Role of exact exchange in the structural and electronic properties of the α and γ phases of cerium: a density functional theory study

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Abstract
Modeling the α–γ isostructural phase transition of cerium (Ce) within the framework of density functional theory is challenging because the 4f electron in Ce is difficult to characterize. The use of a fraction of exact exchange in the hybrid functional (2012 Phys. Rev. Lett. 109 146402) predicts the existence of the α and γ phases but their relative energy is inconsistent with the experiments. In fact, the role of exact exchange in affecting properties of the α and γ phases has not been well investigated. In this regard, we choose a variable amount of exact exchange (0.05–0.4) and systematically explore the properties of the α and γ phases of Ce including cohesive energies, lattice constants, bulk moduli, magnetic moments, and 4f electron numbers. Notably, a small portion of exact exchange close to 0.1 yields an accurate description of these properties, in particular the predicted relative energy between the α and γ phases agrees with the experiment. We further analyze the density of states, partial density of states, band structures and electron densities of the two phases. We observe that the exact exchange substantially affects the γ phase by localizing the 4f electrons, while it tends to delocalize the electrons in the α phase. Our work provides deep insights into the structural and electronic properties of the α and γ phases of Ce by elucidating the role of exact exchange in hybrid functional calculations.

1. Introduction
Understanding the f electrons of rare-earth and actinide materials is considered to be one of the most challenging topics in condensed matter physics. The rare-earth element cerium (Ce) has an electron configuration of [Xe]4f15d16s2, where the 4f electron is considered to play a key role in determining the anomalous isostructural [face-centered-cubic (fcc)] α–γ phase transition of Ce. In detail, the phase transition is accompanied by a volume collapse of about 15% at ambient pressure and room temperature, and has been intensively studied both experimentally and theoretically [1, 2]. However, the origin of changes of the magnetic property [3–7] during the isostructural transition is still inconclusive.

Despite previous investigations, a common consensus has not yet been reached on the detailed transition mechanism such as the role played by the 4f electron during the α–γ phase transition. So far, there are two competing pictures for the driving mechanism of the isostructural transition: the Mott transition [8, 9] and the Kondo volume collapse (KVC) [10, 11]. On the one hand, the Mott transition model points out that the 4f electron plays a key role in the phase transition and the spd electrons are spectators. The picture assumes that the 4f electron is completely localized in the γ phase while it becomes itinerant in the α phase. On the other hand, in the KVC model, there are no essential differences between
the $\alpha$ and $\gamma$ phases. The model points out that the 4f electron is localized in both phases of Ce; the only difference is the scale of the Kondo temperature. Recently, several studies pointed out that the interplay between Mott and Kondo physics may be important in determining the isostructural transition of Ce [12, 13]. It is uncertain which theory correctly reveals the underlying mechanism of the isostructural transition.

The first-principles methods based on the mean field theory are able to provide insightful information for understanding properties of materials; however, these methods face challenges in accurately characterizing the isostructural transition of Ce. The difficulty lies in the simultaneous determination of the two phases according to the total energy versus volume curve in a single theoretical framework. We take the density functional theory (DFT) [14, 15] as an example. First, all of the calculations [16–19] based on the local density approximation (LDA) and generalized gradient approximation (GGA) failed to yield a double-well solution required in characterizing the $\alpha$ and $\gamma$ phases of Ce. Part of the reason is the lack of corrections to the self-interaction errors in these approximations [20, 21], which has a tendency to delocalize electrons. Johansson et al [9] assumed that the 4f electron was delocalized in the $\alpha$ phase but localized in the $\gamma$ phase and obtained the two phases with a revised GGA functional. The local-spin-density (LSD) approximation was adopted to characterize the $\alpha$ phase while the self-interaction-corrected local-spin-density approximation (SIC-LSD) was used to describe the $\gamma$ phase [22, 23]. Similarly, by combing LDA and LDA + $U$ methods, Wang et al [24] obtained the $\alpha$ and $\gamma$ phases.

However, all of the above computational models cannot yield the $\alpha$ and $\gamma$ phases of Ce within a single theory. In recent years, dynamical mean field theory (DMFT) combined with LDA emerged to be an effective method to investigate this issue, in an attempt to describe both phases within a single theory [25–31]. The typical three-peak structure, as observed in experiments [32, 33], can be reproduced in LDA and DMFT studies. Furthermore, the LDA + DMFT scheme has succeeded in capturing the 4f electronic configurations for both phases as well as their optical properties [34, 35]. However, the computational costs of the LDA + DMFT method are much higher than DFT calculations.

