Itinerant-localized crossover and orbital dependent correlations for 4f electrons in cerium-based ternary 122 compounds

Haiyan Lu and Li Huang

Science and Technology on Surface Physics and Chemistry Laboratory, P.O. Box 9-35, Jiangyou 621908, China

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The electronic structures of cerium-based ternary 122 compounds CeM₃Si₂, where M = Ru, Rh, Pd, and Ag, are investigated systematically by using the density functional theory in combination with the single-site dynamical mean-field theory. The momentum-resolved spectral functions, total and 4f partial density of states, self-energy functions, and valence state fluctuations are calculated. The obtained results are in good accord with the available experimental data. It is suggested that, upon increasing atomic number from Ru to Ag, the 4f electrons should become increasingly localized. An itinerant-localized crossover for 4f electrons driven by chemical pressure may emerge when M changes from Pd to Ag. Particularly, according to the low-frequency behaviors of 4f self-energy functions, we identify an orbital selective 4f insulating state in CeAg₃Si₂, which is totally unexpected.

I. INTRODUCTION

The cerium-based heavy fermion systems and intermediate valence compounds exhibit a variety of interesting and exotic properties, such as quantum criticality, quantum phase transition, unconventional superconductivity, non-Fermi-liquid behavior, and valence state fluctuation, just to name a few. They have attracted much attention in recent years. It is generally believed that all these features largely originate in the strongly correlated 4f electrons, which manifest Janus-faced behavior (localized or itinerant) depending on surrounding environment. Naturally, an essential question is raised: how and where the 4f electron changes its nature from itinerant to localized, or vice versa? It has been one of the longstanding research issues in the condensed matter physics.

In cerium-based heavy fermion systems and intermediate valence compounds, Kondo temperature \( T_K \) is an important energy scale. According to the well-known Doniach phase diagram, cerium’s 4f electrons hybridize with conduction electrons and form coherent bands when \( T < T_K \). As one would expect, the quasiparticle masses are strongly renormalized. On the contrary, the 4f electrons acquire the localized character and show incoherent electronic fluctuations when \( T > T_K \). Clearly, there exists a transition from coherent quasiparticles at low temperature to incoherent fluctuating local moments at high temperature, which is usually called itinerant-localized crossover in the literatures. Very recently, this scenario is directly verified by inelastic neutron scattering measurements and \textit{ab initio} many-body calculations for the dynamic magnetic susceptibility of CePd₃.

Note that the 4f itinerant-localized crossover is caused not just by temperature changes, but also by pressure, magnetic field, and chemical substitution. For example, it was demonstrated by both experiments and theoretical calculations that pressure can be used to regulate the 4f states of CeIn₃ from localized to delocalized. As pressure is increased, CeIn₃ will undergo an electronic Lifshitz transition accompanied by significant changes in the Fermi surface topology. CeRu₂Si₂ is a typical heavy-fermion compound with a large electronic specific heat coefficient \( \gamma \). It takes a metamagnetic transition at \( H_m = 7.7 \) Tesla. Extensive de Haas-van Alphen (dHvA) effect experiments discerned the change of 4f states from itinerant 4f electrons below \( H_m \) to localized 4f electrons above \( H_m \).

Another interesting and well-studied example is the cerium-based “115” system, namely CeTIn₅, where \( T = \text{Co, Rh, and Ir} \). In CeCoIn₅ and CeIrIn₅, the 4f electrons are itinerant. Due to the contributions of coherent 4f electrons, they have enlarged Fermi surfaces. However, in CeRhIn₅, localized 4f electrons give rise to small Fermi surface. Clearly, chemical composition plays a pivotal role in tuning their 4f states.

