Insights into correlated 5*f* electronic states in ASn_3 (A = U, Np, Pu) intermetallics

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The 5*f* series dependence of itinerant-localized 5*f* states and strongly correlated electronic states has been systematically investigated in archetypical cubic compounds ASn_3 (A = U, Np, Pu) by using a combination of the density functional theory and the embedded dynamical mean-field approach. The reproducibility of theoretical band structure and x-ray photoemission spectrum for USn₃ not only guarantees the reliability of calculation, but also supports the hypothesis of enhanced localization of 5*f* states with increasing atomic series from uranium to plutonium. The suppression of valence state fluctuations, which is characterized by the strength of valence state fluctuations $\mathcal{V}(USn_3) > \mathcal{V}(NpSn_3) > \mathcal{V}(PuSn_3)$, is quantitatively described. The study reveals that these fluctuations are closely related to the itinerant nature of 5*f* states, as evidenced by significant hybridization between 5*f* states and conduction bands (*c*), as well as pronounced spectral weight around the Fermi level. Particularly, the emergence of prominent quasiparticle multiplets in PuSn₃, distinct from USn₃ and NpSn₃, is attributed to the interplay between competing atomic eigenstates of 5*f* states and significant *f*-*c* hybridization contributes to the occurrence of itinerant-electron antiferromagnetism. It is proposed that a detailed understanding of the electronic structure dependence on the actinide series in ASn_3 (A = U, Np, Pu) intermetallics compounds can provide valuable insights and promote further experimental research in this field.

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I. INTRODUCTION

In correlated electronic systems, strong interactions and the interplay between different degrees of freedom may give rise to the emergence of unprecedented quantum phenomena, including intricate magnetism, heavy-fermion behavior, unconventional superconductivity, and mixed-valence states [1-6]. The extended 5*f* wave function enables partially itinerant 5*f* states that promote active chemical bonding and valence state fluctuations. Due to the narrow 5*f* electronic band, the 5*f* states are easily tuned by external temperature, pressure, chemical doping, and magnetic field. To unveil the itinerant-localized 5*f* states and their relationship with *f*-*c* hybridization, binary ASn_3 (A = U, Np, Pu) compounds are established as an ideal archetype platform to explore the subtle electronic structure and corresponding emergent physics.

ASn₃ (A = U, Np, Pu) crystalize in cubic AuCu₃ structure (space group *Pm*-3*m*) [see Fig. 1(a)] with *A* atom locating at cubic corners and Sn atoms occupying the surface center. As is listed in Table I, the experimental lattice constants are 4.603 Å [7], 4.627 Å [8], and 4.630 Å [9] for USn₃, NpSn₃, and PuSn₃, respectively. It is evident that the lattice constants of these three isostructural compounds are approximately 4.6 Å and slightly stretch from USn₃ to PuSn₃. Since the interatomic distance d_{A-A} exceeds the Hill limit (~3.5 Å) [10], these intermetallics are expected to develop magnetic ordering at low temperature. However, certain paramagnetic ground states [11,12] implicate the crucial role of *f*-*c* hybridization, extending 5f electrons from localization to mobility and dualism [3,13,14].

USn₃ is a heavy-fermion compound with an electronic specific heat coefficient 171 mJ/(mol \times K²) [13], which has been confirmed through the temperature-dependent electronic specific heat coefficient [13] and electronic resistivity experiments [15]. Interestingly, USn3 remains paramagnetism at very low temperature around 1 K, with a single weak de Haas-van Alphen (dHvA) frequency at 0.5 K [16]. It is believed that the paramagnetic ground state arises from f-chybridization, leading to strong spin fluctuations observed in inelastic neutron scattering study [11]. Since USn₃ approaches the verge of magnetic instability, a small doping with Pb may initiate antiferromagnetic ordering [11]. This physical scenario aligns with the observation of a spin density wave magnetic instability at the quantum critical point, as evidenced by ¹¹⁹Sn nuclear spin-echo decay rate measurement [17]. Importantly, x-ray photoemission spectroscopy of USn₃ detects a significant peak near the Fermi level, originating from the contribution of 5f states, along with a shoulder peak at approximately 7 eV from Sn-5p states [18]. However, there have been challenges in replicating these experimental findings using x-ray photoemission spectroscopy. Additionally, the extremal orbits predicted by previous first-principles calculation [19] have not been experimentally verified. This discrepancy may arise from the substantial renormalization of heavy electrons by many-body interactions, which cannot be accurately described within the framework of single-particle band theory.

