Pressure-Driven 5f Localized-Itinerant Transition and Valence Fluctuation in Californium

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A combination of the density functional theory and the single-site dynamical mean-field theory is employed to study the pressure dependence of electronic structure for cubic phase Californium. We predict that its 5f electrons could undergo an orbital-selective localized-itinerant transition under moderate pressure. The volume contraction causes remarkable charge redistribution and valence fluctuation behaviors, which are the driving forces of the divalent-trivalent transition. Additionally, we find that the angular momentum coupling mechanism is hardly affected by pressure. The 5f orbital occupancy is well described by the intermediate coupling scheme.

Introduction. Perhaps the actinides are the most fascinating, but the least understood elements in the Periodic Table. They manifest a plethora of interesting physical properties, such as intricate $P - T$ phase diagrams, low-symmetry crystal structures, multiple valence states, heavy-fermion features, and unconventional superconductivity, but only a few of them were studied by experiments or theoretical calculations [1]. There is no doubt that the physical properties of the actinides are dominated by their electronic structures, specifically, status of their 5f states. The 5f states are usually correlated. There exists tricky interplay between Coulomb interaction, Hund’s exchange, and spin-orbit coupling. The 5f states are also Janus-faced, i.e., they can exhibit either localized or itinerant characteristics depending on their surroundings [2]. The complex nature of the 5f states gives rise to extremely complicated electronic structures and unprecedentedly exotic physics.

Over the last decades, considerable attentions have been given to the light and middle actinides. Of particular interest is plutonium (Pu), which locates at the nexus of an unusual ~ 40% volume change that occurs in the actinides [3]. Clearly, the 5f states of Pu, which go from being delocalized to localized, should be responsible for the dramatic volume change and the other anomalous properties [4, 5]. There have been extensive investigations concerning its magnetism [6–8], electronic structures [9–14], lattice dynamics [15–17], phase transitions and phase stability [18–21]. On the contrary, the late actinides, such as americium (Am), curium (Cm), berkelium (Bk), and californium (Cf), have received much less attentions [22–28]. The reasons are twofold. On one hand, these materials are toxic and radioactive, which makes handling difficult and expensive. On the other hand, it is generally believed that their 5f states are highly localized at ambient pressure, and scarcely contribute to the chemical bonding [26–28]. However, beyond the 5f localized-itinerant transition, we argue that these elements could present many intriguing physical properties under pressure. A typical example is Cf, whose cubic phase could provide an ideal test-bed for investigating the complex behaviors of 5f states.

To our knowledge, Cf is the heaviest actinide on which lattice structure studies can be performed at present [1]. Recently, S. Heathman et al. studied the crystal structure of Cf up to 100 GPa by using both X-ray diffraction and theoretical calculations [29]. They observed four different crystallographic phases. At ambient condition, Cf presents a mixture of Cf-I (double hexagonal-close-packed) and Cf-II (face-centered-cubic) phases. Then the mixture gradually converts to the Cf-II phase under pressure. This transformation is completed at about 14 GPa. Upon additional pressure, the Cf-II phase converts to another mixture of Cf-III (face-centered orthorhombic) and Cf-IV (base-centered orthorhombic) phases, which emerges at about 35 GPa and is retained at least up to 100 GPa. Note that the volume collapse during the II-III transition is about 4.8%, and that during the II-IV transition is about 15%, which are attributed to the delocalization of 5f states again. Cf is also the only actinide to exhibit more than one valence (viz., divalent, intermediate valence, and trivalent states) at near to ambient conditions [1]. Previously theoretical calculations about its 5f – 6d promotion energy suggested that Cf falls into the boundary region between divalent and trivalent metallic bonding [30, 31]. Recent experiments confirmed that its divalent state is metastable, which will transform into the intermediate valence state, and then the trivalent state under moderate pressure [29].

In the present work, we employed a state-of-the-art first-principles many-body approach, namely a combination of the density functional theory and the single-site dynamical mean-field theory (dubbed as DFT + DMFT) [32, 33], to study the electronic structure of cubic Cf-II phase under pressure [34]. This approach has been widely used to study the electronic structures and related physical properties for Pu, Am, Cm, and many other actinide-based materials [7–15]. Our results suggest that external pressure can tune the 5f states in a subtle manner. Several fascinating effects are identified in cubic phase Cf, such as the orbital-selective 5f localized-itinerant transition, divalent-trivalent transition, restricted valence state fluctuation, and collapse of local magnetic moment.

