Kondo scenario of the $\gamma$-\alpha phase transition in single crystalline Cerium thin films

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Abstract

The physical mechanism driving the $\gamma$-$\alpha$ phase transition of face-centre-cubic (fcc) Cerium (Ce) remains controversial until now. In this work, high quality single crystalline fcc-Ce thin films were grown on Graphene/6H-SiC(0001) substrate, and explored by XRD and ARPES measurement. XRD spectra showed a clear $\gamma$-$\alpha$ phase transition at $T_{\gamma-\alpha} \approx 50$ K. However, APRES spectra did not show any signature of $\alpha$-phase emerging in the surface-layer from 300 K to 17 K, which implied that $\alpha$-phase might form at the bulk-layer of our Ce thin films. Besides, an evident Kondo dip near Fermi energy was observed in the APRES spectrum at 80 K, indicating the formation of Kondo singlet states in $\gamma$-Ce. Furthermore, the DFT+DMFT calculations were performed to simulate the electronic structures and the theoretical spectral functions agreed well with the experimental ARPES spectra. In $\gamma$-Ce, the behavior of the self-energy’s imaginary at low frequency not only confirmed that the Kondo singlet states emerged at $T_K \geq 80K$, but also implied that the characteristic temperature of the RKKY interaction ($T_{RKKY}$) among $f$ electrons should be around 40 K. Our theoretical results indicate that the Fermi liquid coherence, i.e., $f$-$f$ indirect bonding, happened after the Kondo dip formation upon cooling. Most importantly, $T_{RKKY}$ was comparable to $T_{\gamma-\alpha}$ observed by the XRD spectra, which suggested the $\gamma$-$\alpha$ phase transition in the fcc-Ce thin films could be explicated in the Kondo scenario.
Cerium is among one of the most amazing elements across the periodic table, due to its complex phase diagram in which up to seven allotropic phases (γ, β, α, α′, α″, η and δ) could be realized in a modest pressure and temperature range [1–7]. And the most intriguing and mysterious part of the phase diagram of Ce is the γ-α phase transition which involves a huge volume change (up to 16.5%) [8]. Great efforts have been devoted to understand the underlying physical mechanism of this unusual phenomena, both from theoretical and experimental points of view. As for the theoretical explanation, historically, there were several versions: (1) the promotional model, in which it was believed that the f-electron of Ce turned from localized (core-level like) to itinerant (valence-like) upon the γ to α transition [9–11]. Therefor the electronic configuration changed from 4f^1[5d6s^2]^{3+} to [4f5d6s^2]^{4+}. However, this argument was proved to be inconsistent with positron-annihilation experiments [12, 13], Compton scattering [14] and inelastic neutron scattering [15, 16], as almost no obviously change in the 4f occupancy was observed. (2) the Mott transition model [17], in which there was no significant modification of the 4f occupancy across the transition. The ratio of on-site Coulomb compulsion energy U and 4f band width W, i.e., U/W, was the key parameter for this model. It was believed that U and W could be deduced from photoemission (PES) and inverse photoemission (IPES) experiments, and the value of U/W underwent obvious change across the α to γ phase transition [17]. However, the determination of U and W was unambiguous and challenging. (3) the Kondo Volume Collapse (KVC) model [18, 19], in which the Kondo hybridization (J_{eff}) between the 4f-electron and the conducting (c) valence electrons was assumed to vary with volume between the γ and α phases. And the rapid (exponential) change in the Kondo energy (k_BTK) as a function of J_{eff} drove the volume collapse phenomena. It should be stressed that the key ingredient in the KVC model is the f-c hybridization, which means f-electrons become indirectly bonding due to the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction [20–23]. Therefore, a direct and clear observation of the f-c hybridization effect is inevitable for the understanding of the γ to α phase transition of Ce metal.

Angle resolved photoemission spectroscopy (ARPES) has been proved to be a powerful tool for the direct characterization of electronic structures of materials. High quality single crystal with well-oriented crystalline surface is a necessity for ARPES experiments. As for Ce, it is quite challenging to meet the above criteria, due to its highly chemically reactive nature. Even though macroscopic scale (up to several millimeters) sized Ce single crystal had
been successfully synthesized and characterized by neutron scattering techniques [24–26], no high quality ARPES spectra on those samples were ever reported up to now. Dispersive band structures were only realized on Ce thin films grown on W(110) substrate [27–29]. However, those works on photoemission demonstrated discrepancies on the 4f electronic structures due to their different interpretations of the crystal structure of Ce films grown on W(110). Information on the evolution of the bulk crystalline structure, especially the atomic stacking sequences perpendicular to the thin film surface, was not properly stated [27–30].