The nature of the 5f states in NpSn₃, whether they are itinerant or localized, is still a topic in debate. One

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FIG. 1. (a) Crystal structure of ASn_3 (A = U, Np, Pu). (b) Schematic picture of the first Brillouin zone of ASn_3 (A = U, Np, Pu). Some high-symmetry *k* points *X* [0.5, 0.0, 0.0], Γ [0.0, 0.0, 0.0], *M* [0.5, 0.5, 0.0], and *R* [0.5, 0.5, 0.5] are marked.

argument for the localized nature of the 5f electrons is based on the fact that the distance between the nearest Np atoms exceeds the Hill criterion [10], which suggests localization. In addition, various experimental findings support the idea of localized 5f electrons, such as the decrease of the electronic specific heat coefficient from paramagnetic state 242 mJ/(mol \times K²) to 88 mJ/(mol \times K²) below Néel temperature 9.5 K [20], temperature dependent electronic properties [21], electrical resistivity, magnetic susceptibility, Mössbaurer spectroscopy, and single crystal neutron scattering experiments [22]. On the other hand, the collinear antiferromagnetic ordering with a small magnetic moment $0.28\mu_B$ [3,23] is detected by Mössbauer spectroscopy and single crystal neutron scattering experiments, which still manif est the partially itinerant 5f states. However, the controversy on the itinerant-electron antiferromagnetic NpSn₃ is owing to the deficiency of advanced calculation methods for the strongly correlated systems [24,25]. It is reported that PuSn₃ displays temperature-independent paramagnetism [12,26] and pseudogap around the Fermi level in low-temperature electrical resistivity [27]. However, reliable experiments are still lacking to fully characterize the electronic structure of this compound. The challenges in Pu-based compounds in turn stimulated theoretical studies, which have made great efforts to determine the crystal structure, bulk modulus, electronic structure, and quantum oscillation [12,28-30]. Nevertheless, the underlying physics of the paramagnetic ground state remains unexplored.

Indeed, there have been extensive theoretical efforts to study uranium pnictides and chalcogenides [31,32]. The band structure, density of states, Fermi surface, and effective elec-

tron mass of USn₃ have been previously investigated by employing first-principles calculations [16,33]. Subsequently, the presence of strong correlation among 5f electrons and significant spin-orbit coupling in ASn_3 (A = U, Np, Pu) compounds complicates the calculations and obscures a comprehensive understanding of their electronic structure and ground state properties. Evidently, the missing narrow flat 5f bands within the traditional density functional theory is attributed to the underestimation of strongly correlated 5felectrons. Furthermore, accurate treatment of spin-orbit coupling is crucial for actinide systems. Especially, the intrinsic mechanism for the paramagnetic ground state of USn₃ and PuSn₃ remains poorly understood. It is worth noting that the hybridization strength between the 5f states and conduction bands plays a crucial role in determining the low-temperature magnetic ordering and the itinerant-localized dual nature of the 5f electrons. Therefore, it is instructive to investigate the dependence of the 5f electronic structure and f-c hybridization on the 5f series in order to unravel the intricate bonding behavior and strongly correlated nature of the 5f states. Such investigations may shed light on the diverse ground state ordering as well as alluring heavy-fermion behavior.

II. METHODS

In order to capture the essence of the strongly correlated 5f electronic states for uranium, neptunium, and plutonium, 5f correlated electronic states dependence on 5felectron series are investigated by means of an integration of the density functional theory and the embedded dynamical mean-field theory (DFT+DMFT). The DFT+DMFT method combines the DFT realistic band structure calculation and a nonperturbative way to tackle the many-body local interaction effects in DMFT [34,35]. Then the DFT+DMFT approach is implemented into DFT and DMFT parts, which are solved separately by using the WIEN2K code [36] and the EDMFTF software package [37].

For current computing capacity, the crystal field splitting and structural relaxation are not included in the DFT+DMFT calculation. For one thing, the relativistic effect plays a pivotal role in the electronic structure for the heavy elements with large spin-orbit coupling. Meanwhile, crystal field splitting contributes to complicated magnetism [38,39] and related multipolar ordering. Since the energy splitting magnitude by crystal field splitting is smaller than that of spin-orbit coupling in actinides, the crystal field splitting is neglected in the calculation to reduce the computing complexity and

TABLE I. Crystal structure parameters, electronic specific heat coefficient, and ground state ordering of ASn_3 (A = U, Np, Pu).