In the present study, we would like to concentrate on the cerium-based ternary “122” system, namely CeM₃Si₂, where \( M = \text{Ru, Rh, Pd, and Ag} \). We think that these compounds can be considered as valuable supplements to the “115” system for examining the chemical substitution driven 4f itinerant-localized crossover. The four compounds crystallize in the body-centered tetragonal ThCr₂Si₂-type structure (see Fig. 1), wherein Ce atoms sit on planes well separated by layers of \( M \) and Si atoms. They are notable for the extremely rich magnetic ordered and superconducting phases at low temperature. The ground state of CeRu₂Si₂ is paramagnetic. As mentioned before, it will undergo a metamagnetic transition at finite magnetic field \( \sim 13 \text{ Tesla} \). CeRh₂Si₂ develops complicated antiferromagnetic order below 36 K, which is the highest Néel temperature among cerium-based heavy-fermion compounds.
more, it would turn into superconductor with $T_c \sim 350$ mK at pressure above 9 kbar. Likewise, CePd$_2$Si$_2$ transforms into antiferromagnetic state with a staggered magnetic moment below 10 K and displays a pressure-induced superconductivity in the range 2 $\sim$ 7 GPa. CeAg$_2$Si$_2$ also exhibits antiferromagnetic ground state with $T_N = 8.6$ K. This magnetic ordered phase is completely suppressed when $p \sim 13$ GPa and superconductivity emerges when $p \sim 11$ GPa. The maximal $T_c$ is 1.25 K at $p = 16$ GPa.

In this cerium-based “122” system, undoubtedly, CeRu$_2$Si$_2$ has attracted most of attentions. Exhaustive experiments (including thermodynamic, transport, and spectroscopic measurements) and theoretical calculations have been conducted to unveil the evolution of its 4f states before and after the metamagnetic transition. It is widely accepted that the metamagnetic transition is accompanied by a 4f itinerant-localized crossover. Under small magnetic field, 4f states indeed contribute to the construction of the Fermi surface, manifesting the itinerant 4f electrons. This was confirmed recently by angle-resolved photoemission spectroscopy (ARPES) experiments and band structure calculations for the Fermi surfaces of CeRu$_2$Si$_2$. However, neutron diffraction experiments and static magnetization measurements don’t support this picture. The results indicated that the itinerant character of the 4f electrons remains almost unchanged during the metamagnetic transition. Hence, this issue is still controversial until now. As for the other compounds in this series, we know a little about their 4f states. Actually, considering their electronic structures, experimental results are rarely reported in the literatures. On the theoretical side, Vildosola et al. studied the spectral properties of CeM$_2$Si$_2$ (where M=Ru, Rh, and Pd) compounds by means of local density approximation (LDA) combined with Anderson impurity model (AIM). The model was solved within extended non-crossing approximation (NCA) and the magnetic quantum critical point of CeM$_2$Si$_2$ was also interpreted by M. Matsumoto et al. by solving the Kondo lattice model with the dynamical mean-field theory (DMFT). In these calculations, the physical models were somewhat oversimplified. Furthermore, the many-body electronic correlation among 4f electrons, spin-orbit coupling, and crystal-field splitting had not been fully taken into accounts. Therefore, it was impossible to obtain reliable results for the detailed electronic structures and related physical properties of CeM$_2$Si$_2$. In this regard, a comprehensive study of the electronic structures of CeM$_2$Si$_2$ by ab initio calculations is highly desirable.

In the present paper, we endeavor to uncover the electronic structures of CeM$_2$Si$_2$ by employing a first-principles many-body approach, namely the density functional theory in combination with the single-site dynamical mean-field theory (dubbed as DFT + DMFT). The band structures, density of states, self-energy functions, and 4f electronic configurations of CeM$_2$Si$_2$ are calculated. We successfully reproduce the ARPES spectra of CeRu$_2$Si$_2$. The other results can be viewed as critical predictions. We find that the 4f localized character increases when M goes from Ru to Ag. A chemical pressure driven 4f itinerant-localized crossover is observed when M changes from Pd to Ag. Especially, there exists an orbital selective 4f insulating state in CeAg$_2$Si$_2$. These results will greatly enrich our knowledge about the 4f states in cerium-based strongly correlated materials.

The rest of this paper is organized as follows. In Sec. II, the DFT + DMFT computational details are introduced. In Sec. III, the calculated results, including the electronic band structures, total and partial 4f density of states, self-energy functions, and 4f valence state fluctuations are presented and discussed. A detailed comparison between the calculated results and the available experimental data is also provided in this section. Finally, Sec. IV serves as a brief conclusion.

