with a much more dispersive La-d band crossing all these f bands. The spin–orbit interaction splits the f bands and opens up a continuous energy gap (see Figure 8) with band inversion between Sm-f/d characters flipping around the SOI-induced gap. These results agree well with those presented in previous works [1]. Band structures of SmB$_6$ with SOI and on-site U ranging from 2 to 8 eV are shown in Figure 9. There are no significant changes in band structures due to all the different U values used. Similar to previous study, the SOI-induced band gap and the band inversion behavior remain, indicating the robust topological phase against strong correlations in SmB$_6$.

![Figure 7](image1.png)  
(a) SmB$_6$ without spin-orbit  
(b) SmB$_6$ with spin-orbit

**Figure 7.** Band structures of SmB$_6$ without (a) and with (b) spin-orbit interaction projected by f and d electrons of Sm.

![Figure 8](image2.png)  
SmB$_6$ without spin-orbit  
SmB$_6$ with spin-orbit

**Figure 8.** Band structure of SmB$_6$ without and with spin-orbit coupling. The right panel is the zoom-in view of the middle panel around $E_f$. 
In comparison with the well-known topological Kondo insulator SmB$_6$, the overall band dispersion of PmB$_6$ as shown in Figure 10 is similar to those of SmB$_6$ (Figures 7–9). Since PmB$_6$ has one less valence electron than SmB$_6$, the Fermi level of PmB$_6$ is relatively lower than that of SmB$_6$. With SOI taken into consideration, PmB$_6$ opens up a continuous gap around $E_f$ as shown in Figure 10b,d. In addition, there is a band inversion around X point with B-p and Pm-d components exchanged near $E_f$. Therefore, PmB$_6$ can host topological nontrivial state, giving rise to the topological Kondo insulator similar to SmB$_6$. The electronic structure of PmB$_6$ around $E_f$ is not sensitive to various U values, as shown in Figure 11. On-site U only affects the highest empty f-band without influencing the overall topological properties, indicating the topological phase is robust in PmB$_6$ against strong correlations.
Figure 10. PBE band structure of PmB$_6$ without SOI (a) and with SOI (b). The size of blue, green and yellow circles show contributions from Pm-f, Pm-d and B-p orbitals, respectively. (c) Zoom-in of (a). (d) Zoom-in of (b). (c,d) demonstrate SOI-induced band inversion and gap opening.

Figure 11. Band structures of PmB$_6$ with SOI and $U = 2, 4, 6, 8$ eV (a–d, respectively). As $U$ is tuned larger, the highest f band is lifted but the band property is not changed near the Fermi level.

Band structures of NdB$_6$ as shown in Figure 12 also demonstrate topologically nontrivial phase. The SOI not only opens up a continuous energy gap around $E_F$ but also gives rise to band inversion around X point. Similar to PmB$_6$, the electronic structure and topological behavior of NdB$_6$ near the Fermi level are insensitive to on-site U value, as can be seen in Figure 13. Only the highest unoccupied f band is noticeably modified by $U$, which is irrelevant to its topology. Consequently, NdB$_6$ is also a topological Kondo insulator.
Figure 12. Band structures of NdB₆ without (a) and with (b) spin-orbit interaction.

Figure 13. Band structures of NdB₆ with SOI using $U = 2$, 4, 6, and 8 eV (a–d, respectively). As $U$ is tuned larger, the highest f band is lifted but the band property is not changed near the Fermi level.

Figure 14 shows PBE ($U = 0$ eV) band structures of EuB₆ without and with SOI as well as PBE + $U$ band structures with $U = 2$ eV and 6 eV. As can be seen in Figure 14a, the f bands are located at $E_f$ with a localized flat band character. In the periodic table, Eu is the neighbor of Sm with one more electron. The additional electron raises the Fermi level of EuB₆ near the half-filling metallic regime. When SOI is included, the f bands separate themselves into two groups with an SOI-induced continuous gap in between. Furthermore, band inversion emerges around the high symmetry point X. As a result, EuB₆ exhibits nontrivial topological phase similar to SmB₆. The band structure of EuB₆...

(a)                                            (b)
EuB$_6$ exhibits nontrivial topological phase similar to SmB$_6$. The band structure of EuB$_6$ is not sensitive to $U$, as shown in Figure 14b–d, with $U = 0–6$ eV, leading EuB$_6$ to robust topological Kondo insulator against strong correlations.

Figure 14. PBE band structure of EuB$_6$ without SOI (a) and with SOI (b). SOI opens up an energy gap around $E_f$ and induces band inversion around X point. PBE + $U$ band structure of EuB$_6$ with on-site $U =$ 2.0 eV (c) and $U =$ 6.0 eV (d). Similar to SmB$_6$, the Hubbard $U$ does not change the band structure noticeably.

4. Conclusions

We have systematically analyzed the electronic structures of rare-earth hexaborides to investigate their topological properties and examine the robustness of the topological phase against strong correlations by varying the Coulomb repulsion $U$. SmB$_6$ is a topological Kondo insulator due to the hybridization gap, and it will not experience topological phase transition by tuning the Coulomb
interaction. YbB₆, which has a hybridization gap, on the contrary, will experience a topology phase transition from a topological Kondo insulator to a topological insulator, and finally become a trivial insulator. Our results of SmB₆ and YbB₆ are in good agreement with previous results [1]. Our study also shows that PmB₆, NdB₆, EuB₆ and SmB₆ exhibit SOI-induced continuous gaps with band inversion, revealing nontrivial topological properties. On the other hand, the weaker SOI in relatively lighter. Lanthanides La, Ce and Pr fail to open up a continuous gap in LaB₆, CeB₆ and PrB₆. Thus LaB₆, CeB₆ and PrB₆ are topologically trivial normal metals with correlated conduction electrons.

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