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Electronic structure of YbB_6 dependent on onsite Coulomb interaction U and internal parameter of B atom*

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Using first-principles calculations in the generalized gradient approximation plus on-site Coulomb interaction (GGA+U) scheme, the effects of internal structural parameters x and U on the electronic structure of YbB_6 are investigated. The results show that the band gap of YbB_6 increases with x increasing, and does not change with U. It not only illustrates the influence of internal structural parameter x on band gap, but also explains the discrepancy between the previous experimental result and the theoretical prediction. In addition, the electronic structure and density of states reveal that there exist the interactions between B atoms in different cages, and that a small band gap can form around the Fermi level (E_F). The present work plays a leading role in ascertaining the relation between crystal structure and electronic property for the further analysis of its topological properties.

Keywords: electronic structure, GGA+U, internal parameter, band gap

PACS: 62.20.D–, 71.15.–m, 31.15.A–, 05.70.–a **DOI:** 10.1088/1674-1056/ab46a1

1. Introduction

Owing to the the fact that topological insulators (TIs) provide a promising background for novel physics arising from their nontrivial bulk electronic structure with gapless surface states on the boundaries, they have aroused the great interest of researchers in recent years. Very recently, the rare-earth hexaborides containing f-electrons in their electronic configurations in this field were found. The compound LnB_6 may exhibit the electronic correlation effects from foreign materials,[1–3] such as topological Mott insulators,[4,5] topological crystalline insulators,[3,6] and topological Kondo insulators (TKIs).[7–9] For example, SmB_6 hopefully becomes a "topological Kondo insulator" theoretically and was confirmed recently by transport,[7,10] photo emission,[11–13] and STM experiments.[14] The prediction of SmB_6 renews the scientific attention to 4f-contained hexaborides. However, the surface states of SmB_6 in the TKI phase only exist at very low temperatures, which restricts its further application in devices.[3,13] Recently, electronic structure and thermal properties of topological insulator of SmB_6 were studied by first-principles calculations.[15,16] And then, plutonium-based 5f compound PuB_6 and the isostructural ytterbium-based 4f compound YbB_6 are frequently considered to be TKIs theoretically when onsite Coulomb interaction is included in the computations to take into account the strong electron correlation effects.[2,17]

However, there are some discrepancies between the experimental result and theoretical prediction of YbB_6. Theoretically, YbB_6 was proposed to be a TKI with the mixed-valence state of Yb based on the calculations from the DFT + Gutzwiller method.[3,9,18] Besides, a new band calculation with an adjustable correlation parameter (Hubbard $U = 4$) revealed that the topological state is derived from band inversion between the d and p bands[17] and the binding energy (BE) of the Yb $4f_{7/2}$ is 0.3 eV. But the ARPES experiments[17,19,20] manifested that the Yb-4f states are located at around 1 eV and 2.3 eV below the E_F, which is contradictory to previous theoretical prediction. Moreover, Min *et al.* obtained an insulating gap of YbB_6 about 100 meV in the ARPES experiment by adopting the modified Becke–Johnson (mBJ) exchange potential and the on-site Coulomb interaction U ($U = 7$).[19] Unfortunately, the resistivity of YbB_6 exhibits a bulk metallic behavior,[21] which is inconsistent with the prediction. At present, the published calculations[3,15,22] indicate the existence of band gap almost without exception based on the experimental crystal structure.[23] However, the lattice constant a for full relaxation and experimental result are quite similar to each other. On the other hand, the DFT+U calculations with increasing U give only a small gradual decrease in the p–d overlap energy without opening of a semiconducting p–d gap even for an unphysically large U value as high as 15 eV. Based on the above mentioned, we guess that the onsite Coulomb interaction (U) and the internal parameters x are the cause of the difference between experimental and theoretical results.

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Therefore, exploring the inconsistencies between the theoretical predictions and experimental observation in YbB_6 systems would be meaningful and hopeful in gaining an insight into the relation of crystal structure with electronic properties for further analyzing its topological properties.