II. METHOD

The DFT + DMFT method combines realistic band structure calculation by DFT with non-perturbative many-body treatment of local interaction effects in DMFT. It has been successfully applied to investigate the physical properties of many cerium-based heavy fermion materials in recent years. Here we adopted the DFT + DMFT method to perform charge fully self-consistent calculations to explore the detailed electronic structures of CeM$_2$Si$_2$. The self-consistent implementation of this method is divided into DFT and DMFT parts, which are solved separately by using the WIEN2k code and the EDMFT package.

In the DFT part, the experimental crystal structures were used. The generalized gradient approximation was adopted to formulate the exchange-correlation functional. The spin-orbit coupling was taken into account in a second-order variational manner. The k-points mesh was 14 $\times$ 14 $\times$ 14 and $R_{MTK_{MAX}} = 7.0$. In the DMFT part, cerium’s 4f orbitals were treated as correlated. The four-fermions interaction matrix was parameterized using the Coulomb interaction $U = 6.0$ eV and the Hund’s exchange $J_H = 0.7$ eV via the Slater integrals. The fully localized limit scheme was used to calculate the double-counting term for impurity self-energy function. The constructed multi-orbital Anderson impurity models were solved using the hybridization expansion continuous-time quantum Monte Carlo impurity solver (dubbed as CT-HYB). Note that 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 ($N \in [0,3]$) for the local Hilbert space to reduce the computational burden. Since the inverse temperature $\beta = 100$ ($T \sim 116.0$ K), it was reasonable to retain only the paramagnetic solutions. The convergence criteria for charge and energy were $10^{-4}$ e and $10^{-4}$ Ry, respectively.

III. RESULTS

A. Momentum-resolved spectral functions

The direct output of self-consistent DFT + DMFT calculations is the Matsubara self-energy functions $\Sigma(i\omega_n)$. They are firstly converted into real-frequency self-energy functions $\Sigma(\omega)$ via analytical continuation procedure. Then $\Sigma(\omega)$ is...


FIG. 2. (Color online). Momentum-resolved spectral functions \( A(k, \omega) \) of CeM_2Si_2 obtained by DFT + DMFT calculations. (a) \( M = \text{Ru} \). (b) \( M = \text{Rh} \). (c) \( M = \text{Pd} \). (d) \( M = \text{Ag} \). The horizontal dashed lines denote the Fermi level.

FIG. 3. (Color online). Electronic density of states of CeM_2Si_2 obtained by DFT + DMFT calculations. (a) Total density of states (thick solid lines) and partial 4f density of states (color-filled regions). (b) Partial 4f density of states near the Fermi level. The data presented in this figure are rescaled for a better view. The vertical dashed lines denote the Fermi level.

used to evaluate the momentum-resolved spectral functions \( A(k, \omega) \) and local spectral functions \( A(\omega) \). In this subsection, we will pay attention to \( A(k, \omega) \) at first.

We tried to calculate the momentum-resolved spectral functions \( A(k, \omega) \) of CeM_2Si_2 along the high-symmetry lines \( X - N - \Gamma - Z \) in the irreducible Brillouin zone [see Fig. 1(b)]. Figure 2 visualizes the calculated results. Surprisingly, though these compounds share similar crystal structures, they display quite different band structures and Fermi surfaces. (i) For \( M = \text{Ru}, \text{Rh}, \text{and Pd} \), the 4f bands dominate when \( \omega > 3.0 \) eV. In this energy range, only spread and blurring heat maps are observed. When \( \omega < 3.0 \) eV, the \( spd \) bands are predominant. They cross the Fermi level and exhibit significant dispersions. For CeAg_2Si_2, the 4f bands are closer to the Fermi level. (ii) For CeRu_2Si_2, there exist intense and almost flat bands near the Fermi energy, which are associated with the spin-orbit splitting 4f_{5/2} and 4f_{7/2} bands. The low-lying 4f_{5/2} bands locate at the Fermi level, while the high-lying 4f_{7/2} bands are at a few hundred meV above the Fermi level. The energy separation between them is approximately 310 meV, which is very close to those observed in Ce metal and some other cerium-based heavy fermion compounds, such as CeIn_3, CeIn_3, and CeB_6. The prominent 4f_{5/2} bands reveal the itinerant behavior of 4f electrons, which is in accord with the paramagnetic ground state and experimentally observed large Fermi surface. When \( M \) goes from Ru to Pd, a consequent reduc-
tion of the intensities (spectral weights) for these flat bands is observed, connoting the growing localization of $4f$ electrons. For $M = \text{Ag}$, the flat bands feature near the Fermi level is nearly invisible, which implies that its $4f$ electrons will approach to the localized limit. (iii) For $M = \text{Ru, Rh, and Pd}$, there exist remarkable $c-f$ hybridizations around the Fermi level. However, for $M = \text{Ag}$, the $c-f$ hybridizations are very weak. (iv) For $M = \text{Rh}$, there is a small Fermi surface pocket (electron type) centered at the $N$ point. While for the other compounds, such pockets are absent.