Cases	d_{A-A} (Å)	$d_{A-\mathrm{Sn}}$ (Å)	$\gamma \ [mJ/(mol \times K^2)]$	Ground state
USn ₃	4.603	3.255	171 ^a	Paramagnetism ^d
NpSn ₃	4.627	3.272	242 ^b	Itinerant-electron antiferromagnetism ^b ($T_N = 9.5 \text{ K}$)
PuSn ₃	4.630	3.274	96°	Paramagnetism ^e

^aSee Ref. [13].

^bSee Ref. [3].

^cSee Ref. [14].

^dSee Ref. [11].

^eSee Ref. [12].



FIG. 2. (a) Momentum-resolved spectral functions $A(\mathbf{k}, \omega)$ of USn₃ at 116 K calculated by the DFT+DMFT method. (b) The calculated band of paramagnetic USn₃ by employing the augmented-spherical-wave method by Cornelius *et al.* [16]. The horizontal lines mean the Fermi level.

improve convergence efficiency. Here strong electronic correlation and large spin-orbit coupling are treated on an equal footing, but omitting the crystal field splitting. For another thing, it is worth noting that the magnetic structure is tuned by actinide atomic distance which regulates the f-c hybridization strength. In principle, structural relaxation should be executed to locate the lowest energy state. Unfortunately, the accurate force calculation of systems with strong spinorbit coupling has not been implemented with the current EDMFTF software package. As mentioned above, the spin-orbit coupling of actinides is significant—especially that of Pu is about 0.4 eV, which cannot be omitted. It is expected that the structural relaxation with force calculation by employing the DFT+DMFT approach with spin-orbit coupling shall be implemented in the near future.

In the DFT calculation, the experimental crystal structures of ASn_3 (A = U, Np, Pu) were utilized. Since the calculated temperature 116 K is above the antiferromagnetic transition temperature of NpSn₃, the system was assumed to be nonmagnetic. The considerable spin-orbit coupling was treated in a second-order variational manner. Besides, the generalized gradient approximation was tested and used to formulate the exchange-correlation functional [40]. The *k*-points' mesh was $15 \times 15 \times 15$ and $R_{\text{MT}}K_{\text{MAX}} = 8.0$.

In the DMFT part, 5f electrons of A atom were treated as correlated. The four-fermions' interaction matrix was parametrized using the Coulomb interaction U = 5.0 eV and the Hund's exchange $J_H = 0.6 \text{ eV}$ via the Slater integrals [41] for ASn_3 (A = U, Np, Pu). It should be noted that the band structure and density of states for U = 4.0 eV, 5.0 eV, and 6.0 eV reveal subtle nuance for ASn_3 (A = U, Np, Pu). The fully localized limit scheme was used to compute the doublecounting term for the impurity self-energy function [42]. The vertex-corrected one-crossing approximation (OCA) impurity solver [43] was employed to solve the resulting multiorbital Anderson impurity models. In order to reduce the computation burden, some good quantum numbers such as N and Jwere chosen to divide the whole Hilbert space [44] into subblocks. Moreover, the truncation approximation for the atomic eigenstates was adopted to gain further acceleration. Explicitly, only those atomic eigenstates whose occupancy *N* satisfy $N \in [N_{\text{low}}, N_{\text{high}}]$ will be taken into account in the local trace evaluation. Finally, the convergence criteria for energy and charge were 10^{-5} Ry and 10^{-5} e, respectively. It is worth mentioning that the direct output of the OCA impurity solver is real axis self-energy $\Sigma(\omega)$, which was used to calculate the momentum-resolved spectral functions $A(\mathbf{k}, \omega)$, density of states $A(\omega)$, renormalization factor *Z*, effective electron mass m^* , and other physical observables.

III. RESULTS

A. Electronic band structures

Here we focus on the momentum-resolved spectral functions $A(\mathbf{k}, \omega)$ of ASn_3 (A = U, Np, Pu) to reveal the inherent nature of 5f electrons. To verify the reliability of our calculations, the band structure of USn₃ along high-symmetry line $R - \Gamma - X - R - M - X - \Gamma - M$ calculated by using the DFT+DMFT method [see Fig. 2(a)] is compared with the available theoretical results [see Fig. 2(b)] by Cornelius et al. [16], where a localized spin density approximation with the augmented-spherical-wave approach [45] is employed. First of all, the essential feature of band structures generally coincide, including the presence of a holelike orbit near the Fermi level at R point and the presence of a holelike orbit below the Fermi level at the X and M points. Nevertheless, it is noticed that the typical holelike orbit at the Γ point in our results shifts towards the Fermi level compared to those in Fig. 2(b). This difference might root from the fact that the narrow 5f electronic bands of uranium atom intersect the conduction bands near the Fermi level, leading to significant hybridization gaps. The conspicuous spectral weight of hybridization between 5fand 5p states of the Sn atom is in accord with the x-ray photoemission spectroscopy of USn₃ [18]. It is postulated that the absence of quasiparticle 5 f bands in literature [16,33] is likely due to the underestimation of strongly correlated 5f electrons without sophisticated treatment of the many-body effects. In this scenario, the conformity with previous theoretical band structure [16] and experimental photoemission spectroscopy [18] further supports the validity of our calculations.