To make a one to one correspondence of 4f-electron properties and the crystalline structures of Ce metal, here in our work, we have synthesized high quality single crystal Ce thin films on graphene substrate grown on 6H-SiC(0001). By a combination of high-resolution STEM at room temperature and varied temperature X-ray diffraction (XRD) down to 15 K, we found that the as-grown Ce thin films surprisingly sustained the γ-phase from 300 K down to around 50 K, which is controversial to commonly accepted phase transition of Ce metal at ambient pressure. And the α-phase emerged in the thin film around 50 K, but the γ-α transformation did not completely finished even at 15 K, resulting in a mixture of α and γ-Ce. The in-situ ARPES experiments were taken at various temperatures, and a strong hybridization was observed for the γ-Ce at low temperature. Besides, theoretical calculations by combining the density functional theory and the dynamical mean-filed theory (DFT+DMFT) methods were carried out to simulate electronic structures of fcc-Ce upon cooling [31, 32]. The calculated spectral functions agreed well with the experimental ARPES spectra. What is more, we predicted the characteristic temperatures of Kondo singlet states formation and f-f indirect bonding, which represent the Kondo f-c hybridization effect and RKKY interaction, respectively [20–23].

RESULTS

Crystal structure characterization. The reflected high-energy electron diffraction (RHEED) pattern of the Graphene/6H-SiC substrate and the as-grown Ce thin film are shown in Fig. 1(a). The incident electron beam was along the (11$\bar{2}$0) direction, i.e., $\bar{\Gamma} \bar{K}$ in the surface Brillouin zone (SBZ) of the 6H-SiC(0001) substrate. Five streaks are indicated by white arrows on the RHEED pattern of Ce thin film. And this five-streak feature persisted
all through the film growth and there was no extra streak, which implies the single crystalline nature of the thin film. It should be noted that the stacking sequence along the $c$-axis of $\beta$-Ce is -ABACABAC-, while it is -ABCABC- perpendicular to the $\gamma$-Ce(111) surface. As the stacking sequence of the first two atomic layers are identical for the two phases, the question arises in which phase the Ce atoms condensed on the substrate. To clarify this, high-resolution transmission electron microscopy (HRSTEM) was used to probe the stacking sequence perpendicular to the sample surface.

A Ce thin film with thickness of 200 nm was used to prepare the sample for HRSTEM experiments. A part of the thin film together with the substrate was cut by focused ion beam (FIB). Fig. 1(b) is a typical HRSTEM image acquired such that the incident electron beam is parallel to the $[1\overline{1}20]_{6H-SiC}/[\overline{1}10]_{Ce}$ direction. The atomic arrays of the SiC substrate and the Ce film are extracted and displayed in Fig. 1(c) and (d), respectively. Due to the low atomic mass of Carbon atoms, only the Silicon atoms are revealed in the HRSTEM pattern. The arrangement of the Si atom arrays in Fig. 1(c) could be well reproduced by simple simulation from the well-known crystal structure of 6H-SiC[38], as shown in Fig. 1(e). In the simulation in Fig. 1(e), the projection is along $[11 \overline{2}0]$ direction and the left and upward arrows denote the $[0001]$ and $[1 \overline{1}00]$ directions, respectively. By omitting the Carbon atoms (golden spheres), the zig-zag chains well reproduce the patterns in Fig. 1(c). Furthermore, the atom column in Fig. 1(d) could be grouped in three types, as marked by green (A), purple (B) and blue (C) spheres. They arrange in perfect -ABCABC- sequence, and are reproduced by the simulation of the $\gamma$-phase Ce with projection along $[1\overline{1}0]$ direction and the column array along $[11\overline{2}]$ direction. It should be stressed that there was no oxidation of the Ce by checking the EELS signal. From the HRSTEM images, the orientation relationship (OR) between Ce and 6H-SiC substrate is expressed as $[111]_{Ce}//[0001]_{6H-SiC}$. Therefore, our HRSTEM results indicate that the as-grown Ce thin film is in the $\gamma$-phase, i.e., having the FCC structure.