Therefore, the effect of internal structural parameter x and U on the band gap of YbB_6 is firstly investigated by the first-principles calculation. Then, the relation of the internal structural parameter x with electronic structure near the Fermi level (E_F) with fixed U is discussed. The rest of this paper is organized as follows. In Section 2, a brief introduction of theoretical methods is presented. The results aregiven and the discussion is made in Section 3. Finally, some conclusions are drawn in Section 4.

2. Theoretical and computational method

The first-principles study of electronic structure is conducted based on the density functional theory (DFT) in conjunction with projector augmented-wave potential (PAW)[24,25] within the GGA+U[26–30] schemes as implemented in the Vienna *ab initio* simulation package (VASP).[31–34] The GGA+U approach is an alternative method to take into account the correlation effects with less computational effort and is frequently used to correct the band gap. It combines the explicit treatment of electronic correlation with a Hubbard-like model[35] for a subset of states in the system. Pseudopotentials with valence states $2s^2 2p$ for B, $5s^2 5p^6 4f^{14} 6s^2$ for Yb are used. The wavefunctions are expanded in a plane-wave basis set with a kinetic-energy cut-off of 550 eV. The $11\times11\times11$ k-points for YbB_6 unit cell with the Monkhorst–Pack scheme are adopted for the Brillouin zone sampling. In all cases, the total energy of self-consistent convergence is 10^{-5} eV/cell and the process is terminated when the atomic force is less than 10^{-3} eV/Å. All the parameters are carefully tested to give satisfactory converged results. The spin–orbit coupling (SOC) is included self-consistently in all calculations. To produce more accurate densities of states, a dense k-point mesh of $19\times19\times19$ is used, and the DOS is computed by the Gaussian smearing method.[31–34]

3. Results and discussion

YbB_6 crystallizes into a cubic CsCl-type structure with a space group of $O_h^1(Pm\bar{3}m)$.[36,37] The Yb and B atoms are respectively located at the $1a$ (0, 0, 0) and $6f$ (1/2, 1/2, x) Wyckoff position, where x is the positional parameter. Figure 1 shows the crystal structure of YbB_6.

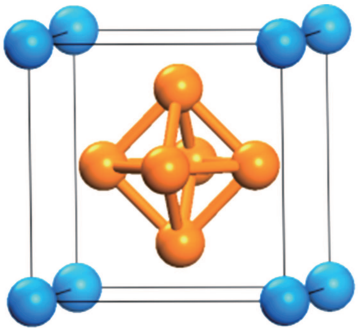


Fig. 1. Crystal structure of YbB_6, where Yb and B atoms are located at $1a$ (0, 0, 0) and $6f$ (1/2, 1/2, x) Wyckoff positions, respectively.

