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Kondo scenario of the γ - α phase transition in single crystalline cerium thin films

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The physical mechanism driving the γ - α 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 γ - α phase transition at $T_{\gamma-\alpha} \approx 50$ K, which is retarded by strain effect from substrate comparing with $T_{\gamma-\alpha}$ (about 140 K) of the bulk Ce metal. However, APRES spectra did not show any signature of α -phase emerging in the surface-layer from 300 to 17 K, which implied that α -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 γ -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 γ -Ce, the behavior of the self-energy's imaginary part at low frequency not only confirmed that the Kondo singlet states emerged at $T_{KS} \geq 80$ K, but also implied that they became coherent states at a lower characteristic temperature ($T_{coh} \sim 40$ K) due to the indirect RKKY interaction among f - f electrons. Besides, T_{coh} from the theoretical simulation was close to $T_{\gamma-\alpha}$ from the XRD spectra. These issues suggested that the Kondo scenario might play an important role in the γ - α phase transition of cerium thin films.

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INTRODUCTION

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 phenomenon, 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}. Therefore 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 scattering¹⁴ and inelastic neutron scattering^{15,16}, as almost no obvious change in the $4f$ occupancy was observed. (2) the Mott transition model¹⁷, in which there was no significant modification of the $4f$ occupancy across the transition. The ratio of on-site Coulomb repulsion 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 transition¹⁷. 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. The original conclusion was that the rapid (exponential) change in the Kondo energy ($k_B T_{KS}$) as a function of J_{eff} drove the volume collapse phenomenon. 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 chemical reactive nature. Even though macroscopic scale (up to several millimeters) sized bulk Ce single crystal had been successfully synthesized and characterized by neutron scattering techniques^{24–26}, no high-quality ARPES spectra on those bulk 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

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stacking sequences perpendicular to the thin film surface, was not properly stated^{27–30}.

To make a one to one correlation 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). We chose this substrate based on the lattice match condition and inertness of graphene (detailed discussion could be found in the Supplementary materials). 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 temperature (141 ± 10 K) of Ce metal at ambient pressure³¹. And the α -phase emerged in the thin film around 50 K, but the γ - α transformation did not completely finish 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-field theory (DFT +DMFT) methods were carried out to simulate electronic structures of fcc-Ce upon cooling^{32,33}. The calculated spectral functions agreed well with the experimental ARPES spectra. Moreover, the characteristic temperatures of Kondo singlet states formation T_{KS} and the formation of coherent heavy quasi-particle states T_{coh} were simulated numerically, which correspond to the local f - c Kondo hybridization and the additional non-local f - f RKKY interaction, respectively^{20–23}.

RESULTS

Crystal-structure characterization

The reflected high-energy electron diffraction (RHEED) patterns of the Graphene/6H-SiC substrate and the as-grown Ce thin film are shown in Fig. 1a. The incident electron beam was along the $\langle 11\bar{2}0 \rangle$ direction, i.e., $\bar{\Gamma}K$ 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 β -Ce is $-ABACABAC-$, while it is $-ABCABC-$ perpendicular to the γ -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). Figure 1b is a typical HRSTEM image acquired such that the incident electron beam is parallel to the $[11\bar{2}0]_{6H-SiC}/[1\bar{1}0]_{Ce}$ direction. The atomic arrays of the SiC substrate and the Ce film are extracted and displayed in Fig. 1c, 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. 1c could be well reproduced by simple simulation from the well-known crystal structure of 6H-SiC³⁴, as shown in Fig. 1e. In the simulation in Fig. 1e, the projection is along $[11\bar{2}0]$ direction and the left and

Fig. 1 RHEED and HRSTEM results. **a** RHEED patterns of Graphene/6H-SiC substrate and as-grown Ce thin film, with incident electron beam along $\langle 11\bar{2}0 \rangle$ direction of the SBZ of 6H-SiC(0001); **b** A typical HRSTEM image of the Ce thin film together with the SiC substrate; **c, d** Arrangement of the Si atoms and Ce atoms; **e, f** Simulations of the atomic stacking sequences of SiC substrate and the Ce thin films, respectively.

