Unraveling strongly correlated 5f electrons in prototypical plutonium borides

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Abstract. To elucidate the localized-itinerant dual nature and orbital dependent correlations of Pu-5f valence electrons in plutonium borides (PuB_x, x=1, 2, 6, 12), the electronic structures are throughout investigated by using the combination of density functional theory and single-site dynamical mean-field method. We not only reproduce the correlated topological insulator of PuB_6, but also predict the metallicity in PuB_x (x=1, 2, 12). It is found that the momentum-resolved spectral functions, density of states, hybridization functions all indicate partially itinerant 5f states in PuB_x (x=1, 2, 6, 12). Especially, quasiparticle multiplets induced noteworthy valence state fluctuations implying the mixed-valence behavior of plutonium borides. Moreover, the itinerant degree of freedom for 5f electrons in PuB_x (x=1, 2, 12) is tuned by hybridization strength between 5f states and conduction bands, which is affected by atomic distance between Pu and B atoms. Lastly, 5f electronic correlations encoded in the electron self-energy functions demonstrate moderate 5f electronic correlations in PuB_6 and orbital selective 5f electronic correlations in PuB_x (x=1, 2, 12). Consequently, the understanding of electronic structure and related crystal structure stability shall shed light on exploring novel 5f electrons states and ongoing experiment research.

Keywords: dynamical mean-field method, electronic correlation, quasiparticle multiplets, valence state fluctuation
1. Introduction

Actinide compounds with partially filled 5f electronic shell exhibit abundant fascinating behavior of fundamental physical interests including heavy-fermion behaviors, unconventional superconductivity, nontrivial topology, complex magnetism and mixed-valence states [1, 2, 3, 4, 5, 6, 7, 8, 9]. These perplexing features are mainly attributed to the intricate electronic structure concerning strongly correlated 5f electrons as well as hybridization between 5f states and conduction bands. Since plutonium (Pu) situates on the boundary between the itinerant and localized 5f states [1] of early and late actinides, Pu metal reveals multiple allotropic crystalline phases [10] and tremendous variations in thermophysical properties. Note that 5f electron is extremely sensitive to external temperature, pressure and chemical doping, so 5f states tend to involve in active chemical bonding and form plenty of Pu-based compounds [11]. The discovery of superconductivity in PuCoGa$_5$ [3, 4, 5, 6] with astonishingly high transition temperature of 18.5 K has renewed an interest in Pu-based compounds. Additionally, plutonium tetraboride (PuB$_4$) and plutonium hexaboride (PuB$_6$) have been reported to be promising correlated topological insulators [7, 8, 9, 12].

![Figure 1](image)

**Figure 1.** (Color online). Crystal structure of plutonium borides, where blue and green spheres denote Pu and B atoms, respectively. (a) PuB. (b) PuB$_2$. (c) PuB$_6$. (d) PuB$_{12}$.

Plutonium borides are typical actinide borides (Th-, U-, Np-, Pu-, Am-borides [15]), which integrate the electronic, optical, mechanical and refractory properties of metal borides [16]. In 1960s plutonium borides were successfully synthesized in spite of the intractable radioactivity and toxicity. The high melting point (~2300 K [14]) and refractory [17] enable their potential use as nuclear fuels. Generally, plutonium borides stabilize in PuB, PuB$_2$, PuB$_4$, PuB$_6$, PuB$_{12}$ and PuB$_{100}$ according to various boron-containings [13, 14]. It is worth noting that PuB$_4$ crystalizes in the tetragonal ThB$_4$-type crystal structure with space group $P4/mmbm$ (No. 127) [13, 11, 17] and PuB$_{100}$ has a large
Unraveling strongly correlated 5f electrons in prototypical plutonium borides

Table 1. Crystal structure parameters of plutonium borides [13, 14] PuB_x (x=1, 2, 6, 12).

