Unraveling the 4f electronic structures of cerium monopnictides

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Abstract

We employed a state-of-the-art first-principles many-body approach, namely the density functional theory in combination with the single-site dynamical mean-field theory, to study the 4f electronic structures in cerium monopnictides (CeX, where X = N, P, As, Sb, and Bi). We find that the 4f electrons in CeN are highly itinerant and mixed-valence, showing a prominent quasiparticle peak near the Fermi level. On the contrary, they become well localized and display weak valence fluctuation in CeBi. It means that a 4f itinerant-localized crossover could emerge upon changing the X atom from N to Bi. Moreover, according to the low-energy behaviors of 4f self-energy functions, we could conclude that the 4f electrons in CeX also demonstrate interesting orbital-selective electronic correlations, which are similar to the other cerium-based heavy fermion compounds.

Keywords: dynamical mean-field theory, electronic correlation, itinerant-localized crossover, valence fluctuation

(Some figures may appear in colour only in the online journal)

1. Introduction

The cerium-based heavy fermion materials, which exhibit a variety of fascinating and exotic properties (including topology, unconventional superconductivity, quantum criticality, mixed-valence behavior, Kondo physics, and so on), have renewed a lot of interests in recent years [1, 2]. It is generally believed that the physical and chemical properties of cerium-based heavy fermion materials are governed by their 4f electronic structures [3–6], which are very sensitive to the surrounding environment, such as external pressure, temperature, element substitution, and electromagnetic field, etc.

For instance, Ce$_3$Bi$_4$Pt$_3$ (a noncentrosymmetric Kondo insulator), is such an archetypal heavy fermion compound [7]. Experimentally, it has been found that a phase transition from topological Kondo insulator (TKI) to Weyl–Kondo semimetal (WKSIM) could be realized via simple Pt–Pd substitution, i.e., from Ce$_3$Bi$_4$Pt$_3$ to Ce$_3$Bi$_4$Pd$_3$ [8]. Further theoretical calculations suggest that the underlying mechanism of the TKI–WKSIM transition is the large mass difference between Pt and Pd atoms, which leads to a big discrepancy in the strength of spin-orbital coupling, and thus has an unprecedentedly drastic influence on the hybridization between 4f and p electrons [9]. These experimental facts manifest that Ce$_3$Bi$_4$Pt$_3$ and its substitution series Ce$_3$Bi$_4$(Pt$_{1-x}$Pd$_x$)$_3$ (0 ≤ x ≤ 1) are versatile platforms for studying the interplay between topology and electronic correlation under the influence of external conditions [10, 11]. In addition, CeTIn$_5$ (T = Co, Rh, and Ir) [3, 4] and CeM$_2$Si$_2$ (M = Ru, Rh, Pd, and Ag) [12] are also classic examples for examining the intriguing properties of cerium-based heavy fermion materials.

In the present work, we turn to another interesting series of cerium-based heavy fermion compounds, namely cerium monopnictides CeX, where X = N, P, As, Sb, and Bi. These compounds crystallize in the rock-salt structure (see figure 1), where the Ce atoms form a face-centered-cubic Bravais lattice, while the X atoms occupy the octahedral voids in the lattice [13]. Owing to the peculiar electronic and magnetic properties (see table 1), the cerium monopnictides have attracted lots of attentions. All of the CeX compounds develop some kinds of antiferromagnetic ordering at low temperature, except for CeN. Especially, CeSb and CeBi exhibit extremely compli-
mixed-valence nature, lattice dynamics, and elastic properties, produced by first-principles calculations [32–37]. Particularly, the electronic spectra of Ce, being itinerant or localized. On the theoretical side, the experimental features in cerium-based heavy fermion materials. We wonder whether Ce could evince similar behaviors or not. Notice that CeN was recognized as an intermediate mixed-valence compound [45–50]. In addition, CeP undergoes an isostructural transition (~8% volume collapse) together with considerable change of 4f valence state under moderate pressure [51]. However, we do not know quite well the other cerium monopnicnides. In order to tackle these problems, we try to study the electronic structures of CeX thoroughly via the density functional theory merged with the single-site dynamical mean-field theory [52]. According to the calculated results, we find that CeX is a good testing bed not only for exploring evolution of 4f electronic states tuned by spin-orbital coupling, but also for studying subtle entanglement between electronic correlation and magnetism.