Fig. 2 Varied temperature X-ray diffraction of a 200-nm thick Ce thin film. **a** Evolution of the (111) diffraction peaks for γ and α -Ce, together with the oxide hump (indicated by black arrow) and the 6H-SiC substrate, as the sample temperature decreased from 300 to 15 K. **b** The lattice constant of γ -Ce and its linear thermal expansion coefficient α_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, 40, and 20 K, demonstrating the emergence of α -phase Ce. **c** FWHMs of the γ -Ce (111) peaks at various temperatures.

upward arrows denote the $[0001]$ and $[\bar{1}\bar{1}00]$ directions, respectively. By omitting the Carbon atoms (golden spheres), the zig-zag chains well reproduce the patterns in Fig. 1c. Furthermore, the atom column in Fig. 1d 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 γ -phase Ce with projection along $[\bar{1}\bar{1}0]$ direction and the column array along $[\bar{1}\bar{1}\bar{2}]$ 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 $[111]_{\text{Ce}}//[0001]_{6\text{H-SiC}}$. Therefore, our HRSTEM results indicate that the as-grown Ce thin film is in the γ -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 to 15 K and the XRD patterns were collected every 20 K except for the lowest temperature (15 K) as shown in Fig. 2a. There are several features among the 2θ range of 24° – 38° : a broad hump near 28° 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 γ -Ce around 30° at all temperatures; emergence of the (111) peak of α -Ce at low temperature; unchanged (0006) peak of the 6H-SiC substrate. It is quite interesting that there was no sign of β -Ce during the phase transition. Figure 2b shows the evolution of the lattice constant (L) of γ -Ce in Fig. 2a and its linear thermal expansion coefficient α_L (defined as $\frac{\Delta L}{L \Delta T}$) versus the temperature. The inset in Fig. 2b demonstrates the (111) diffraction peaks at 20, 40, and 60 K, respectively. The α -Ce (111) diffraction peak emerged below 60 K, which offers a fingerprint for the γ - α phase transition. And the phase transition induced a crossover of the α_L curve around 60 K.

From our XRD results, the γ - α phase transition temperature in thin film lagged far behind the bulk crystal (141 ± 10 K), which can be attributed to the strain effect in our samples with the lattice match of the in-plane lattice parameters of the substrate and the (111) surface of γ -Ce. We qualitatively studied the strain effect through analyzing the full width at half maximum (FWHM) of the XRD diffraction peaks at various temperatures, as peak width contains rich information on the crystallite size, defect (strain, disorder, and defects) of the studied materials. The FWHMs of the γ -Ce(111) peaks at various temperature were extracted by fitting with Lorentzian line-shape, which was convolved with a Gaussian-type instrumental broadening (0.05°), as shown in Fig. 2c. The peak width showed no obviously change from 300 to 180 K

($0.068 \pm 0.009^\circ$), and started to increase to a rather flat plateau between 140 and 40 K ($0.117 \pm 0.004^\circ$) as temperature further decreased. Abrupt change in the peak width happened below 40 K, indicating the phase transition posed obviously effects on the crystalline status of the thin films, which is consistent with the emergence of α -Ce(111) XRD peak at 40 K (inset of Fig. 2b).

The phenomena observed above indicate that the thin film tended to transform from γ -phase to α -phase below 140 K, which is consistent with the phase transition temperature of bulk crystals in the literatures. However, the phase transition did not happen until around 50 K, as a result of the existence of the substrate/thin film interface. It should be noted that, even with the existence of strong interface effect, the lattice of the thin film continued to shrink as temperature decreased, indicating the competition of temperature and interface effects on the phase transition of the thin film. The abrupt change in the peak width at 40 K indicates the interface effects were overwhelmed.