| PuB_x | Space group | d_{Pu-Pu} (Å) | d_{B-B} (Å) | d_{Pu-B} (Å) |
|-------|-------------|---------------|-------------|-------------|
| PuB   | Fm-3m       | 4.92          | 3.48        | 2.46        |
| PuB_2 | P6/mmm      | 3.19          | 1.84        | 2.70        |
| PuB_6 | Pm-3m       | 4.11          | 1.70        | 3.03        |
| PuB_{12} | Fm-3m   | 5.29          | 1.76        | 2.79        |

number of boron atoms in the unit cell. Here we only consider PuB_x (x=1, 2, 6, 12) with relatively high crystal structure symmetry, whose crystallographic parameters measured by X-ray powder diffraction techniques are listed in table 1. Plutonium monoboride (PuB)[Fig. 1(a)] stabilizes in a cubic NaCl-type structure (space group Fm-3m). It is the lowest boron-containing plutonium boride with the absence of uranium and thorium monoborides. Plutonium diboride[Fig. 1(b)] takes a AlB_2-type hexagonal structure (space group P6/mmm) where boron atoms form two-dimensional hexagonal networks with planar layers of metal atoms interposed. Plutonium hexaboride[Fig. 1(c)] has a simple cubic structure (space group Pm-3m), where Pu ions locate at the cubic center and the boron octahedra situate at the cubic corners. Plutonium decaboride[Fig. 1(d)] crystallizes in a cubic structure (space group Fm-3m), where Pu ions and B_{12} units arrange as NaCl-type. Each Pu ion locates in the center of a B_{24} cubo-octahedron which associates B_{12}-polyhedra cages forming a three-dimensional skeleton. In this sense, the basic structural units in plutonium borides are depicted in terms of the B-B bonding configurations, such as B_2-sp^2, B_6-octahedral, and B_{12}-cuboctahedral boron atom clusters. Rich physics relating to complicated electronic structure and exotic topological feature are expected because of the fantastic bonding behavior between Pu and B atoms.

Appreciable experimental progresses in plutonium borides have been achieved on the crystal structure, magnetism, transport, thermodynamics and reactivity [17, 18, 19, 20, 21]. Available Pu-B phase diagram on temperature and boron composition parameter plane clarifies the stable condition and locates the melting points of plutonium borides [17], even though some early results still dispute the existence of PuB [18] owing to the various preparation methods. Besides, entropies have been measured for PuB_2, PuB_4 and PuB_6 at room temperature [19]. It is reported that magnetic susceptibility of PuB_2 slightly depends on temperature [20]. Whereas magnetic susceptibility of PuB_4 and PuB_6 rarely changes against temperature [21], indicating different nature from PuB, PuB_2 and PuB_{12} metal. Recent experimental advances confirmed the correlated topological insulator of PuB_4 through small magnetic moment of Pu atom, insulating like electrical transport and ^{239}\text{Pu} nuclear magnetic resonance. Among several Pu-based compounds which have been predicted to be correlated topological insulators, PuB_4 and PuB_6 are archetypical prototypes to explore the underlying mechanism of the topological feature and strongly correlated 5f electronic states.
PuB₆ has been addressed to exhibit topological feature and mixed-valence behavior for 5f electrons within the combination of dynamical mean-field approach and density functional theory [7]. Furthermore, PuB₆ is proposed to be Racah material with intermediate valence singlet ground state by utilizing local density approximation plus an exact diagonalization method [22]. Subsequently, the surface states signatures reflected topological feature are predicted in scanning tunneling spectroscopy and quasiparticle interference based on a multiorbital tight-binding model [23]. Lately, You Lv et al. theoretically found that PuB₁₂ is the most stable compound among AB₁₂ (A=Th, U, Np, Pu, Am) and a candidate superhard material owing to the outstanding mechanical and thermodynamic properties [24]. Motivated by these findings, it is worth while to survey the electronic structure tuned by boron composition to build a comprehensive picture of strongly correlated 5f electronic states, itinerant-localized dual nature and bonding behavior, so as to pave the way for future angle-resolved photoemission spectroscopy and de Haas-van Alphen (dHvA) oscillation experiments.

In these calculations, theoretical investigations mainly concentrate on PuB₄ and PuB₆, while experimental advances achieve pioneering results on topological insulator in PuB₄. However, present research on PuB, PuB₂ and PuB₁₂ are insufficient. Moreover, the long-standing issue of itinerant-localized dual nature for 5f electrons which is closely linked with crystal stability has rarely been touched. Above all, the accurate electronic structure involving the strong 5f electronic correlation, large spin-orbit coupling, and intricate crystal field splitting have not been fully taken into account. Last but not least, the tight relationship between bonding behavior and crystal structure have not been well addressed. Consequently, it seems hard to acquire reliable electronic structures and related physical properties of plutonium borides.

