The electronic structures of two mixed valence insulators YbB$_6$ and YbB$_{12}$ are studied by using the local density approximation (LDA) supplemented with the Gutzwiller method and dynamic mean field theory (DMFT). 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 non-zero mirror Chern number. The surface calculations find odd (three) and even (four) number of Dirac cones for YbB$_6$ and YbB$_{12}$, respectively.

Topological Insulators (TI) \cite{1, 2} have been extensively studied, but mostly on the s and p orbital systems, such as HgTe \cite{3-5}, and Bi$_2$Se$_3$ family compounds \cite{6-8}, which are free of strong correlation effects. In the presence of strong electron interactions, much fruitful topological phases might be expected, such as the topological Mott \cite{9} or Kondo \cite{10-12} insulators, topological superconductors \cite{2}, and fractional TI \cite{13, 14}. To pursue those 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 non-trivial. Studies on such systems are challenging both theoretically and experimentally. Nevertheless, the mixed valence phenomena provides an important way towards this direction \cite{12, 15, 16}. 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. SmB$_6$, a typical mixed valence compound, has been proposed theoretically as “topological Kondo insulator” \cite{10-12}, and recently been supported by transport \cite{17-20}, photo emission \cite{21-23} and STM \cite{24} experiments.

Here the dispersive 5d conduction band intersects with the 4f energy levels, leading to electron transfer and strong quantum fluctuation among 4f atomic configurations \cite{16}. At sufficiently low temperature, the coherent motion of 4f states are established, resulting in the formation of “heavy fermion” bands, whose non-trivial Z$_2$ topological index \cite{1, 2} can be determined by the single particle Green’s function at zero frequency \cite{25, 26}.

In the present paper, we will focus on another family of binary mixed valence compounds, Ytterbium Borides, and proposed that various correlated topological phases, in particular a new topological crystalline Kondo insulator \cite{27, 29}, can be realized. Among the four typical compounds, YbB$_4$, YbB$_6$, YbB$_{12}$ and YbB$_{66}$, the Yb ions in YbB$_4$ and YbB$_{66}$ are in 2+ or 3+ respectively, while the XPS and XAS data suggest that the valence of Yb in YbB$_6$ and YbB$_{12}$ is around 2.2 \cite{30} and 2.8 \cite{31-34} respectively, indicating the mixed valence nature. As we have proposed in reference \cite{12}, the local density approximation (LDA) combined with the Gutzwiller density functional theory \cite{35} is a powerful tool to compute the ground state and the quasi-particle spectrum of such correlated systems. Using this method, we find that (1) YbB$_6$ is a correlated $Z_2$ topological insulator similar to SmB$_6$ but with much larger band gap (31 vs 10 meV); (2) YbB$_{12}$ is a new topological crystalline Kondo insulator, which can be characterized by the non-trivial mirror Chern number \cite{27, 28}, and shows even number of Dirac cones on its surface.

As shown in Fig. 1 YbB$_6$ has the CsCl-type structure, the same as SmB$_6$, with Yb and B$_6$ octahedral clus-
and 1.57 bohr. The plane-wave cutoff $K_{\text{MT}}$ of Yb and B atoms are taken as 2.50 and 1.57 bohr. The plane-wave cutoff $K_{\text{MT}}$ is given by $R_{\text{MT}}K_{\text{MT}}=7.0$. The spin-orbit coupling (SOC) is included self-consistently in all calculations.

The LDA band structures, shown in Fig. 2(a) and (b), suggest that the major features are very similar to SmB$_6$. Firstly, the Yb-4$f$ 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 latter near the Fermi level in SmB$_6$, the $j=7/2$ manifolds are fully empty, and $j=5/2$ states are close to the Fermi level. Secondly, the low energy band structure is semi-conducting with a minimum gap of about 29 meV along the $X$-$M$ path in YbB$_6$, and a nearly zero indirect gap for YbB$_{12}$. Thirdly, there are clear band inversion features around the $X$ point in both systems. In YbB$_6$, one $5d$ band goes below the $j=7/2$ bands (by about 1.0eV), which reduces the occupation number $n_f$ of the $4f$-states to be around 13.58 (resulting in the Yb valence of +2.42). What is qualitatively different in YbB$_{12}$ is that two $5d$ bands (which strongly hybridize with B-2$s$ and -2$p$ states) sink down below the $j=7/2$ states (by about 0.8eV), and $n_f$ is further reduced to be 13.31, leading to the Yb valence of +2.69. We noticed that the shortest Yb-B bond length in YbB$_{12}$ (2.277 Å) is much shorter than that in YbB$_6$ (by about 0.772 Å), the enhanced $5d$-$2p$ hybridization in YbB$_{12}$ therefore push 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 semi-conducting behavior. Since the $5d$ and the $4f$ states have opposite parity at the X point, and further more there are three $X$ points in the whole BZ, the band inversion in YbB$_6$ happens three (odd) times, which leads to a non-trivial TI with the $Z_2$ indices given as (1:111) [37, 38]. While for YbB$_{12}$, the two times of band inversion at each X point generates totally six (even) times band inversion in the whole BZ, which gives a trivial insulator in the sense of $Z_2=0$.