Additionally, we have done Low-Energy Electron Diffraction (LEED) experiments on Ce thin films at 80 K (see the Supplementary materials for detail). We found that the in-plane lattice parameter of Ce thin film at 80 K is 3.60 ± 0.02 Å, and this value is comparable to the VT-XRD results at 80 K, i.e., ≈ 3.62 Å. Therefore, the surface of Ce thin film remains in the γ -phase at 80 K. The persistent existence of pure γ -Ce down to 60 K makes it possible to study the evolution of the 4f 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 min after growth. Because of the high chemical reactivity of Ce, the duration of the PES measurement was restricted within 1 h after the sample temperature reached the desired value. ARPES spectrum at 80 K is shown in Fig. 3a, with $k_{\parallel}$ along $\bar{\Gamma}\text{K}$ in the surface Brillouin zone. Strongly dispersive electronic bands indicate the high quality of our single crystal film. There are three predominant nondispersive features in the spectra. The broad flat band at a binding energy of ≈ 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 ≈ 250 meV below Fermi level, corresponding to the so-called Kondo resonance and its spin-orbit coupling replica³⁵, and are traditionally labeled as $4f_{5/2}^1$ and $4f_{7/2}^1$, respectively. Those three features could be identified more specifically from the energy distribution curves (EDCs) as shown in Fig. 3b. The $4f^0$ and $4f_{7/2}^1$ bands are marked by red and purple

Fig. 3 Band structures and EDCs fitting results. **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 α , β , and γ , together with $4f^0$, $4f^1_{5/2}$ and $4f^1_{7/2}$ levels. **c** Normal emission and angle-integrated photoemission spectra of **a**.

circles, respectively. And the $4f^1_{5/2}$ signal dominates the intensity near Fermi level. Apart from those $4f$ features, there exist two conduction bands between $4f^0$ and $4f^1_{7/2}$, labeled as β - and γ -band, respectively. Here we also present the normal emission (NE) and angle-integrated photoemission (AIPES) spectra of Fig. 3a in Fig. 3c. The normal emission and AIPES spectra were extracted from Fig. 3a by integrating the EDCs within $\pm 0.02 \text{ \AA}^{-1}$ and $\pm 0.50 \text{ \AA}^{-1}$ around the $\bar{\Gamma}$ point, respectively. At the Fermi energy (E_F), AIPES shows a quite broad peak, which extends to about -0.5 eV, corresponding to the band width of the α 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., β 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 single $4f^0$ state, resulting in an anisotropic broad $4f^0$ peak that can not be fitted by a standard Lorentzian or Gaussian line-shape. However, the situation for the NE spectrum is quite different. Sharp $4f^1_{5/2}$ peak sits near E_F and the $4f^1_{7/2}$ level could be resolved quite well. The NE spectrum could be simulated by a multicomponent function,

$$f(\epsilon) = A_0 + \left[P_3(\epsilon) + \sum_i L(\epsilon, \epsilon_i, w_i) \right] \bullet [F * G](\epsilon). \quad (1)$$

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 line-shape $L(\epsilon, \epsilon_i, w_i)$ centers at ϵ_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 ≈ 18.5 meV was obtained. Three Lorentzian peaks are used to fit the normal emission spectrum. The solid blue curve in Fig. 3c is the fitted result, which nicely reproduces the NE spectrum. The spectral contribution from $4f^0$, $4f^1_{7/2}$ and $4f^1_{5/2}$ are extracted and demonstrated as black solid lines in Fig. 3c. The extracted spectrum resembles the resonance photoemission (PE) results of α -Ce in refs ^{36,37}, 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 $4f^1_{5/2}$ peak near E_F at 80 K invokes 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.