**B. Density of states**

Next, let us focus on the integrated spectral functions of $\text{CeM}_2\text{Si}_2$. Figure 3(a) shows the total density of states $A(\omega)$ and $4f$ partial density of states $A_{4f}(\omega)$. Since the spectral weights at the Fermi level are larger than zero, overall the four compounds are metallic. For $M = \text{Ru}$, we can see sharp quasiparticle peak at the Fermi level, which is largely contributed by the $4f_{5/2}$ states. Another more pronounced peak located at $\sim 310 \text{ meV}$ is mainly associated with the $4f_{7/2}$ states. Note that the ratio of spectral weights of the two peaks is less than 1.0, i.e. $I(4f_{5/2})/I(4f_{7/2}) < 1.0$, which is contrary to those observed in the CeTiN$_2$ compounds. The smooth and broad hump resided from $2 \text{ eV}$ to $6 \text{ eV}$ is mainly assigned to the upper Hubbard bands of cerium’s $4f$ orbitals. On the other hand, the lower Hubbard bands are almost invisible. The density of states of the Ru ion is peaked around binding energy from $1 \text{ eV}$ to $5 \text{ eV}$. As for $\text{CeRh}_2\text{Si}_2$ and $\text{CePd}_2\text{Si}_2$, their local spectral functions resemble the one of $\text{CeRu}_2\text{Si}_2$. The only difference is that the spectral weights of $4f$ electrons in the vicinity of the Fermi level are transferred to high energy regime. As a result, their quasiparticle peaks become less pronounced. As for $\text{CeAg}_2\text{Si}_2$, it shows quite different spectral function. At first, the quasiparticle peak almost disappears. Its contribution to the spectral weight at the Fermi level is trivial, indicating the Ag compound is on the localized side of the phase diagram. Second, the upper Hubbard bands are shifted toward the Fermi level. The lower Hubbard bands emerge around $-2 \text{ eV}$. They become considerable. Third, the major peaks for the density of states of the Ag ion are moved to $-4 \text{ eV} \sim -7 \text{ eV}$. These differences are consistent with those seen in the momentum-resolved spectral functions [see Fig. 2].

Figure 3(b) zooms in the low-energy part of the $4f$ partial density of states. We see that CeRu$_2$Si$_2$ has the highest quasiparticle peak, CeRh$_2$Si$_2$ follows, and CePd$_2$Si$_2$ has smaller quasiparticle peak. However, CeAg$_2$Si$_2$ has no quasiparticle peak left. Only a broad background of the $4f$ spectral weight is seen around the Fermi level. These results suggest that the Ru compound is the most itinerant. Rh and Pd compounds are very similar to Ru compound, but less itinerant. On the other hand, the Ag compound is localized. In Fig. 3(b), we also find that the peak attributed to the $4f_{5/2}$ state of CePd$_2$Si$_2$ is shifted to higher energy, resulting in larger $\Delta_{\text{SOC}}$ (it is equal to the energy level difference between the $4f_{5/2}$ and $4f_{7/2}$ states) than those of the other cerium-based 122 compounds. This abnormal feature is likely attributed to the crystal structure of CePd$_2$Si$_2$. Actually, it has the largest crystal volume $V$, the smallest $c/a$ ratio, and the longest Ce-Ce distance among the Ru, Rh, and Pd compounds (please refer to Table I).

