Topological Crystalline Kondo Insulator in Mixed Valence Ytterbium Borides

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The electronic structures of two mixed valence insulators YbB_6 and YbB_{12} are studied by using the local density approximation supplemented with the Gutzwiller method and dynamic mean field theory. YbB_6 is found to be a moderately correlated Z_2 topological insulator, similar to SmB_6 but having much larger bulk band gap. Notably, YbB_{12} is revealed to be in a new novel quantum state, strongly correlated topological crystalline Kondo insulator, which is characterized by its nonzero mirror Chern number. The surface calculations find an odd (three) and an even (four) number of Dirac cones for YbB_6 and YbB_{12} , respectively.

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Topological insulators (TIs) [1,2] have been extensively studied, but mostly for the s and p orbital systems, such as HgTe [3-5], and Bi₂Se₃ family compounds [6-8], which are free of strong correlation effects. In the presence of strong electron interactions, very fruitful topological phases can be expected, such as the topological Mott [9] or Kondo [10–12] insulators, topological superconductors [2], and fractional TI [13-15]. To pursue these exotic phases, however, an important and necessary step is to find suitable compounds, which are strongly correlated (presumably in d and f orbital systems) and topologically nontrivial. Studies on such systems are challenging both theoretically and experimentally. Nevertheless, the mixed valence phenomenon provides an important way towards this direction [12,16–18]. For instance, in rare-earth mixed valence compounds, the band inversion naturally happens between the correlated 4f and 5d states, which may lead to correlated topological phases. SmB₆, a typical mixed valence compound, has been proposed theoretically as a "topological Kondo insulator" [10–12], and recently has been supported by transport [19–22], photo emission [23–25] and STM [26] experiments. Here the highly dispersive 5d conduction band intersects with the 4f energy levels, leading to electron transfer and strong quantum fluctuation among 4fatomic configurations [17]. At sufficiently low temperature, the hybridization between 4f orbitals and 5d bands will be established, resulting in the formation of "heavy fermion" bands, whose nontrivial Z_2 topological index [1,2] can be determined by the single particle Green's function at zero frequency [27,28].

In the present Letter, we will focus on another family of binary mixed valence compounds, ytterbium borides, and propose that various correlated topological phases, in particular a new topological crystalline Kondo insulator [29–31], can be realized. Among the four typical compounds, YbB₄, YbB₆, YbB₁₂, and YbB₆₆, the Yb ions in YbB₄ and YbB₆₆ are 2+ or 3+ respectively, while both the XPS and XAS data suggest that the valence of Yb in

YbB₆ and YbB₁₂ is around 2.2 [32] and 2.8 [33–36], respectively, indicating the mixed valence nature. As we have proposed in Ref. [12], the local density approximation (LDA) combined with the Gutzwiller density functional theory [37] is a powerful tool to compute the ground state and the quasiparticle spectrum of such correlated systems. Using this method, we find that (1) YbB₆ is a correlated Z_2 topological insulator similar to SmB₆ but with a much larger band gap (31 vs 10 meV), and (2) YbB₁₂ is a new topological crystalline Kondo insulator [29,30,38], which can be characterized by the nontrivial mirror Chern number, and shows an even number of Dirac cones on its surface.

As shown in Fig. 1, YbB₆ has the CsCl-type structure, the same as SmB₆, with the Yb and B_6 octahedral cluster occupying the Cs and Cl site, respectively, while YbB₁₂ takes the NaCl-type structure with the Yb and B_{12} cubo-octahedral cluster replacing the Na and Cl ions, respectively. The LDA part of the calculations has been done by the full potential linearized augmented plane wave method implemented in the WIEN2 κ package [39]. A regular mesh of $12 \times 12 \times 12 k$ points is used, and the muffintin radii (R_{MT}) of Yb and B atoms are taken as 2.50 and 1.57 bohr. The plane-wave cutoff K_{max} is given by $R_{MT}K_{\text{max}} = 7.0$. The spin-orbit coupling (SOC) is included self-consistently in all calculations.