Figure 4a–c shows the ARPES spectra collected at 300, 80, 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)³⁸, with an instrumental broadening of 25, 14.5, 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 α band dominate the spectral weight, with almost 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 $4f^1_{5/2}$ and $4f^1_{7/2}$ level developed. Meanwhile, the valence bands α dispersed toward $\bar{\Gamma}$ point and merged with $4f^1_{5/2}$ level, demonstrating a strong evidence for the notable f - c hybridization, which is the very first one observed in γ -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 α band and $4f^1_{7/2}$ produces noticeable distortion of the α band near -250 meV. We noted that our extracted NES and AIPES, as shown in Fig. 4d, e, resemble the resonance photoemission results of α -Ce in refs ^{36,37} in the following way: similarity in the intensity ratio of $4f^1_{5/2}$ and $4f^1_{7/2}$ states. And what is more important, the position of $4f^0$ ionization peak in our work matches very well with that of γ -phase Ce in refs ^{35–37} (see detail in the Supplementary materials). Therefore, we were probing γ -phase Ce on the thin film surfaces in our ARPES experiments. It is worth noting that a “ γ - α ” phase transition of monolayer Ce on W(110) was reported³⁹ and a splitting of $4f^0$ ionization peak was revealed in a Ce monolayer on W(110) substrate, which was attributed to the formation of Ce $4f$ band and its hybridization with the valence-band states⁴⁰. Our current work differs with this work in the sense that we were

Fig. 4 Evolution of the c - f hybridization with temperature and the PAM model. **a–c** ARPES spectra of 20 nm thick Ce thin films at 300 K, 80, and 17 K, respectively (with RC-FDD correction); **d, e** NE and AIPES spectra of **a–c**, without/with RC-FDD correction; **f** Illustration of strong f - c hybridization within the PAM framework.

dealing with rather thick Ce thin films (dozens of nanometers) and focussing on the f - c hybridization near E_F , not at $4f^0$. 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 γ - α phase transition undergoes beneath the sample surface, i.e., starting from the bulk layers of the sample. Nevertheless, this unexpected phenomenon offers us the possibilities for exploring the evolution of the electronic structure of γ -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 ≈ 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. 4d, e. A similar spectral feature at about 21 meV below E_F was also observed in the superconducting heavy Fermion compound CeCu_2Si_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. The CF splitting in γ -Ce was estimated to be 5.8 meV by inelastic neutron scattering⁴¹, far less than 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 as³⁸,

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

Here ϵ_0 is $4f$ ground state energy, $\epsilon(k)$ is the valence-band dispersion at high temperature, and V_k is the renormalized hybridization strength. As shown in Fig. 4d, e, there is weak nonvanishing spectral weight around -250 meV at 300 K in the NES and AIPES spectra, which corresponds to the $4f_1^{7/2}$ level. We should note that the thermal broadening at 300 K (≈ 26 meV) smeared the $4f_1^{5/2}$ level and gave rise to a continuous upward trend for the NES and AIPES spectra in Fig. 4e from -0.1 to 0.1 eV and above. Here we took the two branches of the dispersive bands at 300 K as unhybridized valence bands, and fitted them by a hole-like parabolic band, and kept its shape 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 γ -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 (defined as a minimal separation of two bands at the same momentum) of ≈ 140 meV and an indirect gap (defined as the global minimal separation of two bands) of ≈ 20 meV, respectively. What is more, the fitting results could reproduce the hybridization behaviors very well at low temperature. This fact indicates that the Fermi crossing of the unhybridized valence

bands remained almost the same upon cooling from 300 to 80 K and 17 K, meaning that we were probing γ -Ce on the sample surfaces in our ARPES experiments.

On the one hand, from the XRD experiments, pure γ -phase exists above the phase transition critical temperature $T_{\gamma-\alpha} \approx 50$ K, while γ - and α -phase obviously coexist below this critical temperature. 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 α -phase could emerge in the bulk first, while the γ -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 γ -phase. In other words, as the temperature decreases, the γ - α phase transition happens more easily in the bulk than in the surface. It is similar with the so-called “surface Kondo breakdown” used to explain unusual quantum oscillations in the topological Kondo insulator SmB_6 ^{42–44}.