By adopting hybrid functionals within the DFT theoretical framework, Casadei et al [36, 37] were able to capture a double minimum volume–energy curve of Ce. The hybrid functionals adopted in these works, such as PBE0 [38] and HSE06 [39], included a fraction of the exact exchange and yielded stable $\alpha$ and $\gamma$ phases of Ce at zero temperature within a single framework. Subsequently, the electronic structure analysis revealed a localization–delocalization behavior of the 4f electron across the $\gamma$–$\alpha$ transition, which was consistent with the scenario of the Mott transition. Moreover, by considering the entropic contributions, the pressure–temperature phase diagram was determined, which was in reasonable agreement with the experiments [1, 2, 40, 41]. However, the energy ordering of the two phases calculated by these hybrid functionals was in contradiction with the extrapolation of the experimental data to zero temperature [26, 41]. In this regard, the correlation energy of electrons was further included by using the random-phase approximation (RPA) [42, 43]. However, the expensive EX + cRPA method was applied to Ce clusters instead of its condensed phases.

According to the adiabatic connection formula, the exchange energy of the hybrid functional is the admixture of a certain amount of the nonlocal Fock exchange energy to a part of local or semilocal density functional exchange energy [44–47]. Perdew et al rationalized the fraction $a = 0.25$ as the default amount of Fock exchange mixed in the standard DFT exchange energy [38]. In general, hybrid functionals provide a more accurate description for localized electrons due to the mitigation of self-interaction errors [48–50], except very rare failure in some transition metals such as vanadium and niobium [51]. However, the optimal ratio of the nonlocal Fock exchange was argued to be system dependent [38, 52]. For example, Paier et al proposed that more nonlocal Fock exchange would be required in large-gap insulators and less in strongly screening materials or itinerant systems such as metals [53, 54]. Later works [55–57] suggested that the fraction of the nonlocal Fock exchange should be related to the screening strength of given systems.

Specifically, the optimal portion of exact exchange in insulating systems depends on the dielectric constant $\epsilon$. Alkauskas et al [56] proposed that the relation between the optimal fraction of exact exchange $a$ and the optical dielectric constant $\epsilon_{\infty}$ can be qualitatively approximated as $a = \frac{1}{\epsilon_{\infty}}$. For strongly screening materials such as metals, it has been argued that the suitable percentages of the Fock exchange are small values close to zero [38, 55]. In this regard, it seems reasonable to use a small portion (<25%) of nonlocal exchange to describe the structural and electronic properties of Ce metal under different external conditions.

To address the above issue, we performed a systematical DFT study with hybrid functionals including PBE0 and HSE06 to investigate the structural and electronic properties of the $\alpha$ and $\gamma$ phases of Ce. We chose a variable amount of exact exchange ($a = 0.05, 0.1, 0.25$ and 0.4) mixed in the hybrid functionals. The results show that a small amount of exact exchange ($a = 0.1$) improves the description of the electronic structures, as well as the energy ordering between the two phases. The paper is organized as follows. We
describe the setups of computational methods in section 2. We present and analyze the DFT results in section 3, and summarize our findings in section 4.

2. Methods

The DFT calculations presented in this work were performed with the Vienna Ab initio Simulation Package (VASP) 5.4.4 [67–70]. In the spin-polarized calculations of an fcc primitive cell with one Ce atom, the periodic boundary conditions and the Monkhorst–Pack method [71] with a $14 \times 14 \times 14$ $\Gamma$-centered $k$-point mesh were used. The ion–electron interactions were treated by the projector-augmented wave (PAW) method; [72, 73] the atomic configuration in the PAW potential of Ce was chosen to be \textit{5s}^2\textit{5p}^6\textit{6s}^2\textit{4f}^{15}\textit{d}^1 with 12 valence electrons. Here we employed the PBE0 functional [38] and HSE06 functional [39] (range separated hybrid functional). The hybrid functionals admix a certain amount of Fock exchange to a local or semilocal density functional, which can be expressed as the simplest formulation:

$$E_{\text{hybrid}} = E_{\text{DFT}}^{\text{xc}} + aE_{\text{xc}}^{\text{EX}} + (1 - a)E_{\text{DFT}}^{\alpha},$$