Orbital-selective 5f localized-itinerant transition. Firstly, we calculate the spectral functions of cubic phase Cf with respect to various pressures (or lattice constants $a_0$). We concentrate on the momentum-resolved spectral functions $A(k, \omega)$, the total density of states $A(\omega)$, and the 5f partial density of states $A_{5f}(\omega)$, which are depicted in Fig. 1(a) and (b), respectively. The results endorse the scenario of pressure-driven electronic Lifshitz transition, which could be divided into three different stages. (i) $a_0 > 9.6$ bohr. There are stripe-like band structures in the momentum-resolved spec-
FIG. 1. (Color online). Pressure-dependent electronic structures of cubic phase Cf. (a) Momentum-resolved spectral functions $A(k, \omega)$. The horizontal lines denote the Fermi level. (b) Total density of states $A(\omega)$ (thick solid lines) and $5f$ partial density of states $A_{5f}(\omega)$ (color-filled regions). (c) Imaginary parts of hybridization functions $\Delta(\omega) = -\text{Im}\Delta(\omega)/\pi$. The $5f_{5/2}$ and $5f_{7/2}$ components are represented by thick solid lines and color-filled regions, respectively. (d) The $5f$ band gap as a function of lattice constants. (e) $\beta |G(\tau = \beta/2)|$ as a function of lattice constants, where $G(\tau)$ is the imaginary-time Green’s function for $5f$ orbitals and $\beta = 1/T$ is the inverse temperature. In panels (d) and (e), the letters “M” and “I” mean metallic and insulating characters, respectively.

tral functions, which are associated with the $5f$ states. These bands are nearly flat and far away from the Fermi level, indicating the localized nature of the $5f$ states. The $5f$ partial density of states show obviously insulating behavior. When $a_0 = 10.2$ bohr, the $5f$ band gap is estimated to be $3.0$ eV. (ii) $a_0 \sim 9.6$ bohr. The occupied $5f$ bands are shifted toward the Fermi level. In consequence, the $5f$ band gap is greatly reduced. (iii) $a_0 < 9.6$ bohr. Strong quasi-particle peak emerges at the Fermi level, which is attributed to the itinerant $5f$ states. The $5f$ band gap is completely closed. We thus speculate that there is a small-to-large Fermi surface transition, accompanied by change of the Fermi surface topology [35, 36].

Then we focus on the hybridization functions $\Delta(\omega)$, which are generally used to measure the hybridization strength between the correlated $5f$ and non-correlated $spd$ bands. Fig. 1(c) depicts the imaginary parts of hybridization functions. The $5f - spd$ hybridization mostly takes place at the unoccupied states. However, when $a_0 < 9.6$ bohr, there is sizeable spectral weight transferring from unoccupied to occupied states. All these features suggest that under pressure, the $5f$ states in Cf should undergo a typical localized-itinerant transition. According to the experimental $P-V$ curve [29], the transition will happen around $10$ GPa. Note that similar transitions have been already observed at the high-pressure phases of Am and Cm [25–28].

Let’s make a further analysis about this localized-itinerant transition. Due to the spin-orbit coupling, the $5f$ orbitals can be split into the $5f_{5/2}$ and $5f_{7/2}$ sub-bands. The most astonished thing is that the localized-itinerant transitions don’t occur simultaneously for the $5f_{5/2}$ and $5f_{7/2}$ states. In Fig. 1(d), the $5f$ band gap as a function of lattice constants is plotted. When $a_0 < 9.6$ bohr (or $a_0 > 9.7$ bohr), both the $5f_{5/2}$ and $5f_{7/2}$ states are metallic (or insulating). However, at the intermediate regime (i.e, $9.6$ bohr $< a_0 < 9.7$ bohr), the $5f_{7/2}$ states become metallic while the $5f_{5/2}$ states still retain insulating. In order to confirm the coexistent zone, we further calculate $\beta G(\tau = \beta/2)$, which is in proportion to $A(\omega = 0)$ when $\beta \to \infty$ [37]. The calculated results are quite similar, as is seen in Fig. 1(e). Therefore, we believe that this localized-itinerant transition is orbital-selective, which is an analogy to the orbital-selective Mott insulator-metal transition for multiorbital correlated electron systems [38, 39].
FIG. 2. (Color online). Valence state transition in cubic phase Cf upon volume compression. (a) Valence. The data are evaluated via the formula: valence = 12 − n_{5f}, where n_{5f} is the 5f orbital occupancy. (b) Number of electrons those are promoted from 5f to spd orbitals. (c) Charge fluctuation \( \chi_c = \frac{(\langle n_{5f}^2 \rangle - \langle n_{5f} \rangle^2)}{\beta} \).