FIG. 3. Momentum-resolved spectral functions $A(\mathbf{k}, \omega)$ of ASn_3 (A = U, Np, Pu) at 116 K calculated by the DFT+DMFT method. The horizontal lines indicate the Fermi level. (a) USn₃. (b) NpSn₃. (c) PuSn₃.

Then we scrutinize the salient traits encoded in the band structure of ASn_3 (A = U, Np, Pu). It is observed that the overall profile of the momentum-resolved spectral functions for USn₃ and NpSn₃ [see Figs. 3(a) and 3(b)] at 116 K share abundant similarities with analogous conduction bands and remarkable dispersionless 5f electronic bands around the Fermi level. Even so, a slight discrepancy indicates a higher intensity of 5f band in NpSn₃ than that in USn₃, which solidifies the itinerant nature of the 5f electrons. Additionally, the increased intensity and subtle structure of Sn-5p electronic bands at the Γ point, approximately 1 eV above the Fermi level, substantiate the itinerant nature of 5f states of the Np atom. Further examination reveals that the band structure of PuSn₃ [see Fig. 3(c)] exhibits distinct flat 5f bands of the Pu atom, as well as holelike conduction bands derived from the Sn-5p state at the Γ point above the Fermi level, positioned at higher energy levels above the Fermi level. Simultaneously, the conduction bands below the Fermi level resemble those found in USn₃ and NpSn₃. Notably, narrow 5f bands become apparent at -0.9 eV, -0.47 eV, and the Fermi level, demonstrating hybridization with ligand states and forming clearly discernible hybridization gaps. Consequently, the significant spectral weight of the 5f electrons, the remarkable quasiparticle bands, and the pronounced hybridization collectively indicate the itinerant and coherent nature of the 5f states in PuSn₃. Thus it can be speculated that the distinct character of 5f electrons stems from a diverse actinide series and the varying strength of hybridization between the 5f-ligand states.

B. Density of states

To unveil the 5f electronic structure of ASn_3 (A = U, Np, Pu), we can analyze the density of states and quasiparticle peaks shown in Figs. 4(a)-4(g). First, the overall shape of the total density of states for USn₃ and NpSn₃ bears remarkable similarities. Both materials exhibit a sharp and narrow quasiparticle peak at the Fermi level, accompanied by a broad "hump" in the energy range of 0.5 eV to 2 eV. The prominent quasiparticle peaks at the Fermi level indicate the itinerancy and coherence of 5f electrons. Due to the influence of spin-orbit coupling, the originally fourteenfold degenerated 5f orbitals split into sixfold degenerate $5f_{5/2}$ and eightfold degenerate $5f_{7/2}$ subbands [see Figs. 4(d)-4(f)]. The dominant contribution to the quasiparticle peak mainly comes from the $5f_{5/2}$ orbital in both USn₃ and NpSn₃. However, there is a slight increase in the spectral weight of the 5f orbital in NpSn₃ compared to USn₃, which leads to a visible spectral weight of $5f_{7/2}$ orbital at the Fermi level in NpSn₃. As is indicated in Table III, the quasiparticle weight Z of $5f_{7/2}$ orbital in NpSn₃ is highest, suggesting significant valence state fluctuations and mixed-valence behavior. This analysis of the density of states and quasiparticle peaks provides insights into the 5f electronic structure of ASn_3 (A = U, Np, Pu) compounds, highlighting similarities and differences in the spectral features, as well as the presence of valence state fluctuations and mixed-valence behavior in NpSn₃.

The density of states of PuSn₃ exhibit a distinct characteristic, as shown in Fig. 4(c). It displays typical atomic multiplets with a sharp quasiparticle peak at the Fermi level and four satellite peaks located above and below it. By examining the partial density of states for the 5f orbitals [see Fig. 4(f)], we observe that the quasiparticle peak primarily arises from the $5f_{5/2}$ orbital. Meanwhile, the two satellite peaks "P1" and "P2" at -0.9 eV and -0.47 eV with energy gap about 0.43 eV are attributed to $5f_{5/2}$ and $5f_{7/2}$ orbitals, respectively. Above the Fermi level, the reflected peaks "P3" and "P4" distribute in 0.47 eV and 0.9 eV relative to the central quasiparticle peak. These five representative peaks, collectively known as "quasiparticle multiplets" commonly exist in plutoniumbased compounds such as Pu₃Ga, PuIn₃, and PuB₆ [46,47]. To understand the origin of these quasiparticle multiplets, it is proposed that "P3" and "P4" peaks are formed by a mixture of $5f_{5/2}$ and $5f_{7/2}$ orbitals. It is worth mentioning that the emergence of these quasiparticle multiplets is attributed to the interplay between the abundant competing atomic eigenstates of the 5 f electrons and the valence state fluctuations of the 5 forbitals, as discussed in Sec. III D.