Due to 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, 35]. For both systems, we take the Hubbard interaction $U$ of 6.0 eV and neglect the Hund’s coupling $J$. From the calculated results (shown in Fig.2(c) and (d)), we find three major modifications coming from the correlation effects. Firstly, 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 interaction tend to suppress the charge fluctuation among different atomic configurations. Secondly, we find renormalization of the $4f$ quasi-particle bands, and the behaviors of YbB$_6$ and YbB$_{12}$ are quite different. The quasi-particle 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 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 $n_f$. Thirdly, we find that the hybridization gap between $4f$ and itinerant $5d$ bands

| \(\Gamma\) | \(3X\) | \(3M(L)\) | \(R(L)\) | \(n_f\) | \(n_f^{\exp}\) | \(z\) |
|---|---|---|---|---|---|---|
| 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 |

$^a$Ref. [30]; $^b$Ref. [31]; $^c$Ref. [32]

FIG. 2: The band structure of (a) YbB$_6$ and (b) YbB$_{12}$ obtained from LDA+SOC calculations. (c) and (d) are their quasi-particle band structures calculated from LDA+SOC+Gutzwiller with $U=6.0$ eV.

TABLE I: The products of parity eigenvalues of the occupied states for TRIM points, YbB$_6$ and YbB$_{12}$ 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 $n_f^{\exp}$. And $z$ is the quasi-particle weight obtained by LDA+Gutzwiller.
FIG. 3: The momentum-resolved spectral function $A_k(\omega)$ of YbB$_6$ (a - c) and YbB$_{12}$ (e - g) at different temperature ($T \approx 290$K, 193K, 116K from top to bottom). (d) YbB$_6$ spectral function $A_\omega$ at the $k$ point with the minimum gap as indicate in (c) with $T \approx 290$K(red), 193K(green), 116K(blue). (i) YbB$_{12}$ spectral function $A_\omega$ at the X point, as indicate in (h), with $T \approx 290$K(red), 193K(green), 116K(blue). (e) and (j) are the probability of atomic eigenstates with occupation number $N_f = 12, 13, 14$ obtained by LDA+DMFT for YbB$_6$ and YbB$_{12}$ at $T \approx 116$K, respectively.

is slightly enlarged to be 31 meV in YbB$_6$ and 6 meV in YbB$_{12}$, being much closer to the experimental values[39-41]. The parity analysis is still applicable for the quasiparticle bands obtained by LDA+Gutzwiller [12, 25, 26], and the results listed in Table I conclude that $Z_2$ indices keep unchanged after including the correlation effects for both materials.

One of the major differences between Kondo insulator and band insulator is the temperature dependence of electronic structures. For a typical band insulator, the band picture is applicable for almost all 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 the Kondo temperature, which has been found to be around 220K for YbB$_{12}$ [33]. In order to calculate the electronic structure at finite temperature, we further apply the LDA+DMFT (dynamical mean field theory) method [42, 43] to both materials. We use the continuous time quantum Monte Carlo method based on the hybridization expansion [44] 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 [45] suggest that two materials behave quite differently. At low temperature ($T=116$K), the spectral functions for both materials are in good agreement with the LDA+Gutzwiller results (plotted in Fig.2). At 290K, however, the spectral function of YbB$_{12}$ is significantly smeared out, while that of YbB$_6$ still keeps unchanged. This indicates that the rigid band picture is applicable to YbB$_6$ but broken down for YbB$_{12}$, which can be viewed as a Kondo Insulator with Kondo temperature around 200K.