Table 1. Lattice constants and key physical properties of CeX [13], where SM denotes semimetal, SC semiconductor, PM paramagnetism, AFM antiferromagnetic state, and $T_N$ the Neel temperature. Notice that CeX usually exhibits some kinds of magnetic ordering, except for CeN.

| X  | $a$ (Å) | Metallicity | Ordering | $T_N$ (K)  |
|----|--------|-------------|----------|------------|
| N  | 5.013  | SM          | PM       | —          |
| P  | 5.942  | SC          | AFM      | 6–9        |
| As | 6.060  | SC          | AFM      | 5–7.5      |
| Sb | 6.400  | SM          | AFM (complicated) | 16       |
| Bi | 6.490  | Metal       | AFM (complicated) | 25       |

The $f-p$ mixing model [42–44] based on the anisotropic hybridization between the Ce-4$f$ level and the ligand X-$p$ band is widely utilized to explain the complex antiferromagnetic ordering phases [13]. However, since the 4$f$ electrons are usually correlated, the traditional first-principles approaches often underestimate the electron correlation and cannot formulate a reliable physical picture of the 4$f$ electronic structures of CeX. Furthermore, large spin-orbital coupling and intricate magnetic ordering states make the theoretical calculations quite difficult. Consequently, it seems tough to acquire an accurate and comprehensive description for the electronic structures of CeX.

Though many efforts have been devoted to understanding the unusual properties of CeX in the past decades, there are still some issues and questions that need to be solved and answered [13, 24, 28, 32–37]. First of all, how do the 4$f$ electronic states evolve when X goes from N to Bi? In general, the lattice constants and strength of spin-orbital coupling should vary with respect to X’s atomic mass. The hybridization between Ce-4$f$ and X-$p$ bands should be modified as well. We suspect that these changes could probably drive a 4$f$ itinerant-localized crossover or transition in this series. Second, how to explain the complicated magnetic ordering states in CeSb and CeBi? Are they related to the increment of 4$f$ electronic localization or anything else? Third, it is suggested that valence state fluctuation and orbital-dependent electronic correlation are universal features in cerium-based heavy fermion materials. We wonder whether Ce could evince similar behaviors or not. Notice that CeN was recognized as an intermediate mixed-valence compound [45–50]. In addition, CeP undergoes an isostructural transition (~8% volume collapse) together with considerable change of 4$f$ valence state under moderate pressure [51]. However, we do not know quite well the other cerium monopnicnides. In order to tackle these problems, we try to study the electronic structures of CeX thoroughly via the density functional theory merged with the single-site dynamical mean-field theory [52]. According to the calculated results, we find that CeX is a good testing bed not only for exploring evolution of 4$f$ electronic states tuned by spin-orbital coupling, but also for studying subtle entanglement between electronic correlation and magnetism.

The rest of this paper is organized as follows. In section 2, the computational details are introduced. In section 3, the electronic band structures, total and partial 4$f$ density of states, hybridization functions, 4$f$ self-energy functions, and histograms of atomic eigenstates are presented. The consistency between calculated and experimental data is illustrated. In section 4, we attempt to clarify some important topics about the double counting scheme, the 4$f$ itinerant-localized crossover, the role played by spin-orbital coupling and the possible relationship between electronic correlation and magnetic ordering states. Finally, section 5 serves as a brief conclusion.