In simple terms, the presence of sufficient competitive atomic eigenstates is necessary for the formation of quasiparticle multiplets. For example, the nominal occupancy of 5f electrons in plutonium is 5.0, which is higher than that of uranium (2.0) and neptunium (3.0). Consequently, the number of occupied 5f states in plutonium is greater than in uranium and neptunium. However, in the case of curium and californium, where the 5f electrons are highly localized and valence state fluctuations are relatively weak, the development of quasiparticle multiplets does not occur even though their nominal occupancy of 5f electrons exceeds 5.0. This is in



FIG. 4. Electronic density of states of ASn_3 (A = U, Np, Pu) at 116 K obtained by the DFT+DMFT method. Total density of states (thick solid lines) and partial 5*f* density of states (color-filled regions) of (a) USn₃, (b) NpSn₃, and (c) PuSn₃. These peaks in figure (c) resulting from the quasiparticle multiplets are denoted with "P1," "P2," "P3," and "P4." The *j*-resolved 5*f* partial density of states with 5*f*_{5/2} and 5*f*_{7/2} components represented by red and green lines, respectively. (d) USn₃, (e) NpSn₃, and (f) PuSn₃.

contrast to PuSn₃, where significant quasiparticle multiplets emerge despite remarkable valence state fluctuations in other ASn_3 (A = U, Np, Pu) compounds.

C. Fermi surface structure

Fermi surface structure is a pivotal physical quantity for characterizing the detailed electronic structure of ASn_3 (A = U, Np, Pu). Figure 5 visualizes the three-dimensional Fermi surface structure at 116 K. There are two doubly degenerated bands crossing the Fermi level (no. of bands: 16 and 17, 18 and 19) for USn₃ and (no. of bands: 18 and 19, 20 and 21) for both NpSn₃ and PuSn₃, which are labeled by α and β , respectively. For USn₃ [see Figs. 5(a1) and 5(a2)], α band occupies eight corners of the first Brillouin zone, while β band takes on an anisotropic and large form. Especially, α band develops a distorted hexahedral structure for NpSn₃ [see Figs. 5(b1) and 5(b2)], while β band displays twelve small scattered fragments at the edge centers of the first Brillouin zone. For PuSn₃ [see Figs. 5(c1) and 5(c2)] the Fermi surface structure of α band takes an ellipsoid shape, in agreement with previous DFT calculations [30]. Nevertheless, the Fermi surface structure of β band assumes an anisotropic shape, differing from the previous results [30]. The discrepancy of β band may arise from the temperature effect and the strongly correlated 5f electronic states. The DFT calculations [30] are performed at zero temperature, which also underestimates the 5f electronic correlation. Besides, it is pointed out that the Fermi surface could be detected by following dHvA quantum oscillation; then the experimental results may clarify possible physical causes behind the paramagnetic ground state of USn₃ and PuSn₃ provided that no Fermi surface nesting is observed.

To better discern the interior structure of the threedimensional Fermi surface, the two-dimensional Fermi surface of α and β bands is plotted in Fig. 6. In accordance with the three-dimensional Fermi surface of USn₃ [see Fig. 6(a)], both α and β bands intersect the Γ -*M* line and *M*-*X* line, while no bands cross the Γ -*X* line. Meanwhile, only α band cuts through the Γ -*X* line for NpSn₃ [see Fig. 6(b)] with α and



FIG. 5. Three-dimensional Fermi surface of ASn_3 (A = U, Np, Pu) at 116 K calculated by the DFT+DMFT method. (a1), (a2) USn₃. (b1), (b2) NpSn₃. (c1), (c2) PuSn₃.

 β bands passing through the Γ -*M* line and *M*-*X* line. Finally, both α and β bands cross the Γ -*X* line and Γ -*M* line for PuSn₃ [see Fig. 6(c)], along with β band intersecting the *M*-*X* line, which is in accordance with the momentum-resolved spectral functions (see Fig. 3).