The surface states (SS) for YbB$_6$ and YbB$_{12}$ (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 Gutzwiller approximation are included. For YbB$_6$, the SS on (001) surface is very similar to that of SmB$_6$ [12], which contains three surface Dirac cones located at $\Gamma$ 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 three fold rotation along [111] axis. Although YbB$_{12}$ is topologically trivial in the sense of $Z_2=0$, the band inversion feature around the X points generates surfaces states as well, which are shown in Fig.4(c) and (d). Unlike YbB$_6$, whose SS has odd number of Dirac points, the SS of YbB$_{12}$ contains four Dirac

FIG. 4: The surface states (SS) of YbB$_6$ 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 $\Gamma$ drawn for (001) and (111) SS, respectively. (c) SS of YbB$_{12}$ (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).
points on the (001) surfaces (near the $\overline{M}$ point along the $\overline{M}$ to $\overline{\Gamma}$ direction), indicating that it is a topological crystalline insulator similar to SnTe [27, 28]. 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 non-zero “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 planes, which can be defined as the Chern number of non-zero “Mirror Chern number” (MCN) within such plane in Fig. 1(d)), and is the consequence of non-zero MCN in YbB$_{12}$ indicates that the ground state of YbB$_{12}$ is a new topological crystalline Kondo insulator [29].

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 YbB$_{3}$ and YbB$_{12}$. Our results verify that YbB$_{3}$ is a moderately correlated $Z_2$ topological insulator, while YbB$_{12}$ is a strongly correlated topological crystalline Kondo insulator with MCN=2. This work was supported by the NSF of China and by the 973 program of China (No. 2011CBA00108 and 2013CBP21700). We acknowledge the helpful discussions with professor P. Coleman and Yulin Chen.

[1] M. Z. Hasan and C. L. Kane, Reviews of Modern Physics 82, 3045 (2010).
[2] X. L. Qi and S. C. Zhang, Reviews of Modern Physics 83, 1057 (2011).
[3] B. A. Bernevig, T. L. Hughes, and S. C. Zhang, Science 314, 1757 (2006).
[4] M. König, S. Wiedmann, C. Bräune, A. Roth, H. Buhmann, L. W. Molenkamp, X.-L. Qi, and S.-C. Zhang, Science 318, 766 (2007).
[5] X. Dai, T. L. Hughes, X.-L. Qi, Z. Fang, and S.-C. Zhang, Phys. Rev. B 77, 125319 (2008).
[6] H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Nature Physics 5, 438 (2009).
[7] Y. Xia, D. Qian, D. Hsieh, L. Wray, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, et al., Nature Physics 5, 398 (2009).
[8] Y. L. Chen, J. G. Analytis, J. H. Chu, Z. K. Liu, S. K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, et al., Science 325, 178 (2009).
[9] D. Pesin and L. Balents, Nat Phys 6, 376 (2010).
[10] M. Dzero, K. Sun, V. Galitski, and P. Coleman, Physical Review Letters 104, 106408 (2010).
[11] M. Dzero, K. Sun, P. Coleman, and V. Galitski, Physical Review B 85, 045130 (2012).
[12] F. Lu, J. Zhao, H. Weng, Z. Fang, and X. Dai, Physical Review Letters 110, 096401 (2013).
[13] D. N. Sheng, Z.-C. Gu, K. Sun, and L. Sheng, Nature Communications 2, 389 (2011).
[14] N. Regnault and B. A. Bernevig, Phys. Rev. X 1, 021014 (2011).
[15] R. M. Martin and J. W. Allen, Journal of Applied Physics 50, 7561 (1979).
[16] P. Coleman, Handbook of Magnetism and Advanced Magnetic Materials (2007).
[17] S. Wolgast, C. Kurdak, K. Sun, J. W. Allen, D.-J. Kim, and Z. Fisk, arXiv.org (2012), 1211.5104v3.
[18] D. Kim, S. Thomas, T. Grant, J. Botimer, Z. Fisk, and J. Xia, arXiv.org (2012), 1211.6769.
[19] S. Thomas, D. Kim, S. B. Chung, T. Grant, Z. Fisk, and J. Xia, arXiv.org (2013), 1307.4133.
[20] G. Li, Z. Xiang, F. Yu, T. Asaba, B. Lawson, P. Cai, C. Tinsman, A. Berkley, S. Wolgast, Y. S. Eo, et al., arXiv.org (2013), 1306.5221v1.
[21] M. Neupane, N. Alidoust, S.-Y. Xu, T. Kondo, D.-J. Kim, C. Liu, I. Belopolski, T.-R. Chang, H.-T. Jeng, T. Durakiewicz, et al., arXiv.org (2013), 1306.6343v1.
[22] J. Jiang, S. Li, T. Zhang, Z. Sun, F. Chen, Z. R. Ye, M. Xu, Q. Q. Ge, S. Y. Tan, X. H. Niu, et al., arXiv.org (2013), 1306.5664v1.
[23] N. Xu, X. Shi, P. K. Biswas, C. E. Matt, R. S. Dhaka, Y. Huang, N. C. Plumb, M. Radovic, J. H. Dil, E. Pommjakushina, et al., arXiv.org (2013), 1306.3676v1.
[24] M. M. Yee, Y. He, A. Soumyanarayanan, D.-J. Kim, Z. Fisk, and J. E. Hoffman, arXiv.org (2013), 1308.1085v1.
[25] Z. Wang, X.-L. Qi, and S.-C. Zhang, Phys. Rev. Lett. 105, 256803 (2010).
[26] Z. Wang and S.-C. Zhang, Physical Review X 2, 031008 (2012).
[27] J. Teo, L. Fu, and C. Kane, Physical Review B 78, 045426 (2008).
[28] T. H. Hsieh, H. Lin, J. Liu, W. Duan, A. Bansil, and L. Fu, Nature Communications 3, 982 (2012).
[29] M.-X. Ye, J. W. Allen, and K. Sun, arXiv.org (2013), 1307.7191.
[30] T. Namba, M. Tomikawa, Y. Mori, N. Shino, S. Imada, S. Suga, S. Kimura, and S. Kunii, Physica B: Condensed Matter 186–188, 557 (1993), ISSN 0921-4526.
[31] M. Kasaya, F. Iga, K. Negishi, S. Nakai, and T. Kasuya, Journal of Magnetism and Magnetic Materials 31 - 34, Part 1, 437 (1983), ISSN 0304-8853.
[32] M. Kasaya, F. Iga, M. Takigawa, and T. Kasuya, Journal of Magnetism and Magnetic Materials 47 - 48, 429 (1985), ISSN 0304-8853.
[33] T. Susaki, A. Sekiyama, K. Kobayashi, T. Mizokawa, A. Fujimori, M. Tsumekawa, T. Muro, T. Matsushita, S. Suga, and H. Ishii, Physical Review Letters 77, 4269 (1996).
[34] Y. Takeda, M. Arita, M. Higashiguchi, K. Shimada, M. Sawada, H. Sato, M. Nakatake, H. Namatame, M. Taniguchi, F. Iga, et al., Physica B: Condensed Matter 351, 286 (2004).
[35] X. Deng, L. Wang, X. Dai, and Z. Fang, Physical Review B 79, 075114 (2009).
[36] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka,
and J. Luitz, *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (2001), ISBN 3-9501031-1-2.