To clarify the lattice structure evolution of the Ce film versus the temperature, ex-situ XRD was used to characterize the lattice structure of the Ce film. A 200 nm Ce thin film sample was cooled from 300 K to 15 K and the XRD patterns were collected every 20 K except for the lowest temperature (15 K) as shown in Fig. 2(a). There are several features among the $2\theta$ range of $24^\circ$ to $38^\circ$: a broad hump near $28^\circ$ which belongs to the oxidized Ce at the sample surface, as oxidation was inevitable during the sample transfer for ex-situ XRD
experiments; persistent (111) peak of $\gamma$-Ce around 30° at all temperatures; emergence of the (111) peak of $\alpha$-Ce at low temperature; unchanged (0006) peak of the 6H-SiC substrate. It is quite interesting that there was no sign of $\beta$-Ce during the phase transition. Fig. 2(b) shows the evolution of the lattice constant ($L$) of $\gamma$-Ce in Fig. 2(a) and its linear thermal expansion coefficient $\alpha_L$ (defined as $\frac{\Delta L}{L \Delta T}$) versus the temperature. The inset in Fig. 2(b) demonstrates the (111) diffraction peaks at 20 K, 40 K and 60 K, respectively. The $\alpha$-Ce (111) diffraction peak emerged below 60 K, which offers a fingerprint for the $\gamma$-$\alpha$ phase transition. And the phase transition induced a crossover of the $\alpha_L$ curve around 60 K. The persistent existence of $\gamma$-Ce down to 60 K makes it possible to study the evolution of the 4$f$ electronic properties versus temperature.

**Photoemission studies.** An *as-grown* Ce thin film sample with thickness of 20 nm was transferred *in-situ* into the ARPES chamber under UHV within 5 minutes after growth. Because of the highly chemical reactivity of Ce, the duration of the PES measurement was restricted within one hour after the sample temperature reached the desired value. ARPES spectrum at 80 K is demonstrated in Fig. 3(a), with $k_\parallel$ along $\bar{\Gamma}\bar{K}$ in the surface Brillouin zone. Strongly dispersive electronic bands indicate the high quality of our single crystal film. There are three predominant non-dispersive features in the spectra. The broad flat band at a binding energy of $\approx$2.0 eV below $E_F$ corresponds to the $4f^1 \rightarrow 4f^0$ ionization peak, and is labeled as $4f^0$. The other two flat bands situate near Fermi level and at $\approx$250 meV below Fermi level, corresponding to the so-called Kondo resonance and its spin-orbit coupling replica [39], and are traditionally labeled as $4f^{1}_{5/2}$ and $4f^{1}_{7/2}$, respectively. Those three features could be identified more specifically from the energy distribution curves (EDCs) as shown in Fig. 3(b). The $4f^0$ and $4f^{1}_{7/2}$ bands are marked by red and purple circles, respectively. And the $4f^{1}_{5/2}$ signal dominates the intensity near Fermi level. Apart from those 4$f$ features, there exist two conduction bands between $4f^0$ and $4f^{1}_{7/2}$, as are labeled as $\beta$- and $\gamma$-band, respectively. Here we also present the normal emission (NE) and angle-integrated photoemission (AIPES) spectra of Fig. 3(a) in Fig. 3(c). The normal emission and AIPES spectra were extracted from Fig. 3(a) by integrating the EDCs within $\pm$0.02 Å$^{-1}$ and $\pm$0.50 Å$^{-1}$ around the $\bar{\Gamma}$ point, respectively. At the Fermi energy ($E_F$), AIPES shows a quite broad peak, which extends to $\approx$ -0.5eV, corresponding to the the band width of the $\alpha$ band. The $4f^{1}_{7/2}$ peak is considerably suppressed in the AIPES and could be barely figured out as a little hump near -200 meV. What is more, the valence bands between $4f^{1}_{7/2}$ and $4f^0$, *i.e.*, $\beta$ and
γ bands, contribute a nearly linear density of states (DOS) to AIPES, as indicated by the dashed green line on the AIPES spectrum. This linear DOS adds up to the bare $4f^0$ state, resulting in a anisotropic broad $4f^0$ peak that cannot be fitted by a standard Lorentzian or Gaussian line shape. However, the situation for the NE spectrum is quite different. Sharp $4f^{1/2}$ peak sits near $E_F$ and the $4f^{3/2}$ level could be resolved quite well. The NE spectrum could be simulated by a multi-component function,

$$f(\epsilon) = A_0 + \left[ P_3(\epsilon) + \sum_i L(\epsilon, \epsilon_i, w_i) \right] \cdot [F * G](\epsilon).$$