The LDA band structures, shown in Figs. 2(a) and 2(b), suggest that the major features are very similar to SmB₆. First, the Yb-4f orbitals, which split into the j=5/2 and j=7/2 manifolds due to the SOC, form two sets of narrow bands with the former fully occupied and the later near the Fermi level (in SmB₆, the j=7/2 manifolds are completely empty, and j=5/2 states are close to the Fermi level). Second, the low energy band structure is semiconducting with a minimum gap of about 29 meV along the X-M path in YbB₆, and a nearly zero indirect gap for YbB₁₂. Third, there are clear band inversion features around the X point in both systems. In YbB₆, one 5d band goes below the j=7/2 bands (by about

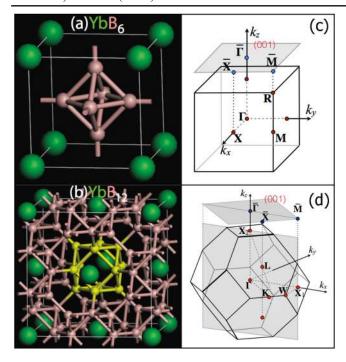


FIG. 1 (color online). (a) The CsCl-type structure of YbB₆ with $Pm\bar{3}m$ space group, and (b) the NaCl-type structure of YbB₁₂ with $Fm\bar{3}m$ space group (B_{12} cubo-octahedral cluster is highlighted). (c) and (d) are the corresponding bulk and surface Brillouin zones.

1.0 eV), which reduces the occupation number n_f of the 4fstates to be around 13.58 (resulting in the Yb valence of +2.42). What is qualitatively different in YbB₁₂ is that there are two 5d bands (strongly hybridized with B-2sand -2p bands) sinking down below the j = 7/2 states (by about 0.8 eV), and n_f is further reduced to be 13.31, leading to the Yb valence being +2.69. We noticed that the shortest Yb-B bond length in YbB₁₂ (2.277 Å) is much shorter than that in YbB₆ (by about 0.772 Å), the enhanced 5d-2p hybridization in YB₁₂ therefore pushes one more 5d state down to be lower than the 4f states at X point. As has been discussed in SmB_6 [12], the hybridization between the 5d and 4f states will open up a gap, and generate the semiconducting behavior. Since the 5d and the 4f states have opposite parity at the X point and there are three X points in the whole BZ, the band inversion in YbB₆ happens three (odd) times, which leads to a nontrivial TI with the Z_2 indices given as (1; 111) [40,41]. While for YbB_{12} , the band inversion happens twice at each X point, which generates totally six (even) times band inversion in the whole BZ, which gives a trivial insulator in the sense of Z_2 .

Because of the partially filled 4f states near the Fermi level, the on-site interactions among the f electrons are expected to play important roles, which can be captured by the LDA + Gutzwiller method [12,37]. For both systems, we take the Hubbard interaction U of 6.0 eV and

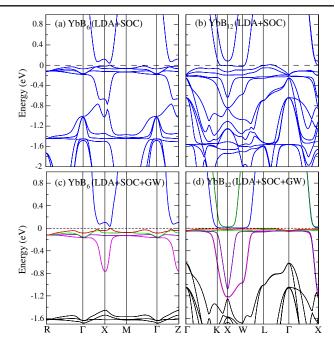


FIG. 2 (color online). The band structure of (a) YbB_6 and (b) YbB_{12} obtained from LDA + SOC calculations. (c) and (d) are their quasiparticle band structures calculated from LDA + SOC + Gutzwiller with U = 6.0 eV.