2. Methods

As mentioned above, since the 4$f$ electrons in CeX are correlated, we have to consider the correlation effect carefully in the calculations. In the present work, we employed the density
functional theory plus single-site dynamical mean-field theory (DFT + DMFT) approach [52]. It incorporates the band picture inheriting from the DFT part, and a non-perturbative treatment to the $4f$ electronic correlation from the DMFT perspective. It has been widely used to study the electronic structures of many cerium-based heavy fermion materials [3, 4, 6, 12, 53–55]. Note that the DFT + DMFT method has been applied to study CeX’s electronic structures a few years ago [33, 35–37, 56]. Those works using the spin-polarized $T$-matrix fluctuation-exchange solver for CeN [33] and the non-crossing approximation as quantum impurity solver could reproduce the Kondo peak around the Fermi level. Recent progress has been achieved in the electronic structure of a large group of cerium-based compounds by combining many-body theory with large databases [57]. It is reported that the localized degree of $4f$ electrons could be obtained from the hybridization functions, which is consistent with available experimental data. These theoretical advances provide a new approach to understand the electronic structure and related physical properties of cerium-based compounds.

Here we used the WIEN2K code [58] to perform the DFT calculations, which implements a full-potential augmented plane wave formalism. The experimental crystal structures of CeX are used. The muffin-tin radii for Ce is 2.5 a.u. and from N to Bi are 2.08 a.u., 2.38 a.u., 2.50 a.u., 2.50 a.u., respectively [59]. The $k$-points mesh for Brillouin zone integration is $21 \times 21 \times 21$. The generalized gradient approximation, namely the Perdew–Burke–Ernzerhof functional [60] is adopted to express the exchange–correlation potential. The spin-orbital coupling of cerium atom is considered in a second-variational procedure and the eigenvalues as well as eigenvectors are computed using the scalar-relativistic wavefunctions. Besides, the effect of spin-orbital coupling of X atoms on electronic structure is also addressed in section 4.

The basic idea of the DMFT is to map the quantum lattice model to a quantum impurity model self-consistently and solve the obtained quantum impurity model by using various quantum impurity solvers [52]. We employ the EDMFT software package [61] to accomplish this job. The constructed multi-orbital quantum impurity models are solved using the hybridization expansion continuous-time quantum Monte Carlo impurity solver (dubbed as CT-HYB) [62–64]. As mentioned before, the Ce-$4f$ orbitals are treated as correlated. The Coulomb interaction matrix was constructed by using the Slater integrals $F^0$, $F^2$, $F^4$ and $F^6$ [65]. The fully rotationally invariant formulation is used for interaction with the Coulomb repulsion interaction $U$ and the Hund’s exchange interaction $J_H$ are 6.0 eV and 0.7 eV, respectively [12, 55]. The fully localized limit (FLL) scheme [66] is used to describe the double counting term in $4f$ self-energy functions. The widely used FLL scheme is suitable for the relatively itinerant $4f$ states of CeN and localized $4f$ states of CeX ($X = P, As, Sb$, and Bi). In order to simplify the calculations, we not only utilize the good quantum numbers $N$ and $J$ to reduce the sizes of matrix blocks of the local Hamiltonian, but also make a truncation for the local Hilbert space [64]. Only those atomic eigenstates with $N \in [0, 3]$ are retained in the calculations. The lazy trace evaluation trick is used to accelerate the Monte Carlo sampling further. Since the inverse temperature $\beta = 100$ ($T \sim 116.0$ K), it is reasonable to retain only the paramagnetic solutions. We perform charge fully self-consistent DFT + DMFT calculations. For each DMFT iteration, $16 \times 10^8$ Monte Carlo steps were performed to reach sufficiently high accuracy. Of the order of 80 DFT + DMFT iterations are required to obtain good convergence for the chemical potential $\mu$, charge density $\rho$, and total energy $E_{\text{DFT+DMFT}}$. The convergence criteria for charge and energy are $10^{-3}$ $e$ and $10^{-5}$ Ry, respectively. The Matsubara self-energy functions $\Sigma(i\omega_n)$ generated in the last 10 DFT + DMFT iterations are collected and then averaged for further post-processing.