D. Valence state fluctuations

Now that alluring quasiparticle multiplets are closely interrelated with valence state fluctuations, the 5*f* electron atomic eigenstates derived from the output of DMFT many-body states contain the valence state fluctuations. p_{Γ} is used to quantify the probability of 5*f* electrons which remain in each atomic eigenstate Γ . Then the average 5f valence electron is defined as $n_{5f} = \sum_{\Gamma} p_{\Gamma} n_{\Gamma}$, where n_{Γ} denotes the number of electrons in each atomic eigenstate Γ . Finally, the probability of $5f^n$ electronic configuration can be written as $P_n = w(5f^n) = \sum_{\Gamma} p_{\Gamma} \delta(n - n_{\Gamma}).$

The calculated probabilities of $5f^n$ electronic configuration for ASn₃ (A = U, Np, Pu) are listed in Table II. Evidently, for USn₃, the probability of $5f^2$ electronic configuration accounts for 67.1%, followed by the probability of $5f^3$ about 29.7%. The probabilities of $5f^1$ and $5f^4$ electronic configurations are about 2.6% and 1.2%, respectively. The conspicuous valence state fluctuations give rise to the 5f electron occupancy $n_{5f} = 2.283$, which deviates from its nominal value 2.0.



FIG. 6. Two-dimensional Fermi surface on the $k_x - k_y$ plane (with $k_z = \pi/2$) of ASn₃ (A = U, Np, Pu) at 116 K calculated by the DFT+DMFT method. (a) USn₃. (b) NpSn₃. (c) PuSn₃. They are visualized with different colors.

TABLE II. Probabilities of $5f^n$ electronic configuration at 116 K for USn₃ ($n \in [0, 4]$), NpSn₃ ($n \in [1, 5]$), and PuSn₃ ($n \in [3, 7]$), 5f occupancy n_{5f} , and x-ray absorption branching ratio \mathcal{B} .

USn ₃	$5f^{0}$	$5f^1$	$5f^{2}$	$5f^3$	$5f^{4}$	n _{5f}	в
	9.048×10^{-5}	0.026	0.671	0.297	0.012	2.283	0.6855
NpSn ₃	$5f^1$	$5f^2$	$5f^{3}$	$5f^4$	$5f^{5}$	n_{5f}	${\mathcal B}$
	9.234×10^{-5}	0.018	0.472	0.496	0.014	3.506	0.7291
PuSn ₃	$5f^{3}$	$5f^4$	$5f^{5}$	$5f^{6}$	$5f^{7}$	n_{5f}	${\mathcal B}$
	9.976×10^{-4}	0.075	0.772	0.150	1.343×10^{-3}	5.076	0.7806

Accordingly, 5 f electrons tend to spend more time on $5f^2$ and $5f^3$ electronic configurations, promoting mixed-valence behavior. In the case of NpSn₃, the competitive probabilities of $5f^3$ and $5f^4$ electronic configurations approximate 47.2% and 49.6%, respectively, which render substantial valence state fluctuations. Together with a small portion of the probabilities of $5f^2$ and $5f^5$ electronic configurations around 1.8% and 1.4%, the 5f electron occupancy $n_{5f} = 3.506$ diverges significantly from its nominal value 3.0. Therefore, NpSn₃ exhibits noteworthy valence state fluctuations and mixedvalence states. Eventually, we focus on the probability of electronic configuration of PuSn₃. The leading probability of $5f^5$ electronic configuration reaches as high as 77.2%. Meanwhile, the probability of $5f^6$ and $5f^4$ attains 15.0% and 7.5%, respectively, neglecting other electronic configurations. In this context, moderate valence state fluctuations regulate the 5f electron occupancy $n_{5f} = 5.076$, which approaches its nominal value 5.0. In order to quantitatively describe the strength of valence state fluctuations, we define the quantity $\mathcal{V} = \sum_{n} P_n(P_n - 1)$, where *n* denotes the occupancy number of 5f electrons. Two extreme cases are listed for illustration. The case for $P_n = 1$, $\mathcal{V} = 0$ signifies the absence of valence state fluctuations with only one electronic configuration. In this context, electrons are extremely localized where they prefer to stay in one electronic configuration. On the contrary, dispersive distribution of electronic configurations generates arresting valence state fluctuations with $\mathcal{V} = 1$. Actually, such ideal systems hardly exist in real materials and \mathcal{V} evaluates 0.689, 0.623, and 0.449 for USn₃, NpSn₃, and PuSn₃, respectively. Accordingly, the strength of valence state fluctuations obeys the following sequence: $\mathcal{V}(USn_3) >$ $\mathcal{V}(NpSn_3) > \mathcal{V}(PuSn_3)$. The order conforms with the qualitative picture that increscent atomic number with growing localization of 5f electrons suppresses valence state fluctuations. It is expected that ongoing research on a wide range of f electronic states for lanthanide and actinide compounds shall shed light on the comprehensive results about the precise description of valence state fluctuations.