Several questions still remain to be answered. First of all, the mechanism of topological feature and its connection with strongly correlated 5f electronic states. Secondly, the evolution pattern of itinerant to localized nature of 5f electrons in plutonium borides. Thirdly, whether the orbital dependent correlations of 5f electrons commonly exist in plutonium borides. To answer the questions above, it is of high priority to examine the fine electronic structures of plutonium borides to evaluate itinerant-localized nature, mixed-valence behavior, orbital selective 5f electronic correlations and related crystal stability.

The rest of this paper is arranged as follows. In Sec. 2, the computational details of DFT + DMFT approach are introduced. In Sec. 3, the electronic band structures, total and partial 5f density of states, valence state fluctuations and 5f self-energy functions are presented. The Pu-B bonding behavior and crystal structure stability, as well as angular momentum coupling scheme are discussed. Finally, Sec. 5 serves as a brief conclusion.
2. Methods

The well-established DFT + DMFT method combines realistic band structure calculation by DFT with the non-perturbative many-body treatment of local interaction effects in DMFT [25, 26]. The DFT + DMFT method has achieved great success in abundant correlated materials. It is really appropriate for describing electronic structures of strongly correlated materials. To account for the strongly correlated 5f electrons, we perform charge fully self-consistent calculations to explore the detailed electronic structure of PuB\textsubscript{x} (x=1, 2, 6, 12) using DFT + DMFT method. The implementation of this method is divided into two separate parts. The DFT part is solved by using the \textsc{wien2k} code [27] which implements a full-potential linear augmented plane-wave (FP-LAPW) formalism. The DMFT part is solved by employing the \textsc{edmftf} package [28] which preserves stationarity of the DFT + DMFT functional, and is able to obtain high precision total energy and force.

In the DFT calculation, the experimental crystal structures for PuB\textsubscript{x} (x=1, 2, 6, 12) were used throughout the calculations [14, 13]. Since the inverse temperature $\beta = 100$ ($T \sim 116.0$ K), it was reasonable to retain only the paramagnetic solutions. The generalized gradient approximation was adopted to formulate the exchange-correlation functional [29]. The spin-orbit coupling was taken into account in a second-order variational manner. The $k$-points' mesh was $15 \times 15 \times 15$ and $R_{MT}K^{MAX} = 8.0$.

In the DMFT part, 5f orbitals of plutonium were treated as correlated. The four-fermions' interaction matrix was parameterized using the Coulomb interaction $U = 5.0$ eV and the Hund’s exchange $J_H = 0.6$ eV via the Slater integrals [30]. The fully localized limit scheme was used to calculate the double-counting term for impurity self-energy function [31]. The vertex-corrected one-crossing approximation (OCA) impurity solver [32] was employed to solve the resulting multi-orbital Anderson impurity models. Meanwhile, the hybridization expansion version of continuous-time quantum Monte Carlo quantum impurity solver (dubbed as CTQMC) [33, 34] was also used to solve the resulting multi-orbital impurity models for comparison. In order to reduce the computational resources required, we not only utilized the good quantum numbers $N$ (total occupancy) and $J$ (total angular momentum) to classify the atomic eigenstates, but also made a severe truncation ($N \in [3, 7]$) for the local Hilbert space [35]. The convergence criteria for charge and energy were $10^{-5}$ e and $10^{-5}$ Ry, respectively. It is worth mentioning that the advantage of OCA impurity solver lies in the real axis self-energy, the direct output $\Sigma(\omega)$ were applied to calculate the momentum-resolved spectral functions $A(k, \omega)$ and density of states $A(\omega)$, as well as other physical observables.