where $E_{\text{DFT}}^{\text{xc}}$ and $E_{\text{DFT}}^{\alpha}$ denote the exchange and correlation energies, respectively. $E_{\text{xc}}^{\text{EX}}$ is the non-local Fock exchange energy with $a$ being the mixing parameter. In this work, the parameter $a$ was set to 0.05, 0.1, 0.25 and 0.4 for both PBE0 and HSE06 functionals, respectively. The kinetic energy cutoff of plane-wave basis was set to 400 eV and the electronic iteration convergence threshold was set to $10^{-6}$ eV. We employed the Gaussian smearing method with a smearing width of 0.001 eV. The stability of crystal structure is characterized by the cohesive energy, of which a smaller value (more negative) means the corresponding crystal structure is more stable. Here the computed cohesive energy $E_{\text{coh}}$ is defined as

$$E_{\text{coh}} = \sum_i E_i - E_{\text{bulk}},$$

where $E_{\text{bulk}}$ and $E_i$ denote the total energy of the bulk Ce system, and a single Ce atom with the index being $i$, which was put in a $15 \times 15 \times 15$ Å box with the $\Gamma$-only $k$-point and spin-polarized calculation being performed. In order to obtain converged energy curves with respect to different lattice constants for the $\alpha$ and $\gamma$ phases of Ce, the ground-state wave functions at one particular lattice constant can be used as initial guess wave functions of the calculations at a smaller lattice constant following the procedure adopted in reference [37]. In this way, two distinct self-consistent solutions were obtained with the same lattice constant.

3. Results and discussions

3.1. Bulk properties

We investigate the effects of the mixing parameter $a$ of hybrid functionals on the bulk properties of Ce, which mainly include equilibrium lattice constants $a_0$, cohesive energies $E_{\text{coh}}$, bulk moduli $B$, and energy differences $\Delta E$ of the $\alpha$ and $\gamma$ phases of Ce. Based on the data shown in table 1, we find that the HSE06 functional provides almost identical results to those obtained by the PBE0 functional. For example, when $a$ is set to 0.25, both hybrid functionals yield the same equilibrium lattice constants $a_0$ for the $\alpha$ (4.66 Å) and $\gamma$ (5.25 Å) phases. Similarly, the two functionals yield close bulk moduli $B$ and energy differences $\Delta E$. Therefore, our following discussions are mainly based on the PBE0 results. In addition, the relative errors of equilibrium lattice constants of the $\alpha$ and $\gamma$ phases between our results and the all-electron DFT calculations [36, 37] are 0.65% and 0.57%, respectively. Furthermore, our computed bulk moduli $B$ only show a small deviation from the data obtained by all-electron calculations, suggesting that the usage of the PAW potential is reasonable as compared to the all-electron calculations.

Notably, when the mixing parameter $a$ changes from 0.4 to 0.1, the equilibrium lattice constant $a_0$ of the $\gamma$ phase decreases monotonically from 5.31 to 5.15 Å, getting closer to the experimental value of 5.1610 Å [64]. Meanwhile, $a_0$ of the $\alpha$ phase varies from 4.65 to 4.69 Å, which agrees reasonably with the experimental value of 4.824 Å [61]. In table 1, we do not show results with $a = 0.05$ because no energy minimum is found for the $\gamma$ phase. The changes of the lattice constants imply that the exact exchange has a larger effect on the $\gamma$ phase than the $\alpha$ phase, which we will discuss later.

Figure 1 shows the cohesive energy curves of both $\alpha$ and $\gamma$ phases of Ce in terms of different lattice constants, where results from PBE0 ($a = 0.05, 0.1, 0.25$ and 0.4) and PBE (black dot line) are shown. Compared to the PBE result, the cohesive energy curve of $a = 0.05$ exhibits a tendency to split into two curves. Interestingly, as the fraction $a$ increases from 0.05 to 0.1, the two cohesive energy curves corresponding to the two phases clearly emerge, and the $\alpha$ phase is predicted to be more stable than the $\gamma$
Fock exchange is system dependent [38, 52], and is related to the inverse dielectric constant [55–57]. Since properties of Ce, nonlocal exchange into hybrid functionals to describe the structural and electronic metals like Ce have large dielectric constants, it is reasonable to introduce a relatively small portion of the exact exchange on the 4f electrons of Ce. As mentioned in section 1, the optimal ratio of the nonlocal exchange is set to 0.1, 0.25 and 0.4.