E. Self-energy functions

Inspiringly, the electronic correlations are encoded in the electron self-energy functions [34,35,39,48]. The renormalization factor Z which embodies the electronic correlation strength can be deduced from the real part of self-energy functions on the real axis via the following equation [34]:

$$Z^{-1} = \frac{m^{\star}}{m_e} = 1 - \left. \frac{\partial \operatorname{Re}\Sigma(\omega)}{\partial \omega} \right|_{\omega=0}.$$
 (1)

TABLE III. Effective electron mass m^* and quasiparticle weight Z of $5f_{5/2}$ and $5f_{7/2}$ states for ASn₃ (A = U, Np, Pu) at 116 K.

	5 <i>f</i> 5	5/2	5 <i>f</i> -	1/2
Compounds	m^*/m_e	Ζ	m^*/m_e	Ζ
USn ₃	18.717	0.053	17.233	0.058
NpSn ₃	18.673	0.054	1.890	0.529
PuSn ₃	29.111	0.034	13.873	0.072

Here renormalization factor Z quantitatively describes the quasiparticle weight and band compression degree of correlated electronic bands, which is inversely proportional to the effective electron mass m^* . Table III lists the computed effective electron mass m^* and renormalization factor Z of $5f_{5/2}$ and $5f_{7/2}$ states for ASn₃ (A = U, Np, Pu) at 116 K. For USn₃, sizable effective electron mass for both $5f_{5/2}$ and $5f_{7/2}$ states implicates the strongly correlated 5f electronic states, accompanied by suppressed quasiparticle weight Z. Fortunately, the computed effective electron mass of $5f_{5/2}$ and $5f_{7/2}$ states is about $17m_e$ for USn₃, which approaches the upper limit of the detected effective electron mass in the range of $5m_e$ -15 m_e by dHvA experiments [16]. Similarly, PuSn₃ reveals strong correlation strength among 5f electrons where the effective electron mass of the $5f_{5/2}$ state is much larger than the $5f_{7/2}$ state. As is mentioned in Sec. III B, the finite distribution of spectral weight of the $5f_{7/2}$ state of NpSn₃ arises from the smooth variation across the Fermi level, indicating a small effective electron mass of the $5f_{7/2}$ state with significant quasiparticle weight Z. The comparatively weak electron correlation of the $5f_{7/2}$ state compares to that of the $5f_{5/2}$ state, evincing the orbital dependent trait. It is speculated that the orbital selective correlation of $5f_{5/2}$ and $5f_{7/2}$ states for NpSn₃ holds possible linkage with itinerant antiferromagnetic ordering.

IV. DISCUSSION

In this section, we discuss the hybridization between 5f states and conduction bands to elucidate the paramagnetic ground state of USn₃ and PuSn₃, as well as the antiferromagnetic ordering observed in NpSn₃. Additionally, we aim to interpret the angular momentum coupling scheme using x-ray absorption spectroscopy. Lastly, we partially comprehend the heavy-fermion behavior of USn₃ by estimating the electronic specific heat coefficient.

5*f* series dependence of electronic structure. As the atomic number increases from uranium to plutonium, the f - chybridization strength and the corresponding bonding behavior undergo changes. The key features are summarized in Table IV, where the spectral weight of 5*f* states near the Fermi level indicates a tendency for hybridization with Sn-5*p* bands, leading to the formation of partially itinerant 5*f* states. The bonding behavior is further evidenced in the significant valence state fluctuations and apparent mixed-valence behavior for ASn_3 (A = U, Np, Pu). It is speculated that a larger atomic actinide distance may weaken f - c hybridization, thereby reducing the itinerant degree of freedom and restraining valence state fluctuations. Surprisingly, prominent

TABLE IV. Valence state fluctuations, quasiparticle multiplets, and correlation strength of 5f electronic states in ASn₃ (A = U, Np, Pu).