neglect the Hund's coupling J. From the calculated results [shown in Figs. 2(c) and 2(d)], we find three major modifications coming from the correlation effects. First, the 4f occupation number is further pushed towards its integer limit, namely towards $n_f \sim 13.0$ for YbB $_{12}$ and $n_f \sim 14.0$ for YbB $_6$, respectively, being in better agreement with the experimental data (see Table I). This is simply due to the fact that the strong Coulomb interactions tend to suppress the charge fluctuation among different atomic configurations. Second, we find the renormalization of the 4f quasiparticle bands, and the behaviors of YbB $_6$ and YbB $_{12}$ are quite different. The quasiparticle weight z is 0.87 for YbB $_6$ but reaches very low 0.28 for YbB $_{12}$, indicating that the former is an intermediately correlated

TABLE I. The products of parity eigenvalues of the occupied states for TRIM points, Γ , X, R, and M for YbB₆ and Γ , X, L, and L for YbB₁₂ in the BZ. n_f is the occupation number of 4f orbitals by LDA + Gutzwiller, compared with LDA results in the brackets and the experimental one $n_f^{\rm exp}$. And z is the quasiparticle weight obtained by the LDA + Gutzwiller method.

	Γ	3 <i>X</i>	3 <i>M</i> (<i>L</i>)	R(L)	$n_f^{\rm exp}$	$n_f^{\rm exp}$	z
YbB ₆	+	_	+	+	13.80(13.58)	13.8^{a}	0.87
YbB ₁₂	+	+	+	+	13.11(13.31)	13.14^b , 13.12^c	0.28

^aRef. [32].

^bRef. [35].

^cRef. [36].

insulator while the latter is very close to the strong coupling description, the Kondo insulator. Since the same interaction parameters are used for both materials, the big difference in z is due to the different 4f occupations n_f . Third, we find that the hybridization gap between 4f and itinerant 5d bands is slightly enlarged to be 31 meV in YbB₆ and 6 meV in YbB₁₂, being much closer to the experimental values [42–44]. The parity analysis is still applicable for the quasiparticle bands obtained by the LDA+Gutzwiller method [12,27,28], and the results listed in Table I conclude that Z_2 indices stay unchanged after including the correlation effects for both materials.

One of the major differences between the Kondo insulator and band insulator is the temperature dependence of the electronic structure. For a typical band insulator, the band picture is applicable for almost all of the temperature range and the rigid band approximation is usually adopted, while for a Kondo insulator, the coherent hybridization between the localized f orbitals and the conduction bands (leading to insulating behavior) only occurs below

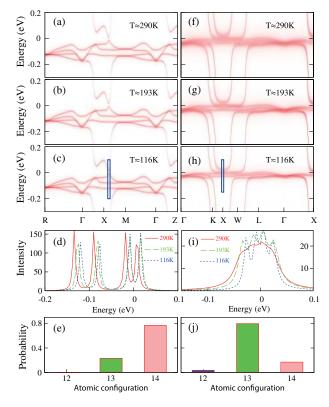


FIG. 3 (color online). The momentum-resolved spectral function $A_k(\omega)$ of YbB₆ (a)–(c) and YbB₁₂ (e)–(g) at different temperatures ($T\approx 290$ K, 193 K, 116 K from top to bottom). (d) YbB₆ spectral function $A(\omega)$ at the k point with the minimum gap as indicated in (c) with $T\approx 290$ K (red), 193 K (green), 116 K (blue). (i) YbB₁₂ spectral function $A(\omega)$ at the X point, as indicated in (h), with $T\approx 290$ K (red), 193 K (green), 116 K (blue). (e) and (j) are the probability of atomic eigenstates with occupation number $N_f=12$, 13, 14 obtained by the LDA + DMFT method for YbB₆ and YbB₁₂ at $T\approx 116$ K, respectively.