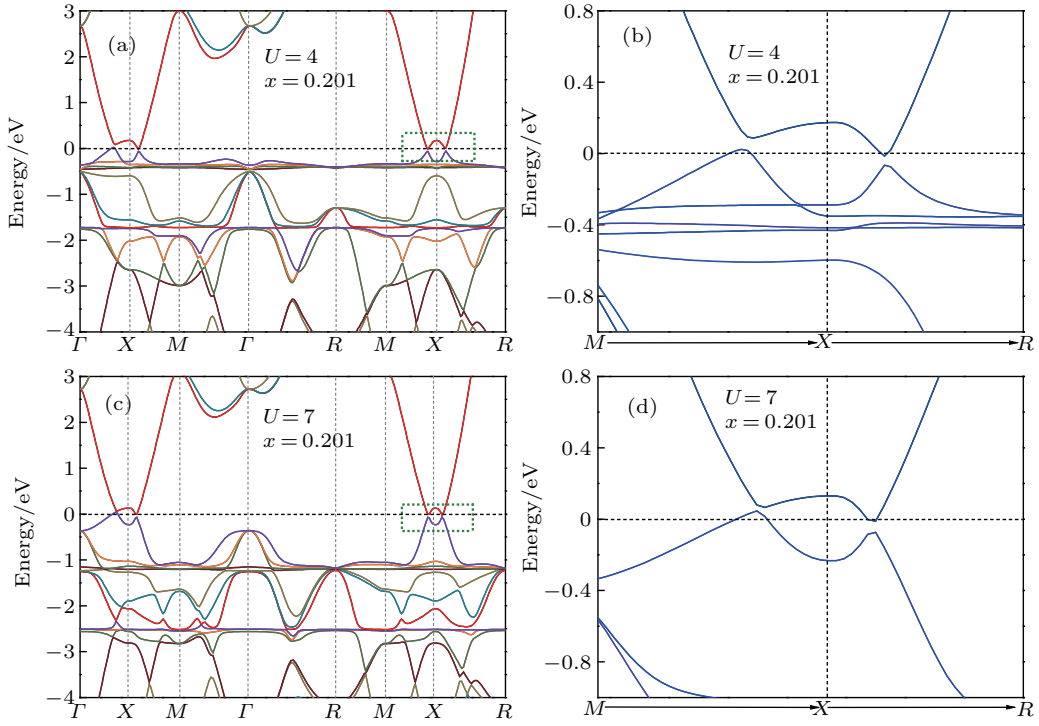


Fig. 2. First-principles calculation-based band structure of YbB_6 with different values of internal structural parameter x and U ($U = 4$ eV (a) and 7 eV (c)). (b) and (d) Zoomed part of band structure in panels (a) and (c) near E_F, respectively.

All the groups well versed in topological properties adopt experimental crystallographic structure[23] in the calculation. The experimental lattice constant a and the positional parameter x are 4.144 Å and 0.207, respectively. The equilibrium crystal structure is obtained theoretically by minimizing the total energy in the two-dimensional parameter space (a, x). The GGA+U ($U = 6.5$) relaxed minimum value is located at 4.140 Å and $x = 0.201$. The lattice constant shows that it is in good agreement with experimental result. However, the x is not in good agreement with the experimental result. On the other hand, as shown in Fig. 2, the band gap is not found by using the present equilibrium crystal structure with the different values of U but it appeared in previous researches[3,15] based on the DFT + SOC+U ($U = 4$ eV) and GGA + GW+U ($U = 7$).

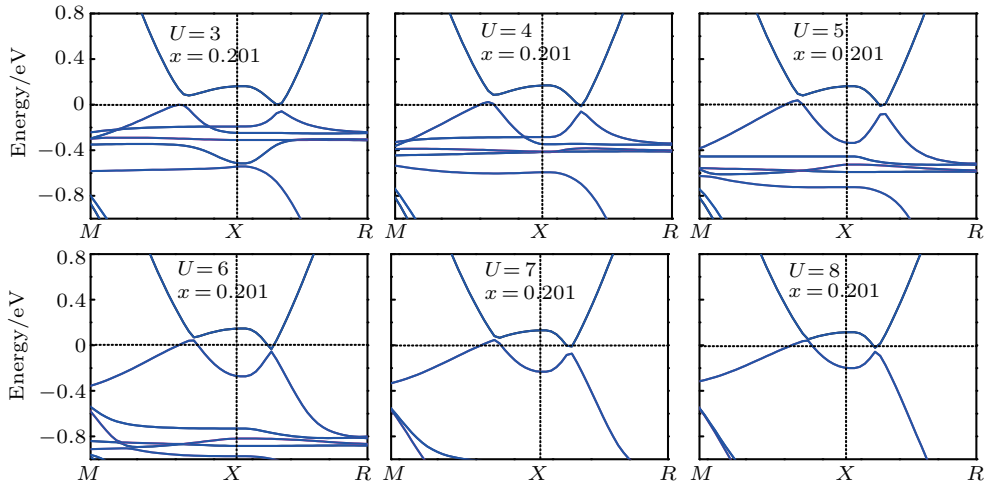


Fig. 3. Energy band structures along principal high-symmetry direction of YbB_6 for varying U with $x = 0.201$.