3. Results

3.1. Atomic multiplets

The pioneering advances have authenticated multiplet peaks near the Fermi level in Pu metal via observed photoemission spectroscopy and calculated quasiparticle
Unraveling strongly correlated 5f electrons in prototypical plutonium borides

Figure 2. (Color online). Electronic density of states and hybridization functions for PuBx (x=1, 2, 6, 12) at 116 K obtained by DFT + DMFT method. (a1) Partial 5f density of states for PuB, PuB2, and PuB12. (a2) Partial 5f density of states for PuB6. (b1)-(b4) The j-resolved 5f partial density of states with 5f5/2 and 5f7/2 components represented by purple and green lines, respectively for PuB, PuB2, PuB6 and PuB12, from top to bottom. (c1)-(c4) Hybridization functions denoted by red and cyan lines, respectively for PuB, PuB2, PuB6 and PuB12, from top to bottom.

multiplets, originating from 5f valence fluctuations and atomic multiplets [36, 37]. The atomic multiplets for 5f electrons are believed to be generic in many Pu-based compounds [7, 38]. In order to elucidate the quasiparticle multiplets and itinerant degree of 5f electrons, it is imperative to investigate the evolution of 5f correlated electronic states upon boron composition. Figure 2 delineates the density of states and hybridization functions of plutonium borides at 116 K. Figure 2(a1) sketches the entire profile of 5f density of states for PuB, PuB2 and PuB12, which share a similar single peak in the Fermi level but with slightly different spectral weights. Meanwhile, Fig. 2(a2) shows 5f density of states of PuB6 which is distinctly different from the other three compounds and exhibits a much higher shoulder peak. A diminutive dip is discovered in the Fermi level which is associated with the onset of a pseudogap, in accordance with previous calculations [7]. Additionally, two sharp peaks at −0.025 eV and −0.06 eV also emerge in the vicinity of Fermi level.

The origin of these atomic multiplets is primarily encoded in the 5f partial density of states [see Fig. 2(b1)-(b4)]. Firstly, the fourteen-fold degenerated 5f states are split
Unraveling strongly correlated 5f electrons in prototypical plutonium borides

Figure 3. (Color online). Momentum-resolved spectral functions $A(k, \omega)$ of plutonium borides at 116 K calculated by DFT + DMFT method. (a) PuB. The coordinates for the high-symmetry points are $X [0.0, 0.5, 0.5], L [0.0, 0.5, 0.0], W [0.5, 0.75, 0.25]$. (b) PuB$_2$. The coordinates for the high-symmetry points are $A [0.0, 0.0, 0.5], M [0.5, 0.0, 0.0], L [0.5, 0.5, 0.5]$. (c) PuB$_6$. The coordinates for the high-symmetry points are $X [0.5, 0.0, 0.0], M [0.5, 0.5, 0.0], R [0.5, 0.5, 0.5]$. (d) PuB$_{12}$. The coordinates for the high-symmetry points are the same with PuB. An enlarged view of panel (e) PuB, (f) PuB$_2$, (g) PuB$_6$, (h) PuB$_{12}$ in the energy window $\omega \in [-1.5, 1.0]$ eV. The horizontal lines denote the Fermi level.

Figure 4. (Color online). (a) Three-dimensional Fermi surface and (b) two-dimensional Fermi surface of PuB$_6$ at 116 K calculated by the DFT + DMFT method. Two-dimensional Fermi surface are on the $k_x - k_y$ plane (with $k_z = \pi/2$).

into six-fold degenerated $5f_{5/2}$ and eight-fold degenerated $5f_{7/2}$ subbands stemming from spin-orbit coupling [1, 39, 37]. A quasiparticle peak develops in the Fermi level, mostly belonging to $5f_{5/2}$ orbital, which implicates metallic behavior for PuB, PuB$_2$ and PuB$_{12}$.
Unraveling strongly correlated $5f$ electrons in prototypical plutonium borides

Concurrently, two satellite peaks of PuB$_6$ at –0.9 eV and –0.5 eV with energy gap about 0.4 eV are ascribed to $5f_{5/2}$ and $5f_{7/2}$ orbitals, respectively. In contrast, the reflected peaks above the Fermi level degrade into broad humps. Naturally, it is expected that the atomic multiplets are induced by $5f$ valence fluctuations, which leave fingerprints on the $5f$ photoemission spectroscopy of PuB$_6$. Secondly, the quasiparticle weight of plutonium borides which are somewhat similar for PuB, PuB$_2$ and PuB$_{12}$ despite their diverse crystal structures. Thirdly, hybridization functions [see Fig. 2(c1)-(c4)] depicts the hybridization strength between $5f$ electrons and conduction bands ($c-f$). As can be seen, the strongest hybridization strength of PuB coincides with the shortest Pu-B distance 2.46 Å in Tab. 1. In this scenario, the Pu-B distance regulated hybridization strength varies with boron composition.