(1)

Here, $A_0$ is the overall constant background due to the experimental noise, $P_3(\epsilon)$ is a cubic polynomial that simulates the spectral contributions from valence bands, and Lorentzian lineshape $L(\epsilon, \epsilon_i, w_i)$ centers at $\epsilon_i$ with a full width at half maximum (FWHM) of $w_i$. $[F * G](\epsilon)$ corresponds to the convolution of the Fermi-Dirac distribution and a Gaussian instrumental broadening. The Gaussian broadening was estimated by fitting the AIPES of an amorphous gold sample at 80 K and a broadening of $\approx 18.5$ meV was obtained. Three Lorentzian peaks are used to fit the normal emission spectrum. The solid blue curve in Fig. 3(c) is the fitted result which nicely reproduces the NE spectrum. The spectral contribution from $4f^0$, $4f^{1/2}$ and $4f^{3/2}$ are extracted and demonstrated as black solid lines in Fig. 3(c). The extracted spectrum resembles the resonance photoemission (PE) results of $\alpha$-Ce in Refs. 40 and 41, in which the $4f$ signals of Ce are resonantly enhanced due to the $4d \rightarrow 4f$ absorption threshold and the PE cross section of valence electrons are low. Our observed distribution of $4f$ electronic states is quite striking, as the previous VT-XRD experiments showed clearly the Ce thin film retains γ phase above 60 K. However, we should keep in mind that, in the Kondo scenario, Kondo effect would manifest itself as the system is cooled near or lower than the Kondo temperature $T_K$, strengthening the hybridization of $f$ states with valence states ($f$-c). The intense $4f^{1/2}$ peak near $E_F$ at 80 K motivates a carefully investigation of the electronic structures close to $E_F$ at various temperatures in pursuit of the possible $f$-$c$ hybridization evidence in Ce metal.

Fig. 4(a)-(c) show the ARPES spectra collected at 300 K, 80 K and 17 K, within an energy range from 600 meV below $E_F$ to 100 meV above $E_F$. To have a better view of the fine structures near $E_F$, the spectra were divided by the corresponding resolution-convoluted Fermi-Dirac distribution (RC-FDD) [42], with an instrumental broadening of 25 meV, 14.5 meV and 10 meV, respectively. Obviously, the spectrum at 300 K has the largest momentum
and energy broadening due to the thermal effect at high temperature. The two branches of $\alpha$ band dominate the spectral weight, with vanishing $4f^1$ features, indicating a localized nature of the $4f$ electrons at 300 K. As the temperature dropped to 80 K, the spectral weight of $4f_{5/2}^1$ and $4f_{7/2}^1$ level developed. Meanwhile, the valence bands $\alpha$ dispersed toward $\bar{\Gamma}$ point and merged with $4f_{5/2}^1$ level, demonstrating a strong evidence for the notable $f$-$c$ hybridization, which is the very first one observed in $\gamma$-Ce at low temperature. Further cooling Ce thin film down to 17 K gave no fundamental change in the ARPES spectrum, except that the dispersions are sharper and even the hybridization between $\alpha$ band and $4f_{7/2}^1$ produces noticeable distortion of the $\alpha$ band near -250 meV. The photon energy that we used is quite surface sensitive, i.e., it could probe only a few atomic layers on the sample surface. The similarities in the ARPES spectra indicate that the sample surfaces possess the same phase structure at 80 K and 17 K. Taking the VT-XRD experiments in Fig. 2 into consideration, we could conclude that the $\gamma$-$\alpha$ phase transition undergoes beneath the sample surface, i.e., starting from the bulk layers of the sample. Nevertheless, this unexpected phenomena offers us the possibilities for exploring the evolution of the electronic structure of $\gamma$-Ce at low temperature, especially the localized to itinerant transition of $4f$ electrons in Ce.