**C. Self-energy functions**

Figure 4 shows the Matsubara self-energy functions for $4f$ states of $\text{CeM}_2\text{Si}_2$. In general, we can use the following equation to fit the imaginary part of low-frequency Matsubara self-energy function:

$$-\Im\Sigma(i\omega_n) = A(i\omega_n)^\alpha + \gamma.$$ (1)

Here, $A$ is a fitting parameter. The exponent parameter $\alpha$ can be used to examine whether the Landau Fermi-liquid theory is fulfilled. According to self-energy data presented in Fig. 4, we find that the extracted $\alpha$ parameters are less than 1.0. It manifests the behaviors of $4f$ electrons in these compounds deviate from the description of the Landau Fermi-liquid theory. The $\gamma$ parameter denotes the low-energy scattering rate of $4f$ electrons. It is equivalent to $\Im\Sigma(i\omega_n \rightarrow 0)$. For the $4f_{5/2}$ states, $\gamma$ approaches zero. While for the $4f_{7/2}$ states, $\gamma$ is much larger than zero. We can conclude that the systems resemble the non-Fermi-liquid state. Furthermore, their quasiparticle weights $Z$ and the electron effective masses $m^*$ should show very strong orbital dependence.

Finally, we notice that for $M = \text{Ru, Rh, and Pd}$, the self-energy functions for both the $4f_{5/2}$ and $4f_{7/2}$ components exhibit metallic features. However, for CeAg$_2$Si$_2$, the situation is a bit different. Its $4f_{5/2}$ component shows metallic behavior ($Z \approx 0.65$, $m^* \approx 1.55m_e$), while its $4f_{5/2}$ component is
insulating \((Z \approx 0.012, m^* \approx 84.90 m_e)\). Clearly, the 4f electrons in the 4f\(_{5/2}\) state are more correlated. We can regard this scenario as an orbital selective 4f insulating state, which is an analogy to the orbital selective Mott phase identified in transition metal compounds, such as Ca\(_{2-x}\)Sr\(_x\)RuO\(_4\)\(^3\).}

D. Valence state fluctuations

Now let us concentrate on 4f valence state fluctuations and electronic configurations in the four compounds. The CT-HYB quantum impurity solver is capable of computing the valence state histogram (or equivalently atomic eigenstate probability) \(p_\Gamma\) for 4f electrons, which presents the probability to find out a 4f valence electron in a given atomic eigenstate \(|\psi_\Gamma\rangle\) (labeled by good quantum numbers \(N\) and \(J\) as mentioned in Sec. II)\(^5\). Fig. 5(a-d) illustrate the calculated 4f valence state histograms of Ce\(_M\)\(_2\)Si\(_2\) (where \(M = \text{Ru, Rh, Pd, and Ag, from top to bottom}\) by DFT + DMFT calculations.)

\(FIG. 5.\) (Color online). (a)-(d) Valence state histograms of Ce\(_M\)\(_2\)Si\(_2\) by DFT + DMFT calculations. Here we used three good quantum numbers to label the atomic eigenstates. They are \(N\) (total occupancy), \(J\) (total angular momentum), and \(\gamma\) (\(\gamma\) stands for the rest of the atomic quantum numbers, such as \(J_z\)). Note that the contribution from \(N = 3\) atomic eigenstates is too trivial to be visualized in these panels. (e)-(h) Probabilities of 4f\(_0\) (violet), 4f\(_1\) (orange), and 4f\(_2\) (red) configurations for Ce\(_M\)\(_2\)Si\(_2\) (where \(M = \text{Ru, Rh, Pd, and Ag, from top to bottom}\) by DFT + DMFT calculations.)
FIG. 6. (Color online). (a) Momentum-resolved spectral functions $A(k, \omega)$ of CeRu$_2$Si$_2$ obtained by DFT + DMFT calculations. (b) and (c) ARPES spectra of CeRu$_2$Si$_2$ measured at 20 K. The colored dashed lines representing each band are guides to the eye. These figures are reproduced from Ref. [31].