3.2. Momentum-resolved spectral functions

Now it is instructive to examine the momentum-resolved spectral functions which imprint intriguing features of plutonium borides [see Fig. 3]. At first, the reliability of our calculated band structures is evaluated by referring to the band structure of PuB$_6$ [7] derived via adopting the continuous-time quantum Monte Carlo impurity solver. The overall band profile obtained from OCA and CTQMC impurity solvers share very semblable characteristics. As is shown in Fig. 3(c), three salient flat narrow electronic bands parallel around the Fermi level which are contributed by $5f$ states. Owing to the strong correlation among $5f$ electrons, the electronic bands calculated by DFT + DMFT method are dramatically renormalized compared to the standard DFT results. After a close inspection, one may notice a weeny gap around the $X$ point just at

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**Figure 5.** (Color online). Valence state fluctuations in plutonium borides at 116 K computed by DFT + DMFT method. (a) Distribution probability of $5f$ atomic eigenstates. (b) $5f$ occupancy with respect to boron composition.
Unraveling strongly correlated 5f electrons in prototypical plutonium borides

the Fermi level [see Fig. 3(g)], rooting from a band inversion between Pu-6d and Pu-5f orbitals. The band inversion hints a possible correlated topological insulator of PuB₆ which was affirmed by surface states analysis [7]. Below the Fermi level, there exist two dispersionless 5f electronic bands at −0.5 eV and −0.9 eV, respectively, which are split by spin-orbit coupling with an energy gap of 0.4 eV between 5f₅/₂ and 5f₇/₂ states. It should be pointed out that the energy gap of Pu-based compounds is larger than that of cerium-based compounds due to a heavier nucleus of Pu atom. Particularly, these narrow bands prominently hybridize with conduction bands along X - Γ high-symmetry line, opening evident hybridization gaps. Combined with the density of states in Fig. 2, the conspicuous c – f hybridization evinces the itinerant tendency of 5f states. Moreover, the electronic structure could be visualized in the Fermi surface topology [see Fig. 4(a)] which is usually detected by subsequent dHvA quantum oscillation. Only one doubly degenerated bands cross the Fermi level (No. of bands: 24 and 25), which take six pretty parabolic shapes and agree with the band trait in Fig. 3(c). It is noticeable that a representative electron pocket appears along the Γ - M high-symmetry line in the energy region of 0 eV ∼ 1 eV which is attributed to conduction band. Despite the absence 5f quasiparticle weight at −0.5 eV and −0.9 eV computed from CTQMC, the basic features of energy bands are consistent with each other, evincing the validity of our results. A discrepancy in 5f quasiparticle intensity below Fermi level might come from the overamplification of correlation effects in the OCA impurity solver.

Then we turn to the electronic band structures of PuB, PuB₂ and PuB₁₂. At first glance, 5f electronic bands are not quite obvious as those in PuB₆ because of their small quasiparticle weight and faint band intensity. In the enlarged band structure near the Fermi level [see Fig. 3(e), (f) and (h)], the conduction bands develop certain degree of bending when they meet 5f states near the Fermi level. The advent of flat bands suggest the partially itinerant 5f states. For PuB, these prominent conduction bands intersect the Fermi level and mainly distribute in the energy range of −2 eV to 2 eV, inducing hole and electron pockets at Γ and L points, respectively. For PuB₂, anomalous conduction bands mainly crowd below the Fermi level, revealing different nature from the other three compounds. Concerning PuB₁₂, two conduction bands with nearly linear dispersion locate about −1 eV to 3 eV, while most of the conduction bands gather below the Fermi level. It should be pointed out that the crystal structure of plutonium borides mediates the Pu-B bonding character, which in turn tunes the itinerant-localized nature of 5f states. So far the calculated electronic band structure of plutonium borides serves as critical prediction for future angle-resolved photoemission spectroscopy (ARPES) experiment.