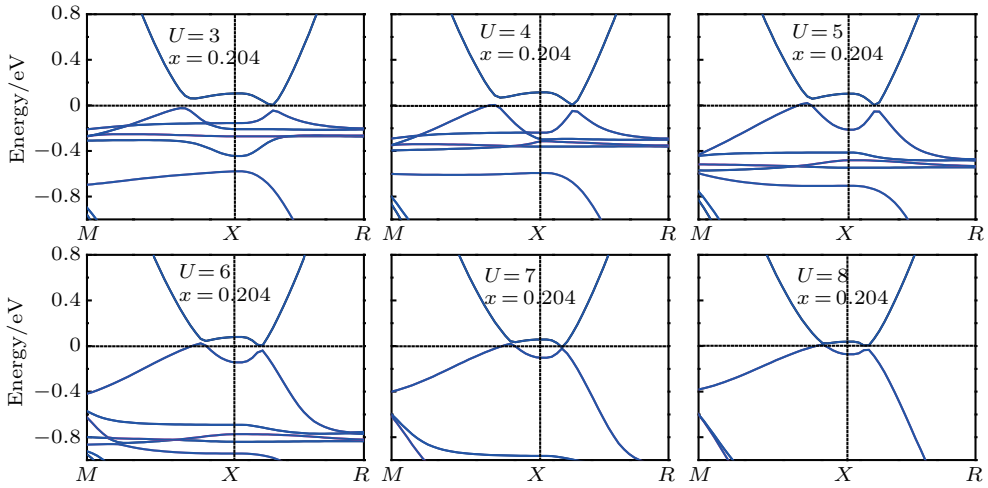


Fig. 4. Energy band structures along principal high-symmetry direction of YbB_6 for varying U with $x = 0.204$.

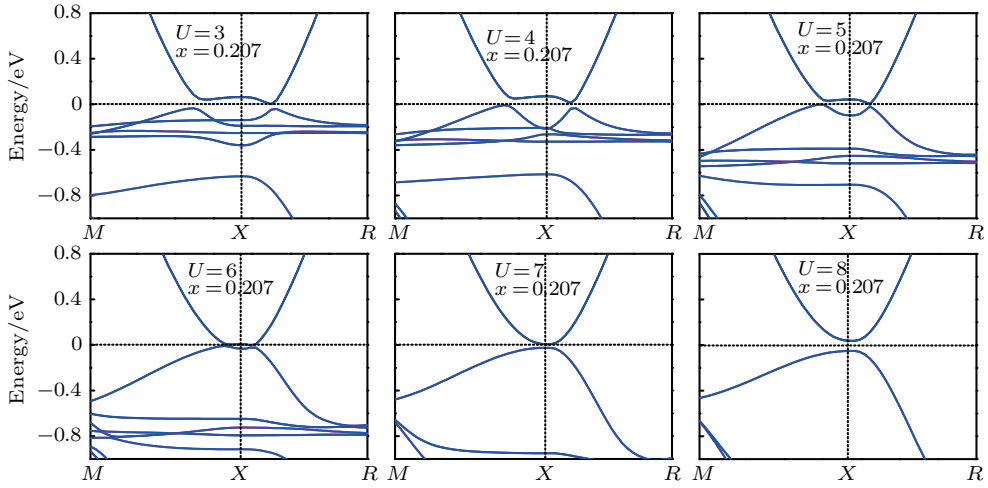


Fig. 5. Energy band structures along principal high-symmetry direction of YbB_6 for varying U with $x = 0.207$.

In view of the above, it is necessary to investigate the electronic structures of YbB_6 with three representative values of x within a range of U. As depicted in Figs. 3–5, as the values of U range from 3 to 8, the band gap between Yb-5d state and B-2p state is not discovered with $x = 0.201$ or 0.204. When x is equal to 0.207, the band gap between Yb-5d state and B-2p state is closed and reopened with the increase of U.[22] Therefore, we affirm that the positional parameter x plays a significant role in forming the band gap while the U is not the main factor.