Moreover, we find that the increased equilibrium lattice constant of the α-phases leads to a small decrease for the γ-phases [62]. Meanwhile, the computed magnetic moments for the α-phases of Ce approach zero for all of the three values of α, which may arise from the difference between the all-electron potential and the PAW potential of Ce. Nevertheless, the α phase is predicted to be 0.59 eV less stable than the γ phase when α = 0.25, which agrees with previous all-electron calculations but is in contradiction with the experiments; the incorrect energy ordering becomes more severe with an increase of α, where the γ phase is 1.09 eV more stable than the α phase. Based on the above analysis, we conclude that the fraction of exact exchange plays an essential role in the evaluation of the energy difference between the α and γ phases, which may be determined by the effects of exact exchange on the 4f electrons of Ce. As mentioned in section 1, the optimal ratio of the nonlocal Fock exchange is system dependent [38, 52], and is related to the inverse dielectric constant [55–57]. Since metals like Ce have large dielectric constants, it is reasonable to introduce a relatively small portion of nonlocal exchange into hybrid functionals to describe the structural and electronic properties of Ce.

Table 1 also lists the computed bulk moduli, which are obtained by utilizing the Murnaghan equation of state [74]. Although the errors of computed bulk moduli from PBE0 are relatively large especially for the α phase, these values are in general smaller than results from other computational methods [SIC-LSD, LDA + U, VMC, and LRDMC]. Moreover, we find that the increased equilibrium lattice constant of the α phase leads to a small decrease for the bulk modulus. In summary, the bulk moduli from these first-principles methods are still substantially larger than the experimental value, which remains as an unresolved puzzle.

By adopting the hybrid functional in DFT calculations, the magnetic moments for the α phase of Ce approach zero for all of the three values of α, which are consistent with the experimental value [62]. Meanwhile, the computed magnetic moments for the γ phase of Ce are 1.45, 1.26, and 1.17 μB for α = 0.4, 0.25, and 0.1, respectively. The results obtained from α = 0.1 (1.17 μB) are closer than the other two values when compared to the experimental value of μ ≈ 1 μB [63]. Since the PBE functional cannot predict the existence of the γ phase, we obtain a magnetic moment of 0.008 μB for the α phase. If the magnetic moments of the γ phase are decomposed into contributions from f(d) electrons of each atom, only those magnetic moments within a radius cutoff (Wigner–Seitz radius) can be obtained by using the current algorithms implemented in VASP, and the magnetic moments contributed by the interstitial region of the cell are missing. Therefore, the summation of the magnetic moments contributed by the f and d electrons must be smaller than the total magnetic moments shown in table 1. In fact, we find the total magnetic moments are 0.97 (0.12), 0.95 (0.08), and 0.90 (0.06) μB for α = 0.4, 0.25, and 0.1, respectively. The result suggests that both f and d electrons contribute to the change of magnetic moments.

### 3.2. Occupation numbers of 4f electrons

The occupation numbers of the 4f electrons in both α and γ phases of Ce have been measured from several experiments [63, 66, 75–77]. For example, Wülloud et al reported an estimation of the 4f electron occupations n_{4f} ≈ 0.85/0.90 for α-Ce, and n_{4f} ≈ 1 for γ-Ce [63]. Rueff et al combined the resonant