3.3. Valence state fluctuations

It is well established that δ-Pu displays obvious mixed-valence behavior with noninteger occupation number deviating from nominal value 5.0. The 5f electron atomic eigenstates derived from the output of DMFT many-body states elaborate the valence
Unraveling strongly correlated 5f electrons in prototypical plutonium borides

state fluctuations and related mixed-valence behavior. Here \( p_\Gamma \) is used to quantify the probability of 5f electrons which stay in each atomic eigenstate \( \Gamma \). Then the average 5f valence electron is defined as \( \langle n_{5f} \rangle = \sum_\Gamma p_\Gamma n_\Gamma \), where \( n_\Gamma \) denotes the number of electrons in each atomic eigenstate \( \Gamma \). Finally, the probability of 5f\( n \) electronic configuration can be expressed as \( \langle w(5f^n) \rangle = \sum_\Gamma p_\Gamma \delta(n - n_\Gamma) \).

The calculated probabilities of 5f\( n \) electronic configuration for plutonium borides are visualized in Fig. 5. Apparently, the probability of 5f5 electronic configuration is dominating, followed by a comparative proportion of 5f4 and 5f6 electronic configurations which fluctuate around 15%. It is noticed that the contributions of 5f3 and 5f7 electronic configurations are too small to be noticed similar to most plutonium compounds [7, 38]. According to the pattern of electronic configuration dependence on boron composition, plutonium borides are classified into two groups. PuB\( _6 \) stands out from the other three compounds with a considerably larger percentage of 5f6 electronic configuration accounting for 27.8%. Besides the predominant 5f5 electronic configuration comes up to 67.9%, the ratio of 5f4 electronic configuration only limits to 3.8%. The fact lies in that 5f valence electrons are prone to spend more time in the 5f5 and 5f6 electronic configurations rendering valence fluctuations and promoting quasiparticle multiplets. The regulated 5f valence electron \( \langle n_{5f} \rangle = 5.25 \) is evocative of mixed valence behavior in reminiscence of that in \( \delta \)-Pu [40]. On the other hand, the probability of 5f5 electronic configuration approaches 80%, followed by the comparable probabilities of 5f4 and 5f6 electronic configurations accounting for approximate 10% of PuB, PuB\( _2 \), PuB\( _{12} \). It means that a fairly smaller 5f valence electron (less than 5.0) originate from a lower percentage of 5f6 electronic configuration. Accordingly, the valence state fluctuations also distinguish PuB\( _6 \) from the other three compounds.

3.4. Self-energy functions

| \( 5f_{5/2} \) | \( 5f_{7/2} \) |
|----------------|----------------|
| \( m^*/m_e \) | \( Z \) | \( m^*/m_e \) | \( Z \) |
| PuB | 51.762 | 0.019 | 6.869 | 0.146 |
| PuB\( _2 \) | 48.343 | 0.021 | 5.872 | 0.170 |
| PuB\( _6 \) | 11.587 | 0.086 | 18.047 | 0.055 |
| PuB\( _{12} \) | 35.989 | 0.028 | 5.269 | 0.190 |

Usually, the electronic correlations are encapsulated in the electron self-energy functions [25, 26]. \( Z \) denotes the quasiparticle weight or renormalization factor, which means the electronic correlation strength and can be acquired from the real part of
Unraveling strongly correlated 5f electrons in prototypical plutonium borides

self-energy functions via the following Eq. [25]:

\[ Z^{-1} = \frac{m^*}{m_e} = 1 - \frac{\partial}{\partial \omega} \text{Re} \Sigma(\omega) \bigg|_{\omega=0}. \]  

The evaluated electron effective mass \( m^* \) and quasi-particle weight \( Z \) for 5f_{5/2} and 5f_{7/2} states [25] according to Eq. 1 are listed in table 2. Firstly, the electron effective masses of PuB_6 with both 5f_{5/2} and 5f_{7/2} states are comparatively large, accompanied by diminutive renormalization factors, implying the moderate electronic correlations and intensive localization of 5f states. The trend is in accordance with the low-energy electron scattering in the high-energy regime for PuB_6. Secondly, the electron effective masses of 5f_{5/2} states are much larger than 5f_{7/2} states for PuB, PuB_2 and PuB_{12}, which manifests heavily renormalized 5f_{5/2} bands and strongly correlated 5f_{5/2} states. On the contrary, less renormalized 5f_{7/2} states suggest relatively weakly correlated 5f_{7/2} states. Thirdly, slight variations of electron effective masses among PuB, PuB_2 and PuB_{12} result from diverse band renormalization strengths. Therefore electronic correlation strength and itinerancy degree of freedom are distinct for 5f_{5/2} and 5f_{7/2} states, which are associated with the intrinsic correlated electronic characteristic, further verifying the orbital selective correlated states.