3. Results

3.1. Momentum-resolved spectral functions

At first, we performed analytical continuation on the Matsubara self-energy functions $\Sigma(i\omega_n)$ by using the maximum entropy method [67]. Then the obtained self-energy functions on real axis $\Sigma(\omega)$ are used to calculate the momentum-resolved spectral functions $A(k, \omega)$ and density of states $\rho(\omega)$ [61].

The momentum-resolved spectral functions $A(k, \omega)$ of CeX along the high-symmetry lines $X-\Gamma-W$ in the first irreducible Brillouin zone are shown in figure 2. Clearly, this series can be roughly classified into two kinds. As for CeN, the most prominent feature is the intense flat band structure near the Fermi level, which is likely from the contributions of $4f$ orbitals. It indicates that the $4f$ electrons in CeN are itinerant and take part in active chemical bonding. As for CeP, CeAs, CeSb, and CeBi, the situations are somewhat different. Their spectral functions share some common characteristics: (i) for CeP and CeAs, the flat band features near the Fermi level are still discernible, but they become much dimmer and weaker than that observed in CeN. For CeSb and CeBi, the flat bands around the Fermi level are almost invisible, implying the completely localized $4f$ orbitals. (ii) The ligand $p$ bands are slightly renormalized and shifted toward the Fermi level as compared to those of CeN. We also notice hole pockets at the $\Gamma$-point corresponding to $X-5p$ bands, and electron pockets at the $X$-point belonging to Ce-$5d$ states [28]. (iii) The $4f-p$ hybridization is apparent when $\omega > 2.0$ eV.

3.2. Density of states and hybridization functions

In figures 3(a) and (b), the total and $4f$ partial density of states of CeX are shown, respectively. For CeN, there exist sharp and strong quasiparticle resonance peaks in the vicinity of Fermi level, and a large ‘hump’ between 3 eV and 8 eV. According to figure 3(b), the quasiparticle resonance peaks consist of the low-lying $4f_{5/2}$ [see figure 3(b2)] and high-lying $4f_{7/2}$ [see figure 3(b1)] states. The splitting energy between these two states is approximately 300 meV, which is in accordance with those measured in the other cerium-based heavy fermion compounds [3, 4]. The predominant contribution to the ‘hump’ comes from the upper Hubbard bands. The central energy is about 4.5 eV. Since most of the $4f$ states are unoccupied, the majority of $4f$ spectral weights is above the Fermi level. The lower Hubbard bands are extremely weak. Concerning the rest
of cerium monopnictides, the quasiparticle resonance peaks are greatly reduced. For CeSb and CeBi, these peaks nearly disappear. The upper Hubbard bands are shifted obviously to the Fermi level, which suggest again that the Ce-4f orbitals become more localized and correlated when X = P, As, Sb, and Bi than X = N.

Figures 3(c2) and (c1) depicts hybridization functions for the 4f_{5/2} and 4f_{7/2} states, respectively. It is observed that whether the 4f_{5/2} state or the 4f_{7/2} state, -3Δ(ω = 0)/π (i.e., the 4f hybridization function at the Fermi level) in CeN is always larger than those in CeX (where X = P, As, Sb, and Bi). It means that when X changes from N to Bi, the hybridization between Ce-4f and X’s ligand orbitals is gradually suppressed.