FIG. 7. (Color online). Electronic density of states of Ce$_M$$_2$Si$_2$. (a) $M = $ Ru. (b) $M = $ Pd. (c) $M = $ Ag. The calculated and experimental data are represented by solid thick lines and empty circles, respectively. The calculated data are multiplied by the Fermi-Dirac distribution function. The experimental data are extracted from Ref. [51] (for CeRu$_2$Si$_2$) and [34] (for CePd$_2$Si$_2$ and CeAg$_2$Si$_2$).

histograms for Ce$_M$$_2$Si$_2$. It is easy to notice that the atomic eigenstate $|N = 1, J = 2.5, \gamma = 0 \rangle$ is overwhelmingly dominant, followed by the two atomic eigenstates $|N = 0, J = 0.0, \gamma = 0 \rangle$ and $|N = 1, J = 3.5, \gamma = 0 \rangle$. The probabilities for the remaining atomic eigenstates are negligible. For example, in CeRu$_2$Si$_2$, the probabilities for the three atomic eigenstates are approximately 85.5%, 4.5%, and 2.9%, respectively. As the transition metal ion $M$ varies from Ru to Ag, the probability for the atomic eigenstate $|N = 1, J = 2.5, \gamma = 0 \rangle$ grows up slightly. Accordingly, the probabilities for the atomic eigenstates $|N = 0, J = 0.0, \gamma = 0 \rangle$ and $|N = 1, J = 3.5, \gamma = 0 \rangle$ are reduced. It is suggested that the redistribution of atomic eigenstates probabilities strongly depends on the atomic number of the transition metal ion $M$. The $4f$ valence state electrons favor to stay at the ground state $|N = 1, J = 2.5, \gamma = 0 \rangle$ more and more.

Since the atomic eigenstates probabilities $p_{\Gamma}$ have been calculated, we can sum up them with respect to $N$ to get the distribution of $4f$ electronic configurations. It will provide some useful information about the $4f$ valence state fluctuations of the system. Fig. 5(e-h) shows the distribution of $4f$ electronic configurations of Ce$_M$$_2$Si$_2$. Apparently, the $4f^1$ configuration always dominates ($\sim$ 90%). The $4f^2$ and $4f^0$ configurations are less important. They account for $< 7\%$ and $< 5\%$, respectively. The proportion for the $4f^3$ configuration is trivial and can be ignored surely. Similar data have been reported for some other cerium-based heavy fermion compounds. We find that the proportion of the $4f^1$ configuration slightly rises, while those of the $4f^2$ and $4f^0$ configurations monotonically decline in connection with the atomic number of transition metal ion $M$. It means that the $4f$ valence state fluctuation becomes the most remarkable in CeRu$_2$Si$_2$. When $M$ goes from Ru to Ag, the $4f$ valence state fluctuation will be suppressed gradually.

E. Compared with experimental results

The experimental results concerning with the electronic structures of the four cerium-based 122 compounds, except CeRu$_2$Si$_2$, are very limited in the literatures. As a consequence, most of the calculated results presented above can be considered as critical predictions. In this subsection, we would like to compare our results with the available experi-
CeRu$_2$Si$_2$  CeRh$_2$Si$_2$  CePd$_2$Si$_2$  CeAg$_2$Si$_2$

FIG. 8. (Color online). The sketch of the itinerancy/localization of the four cerium-based 122 compounds. In our view, the 4$f$ itinerant-localized crossover lies between the Pd compound and the Ag compound.

| $M$  | $V$ (Å$^3$) | $c/a$ | $d_{CeCe}$ (Å) | $d_{CeM}$ (Å) |
|------|-------------|-------|----------------|--------------|
| Ru   | 192.93      | 2.34  | 4.185          | 3.22         |
| Rh   | 190.97      | 2.49  | 4.086          | 3.26         |
| Pd   | 198.34      | 2.34  | 4.221          | 3.25         |
| Ag   | 214.31      | 2.51  | 4.233          | 3.40         |