4. Discussions

In this section, both itinerant-localized dual nature and strongly correlated 5f electronic state are explored of plutonium borides to unravel the bonding behavior and underlying mechanism of crystal stability.

**Bonding behavior and crystal stability.** It is generally believed that itinerant 5f states prefer to hybridize with conduction bands and open hybridization gaps. Subsequently, noteworthy atomic multiplets and significant valence state fluctuations along with strong mixed-valence behavior are often visualized in such system. Just as the case for temperature driven itinerant 5f electron is commonly weakly correlated, you may wonder whether the situation always holds in pressure driven or chemical doping 5f electron systems. Take PuB_6 for example, the largest Pu-B distance of the four compounds [see Tab. 2] stretches the Pu-B bonding radius so as to weaken the wavefunction overlap between Pu and B atoms. Hence the attenuated bonding strength may boost localized 5f electrons, which interprets a pseudogap at the Fermi level in the calculated density of states. It is emphasized that the potential topological feature is tightly related to the correlated 5f orbitals which hybridize with 6d orbitals to induce the band inversion, corroborating a correlated topological insulator of PuB_6.

As is mentioned above, partial itinerancy of 5f states embody the \( c-f \) hybridization gap below the Fermi level, finite quasiparticle weight, evident atomic multiplets and remarkable valence state fluctuations. In this respect, 5f states reveal itinerant-localized dual nature which remains a long-standing issue in condensed matter physics. On the other hand, electron effective masses derived from self-energy functions implicate medium electronic correlation of both \( J = 5/2 \) and \( J = 7/2 \) states, which is in conformity
with the pattern in temperature driven itinerant $5f$ states. In contrast to PuB$_6$, the observed band intensity of PuB, PuB$_2$ and PuB$_{12}$ is not quite prominent near the Fermi level together with moderate valence state fluctuations, hinting pretty strongly correlated $5f$ electronic states. Actually, an established picture portrays that itinerant $5f$ states are moderately correlated, while localized $5f$ states are inclined to be strongly correlated in most temperature and chemical doping $5f$ electron systems.

Even so, some delicate differences still exist in quasiparticle weight [see Fig. 2(b1)-(b4)] and hybridization strength [see Fig. 2(c1)-(c4)]. It is noted that the spectral weight obeys the sequence as PuB$_2$ > PuB > PuB$_{12}$, which accords with the series derived from hybridization strength. It is illuminating to examine the detail of crystal structure parameters listed in table 1. Interestingly, the typical Pu-Pu distance follows the order as PuB$_2$ < PuB < PuB$_{12}$, which stresses the atomic distance affecting the itinerant degree of freedom for $5f$ electrons. Furthermore, $5f$ electron occupancy signifies the mixed valence nature which could be measured by the electron energy-loss spectroscopy and X-ray absorption spectroscopy [41]. Actually, when $5f$ and $6d$ orbitals of Pu atom hybridize with the $2s$ and $2p$ orbitals of boron atom, the fluctuating $5f$ electron enables Pu-B bonding, which subsequently alters the charge distribution and finally influences the crystal structure stability of plutonium borides. The hypothesis could be generalized to understand the stability of Th- and Am-diborides [15]. The lack of $5f$ electron for Th atom makes it hard to bond with $2p$ orbital of boron atom so that the poor-boron compound like ThB$_2$ hardly exists in nature. Likewise, a large element number increases the atomic distance, which induces a more localized $5f$ state. The weak bonding between Am and B atom is unable to stabilize AmB$_2$, where boron composition is rather low in diboride.