The density of states of CeX has been extensively studied by using PES several decades ago. In order to verify the correctness of our calculations, we try to compare the calculated results with the available experimental data in figure 4. Let us concentrate on CeN at first. The representative two-peak structure with a small shoulder peak around -2 eV is correctly reproduced by our DFT + DMFT calculations [34, 46, 50]. For the unoccupied state, the broad ‘hump’ between 3 eV and 8 eV is successfully captured. This feature is ascribed to the 4f^2 atomic multisets. As for CeP and CeSb, the calculated results are in reasonably good agreement with the experimental spectra, including the shoulder peaks near -3 eV and a small quasiparticle resonance peak in CeP. However, the main peak of CeAs is about 1 eV difference between calculation and experimental results. The small discrepancies between the theoretical and experimental spectra are likely attributed to the uncertainty in the Coulomb interaction parameters and the use of oversimplified double counting scheme [66]. Thus, we come to a conclusion that our DFT + DMFT calculated results are reliable and reasonable.

3.3. Self-energy functions

In general, the electronic correlation effect is encapsulated by the self-energy function [68]. Traditionally, the self-energy functions can be calculated via the Dyson’ equation [52]. The resulting data are usually fluctuating and full of noise. In the present work, in order to obtain high-precision data for the self-energy functions, we try to measure them directly in the CT-HYB quantum impurity solver [64]. In figure 5, the imaginary parts of 4f self-energy functions are illustrated. First of all, the low-frequency parts of self-energy functions show very strong orbital differentiation. The low-frequency behaviors of the 4f_{5/2} and 4f_{7/2} states are completely different, which means that the 4f electronic correlation in CeX is probably orbital dependent. It is not at all surprised because this phenomenon has been identified in many cerium-based heavy fermion materials [12, 54] and strongly correlated 5f electron systems [69] a few years ago. Second, the 4f self-energy functions of CeN are quite distinctive from those of the other cerium monopnictides. For example, the low-frequency part of 4f_{5/2} state of CeN exhibits remarkable quasi-linear behavior. It signifies a (heavy) Fermi-liquid state. However, the corresponding parts of CeX are convex (X = P and As) or concave (X = Sb and Bi). Third, the intercept of self-energy function in y-axis is approximately zero for CeN. While for the other cerium monopnictides, the intercepts are finite. It means that the low-energy scattering of 4f electrons in CeX is much smaller than those in the rest of cerium monopnictides. Fourth, the low-energy scattering of the 4f_{7/2} states is usually smaller than that of the 4f_{5/2} states.

Based on the self-energy data, the quasiparticle weight Z and effective electron mass m* can be evaluated via the following equation [52]:

$$Z^{-1} = \frac{m^*}{m_e} \approx 1 - \frac{\sum_i \Delta(\omega_0)}{\omega_0},$$

where \(\omega_0 = \pi/\beta\) and \(m_e\) denotes the mass of non-interacting band electron. The calculated Z and m* are summarized in table 2. We find that the 4f_{7/2} states are less renormalized. Its Z \(\approx 0.4–0.7\) and \(m^* \approx 1.3–2.5 m_e\). However, the 4f_{5/2} states are strongly renormalized. Notice that CeAs exhibits the largest \(m^*\) and smallest Z, implying that its 4f electrons are probably the most correlated. It can be phenomenologically understood as the competition between the two forces below. The first one is the increase of 4f electronic correlation with increasing lattice constants of CeX (table 1). The reverse one is that 4f states tend to become less correlated with enlarging X atoms. The interplay of these two factors gives rise to the strongest 4f electronic correlation of CeAs among the CeX compounds. Since the ratio \(R \equiv Z(4f_{7/2})/Z(4f_{5/2})\) is so large \((R \sim 1.25\) for CeN, and \(R > 20\) for CeP, CeAs, CeSb, and
Figure 3. Electronic density of states of CeX (X = N, P, As, Sb, and Bi). (a) Total density of states (thick solid lines) and partial 4f density of states (color-filled regions). (b) The \( j \)-resolved 4f partial density of states. The 4f\(5/2\) and 4f\(7/2\) components are represented in (b2) and (b1), respectively. (c) Imaginary parts of hybridization functions. The 4f\(5/2\) and 4f\(7/2\) components are depicted in (c2) and (c1), respectively. The vertical dashed lines denote the Fermi level. All of the data presented in panels (b1), (b2) and (c1), (c2) are rescaled for a better view.