Usually, in the Kondo scenario for Ce metals and compounds, the Kondo resonance (KR), an enhanced electron density of states (DOS), has a maximum above $E_F$. And PES experiments have merely access to the tail the KR below $E_F$. Surprisingly, the RC-FDD corrected ARPES spectra at 80 and 17 K revealed a weakly dispersed bands $\approx 24$ meV below $E_F$, sufficiently high in binding energy to be resolved within the instrumental resolution, as could be seen from the NE and AIPES spectra in Fig. 4(d) and (e). A similar spectral feature at about 21 meV below $E_F$ was also observed in the superconducting heavy Fermion compound $\text{CeCu}_2\text{Si}_2$ [22], which arises from the virtual transition from the excited crystal field (CF) splitting to the ground $4f^1$ state and thus has a much lower spectral weight than the corresponding KR peak. Our spectra at 80 K and 17 K show no KR peak above $E_F$. What is more, the CF splitting in $\gamma$-Ce was estimated to be 5.8 meV by inelastic neutron scattering [43], far less that 24 meV. Therefore, the spectral feature near 24 meV below $E_F$ is a pure demonstration of the ground state hybridized with valence states. To investigate the $k$-dependent $f$-$c$ hybridization, we introduce the phenomenological periodic Anderson
model (PAM), which gives the band dispersion describing the hybridization as \[ (2) \]

\[
E_k^\pm = \frac{\epsilon_0 + \epsilon(k) \pm \sqrt{\epsilon_0 - \epsilon(k)^2 + 4|V_k|^2}}{2}.
\]

Here \( \epsilon_0 \) is 4f ground state energy, \( \epsilon(k) \) is the valence band dispersion at high temperature, and \( V_k \) is the renormalized hybridization strength. There is negligible 4f\(^1\) spectral weight at 300 K in the NES and AIPES spectra. The unhybridized valence band \( \epsilon(k) \) could be fitted by a hole-like parabolic band, and its shape was fixed for the fittings at low temperature. As the temperature dropped to 80 K, the dispersions below \( E_F \) could be fitted perfectly by Eq. 2 and give \( \epsilon_0 = -4.0 \pm 2.6 \) meV, and \( V_k = 71 \pm 5 \) meV, respectively. The fitting results indicate that the ground state of \( \gamma \)-Ce, i.e., 4f\(^1\) has a position just several meV below \( E_F \). Moreover, as a result of the strong \( f-c \) hybridization strength \( V_k \), the resultant final states have a direct gap of \( \approx 140 \) meV and an indirect gap of \( \approx 20 \) meV (the definitions for the two gaps are given in Ref. [42], respectively.

On the one hand, from the XRD experiments, pure \( \gamma \)-phase exists above the phase transition critical temperature \( T_{\gamma-\alpha} \approx 50 \)K, while \( \gamma \)-phase and \( \alpha \)-phase obviously coexist below the \( T_c \). However, on the other hand, the ARPES spectra above and below \( T_{\gamma-\alpha} \) are similar, which means there is just only one phase in the surface layers of the sample in the whole temperature region. Therefore, it can be deduced that below the phase transition critical temperature, the \( \alpha \)-phase could emerge in the bulk first, while the \( \gamma \)-phase remained unchanged in the surface. Although the bare Coulomb interaction strength \( U \) and \( J \) are similar in the surface and bulk, their effective strength in the surface might be much larger than those in the bulk due to the weaker screening effect from the surface \( c \)-electrons. This means that the \( f \)-electrons in the surface are more localized than those in the bulk, which results in a smaller cohesive energy between the Ce atoms in the surface region. Therefore, the environment of the surface favors the survival of \( \gamma \)-phase. In other words, as the temperature decreases, the \( \gamma-\alpha \) phase transition happens more easily in the bulk than in the surface.