[37] L. Fu, C. Kane, and E. Mele, Physical Review Letters **98**, 106803 (2007).

[38] L. Fu and C. Kane, Physical Review B **76**, 045302 (2007).

[39] H. Werheit, T. Au, R. Schmechel, Y. B. Paderno, and E. S. Konovalova, Journal of Solid State Chemistry **154**, 87 (2000).

[40] Y. Takeda, M. Arita, M. Higashiguchi, K. Shimada, H. Namatame, M. Taniguchi, F. Iga, and T. Takahatake, Physical Review B **73**, 033202 (2006).

[41] T. Susaki, Y. Takeda, M. Arita, K. Mamiya, A. Fujimori, K. Shimada, H. Namatame, M. Taniguchi, N. Shimizu, and F. Iga, Physical Review Letters **82**, 992 (1999).

[42] A. Georges, W. Krauth, and M. J. Rozenberg, Reviews of Modern Physics **68**, 13 (1996).

[43] G. Kotliar, S. Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet, and C. Marianetti, Reviews of Modern Physics **78**, 865 (2006).

[44] E. Gull, A. J. Millis, A. I. Lichtenstein, A. N. Rubtsov, M. Troyer, and P. Werner, Reviews of Modern Physics **83**, 349 (2011).

[45] K. Haule, C.-H. Yee, and K. Kim, Physical Review B **81**, 195107 (2010).

[46] Y. Tanaka, Z. Ren, T. Sato, K. Nakayama, S. Souma, T. Takahashi, K. Segawa, and Y. Ando, Nature Physics **8**, 800 (2012).

[47] P. Dziawa, B. J. Kowalski, K. Dybko, R. Buczko, A. Szczerbakow, M. Szot, E. Lusakowska, T. Balasubramanian, B. M. Wojek, M. H. Berntsen, et al., NATURE MATERIALS **11**, 1023 (2012).

[48] R. Yu, X. L. Qi, A. Bernevig, Z. Fang, and X. Dai, Phys. Rev. B **84**, 075119 (2011).