Figure 4. (a)–(d) Comparisons of theoretical and experimental density of states for CeN, CeP, CeAs, and CeSb, respectively. In panel (a), the UPS data (filled red circles) and BIS data (filled green circles) are taken from references [46] and [50], respectively. In panels (b)–(d), the experimental UPS data are taken from reference [46]. The Fermi levels \( E_F \) are represented by vertical dashed lines. Notice that the spectral data have been rescaled and normalized for a better visualization.

Figure 5. Imaginary parts of Matsubara 4f self-energy functions. (a) 4f\(5/2\) components. (b) 4f\(7/2\) components. The self-energy data are measured directly in the CT-HYB quantum impurity solver, instead of being calculated by Dyson’s equation.

3.4. Valence state fluctuations

Valence state fluctuation or mixed-valence behavior is a common feature in many cerium-based heavy fermion materials [12]. In the present work, by utilizing the atomic eigenvalue probability \( p_\Gamma \), which stands for the probability to find out a 4f valence electron in a given atomic eigenstate \( |\psi_\Gamma\rangle \), we can make a reliable estimation about the magnitude of valence state fluctuation in CeX. The CT-HYB quantum impurity solver is capable of recording the atomic eigenvalue probability \( p_\Gamma \) [64]. In figure 6, the calculated results for CeX are illustrated as histograms. Here, the atomic eigenstates \( |\psi_\Gamma\rangle \) are labelled by using some good quantum numbers such as total occupation \( N \) and total angular momentum \( J \). Generally, the atomic eigenstates are rearranged into three groups, namely, \( N = 0, N = 1 \) and \( N = 2 \), which obey increasing energy sequence.
Their probabilities account for 22% and 20%, respectively. Therefore, it is suggested that the 4f electrons in CeN favor to fluctuate among the above three principle competing atomic eigenstates and become itinerant through hybridization with ligand electrons. When X changes from N to P, As, Sb, and Bi, the corresponding atomic eigenstate probability for $|N = 1, J = 2.5, \gamma = 0\rangle$ soars from 50% to 90%. At the same time, the atomic eigenstates probabilities for $|N = 0, J = 0, \gamma = 0\rangle$ and $|N = 1, J = 3.5, \gamma = 0\rangle$ decrease rapidly. For CeP and CeAs, they account for less than 4%. For CeSb and CeBi, they are less than 1% and are nearly invisible in figures 6(d) and (e). It seems that the 4f electrons in CeP, CeAs, CeSb, and CeBi are very localized, and virtually confined to the primary atomic eigenstate $|N = 1, J = 2.5, \gamma = 0\rangle$. Meanwhile, the corresponding valence state fluctuations are very weak. In short, the redistribution of atomic eigenstates probabilities strongly relies on the atomic number X.

By summing up the atomic eigenstates probabilities $p_{N\gamma}$ with respect to N, we can derive the distribution of 4f electronic configurations. It will provide further information about the 4f valence state fluctuations and mixed-valence behaviors. In CeN, on one hand, the 4f$^1$ configuration is predominant and its probability is about 70%. On the other hand, the probabilities of the 4f$^2$ and 4f$^3$ configurations are about 20% and 9.2%, respectively. It indicates the mixed-valence nature of CeN, which accords with the findings of previous experiments [45–50]. For X = P, As, Sb, and Bi, the 4f$^1$ configuration actually becomes more overwhelming. Its probability is larger than 90%, while those of the 4f$^2$ and 4f$^3$ configurations decline to less than 6%. It means that the 4f valence state fluctuation in CeN is the most remarkable. When X grows from N to Bi, the 4f valence state fluctuations will be greatly suppressed. In consequence, the mixed-valence behaviors will become very trivial.