**DFT+DMFT calculations.** From our theoretical calculations, the momentum-
resolved spectral functions along high symmetry path at 300 K, 80 K and 20 K for \( \gamma \)-Ce are shown in Fig. 5(a)-(c). We could observe that the flat hybridization bands emerge at 80 K and become more evident at 20 K, which are not present at 300 K. For comparison, in Fig. 5(d), we can clearly observe that the effective \( f-c \) hybridization is much stronger in the \( \alpha \)-phase at relatively high temperature, i.e., 80 K, such as the flat hybridization bands
near $E_F$ become more evident and the other low-energy excitation bands shift closer to $E_F$. Besides, there exist many other characteristic differences between the two phases, such as two much larger electronic Fermi surfaces appear at $K$-$\Gamma$ and $L$-$K$ path which did not form well at $\gamma$-phase even at 20 K. These agree well with previous theoretical calculation results based on the continuous-time quantum Monte Carlo impurity solver [29].

The lifetime of quasi-particle could be indirectly reflected by the magnitude of the self-energy’s imaginary part, i.e., $\text{Im} \Sigma(\omega, T)$. Therefore, certain crossover feature could be observed from the behavior of $-\text{Im} \Sigma(\omega, T)$ varied with the frequency ($\omega$) and temperature ($T$) [11]. Since the low-energy excited heavy quasi-particle is mainly composed of the 4f-electrons with $J = 5/2$, curves of $-\text{Im} \Sigma_{5/2}(\omega, T)$ versus $\omega$ at different temperatures for $\gamma$-Ce are plotted in Fig. 6(a). An evident dip near the static limit ($\omega \to 0$) emerged gradually as cooling below $T_K \approx 80$ K, representing the formation of the flat hybridization bands due to the localized Kondo hybridization. It could be also confirmed by our experimental ARPES spectra and theoretical momentum-resolved spectral functions. The functions $-\text{Im} \Sigma_{5/2}(\omega = 0, T)$ are plotted as red points and fitted by the red lines in Fig. 6(b)-(c), for $\gamma$ and $\alpha$ phase, respectively. Besides, their logarithmic temperature derivatives $-d\text{Im} \Sigma_{5/2}(\omega = 0, T)/d\ln T$ are calculated and shown as black lines. Although the magnitude of the imaginary part decreases monotonously as temperature decreases, its logarithmic temperature derivative gives a maximum at a characteristic temperature $T_{RKKY}$, which corresponds to the coherence of the heavy quasi-particles [21, 23, 44]. Therefore, the heavy Fermion liquid coherence happens following the formation of localized Kondo singlet states in the $\gamma$-Ce, while they happen nearly at the same temperature in the heavy Fermion material CeCu$_2$Si$_2$ [22]. In addition, $T_{RKKY}$ changes from 40 K for $\gamma$-Ce to 129 K for $\alpha$-Ce.

DISCUSSIONS

Our results demonstrate that the Kondo hybridization and RKKY interaction successively dominate in the $\gamma$-phase as temperature decreases, which are the two most important features of Kondo scenario pointed out by many research works [20, 23, 44]. Both of flat band and Kondo dip (about 20 meV) near $E_F$ are observed by our ARPES results at low temperature (80 K and 17 K). Meanwhile, the DFT+DMFT calculations confirm the characteristic temperature of Kondo singlet state formation $T_K$ is about 80 K by observing the
low-frequency dip property of $-\text{Im} \Sigma_{5/2}(\omega, T)$. Most importantly, the $\gamma$-$\alpha$ phase transition temperature $T_{\gamma-\alpha}$ (about 50 K) observed from XRD experiment as temperature decreasing agrees well with the heavy Fermion liquid coherence temperature $T_{RKKY}$ (about 40K) of $\gamma$-Ce by the DFT+DMFT calculations.

Moreover, the Kondo scenario is assumed to work through a positive feedback mechanism together with lattice contraction in the $\gamma - \alpha$ phase transition as temperature decreasing. Firstly, assuming the lattice constant $a_{\text{lat}}$ remains fixed, the strength of $f$-$c$ electron hybridization $V_{fc}$ becomes more and more stronger as $T$ decreases, which would enforce $f$-electrons beginning to bond indirectly at a critical temperature $T_{RKKY}$. Secondly, the additional bonding would make the ions at different sites attractive, which means that both the energy bands of $f$- and $c$-electrons become wider and their hybridization becomes stronger. Such these positive feedback processes would repeat again and again, which would induce a first-order isomorphic volume phase transformation at last. Besides, as observed in many previous experimental works\cite{6, 7}, the phase transition temperature from $\alpha$ to $\gamma$ is greater than that from $\gamma$ to $\alpha$, as much stronger thermal fluctuation is demanded to break the $f$-electron coherent bonding in $\alpha$-Ce.