TABLE I. Crystal structure parameters of Ce$_M$$_2$Si$_2$, where $M$ = Ru, Rh, Pd, and Ag.$^{31}$

The electronic structures of CeRu$_2$Si$_2$ have been studied by DFT calculations.$^{35,36}$ In the previous calculations, the 4$f$ electrons of cerium are assumed to be fully itinerant. Since the 4$f$ electrons in CeRu$_2$Si$_2$ are mostly itinerant, this treatment is reasonable. However, traditional DFT method cannot be used to study the dual nature of 4$f$ electrons. On the contrary, the DFT + DMFT method provides a reliable tool to study the electronic structures of cerium-based heavy fermion and intermediate valence materials, regardless of the itinerancy or localization of 4$f$ electrons.

Next, we would like to seek the underlying mechanism and driving force for the 4$f$ itinerant-localized crossover. Firstly, the four compounds share similar ThCr$_2$Si$_2$-type crystal structures as stated before (see Fig. 1), but with different structural parameters (see Tab. I). We find that none of these structural parameters, including crystal volume, $c/a$ ratio, bond distances between Ce and $M$ atoms, can explain the trend of itinerant to localized crossover in these compounds. Thus, the structure itself is not the driving force of the crossover. Second, the four compounds exhibit considerable 4$f$ valence state fluctuations. The 4$f$ itinerant-localized crossover is accompanied with the change of valence state fluctuation. However, the change is too small to drive an electronic transition. Finally, the cerium-based 122 materials are very sensitive to the substitution of the transition metal ion layer. Besides, the Ru, Rh, Pd, and Ag ions are not isovalent. Thus, we believe that the chemical substitution (or chemical pressure) is indeed the driving force of the itinerant-localized crossover.

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IV. CONCLUDING REMARKS

In the present work, we performed ab initio many-body calculations to study the electronic structures of four cerium-based 122 compounds, Ce$_M$$_2$Si$_2$, where $M$ = Ru, Rh, Pd, and Ag. We obtained the momentum-resolved spectral functions $A(k, \omega)$, the total and 4$f$ partial density of states, Matsubara self-energy functions, and 4$f$ valence state fluctuations. We find that from $M$ = Ru, to Rh, Pd, and Ag, the 4$f$ electrons become more and more localized. The compounds with $M$ = Pd and $M$ = Ag stand on the itinerant and localized sides in the phase diagram, respectively. This itinerant-localized crossover is driven by the chemical pressure, and accompanied by change of 4$f$ valence state fluctuation. Of the most interesting is that we identify an orbital selective 4$f$ insulating state in CeAg$_2$Si$_2$, where the 4$f_{5/2}$ states are metallic while the 4$f_{7/2}$ states keep insulating. Our results are in closely consistent with the available experiments. Most of the calculated results even serve as useful predictions.

We would like to point out that the itinerant-localized crossover and 4$f$ valence state fluctuation are common in many rare-earth heavy fermion systems, which has been a longstanding issue and yet to be answered. The study on the electronic structures and valence state fluctuations of typical Ce$_M$$_2$Si$_2$ compounds sheds light on the subject, which needs further experimental and theoretical confirmations.

FIG. 8. (Color online). The sketch of the itinerancy/localization of the four cerium-based 122 compounds. In our view, the 4$f$ itinerant-localized crossover lies between the Pd compound and the Ag compound.