FIG. 3. (Color online). Valence state fluctuation in cubic phase Cf upon volume compression. (a)-(c) Probabilities of the 5f atomic eigenstates (or equivalently valence state histograms) for various lattice volumes. (d)-(f) Distributions of 5f atomic eigenstates with respect to N for various lattice volumes. In these panels, only the contributions from the \( N = 8, 9, \) and 10 atomic eigenstates are shown. The contributions from the other atomic eigenstates are too trivial to be seen. (g) Distributions of 5f atomic eigenstates with respect to volume compression. (h) Averaged total angular momentum \( J_{av} \) as a function of lattice constants.

Valence state transition and charge redistribution. As mentioned before, a valence state transition (divalent-trivalent) would take place upon volume compression [29–31]. Previous studies suggested that the low 5f − 6d promotion energy will facilitate this transition, but the underlying mechanism remains unclear so far. In the present work, we investigate the pressure-driven charge fluctuation, and find some useful clues. Firstly, even if the structural transition is ignored and
only the Cf-II phase is considered, we can reproduce the valence state transition [see Fig. 2(a)]. Second, the 5f electrons are mainly promoted to the 6d orbitals, but the electron transfer from 5f to 6p (or 7s) orbitals can not be neglected as well [see Fig. 2(b)]. Third, the charge fluctuation \( \chi_c \) reaches its local maxima at \( a_0 \sim 9.3 \) bohr [see Fig. 2(c)]. Growing 5f-\( spd \) hybridization and the crossover of 5f\(^{10} \) and 5f\(^{9} \) levels may explain this peak. Since \( \chi_c \) is proportional to the system's compressibility [32], it is reasonable to predict that this maxima leads to softening of the entire electronic liquid, which will manifest in the \( P-V \) curve of Cf, in analogy to the fluctuating valence metal Yb [40].

Valence state transition and atomic eigenvalues fluctuation. The valence state histogram \( p_T \) represents the probability to find a valence electron in a given atomic eigenstate \( |\psi_T \rangle \), which is in general labelled by assorted good quantum numbers, such as \( N \) (occupancy), \( J \) (total angular momentum), and \( \gamma \) (it stands for the rest good quantum numbers). It is a versatile tool to study the electronic configurations of realistic materials [9]. In Fig. 3(a)-(c), the valence state histograms for three typical cases \( (a_0 = 9.0, 9.6, \text{and } 10.2 \) bohr) are shown. The corresponding distributions of 5f atomic eigenstates with respect to \( N \) are illustrated in Fig. 3(d)-(f). When \( a_0 = 10.2 \) bohr, the atomic eigenvalues fluctuation is very weak. The 5f electrons are virtually locked into the 5f\(^{10} \) configuration, and the valence state histogram is peaked only at the ground state of the atom (i.e., \( |N = 10, J = 8, \gamma = 0 \rangle \)). Cf behaves like a divalent metal (valence \( \sim 2.0 \), \( n_{5f} \sim 10.0 \)). When \( a_0 = 9.6 \) bohr, the atomic eigenvalues fluctuation gets to be significant. Though the 5f\(^{10} \) configuration remains predominant, the contributions from the 5f\(^{9} \) configuration are not trivial. As a result, Cf begins to exhibit mixed-valence properties (valence \( \sim 2.2 \), \( n_{5f} \sim 9.8 \)). When \( a_0 = 9.0 \) bohr, the dominant atomic eigenstate is \( |N = 9, J = 7.5, \gamma = 0 \rangle \), which is also the ground state of the atom. The atomic eigenstate \( |N = 10, J = 8, \gamma = 0 \rangle \) becomes less important. It appears that the 5f electrons live a double life, spending nearly all the time in the two states. In other words, the atomic eigenstates fluctuation only involves two principal states. The other atomic eigenstates are practically excluded. We call this behavior as "restricted atomic eigenstate fluctuation", which distinguishes Cf from the other typical mixed-valence materials, such as Pu \( [8,9] \). At this moment, Cf is nearly a trivalent metal (valence \( \sim 2.7 \), \( n_{5f} \sim 9.3 \)). Fig. 3(g) shows the probabilities for the 5f\(^{8} \) - 5f\(^{11} \) configurations. The probabilities for the 5f\(^{10} \) configuration increase monotonously against the lattice constants, while the trends for the other configurations are opposite. Besides, we find that there is a cross for the 5f\(^{10} \) and 5f\(^{9} \) configurations at \( a_0 \sim 9.3 \) bohr, which is related to the local maxima spotted in the local charge fluctuation \( \chi_c \). Accordingly, we believe that the charge redistribution and atomic eigenstates fluctuation are probably the driving forces for the divalent-trivalent transition.