DFT + DMFT calculations

From our theoretical calculations, the momentum-resolved spectral functions along high-symmetry path at 300, 80, and 20 K for γ -Ce are shown in Fig. 5a–c. The two f levels, i.e., $4f_{5/2}^7$ and $4f_{7/2}^8$ locate near E_F and about 280 meV below E_F , respectively. And their contribution to the density of states could be found in Supplementary Fig. 3, where we could clearly see the nonvanishing $4f^1$ spectral weight even at 300 K. 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. 5d, we can clearly observe that the effective f - c hybridization is much stronger in the α -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 - Γ and L - K path, which did not form well at γ -phase

Fig. 5 DFT+DMFT calculations. **a–c** Momentum-resolved spectral functions $A(k, \omega)$ along the high-symmetry lines in the Brillouin zone obtained by DFT+DMFT calculations of γ -Ce at 300, 80, and 20 K. **d** Spectral functions $A(k, \omega)$ of α -Ce at 80 K.

even at 20 K. These agree well with previous theoretical calculation results based on the continuous-time quantum Monte Carlo impurity solver²⁹.

In order to give a deeper investigation of this system, we need to analysis the self-energy as it encodes all the electronic correlations in DFT + DMFT calculation. 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 (ω) and temperature (T)⁴⁵. 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 ω at different temperatures for γ -Ce are plotted in Fig. 6a. An evident dip near the static limit ($\omega \rightarrow 0$) emerged gradually as cooling below $T_{K5} \approx 80$ K, representing the formation of the flat hybridization bands due to the localized Kondo hybridization, which can be seen clearly from the derivative of $-\text{Im}\Sigma_{5/2}(\omega, T)$ with respect to energy ω in the Supplementary Fig. 3c. 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. 6b, c, for γ - and α -phase, respectively. Here we have adopted a four-parameter logistic fitting function, i.e., $y = (A_1 - A_2)/[1 + (T/T_0)^p] + A_2$ (where A_1 , A_2 , T_0 , and p are the fitting parameters), which is widely used to elucidate the turning point of the change of rate of a curve versus certain physical quantity. Besides, their logarithmic temperature derivatives $-\text{dIm}\Sigma_{5/2}(\omega = 0, T)/\text{dln}T$ 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_{coh} , which corresponds to the coherence of the heavy quasi-particles^{21,23,45}. Therefore, the heavy Fermion liquid coherence happens following the formation of localized Kondo singlet states in the γ -Ce, while they happen nearly at the same temperature in the heavy Fermion material CeCu_2Si_2 ²². In addition, T_{coh} changes from 40 K for γ -Ce to 129 K for α -Ce.

DISCUSSION

From our XRD and ARPES experiments, we observed that the γ - α phase transition occurred at ≈ 50 K in the bulk of thin film and the surface remained in the γ -phase down to 17 K. It means that the γ -phase in the surface is much more robust than that in the bulk, which can not be solely explained by the strain effect from substrate, due to the fact that the strain effect on the topmost surface is weaker than that in the bulk. Hence, there should be other factors besides strain effect that leads to the different performance of bulk and surface. With the appearance of the Kondo dip in our ARPES results below 80 K, the Kondo effect might be the proper mechanism.

To clarify the role of Kondo effect, we have performed DFT + DMFT simulation to explore the Kondo hybridization and RKKY interaction, which are the two most important features of Kondo effect^{20–23,45}. Firstly, DFT + DMFT calculations confirm that the characteristic temperature of Kondo singlet state formation T_{K5} is about 80 K by observing the low-frequency dip property of $-\text{Im}[\Sigma_{5/2}(\omega, T)]$, which agreed well with our ARPES results. Moreover, the characteristic temperature of the heavy fermion liquid coherence due to the RKKY interaction from simulation is about 40 K, which is in the neighbourhood of $T_{\gamma-\alpha}$ (about 50 K) from the XRD spectra. Therefore, the Kondo effect has a close relationship with the γ - α phase transition. And our work suggests that Kondo scenario might be the mechanism of the phase transition.