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F. Discussion

Based on the calculated results, we can make a preliminary conclusion about the itinerancy or localization of 4$f$ electrons for the four cerium-based 122 compounds (see Fig. 8). We find that the 4$f$ electrons become increasingly localized from $M$ = Ru, to Rh, Pd, and Ag. They are maximum itinerant for $M$ = Ru, and maximum localized for $M$ = Ag. Furthermore, these exists a 4$f$ itinerant-localized crossover between $M$ = Pd and $M$ = Ag. This trend coincide with the increasing atomic number of transition metal ion $M$. Next, we would like to seek the underlying mechanism and driving force for the 4$f$ itinerant-localized crossover. Firstly, the four compounds share similar ThCr$_2$Si$_2$-type crystal structures as stated before (see Fig. 1), but with different structural parameters (see Tab. I). We find that none of these structural parameters, including crystal volume, $c/a$ ratio, bond distances between Ce and $M$ atoms, can explain the trend of itinerant to localized crossover in these compounds. Thus, the structure itself is not the driving force of the crossover. Second, the four compounds exhibit considerable 4$f$ valence state fluctuations. The 4$f$ itinerant-localized crossover is accompanied with the change of valence state fluctuation. However, the change is too small to drive an electronic transition. Finally, the cerium-based 122 materials are very sensitive to the substitution of the transition metal ion layer. Besides, the Ru, Rh, Pd, and Ag ions are not isovalent. Thus, we believe that the chemical substitution (or chemical pressure) is indeed the driving force of the itinerant-localized crossover.

The electronic structures of CeRu$_2$Si$_2$ have been studied by DFT calculations.$^{35,36}$ In the previous calculations, the 4$f$ electrons of cerium are assumed to be fully itinerant. Since the 4$f$ electrons in CeRu$_2$Si$_2$ are mostly itinerant, this treatment is reasonable. However, traditional DFT method cannot be used to study the dual nature of 4$f$ electrons. On the contrary, the DFT + DMFT method provides a reliable tool to study the electronic structures of cerium-based heavy fermion and intermediate valence materials, regardless of the itinerancy or localization of 4$f$ electrons.

IV. CONCLUDING REMARKS

In the present work, we performed ab initio many-body calculations to study the electronic structures of four cerium-based 122 compounds, Ce$_M$$_2$Si$_2$, where $M$ = Ru, Rh, Pd, and Ag. We obtained the momentum-resolved spectral functions $A(k, \omega)$, the total and 4$f$ partial density of states, Matsubara self-energy functions, and 4$f$ valence state fluctuations. We find that from $M$ = Ru, to Rh, Pd, and Ag, the 4$f$ electrons become more and more localized. The compounds with $M$ = Pd and $M$ = Ag stand on the itinerant and localized sides in the phase diagram, respectively. This itinerant-localized crossover is driven by the chemical pressure, and accompanied by change of 4$f$ valence state fluctuation. Of the most interesting is that we identify an orbital selective 4$f$ insulating state in CeAg$_2$Si$_2$, where the 4$f_{5/2}$ states are metallic while the 4$f_{7/2}$ states keep insulating. Our results are in closely consistent with the available experiments. Most of the calculated results even serve as useful predictions.

We would like to point out that the itinerant-localized crossover and 4$f$ valence state fluctuation are common in many rare-earth heavy fermion systems, which has been a longstanding issue and yet to be answered. The study on the electronic structures and valence state fluctuations of typical Ce$_M$$_2$Si$_2$ compounds sheds light on the subject, which needs further experimental and theoretical confirmations.

TABLE I. Crystal structure parameters of Ce$_M$$_2$Si$_2$, where $M$ = Ru, Rh, Pd, and Ag.$^{31}$

| $M$  | $V$ (Å$^3$) | $c/a$ | $d_{CeCe}$ (Å) | $d_{CeM}$ (Å) |
|------|-------------|-------|----------------|--------------|
| Ru   | 192.93      | 2.34  | 4.185          | 3.22         |
| Rh   | 190.97      | 2.49  | 4.086          | 3.26         |
| Pd   | 198.34      | 2.34  | 4.221          | 3.25         |
| Ag   | 214.31      | 2.51  | 4.233          | 3.40         |

F. Discussion

Based on the calculated results, we can make a preliminary conclusion about the itinerancy or localization of 4$f$ electrons for the four cerium-based 122 compounds (see Fig. 8). We find that the 4$f$ electrons become increasingly localized from $M$ = Ru, to Rh, Pd, and Ag. They are maximum itinerant for $M$ = Ru, and maximum localized for $M$ = Ag. Furthermore, there exists a 4$f$ itinerant-localized crossover between $M$ = Pd and $M$ = Ag. This trend coincide with the increasing atomic number of transition metal ion $M$.
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