**CONCLUSIONS**

In our work, we have experimentally and theoretically investigated the physical mechanism of the $\gamma$-$\alpha$ phase transition in Cerium. We have synthesized high quality single crystalline Cerium thin films. ARPES spectra demonstrated the hybridization of $f$ level with conduction bands and the formation of a Kondo dip upon cooling the sample from 300 K to low temperature. From DFT+DMFT calculations, we found a relatively high energy scale $T_K$ around 80 K, which acted as the precursor of low temperature coherence $T_{RKKY}$. Our ARPES results at low temperature indicated the absence of $\alpha$-phase at the sample surface, while varied temperature XRD demonstrated the $\gamma$-$\alpha$ phase transition occurred around 50 K. This could be explained by the stronger $f$-$c$ hybridization in the bulk than that at the surface. The calculated coherence temperature $T_{RKKY}$ agreed quite well with the phase transition temperature $T_{\gamma-\alpha}$ from XRD. Overall, Our experimental and theoretical results supported the Kondo scenario in the $\gamma$-$\alpha$ phase transition in Cerium.
METHODS

Sample preparation. High quality Ce thin films were synthesized by molecular beam epitaxy (MBE). Ce source with 99.95% purity was used and was thoroughly degassed at 1660 °C before evaporation to the graphene substrate grown on 6H-SiC(0001). The graphene substrate was prepared following the recipe as described in Ref. 33 and 34, with some modification to optimize the quality of the as-grown graphene. N-doped 6H-SiC(0001) was first annealed in UHV at 600 °C for at least 3 hours to remove the absorbed gases or organic molecules. After annealing at ∼950 °C for 18 minutes under Si flux to produce a (3×3) reconstruction, the substrate was heated to ∼ 1400 °C for 10 minutes to form graphene.

The Ce source was kept at 1620 °C during the evaporation. The base pressure of our MBE system is better than 5.0 × 10^{-11} mbar and rise to less than 2.0 × 10^{-10} mbar during Ce evaporation. Even under this ultra high vacuum environment, special care should be taken to avoid the in-situ oxidation of the thin films by trace amount residual gases in the UHV chamber during the evaporation process. The Ce source must be degassed at 1660 °C for at least 4 hours before each deposition. The thermal radiation from the hot Ce source should be also taken into consideration, as it might heat up the substrate and result in the oxidization of the Ce films by the residual oxygen in the MBE growth chamber. During our MBE growth, the substrate temperature was kept at ∼ 80 °C. The flux rate of Ce was determined by Quartz crystal micro-balance (QCM) and was ∼ 0.127 Å/S at 1620 °C.

ARPES experiments. For the photoemission spectroscopy experiment, the spectra were excited by the He Iα (21.2 eV) resonance line of a commercial Helium gas discharge lamp. The light was guided to the analysis chamber by a quartz capillary. In virtue of the efficient four-stage differential pumping system, the pressure in the analysis chamber was better than 1.0 × 10^{-10} mbar during our experiments, satisfying the harsh criteria for probing the physical properties of chemically high reactive lanthanide/actinide elements. A VG Scienta R4000 energy analyzer was used to collect the photoelectrons.

HR-STEM experiments. The HAADF-STEM experiment was performed in a FEI Titan G2 80-200 at 300 kV, which was equipped with an aberration corrector and provided us a sufficiently high spatial resolution (∼ 0.7 Å). The convergence angle of the probe was ∼ 21.4 mrad and the screen beam current was about 0.5 nA. Before the experiment, all of the low-order aberrations have been adjusted to an acceptable level. For high-resolution STEM
imaging, the size of the HRSTEM micrography was $1024 \times 1024$ pixels, with a dwell time of $8 \mu s$.