### 4. Discussions

In this section, we would like to discuss some important issues and questions.

**Choice of double counting scheme.** Since the double counting term plays a vital role in describing the electronic structure, we briefly compare the FLL and around mean field (AMF) double counting schemes to select the adequate one. It is well known that the FLL double counting scheme is suitable for localized 4f systems, such as CeX, X = P, As, Sb, and Bi. It is supposed not applicable to metallic delocalized 4f states of CeN. Here we examine the AMF double counting scheme [70] based on the mean-field theory which considers uniform occupation of the correlated states and is capable to compute the relatively itinerant systems. At first glance, figure 7 shows that the main Kondo resonance around the Fermi level is captured with both using FLL and AMF double counting schemes. With a close inspection, the peak just above the Fermi level in BIS spectra is better reproduced by FLL double counting scheme than the AMF double counting scheme. Consequently, it is guessed that FLL double counting scheme is suitable for CeX, X = N, P, As, Sb, and Bi.
Figure 7. Comparisons of theoretical and experimental total density of states for CeN with FLL (a) and AMF (b) double counting schemes, respectively.

Figure 8. Total density of states (a) and partial 4f density of states (b) for CeN and CeBi, where thick solid lines denote the density of states with spin-orbital coupling of N (Bi) atom and color-filled regions mean the density of states without spin-orbital coupling of N (Bi) atom.

4f itinerant-localized crossover or transition. According to the momentum-resolved spectral functions and density of states, we believe that the 4f electrons in CeN are itinerant, while they tend to be localized in CeP, CeAs, CeSb, and CeBi. In other words, the 4f itinerant-localized crossover may occur between CeN and CeP. Provided that the N atom in CeN is substituted gradually by X atoms (X = P, As, Sb, or Bi), a 4f itinerant-localized crossover is naturally expected. Then a new question rises: what’s the driving force of this crossover? First, when X grows from N to Bi, the lattice constants of CeX increase monotonously [13]. The unit cell volume of CeBi is almost twice of the one of CeN (see table 1). The larger Ce–Ce bond length is, the more localized the 4f electrons become. Second, we think that the spin-orbital coupling effect of X’s p orbitals should play a nontrivial role in this crossover. Generally, the spin-orbital coupling is stronger for the heavier elements, where the electrons acquire large velocities near the nucleus. So, $\lambda_{\text{Bi},6p} > \lambda_{\text{Sb},5p} > \lambda_{\text{As},4p} > \lambda_{\text{P},3p} > \lambda_{\text{N},2p}$, where $\lambda$ denotes the strength of spin-orbital coupling. Thus, the hybridization between Ce’s 4f and X’s np ($n = 2$–6) orbitals should be tuned inevitably by the spin-orbital coupling. Notice that this mechanism is quite similar to the TKI–WKSM transition observed in $\text{Ce}_3\text{Bi}_4(\text{Pt}_{1-x}\text{Pd}_x)_3$ series, which is actually driven by the difference in spin-orbital coupling between Pt and Pd atoms [7–9].

To further explore the effect of spin-orbital coupling (SOC) on 4f states evolution against increasing X atom, we examined the electronic structure with and without SOC for two typical compounds CeN and CeBi. As is shown in figure 8, the total density of states and partial 4f density of states for CeN are almost the same. For CeBi, 4f states are mostly localized with tiny spectral weight near the Fermi level, so the broad ‘hump’ between 2 eV and 6 eV is slightly different with SOC and without SOC. By that analogy, density of states for CeP, CeAs and CeSb are similar with SOC and without SOC. It is discovered that spin-orbital coupling effect of X atoms may not play a key role in the itinerant-localized crossover of 4f electrons as previously expected.