Compounds	USn ₃	NpSn ₃	PuSn ₃
Valence state fluctuations	0.689	0.623	0.449
Quasiparticle multiplets	Weak	Weak	Strong
Correlation strength of $5f$ states	Moderate	Moderate and orbital selective	Moderate

quasiparticle multiplets are observed in PuSn₃, which can be attributed to the interplay between competing atomic eigenstates and valence state fluctuations. The distinction in PuSn₃ authenticates that the Pu atom is located on the edge of itinerant-localized 5f states. In this sense, USn₃ and NpSn₃ tend to develop a paramagnetic ground state on account of substantial f - c hybridization. Subsequently, NpSn₃ exhibits itinerant-antiferromagnetic ordering with a small magnetic moment of the Np atom. This is mainly attributed to the two competitive electronic configurations $5f^3$ and $5f^4$ rendering noteworthy valence state fluctuations and mixed-valence nature, which is analogous to the itinerant 5f-electron antiferromagnet UGa₃ with prominent c - f hybridization [16].

Angular momentum coupling scheme. For the actinides with intricate spin-orbit coupling, 5f electrons occupy the $5f_{5/2}$ and $5f_{7/2}$ subbands. Since the evolution trend of 5f electron in the $5f_{5/2}$ and $5f_{7/2}$ levels with respect to the incremental atomic radius is crucial, the angular momentum coupling scheme serves as the primary determinant factor. In multielectronic systems, there exist three ways of angular momentum coupling and electronic interaction, including Russell-Saunders (LS) coupling, jj coupling, and intermediate coupling (IC) [5]. For the ground state of heavy actinides, the intermediate coupling scheme is usually the favorite. A natural question rises about the 5f orbital occupancy and angular momentum coupling scheme for ASn_3 (A = U, Np, Pu).

X-ray absorption spectroscopy is a powerful technique to measure the electronic transitions between core 4*d* and valence 5*f* states, allowing us to determine the occupancy of 5*f* electrons of actinides. The strong spin-orbit coupling for the 4*d* states leads 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 \mathcal{B} is defined as the relative strength of the $4d_{5/2}$ absorption line [49]. It calibrates the spin-orbit coupling interaction strength in the 5*f* shell. Under the approximation that the electrostatic interaction between core and valence electrons is ignored, the expression for \mathcal{B} is written as [6]

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

where $n_{7/2}$ and $n_{5/2}$ are the 5*f* occupation numbers for the $5f_{7/2}$ and $5f_{5/2}$ states, respectively. The computed results are listed in Table II, obeying $\mathcal{B}(PuSn_3) > \mathcal{B}(NpSn_3) > \mathcal{B}(USn_3)$. The sequence evinces that the angular momentum coupling scheme of three compounds belongs to the intermediate coupling scheme, which is analogous to that in heavy actinides Pu [50] and Cm [51].

Electronic heat capacity. In order to explore the heavyfermion behavior of USn₃, we estimate the specific heat coefficient within the framework of Fermi-liquid theory. Considering the electronic degree of freedom and lattice vibrations, the heat capacity of solid includes two parts $C_v(T) =$ $\gamma T + \beta T^3$. The linear part of heat capacity γT corresponds to the linear specific heat coefficient γ , which is expressed by the following equation:

$$\gamma = \pi k_B^2 \sum_{\alpha} \frac{A_{\alpha}(0)}{Z_{\alpha}},\tag{3}$$

where α means the orbital index, $A_{\alpha}(0)$ denotes the spectral weight at the Fermi level, and Z_{α} is the orbital-resolved renormalization factor [34]. By excluding the contributions from the conduction bands, the calculated electronic specific heat coefficient of 5*f* states at 38.67 K is approximately 172.36 mJ/(mol × K²), which remarkably coincides with the experimental electronic specific heat coefficient of 171 mJ/(mol × K²) [13]. This consistency between the theoretical calculations and experimental results enhances our understanding of the heavy-fermion behavior exhibited by USn₃.

V. CONCLUSION

In summary, we employ the density functional theory in combination with embedded dynamical mean-field theory to extensively study the strongly correlated 5f electronic states of isostructural compounds ASn_3 (A = U, Np, Pu). The apparent quasiparticle weight of 5f states emerges around the Fermi level, accompanied by the narrow 5f electronic band. Both remarkable f-c hybridization and dramatic valence state fluctuations indicate the itinerancy of 5f electrons, facilitating the formation of the paramagnetic ground state in USn₃ and PuSn₃. Generally, correlated 5f electrons are encoded in the renormalized bands and large effective electron mass, which exhibit orbital selective correlation of $5f_{5/2}$ and $5f_{7/2}$ states for NpSn₃. Importantly, the intermediate angular momentum coupling scheme is conducive to probing the occupancy of 5f electrons and emergent physical properties. Consequently, the evolution pattern of strongly correlated 5f electron and itinerant-localized 5f states' dependence on the actinide series provides valuable implications for future research on actinides.

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