To further investigate the connection between band gap and internal parameters x, another theoretical calculation is first performed within GGA + SOC+U, in which the experimental $U = 6.5$ is used. Figure 6 shows the band structure of YbB_6 with experimental internal parameters at $U = 6.5$, the non-dispersive Yb-4f bands are located at about 1 eV and 2.3 eV below Fermi energy (E_F), respectively. The energy difference between the two multiplets is 1.3 eV, which is consistent with previous experimental results.[17,19,20] Then, figures 7(a)–7(c) show the contributions of B-2p, Yb-4d and Yb-4f orbitals as a function of x near the E_F with the different values of internal parameter x, respectively. We find that the p–d overlap decreases with x increasing, and the Yb-5d orbitals are ultimately away from the Yb-4f orbitals which remain at nearly the same binding energy. Therefore, the Yb-4f band exhibits an decreasing overlap of Yb-5d and also implies a decreasing mixed-valency. More importantly, the Yb-5d moves up and B-2p moves in the opposite direction, which is a source of small band gap.

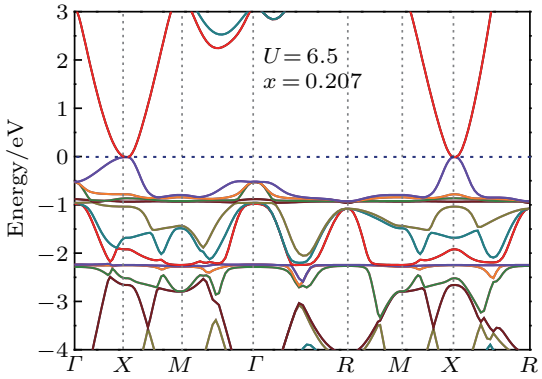


Fig. 6. Energy band structure along principal high-symmetry direction of YbB_6 with $U = 6.5$ and $x = 0.207$.

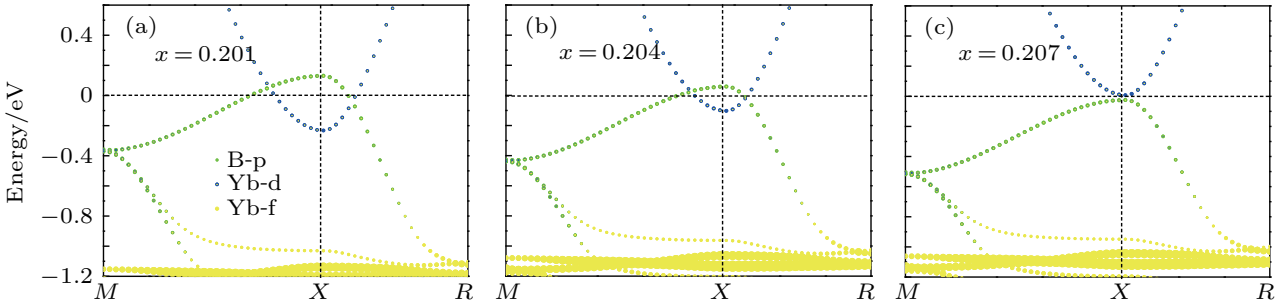


Fig. 7. Zoom-in views of band structure around the E_F with different values of internal parameter x ($x = 0.201$ (a), 0.204 (b), and 0.207 (c)).