**X-ray absorption branching ratio and $5f$ occupancy.** The evolution pattern of $5f$ electrons occupancy in the $5f_{5/2}$ and $5f_{7/2}$ levels across this series is a particularly fundamental question about actinides. Generally, it is determined by the angular momentum coupling scheme of each actinide. Depending on the relative strength of spin-orbit coupling and electrostatic interaction, the angular momenta of multielectronic systems have three ways to couple with each other: Russell-Saunders (LS) coupling, $jj$ coupling, and intermediate coupling (IC) [1]. For the ground states of late actinides, intermediate coupling is usually the favorite. A natural question rises with the $5f$ orbital occupancy and angular momentum coupling scheme for PuB$_x$ ($x=1, 2, 6, 12$).

X-ray absorption spectroscopy is a powerful probe for the electronic transitions between core $4d$ and valence $5f$ states. The strong spin-orbital coupling for the $4d$ states give rise to two absorption lines, representing the $4d_{5/2} \rightarrow 5f$ and $4d_{3/2} \rightarrow 5f$ transitions, respectively. The X-ray absorption branching ratio $B$ is defined as the relative strength of the $4d_{5/2}$ absorption line [42]. It measures the strength of the spin-orbit coupling interaction in the $5f$ shell. If the electrostatic interaction between core and valence electrons is ignored, the expression for $B$ is as follows [40]:

$$B = \frac{3}{5} - \frac{4}{15} \frac{1}{14 - n_{5/2} - n_{7/2}} \left( \frac{3}{2} n_{7/2} - 2n_{5/2} \right),$$

(2)
Unraveling strongly correlated $5f$ electrons in prototypical plutonium borides

where $n_{7/2}$ and $n_{5/2}$ are the $5f$ occupation numbers for the $5f_{7/2}$ and $5f_{5/2}$ states, respectively. The calculated results are listed in table 3, giving $B(\text{PuB}_6) > B(\text{PuB}_2) > B(\text{PuB}) \approx B(\text{PuB}_2)$. That means the angular momentum coupling scheme of four compounds are assigned to intermediate coupling, which is similar to that in heavy actinides Pu [37] and Cm [43].

Table 3. The weights for $5f$ electronic configurations $w(5f^n)$, $5f$ orbital occupancy ($n_{5/2}$, $n_{7/2}$, and $n_{5f}$), and X-ray absorption branching ratio $B$ for PuB$x$ ($x=1$, 2, 6, 12).

| cases  | $w(5f^4)$ | $w(5f^5)$ | $w(5f^6)$ | $n_{5/2}$ | $n_{7/2}$ | $n_{5f}$ | $B$     |
|--------|-----------|-----------|-----------|-----------|-----------|----------|---------|
| PuB    | 14.09%    | 76.28%    | 9.27%     | 3.77      | 1.17      | 4.94     | 0.7706  |
| PuB$_2$| 14.49%    | 73.80%    | 11.22%    | 3.77      | 1.19      | 4.96     | 0.7702  |
| PuB$_6$| 3.79%     | 67.96%    | 27.84%    | 4.02      | 1.23      | 5.25     | 0.7888  |
| PuB$_{12}$| 14.91%  | 76.30%    | 8.38%     | 3.78      | 1.15      | 4.92     | 0.7714  |

5. Conclusions

The detailed electronic structures of plutonium borides embracing momentum-resolved spectral functions, density of states, valence state fluctuations and self-energy functions are comprehensively studied by employing the traditional density functional theory combined with single-site dynamical mean-field approach. It is found that PuB$_6$ is distinguished from PuB$_x$ ($x=1$, 2, 12), evincing topological feature with mixed-valence behavior. Meanwhile, the metallic PuB$_x$ ($x=1$, 2, 12) implicate tunable itinerancy of $5f$ electrons which is virtually affected by $c-f$ hybridization. By tuning boron composition, the hybridization strength varies against Pu-B distance, which might be the vital factor in the growing localization of $5f$ states along with enlarging Pu-B distance. The regulated charge distribution and bonding behavior contribute to the lattice stability of plutonium borides. Actually, itinerant-localized nature interconnecting with $5f$ electronic correlation means that localized $5f$ states is probably strongly correlated. Overall, the calculated momentum-resolved spectral functions and density of states serve as crucial predictions which deserve further experimental corroboration.

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Unraveling strongly correlated 5f electrons in prototypical plutonium borides

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