Apart from the valence and the 5f occupancy, it is also helpful to study the evolution of the other physical quantities with respect to the lattice constants. We calculate the averaged total angular momentum \( J_n \) via the following equation:

\[
J_n = \sum_p p_f J_f, \quad \text{where } J_f \text{ denotes the total angular momentum for the atomic eigenstate } |\psi_f \rangle. \]

The results are plotted at Fig. 3(h). As expected, we observe sizeable collapse for \( J_n \) under pressure. Note that \( J_n \) declines more quickly when \( a_0 < 9.6 \) bohr. Since \( J_n \) is tightly connected with the local magnetic moment \( \mu \). It is plausible to suspect that \( \mu \) should exhibit the same tendency, which is similar to the high-spin to low-spin transition in multi-orbital Mott systems [41].

5f orbital occupancy and angular momentum coupling. As is well known, there are two standard ways to couple the angular momenta of multi-electronic systems: Russell-Saunders (LS) and \( jj \) coupling. Provided that the spin-orbit coupling is weak compared to the electrostatic interactions, the LS coupling is favourable, or else the \( jj \) coupling wins [1]. As for the actinides, however, both the spin-orbit coupling and the electrostatic interactions are important. In this regard, the intermediate coupling (IC) scheme which takes both interactions into account is more appropriate [42]. One exception to this rule is uranium, which exhibits LS coupling. What’s the angular momentum coupling scheme for Cf? Will it be changed under pressure? In order to answer these questions, we calculate its 5f orbital occupancy (see Fig. 4). The calculated values obviously favor the IC scheme. For example, given that \( n_{5f} \sim 10.0 \) \( (a_0 = 10.2 \) bohr\), the calculated \( n_{7/2} \) is approximately 4.23 [43]. However, the theoretical occupation numbers for 5f\(^{7} \) states are 4.86, 4.0, and 4.18 by LS, \( jj \), and IC coupling schemes, respectively. The corresponding errors are 14.9%, -5.4%, and -1.2%, respectively. Hence, we infer that the IC scheme still holds for Cf at ambient condition. Furthermore, the angular momentum coupling scheme won’t be changed over the entire pressure (or volume) range of interest. Because the 5f orbital occupancy can be used to calculate the X-ray branching ratio, the electron energy-loss spectroscopy

![Graph](image_url)
and X-ray absorption spectroscopy can be employed to validate our results.

Conclusions. We have examined the pressure-driven 5f localized-itinerant transition and valence fluctuation in cubic phase Cf by using the DFT + DMFT approach. We believe that the 5f localized-itinerant transition is orbital-selective. There exists a considerable volume range where the insulating 5f5/2 state and the metallic 5f3/2 state could coexist. We also interpret the divalent-trivalent transition as a result of charge redistribution and valence state fluctuation. The valence state fluctuation is greatly restricted. It mainly involved two atomic eigenstates, in contrast to common fluctuating valence materials. Perhaps most importantly we confirm that Cf still obeys the IC scheme, which is not affected by pressure. Our results reveal that the 5f electronic structures for the late actinides under pressure are very interesting. Further theoretical and experimental investigations are highly desired.

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