| Methods     | a (Å) | a_0 | E_{coh} (eV) | B (GPa) | μ(μ_B) | n_{4f} | α-Ce | γ-Ce | ΔE (eV) |
|-------------|-------|-----|--------------|---------|--------|--------|------|------|--------|
| PBE0        | 0.1   | 4.69| 3.947        | 42.3    | 0.02   | 0.88   | 5.15 | 3.914| 26.5   |
|             | 0.25  | 4.66| 3.150        | 47.9    | 0.02   | 0.73   | 5.25 | 3.739| 1.26   |
|             | 0.4   | 4.65| 2.484        | 49.2    | 0.01   | 0.59   | 5.31 | 3.575| 1.45   |
| HSE06       | 0.1   | 4.69| 3.996        | 41.5    | 0.01   | 0.89   | 5.13 | 3.955| 23.3   |
|             | 0.25  | 4.66| 3.263        | 46.3    | 0.04   | 0.73   | 5.25 | 3.829| 1.19   |
|             | 0.4   | 4.65| 2.658        | 49.0    | 0.01   | 0.57   | 5.31 | 3.724| 2.00   |
| PBE0 [37]   | 0.25  | 4.63| 3.76         | 50.5    | 0.20   | 0.73   | 5.22 | 4.35 | 1.00   |
| SIC-LSD     | 0.1   | 4.69| 4.43         |         |        |        | 5.14 | 3.4  |        |
|             | 0.25  | 4.66| 4.326        |         |        |        | 5.04 | 3.4  |        |
|             | 0.4   | 4.65| 2.658        |         |        |        | 4.976| 3.8  |        |
| LDA + U [59]| 0.1   | 4.69| 5.09         |         |        |        | 5.055| 45  |        |
|             | 0.25  | 4.66| 4.326        |         |        |        | 4.976| 38  |        |
|             | 0.4   | 4.65| 2.658        |         |        |        | 5.055| 45  |        |
| Exp.        | 0.25  | 4.63| 3.76         | 50.5    | 0.20   | 0.73   | 5.22 | 4.35 | 1.00   |
|             | 0.4   | 4.65| 2.658        | 49.0    | 0.01   | 0.57   | 5.31 | 3.724| 2.00   |
inelastic x-ray scattering experiments with the DMFT calculation to yield $n_{4f} \approx 0.81$ for the $\alpha$ phase and $n_{4f} \approx 0.97$ for the $\gamma$ phase [66]. Table 1 shows the computed occupation numbers of $4f$ electrons in the two phases as a function of $a$ used in the hybrid functional calculations. As $a$ decreases from 0.4 to 0.1, $n_{4f}$ of the $\alpha$ phase increases linearly from 0.59 to 0.88, while the value keeps as a constant of 0.98 in the $\gamma$ phase. Therefore, the $4f$ electron occupations computed by $a = 0.1$ are consistent with the experimental values.

Interestingly, the amount of exact exchange affects the lattice constant of the $\gamma$ phase more severely than that of the $\alpha$ phase, but here for the $f$-electron number, an opposite behavior is observed. Meanwhile, as $a$ decreases from 0.4 to 0.1, the number of $d$ electrons of the $\alpha$ phase decrease from 1.28 to 1.14, while the number of $d$ electrons in the $\gamma$ phase increases from 0.70 to 0.81. The result suggests that the mixing ratio $a$ also affects the $d$ electrons, which further interact with the $4f$ electrons. Note that only the electron density in a sphere with a cutoff radius $r_c = 1.323$ Å (Wigner–Seitz radius) in the Wigner–Seitz cell is taken to calculate the electron numbers. With this criterion, the almost unchanged $4f$ electron number in the $\gamma$ phase suggests that the $4f$ electron is localized in this phase. In stark contrast, the $4f$ electron in the $\alpha$ phase is more delocalized than that in the $\gamma$ phase. The number of $4f$ electrons out of the sphere in the $\alpha$ phase is about 0.41, 0.26, and 0.12 for $a = 0.4$, 0.25 and 0.1, respectively. This implies the $4f$ electron becomes more localized for the $\alpha$ phase as $a$ decreases from 0.4 to 0.1.

We further compute the contributions of seven $4f$ orbitals to the occupation number of the $4f$ electrons. Table 2 shows the components of $4f$ orbitals as a function of $a$ in the PBE0 functional for both $\alpha$ and $\gamma$ phases. The two spin components are summed for brevity. In particular, the PBE results are included when setting $a = 0$. Note that the minimum of $\gamma$ phase does not emerge when $a$ is set to 0.05 as shown in figure 1, so that the lattice constant is taken as 5.50 Å in the calculation of $\gamma$ phase for $a = 0.05$. We observe that the second $4f$ orbital with the $xyz$ symmetry dominates among the seven $4f$ orbitals for all $a$ values, which is more apparent in the $\gamma$ phase. Furthermore, the two phases exhibit opposite trends in the occupation of the $4f$ $xyz$ orbital as $a$ decreases from 0.4 to 0.05. On the one hand, the component of the $xyz$ orbital increases from 0.206 to 0.279 for the $\alpha$ phase. On the other hand, the contribution of the $xyz$ $4f$ orbital decreases from 0.962 to 0.835 for the $\gamma$ phase. Importantly, we notice that the contributions of the seven $4f$ orbitals from PBE are close to those from PBE0 for the $\alpha$-Ce because PBE itself describes the $\alpha$ phase. However, the PBE results show a substantially different occupation pattern compared to those from PBE0 for the $\gamma$ phase even for $a = 0.05$, demonstrating that the exact exchange imposes minor effect on the $\alpha$ phase but significantly alters the electronic structure of the $\gamma$ phase.