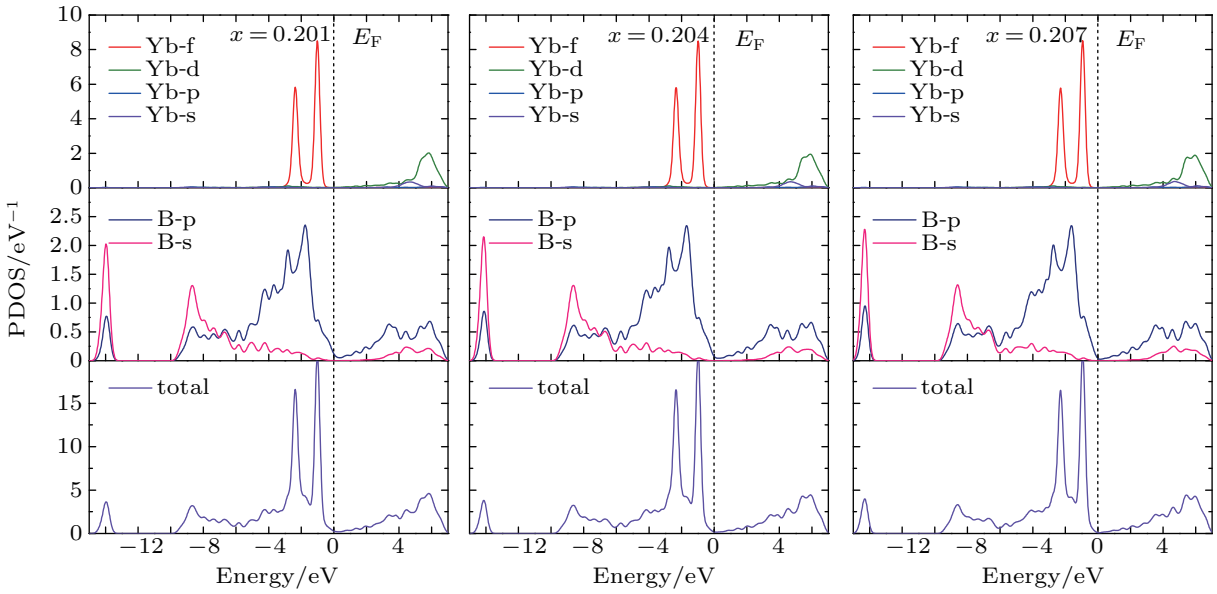


Fig. 8. Total and angular-momentum-projected densities of states of YbB_6 with different values of internal parameter x.

Furthermore, the curves of total and partial density of states (PDOS) of YbB_6 with different values of internal parameter x at $U = 6.5$ are presented in Fig. 8. The hybridization of 2s and 2p of B dominates the lower bonding peak located at -14 eV below the E_F. The B 2s and 2p interactions from intraoctahedron contribute mainly to the upper bonding peaks in an energy range from -10 eV to -6 eV. The upper subgroup, which is in a range from -6 eV to the Fermi level, is composed of B 2p and Yb 4f orbital. The contributions are primarily from the interoctahedral bonds except around the Fermi level where the intraoctahedral B–B bonds become important again. Nevertheless, both B-p and Yb-d states are distributed on both sides of the E_F. As illustrated in Fig. 8, the band overlap in the Fermi level appears between B-s and Yb-d state, and the Yb atom is further apart from B cage with the increase of x. And then it results in the promotion of dispersed conduction band. The intra-cage bonding states come down in energy, resulting in the opening of a small gap. From the above, we can see that the internal parameter x has an influence on the band gap and density of states of YbB_6.

4. Conclusions

The effects of internal parameter x and the value of U on the band gap and density of states of YbB_6 are explored by means of first-principles generalized gradient approximation GGA$+U$. The electronic structures of YbB_6 for three representative values of x within a range of U are calculated, and the results indicate that the internal structural parameter x plays an important role in determining the band gap. Our results explain the discrepancy between experimental and theoretical results. Furthermore, the zoom-in views of band structure around the E_F and density of states are discussed to further illustrate the relation between the internal structural parameter x and band gap. The Yb-4f orbitals are located at around 1 eV below the E_F, p–d overlaps decrease with x increasing, and these bands around the Fermi level are unclear currently. We expect the present reserach to be able to present a basis for further experimental and theoretical studies of this promising material and other topological insulators band gap.

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