Evolution of 4f electronic structures in CeX. The 4f electronic structures of CeX share some common features. The 4f electrons are all correlated. The electronic correlations are orbital dependent, i.e., the 4f_{5/2} states are much more correlated than the 4f_{7/2} states. The evidence is that the quasiparticle weight $Z$ (or effective electron mass $m^*$) of the 4f_{5/2} states is much smaller (or larger) than the one of the 4f_{7/2} states. On the other hand, the 4f electronic structures of CeN differ from all the other CeX compounds obviously. The 4f electrons in CeN are itinerant, with strong valence state fluctuation. We can observe the quasiparticle resonance peak in the Fermi level and Fermi-liquid-like behavior in the low-frequency parts of 4f self-energy functions. Conversely, the 4f electrons in the other CeX compounds are totally localized. The 4f–p hybridization near the Fermi level and valence state fluctuation are rather weak. Apparently, their self-energy functions deviate from the description of Landau Fermi-liquid theory. They are also not mixed-valence compounds under ambient condition, though there are some experimental evidences that these compounds might come to be mixed-valence under moderate pressure [51].
Electronic correlation and magnetism in CeX. Usually the ground states of CeX (X = P, As, Sb, and Bi) are antiferromagnetic, except for the paramagnetic CeN [13]. It is easy to understand because the 4f electrons in CeX are localized and tend to form local moments. Among these compounds, CeSb and CeBi are well known due to their complicated magnetic phase diagram under pressure or under magnetic field [14–17]. Previous studies suggested that these unusual magnetic properties originate from the small crystal field splitting. They guessed that the crystal field excited state with T2g character is pulled down below the crystal field ground state Γ7 owing to the 4f localization and 4f−p mixing effect. Then stacking magnetic structures are formed with strongly polarized Γs Ce layer and paramagnetic Γ7 Ce layer. This scenario looks good, but it requires the cubic symmetry. However, when CeSb and CeBi transform from paramagnetic phase to ordered phases, their crystal structures also distort from the cubic ones to the tetragonal ones [13]. Furthermore, their lattice constants in the tetragonal structures (along a-axis and c-axis) diminish with decreasing temperature when T < Tc. Thus, the above model may be not enough to explain the atypical magnetic properties of CeX. A credible model for this problem should at least take the temperature-dependent crystal structures and the corresponding crystal field splitting into considerations. Anyway, we anticipate that the 4f electronic correlations should play an important role in the electronic structures and magnetic properties of CeSb and CeBi with tetragonal symmetry. More DFT + DMFT calculations are being undertaken.

5. Conclusion

In summary, the 4f electronic structures of cerium-based monopnictides CeX (X = N, P, As, Sb, and Bi) have been systematically investigated by using the DFT + DMFT approach. The momentum-resolved spectral functions A(k, ω), total and 4f partial density of states A(ω) and A_{4f}(ω), hybridization functions, Matsubara self-energy functions, and 4f valence state fluctuations are studied. The calculated results are consistent with the available experimental data. However, since the experimental data are very limited, most of the calculated results act as useful predictions. It is confirmed that 4f states of CeN are the most itinerant among the five compounds and display mixed-valence behavior. It is proposed that the 4f itinerant-localized crossover probably takes place between CeN and CeP, which is accompanied by vanishing of quasiparticle resonance peak at the Fermi level and regression of 4f valence state fluctuation. In particular, the orbital-dependent 4f correlations are identical in CeX. Their 4f_{3/2} orbitals are more correlated and more renormalized than the 4f_{7/2} orbitals, which is in analogy with the other cerium-based heavy fermion compounds. Finally, we would like to point out that the 4f electronic structure is tightly connected with the magnetism of CeX. In order to interpret the intricate magnetic orderings in CeSb and CeBi, which remains a long standing issue and yet to be answered, a deep understanding about the 4f electronic structures of CeX is indispensable. The present study about CeX’s 4f electronic structures fills in this gap, and enriches our knowledge about the exotic properties of cerium-based heavy fermion compounds. However, further experimental and theoretical validations are still highly desired.

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