the Kondo temperature, which has been found to be around 220 K for YbB₁₂ [35]. In order to calculate the electronic structure at finite temperature, we further apply the LDA + DMFT (dynamical mean field theory) method [45,46] to both materials. We use the continuous time quantum Monte Carlo method based on the hybridization expansion [47] for the impurity solver of DMFT, and take the same interaction parameters. The electronic spectral functions (shown in Fig. 3) obtained by the maximum entropy method [48] suggest that the two materials behave quite differently. At low temperature (T = 116K), the spectral functions for both materials are in good agreement with the LDA + Gutzwiller results (plotted in Fig. 2). At 290 K, however, the spectral function of YbB₁₂ is significantly smeared out, while that of YbB6 still stays unchanged, indicating that the rigid band picture is applicable to YbB₆ but broken down for YbB₁₂, which can be viewed as a Kondo Insulator with Kondo temperature around 200 K.

The surface states (SSs) for YbB₆ and YbB₁₂ (shown in Fig. 4) are obtained by using the Green's function method based on the tight-binding model constructed from the maximally localized Wannier functions. The correlation corrections from the Gutzwiller approximation are included. For YbB₆, the SS on the (001) surface is very similar to that of SmB₆ [12], which contains three surface Dirac cones located at $\bar{\Gamma}$ and two \bar{X} points; for its (111) surface we also find three Dirac cones located at \bar{M} , which are symmetric due to the threefold rotation along the [111]

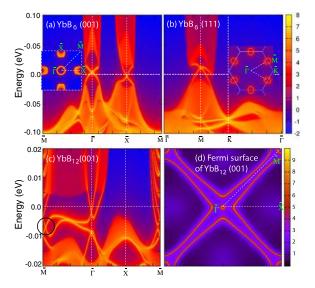


FIG. 4 (color online). The surface states (SSs) of YbB₆ for its (a) (001) and (b) (111) surface from LDA + Gutzwiller calculation. Insets are the Fermi surfaces with chemical potential 5 meV above and below the Dirac point at $\bar{\Gamma}$ drawn for (001) and (111) SSs, respectively. (c) SS of YbB₁₂ (001) surface from LDA + Gutzwiller calculation and (d) its Fermi surface at Fermi level. The Dirac cone due to nonzero MCN is indicated by a circle in (c).

axis. Although YbB₁₂ is topologically trivial in the sense of Z_2 , the band inversion feature around the X points generates SSs as well, which are shown in Figs. 4(c) and 4(d). Unlike YbB₆, whose SS has odd number of Dirac points, the SS of YbB₁₂ contains four Dirac points on the (001) surfaces (near the \bar{M} point along the \bar{M} to Γ direction), indicating that it is a topological crystalline insulator similar to SnTe [29,30,49,50]. The even number of Dirac points are protected by the reflection symmetry respect to the (100) or (010) planes [i.e., the $\Gamma X_1 X_2$ plane in Fig. 1(d)], and is the consequence of the nonzero "mirror Chern number" (MCN) within such planes, which can be defined as the Chern number of half of the occupied states (distinguished by the different eigenvalues of mirror symmetry) [29,30]. We apply the Wilson loop method introduced in Ref. [51] to calculate the MCN of YbB_{12} , and get MCN = 2 for the $\Gamma X_1 X_2$ plane, which is consistent with the SS behavior observed on (001) surface. In fact, the nonzero MCN obtained for the (100) mirror plane implies the appearance of SS on any surface with index (0nm). Unlike the situation in SnTe, however, here the possible topological SS can appear only below the Kondo temperature, when the local 4f moments are effectively screened by the conduction bands and the heavy quasiparticles appear. Therefore, the nonzero MCN in YbB₁₂ indicates that the ground state of YbB₁₂ is a new topological crystalline Kondo insulator [31].

In summary, we have applied the LDA + Gutzwiller and LDA + DMFT methods to study the possible correlated topological phases in two mixed valence Yb compounds, YbB₆ and YbB₁₂. Our results verify that YbB₆ is a moderately correlated Z_2 topological insulator, while YbB₁₂ is a strongly correlated topological crystalline Kondo insulator with MCN = 2.

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