**Theoretical calculations.** To explore the properties of electronic structure and microscopy mechanism of the phase transition of Ce, we performed the theoretical calculations combining the density functional theory and the dynamical mean-field theory method (DFT+DMFT) based on the eDMFT software package \[31\]. We used WIEN2k package based on the full-potential linearized augmented plane-wave (LAPW) method for the density function theory part \[32, 35\]. The lattice parameters were taken from our XRD experiments. Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) was used for the exchange-correlation functional with 5000 k-point meshes for the whole Brillouin zone and as the Ce-ion is so heavy, the spin-orbital coupling (SOC) effect was considered. During all the calculations, we set the Muffin-tin radii to 2.50 a.u., $R_{MTK_{\text{MAX}}} = 8.0$ and $G_{\text{MAX}} = 14.0$. For the DMFT part, the one-crossing approximation (OCA) was used as the impurity solver as the DMFT method mapping the derived lattice model to a single-impurity model \[31, 36, 37\]. The Coulomb interaction $U$ on the Ce f-orbital was set to 6.0 eV with Hund interaction $J$ to 0.7 eV.

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**Author contributions**

X. G. Zhu, Yu Liu and Y. W. Zhao contributed equally to this work. X.G., Y.Z., Y.D., W.F., Y.H., W.Z., D.H. and Yi.L. carried out the growth of thin films and XRD experiments. Y.W. and C.L. performed the HR-STEM experiments. Yu.L., D.J. and X.B. did the theoretical calculations. X.G., S.Y., Q.L., L.Z. and Q.Y. performed the ARPES measurements. X.G., H.F. and X.C. conceived the experiments and wrote the manuscript.
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FIG. 1. (Color online) (a) RHEED pattern of Graphene/6H-SiC substrate and as-grown Ce thin film, with incident electron beam along ⟨1120⟩ direction of the SBZ of 6H-SiC(0001); (b) a typical HRSTEM image of the Ce thin film together with the SiC substrate; (c) and (d) arrangement of the Si atoms and Ce atoms; (e) and (f) simulations of the atomic stacking sequences of SiC substrate and the Ce thin films, respectively.
FIG. 2. (Color online) Varied temperature X-Ray Diffraction of a 200 nm thick Ce thin film. (a) Evolution of the (111) diffraction peaks for $\gamma$ and $\alpha$-Ce, together with the oxide hump (indicated by black arrow) and the 6H-SiC substrate, as the sample temperature decreased from 300 K to 15 K. (b) The lattice constant of $\gamma$-Ce and its linear thermal expansion coefficient $\alpha_L$ (defined in the text) versus the temperature were extracted from (a). The inset enlarges the (111) diffraction peaks of the Ce thin film at 60 K, 40 K and 20 K, demonstrating the emergence of $\alpha$-phase Ce.
FIG. 3. (Color online) (a) Large-scale ARPES spectrum of Ce thin film at T=80 K. (b) Energy distribution curves (EDCs) of (a), demonstrating the three conduction bands $\alpha$, $\beta$ and $\gamma$, together with $4f^0$, $4f_{5/2}^1$ and $4f_{7/2}^1$ levels. (c) Normal emission and angle-integrated photoemission spectra of (a).
FIG. 4. (Color online) (a)-(c) ARPES spectra of 20 nm thick Ce thin films at 300 K, 80 K, and 17 K, respectively (RC-FDD corrected); (d) and (e) NE and AIPES spectra of (a)-(c), without/with RC-FDD correction; (f) illustration of strong $f$-$c$ hybridization within the PAM framework.
FIG. 5. (Color online) (a)-(c) Momentum-resolved spectral functions $A(k,\omega)$ along the high-symmetry lines in the Brillouin zone obtained by DFT+DMFT calculations of $\gamma$-Ce at 300 K, 80 K and 20 K. (d) Spectral functions $A(k,\omega)$ of $\alpha$-Ce at 80 K.
FIG. 6. (Color online) (a) The magnitude of the imaginary part of the 4f ($J = 5/2$) self-energy ($-\text{Im} \Sigma(\omega,T)$) versus energy $\omega$ at different temperatures; (b)-(c) the temperature derivative of $-\text{Im} \Sigma(\omega,T)$ at zero energy ($\omega = 0$) for $\gamma$-Ce and $\alpha$-Ce, respectively. The results show a maximum temperature derivative at about 40 K for $\gamma$-Ce and 129 K for $\alpha$-Ce.