Moreover, the Kondo scenario is assumed to work through a positive-feedback mechanism together with lattice contraction in the γ - α phase transition as temperature decreases. Firstly, as temperature decreases, if the lattice constant a_{lat} is fixed at the

Fig. 6 Evolution of the imaginary part of the self-energy versus temperatures. **a** The magnitude of the imaginary part of the $4f$ ($J = 5/2$) self-energy ($-\text{Im}\Sigma(\omega, T)$) versus energy ω at different temperatures; **b, c** The temperature derivative of $-\text{Im}\Sigma(\omega, T)$ at zero energy ($\omega = 0$) for γ -Ce and α -Ce, respectively. The results show a maximum temperature derivative at about 40 K for γ -Ce and 129 K for α -Ce.

same value, the strength of effective f - c electron hybridization V_{fc} becomes stronger as T decreasing, which enforces f -electrons to bond indirectly at the critical temperature T_{coh} . Secondly, the f - f indirectly 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 positive feedback processes would repeat again and again, and induce a first-order isomorphous volume phase transition at last. Besides, as observed in many previous experimental works^{6,7}, the phase transition temperature from α to γ is greater than that from γ to α , as much stronger thermal fluctuation is demanded to break the f -electron coherent bonding in α -Ce.

The above-mentioned positive feedback would mean a “hysteresis” phenomenon in the transport and XRD experiments for cerium, which has already been studied in literatures for bulk Ce metal^{6,7,46,47}. As for our 200-nm thin film, we also observed hysteresis in the resistivity between cooling and warming, as shown in Supplementary Fig. 5. Although the resistivity curves for bulk Ce metal and Ce thin film differed in the detail, the phenomenon of hysteresis was robust in both bulk Ce metal and Ce thin film, and the “positive feedback” scenario might be reasonable.

To summarize, we have experimentally and theoretically investigated the physical mechanism of the γ - α phase transition in high-quality single crystalline cerium thin films. ARPES spectra show the hybridization of f level with conduction bands and the formation of a Kondo dip upon cooling the sample from 300 to 17 K, and our ARPES results at low temperature indicated the absence of α -phase at the sample surface. The varied temperature XRD demonstrated that the γ - α phase transition occurred around 50 K, which is retarded by strain effect from substrate comparing with $T_{\gamma-\alpha}$ (about 140 K) of the bulk Ce metal. The Kondo effect can be taken advantage to describe these phenomena. From our DFT + DMFT calculations, we obtained the characteristic temperature of Kondo hybridization T_{KS} at about 80 K and the characteristic temperature of heavy fermion liquid coherence T_{coh} at about 40 K. The former one agreed with the ARPES results, and the latter one is in the neighborhood of $T_{\gamma-\alpha}$ from XRD experiments. Therefore, our experimental and theoretical results proposed that the Kondo scenario might play an important role in the γ - α phase transition of cerium thin films.

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 refs^{48,49}, 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 h to remove the absorbed gases or organic molecules. After annealing at ~950 °C for 18 min under Si flux to produce a (3×3) reconstruction, the substrate was heated to ~1400 °C for 10 min 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 h 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 oxidation 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 microbalance (QCM) and was ~0.127 Å/S at 1620 °C.

VT-XRD experiments

For the varied temperature XRD experiment, the Ce thin films were packed in a glove box under Argon atmosphere after taken out from the MBE chamber, and then transferred to a Panalytical Empyrean X-ray Diffractometer. The sample stage of the diffractometer could be cooled by a close-cycled Helium refrigerator and heated by the heating stage. The sample temperature could be set continuously from room temperature to 15 K. We have taken the XRD spectra on a 200-nm thick Ce thin film from 300 to 20 K with 20 K intervals, and also at the lowest achievable temperature 15 K.

ARPES experiments

For the photoemission spectroscopy experiment, the spectra were excited by the He I α (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.

HRSTEM 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 micrograph was 1024×1024 pixels, with a dwell time of 8 μ 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 package³². We used WIEN2k package based on the full-potential linearized augmented plane-wave (LAPW) method for the density function theory part^{33,50}. 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., $R_{MT} K_{MAX} = 8.0$ and $G_{MAX} = 14.0$. 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^{32,51,52}. The Coulomb interaction U on the Ce f -orbital was set to 6.0 eV with Hund interaction J to 0.7 eV.

DATA AVAILABILITY

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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AUTHOR CONTRIBUTIONS

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 HRSTEM experiments. Yu.L., Y.C., 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.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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