3.3. Density of states
Previous experiments [32, 33] have confirmed the characteristic three-peak structure of Ce located approximately at $-2$, 0, and 4 eV with respect to the Fermi level in the energy spectrum, which was
Table 2. Contributions of seven 4f orbitals to the 4f electron number of the $\alpha$ and $\gamma$ phases. The mixing parameter of exact exchange $a$ in the PBE0 functional is chosen to be 0.05, 0.1, 0.25 and 0.4. The result from the PBE functional is shown with $a = 0$. The two spin components are summed for brevity.

| 4f orbitals | $\alpha$-Ce | $\gamma$-Ce |
|-------------|-------------|-------------|
| $y^3 - 3yx^2$ | 0.177 | 0.05 | 0.041 | 0.005 | 0.003 |
| $xyz$ | 0.278 | 0.075 | 0.037 | 0.023 | 0.001 |
| $yz^2 - yr^2$ | 0.276 | 0.073 | 0.038 | 0.024 | 0.001 |
| $zx^2 - 3y^2$ | 0.174 | 0.069 | 0.036 | 0.021 | 0.001 |
| $xz^2 - 3zr^2$ | 0.174 | 0.069 | 0.036 | 0.021 | 0.001 |
| $zx^2 - zy^2$ | 0.093 | 0.079 | 0.047 | 0.025 | 0.014 |
| $x^3 - 3xy^2$ | 0.058 | 0.044 | 0.004 | 0.004 | 0.001 |
| $xyz$ | 0.133 | 0.124 | 0.107 | 0.081 | 0.002 |

Figure 2. DOS of the $\alpha$- and $\gamma$-phases of Ce. The PBE0 functional is adopted with $a = 0.1$ (red), 0.25 (green), and 0.4 (blue). The equilibrium lattice constants listed in table 1 are taken. The DOS is the sum of the spin up and spin down DOS. Experimental data [63, 78] are shown for comparison.

reproduced by LDA + DMFT calculations [26, 28, 29]. In fact, our results are consistent with previous DFT results [37], which do not quantitatively agree with the experimental spectrum. However, we still consider DFT can be useful in providing ground-state energetic information of Ce, and the analysis of the density of states (DOS) and band structures from DFT provides more information about the 4f electron of Ce.

Figure 2 illustrates the DOS of the two phases of Ce from the PBE0 functional, as well as those from the experiments [63, 78]. The computed DOS is the sum of the spin up and spin down components. An approximated three-peak structure is captured in the $\gamma$ phase for all of the $a$ values, though the peak positions and intensities are not consistent with the experimental ones. When $a = 0.1$ is used for the $\alpha$ phase, we observe a peak locates around $-2$ to 0 eV below the Fermi level and another large peak at 1.0 eV above the Fermi level. As the parameter $a$ increases from 0.1 to 0.4 for both solid phases, these peaks move further away from the Fermi level, which is related to the localization features of the 4f electrons. We further plot the partial density of states (PDOS) in figure 3, from which we observe the peaks around the Fermi level in the $\alpha$ and $\gamma$ phases arise mainly from the 4f electrons. For example, in the $\gamma$ phase, the peak located below the Fermi level and the shoulder structure above the Fermi level next to the large peak are mainly caused by 4f orbitals in the spin-up and spin-down channels, respectively. In contrast, for the DOS of the $\alpha$ phase, the two spin channels yield similar DOS, and the occupied states are mainly contributed by both d and f electrons.
3.4. Band structures
The band structures of the $\alpha$ and $\gamma$ phases computed by the PBE0 functional with $a = 0.1$ and 0.25 are reported in figure 4. Since the $\alpha$ phase has almost zero magnetic moments, the spin-up and spin-down components of band structures are almost identical. A distinct feature of the bands in the $\gamma$ phase is a flat band located at around $-1$ eV below Fermi level when $a = 0.1$. The flat band in 4f character shows small dispersion, implying that the 4f electron has a large effective mass and tends to be localized in the $\gamma$ phase. In fact, the flat band exhibits the localized feature of the $xyz$ orbital and its contribution to the electron number is 0.868 (listed in table 2). As for $a = 0.25$, the flat band shifts to around $-3$ eV below the Fermi level and becomes more flat, suggesting that the 4f electron is more localized. The localized feature is further confirmed by noticing that the electron number contributed by the $xyz$ orbital increases from 0.868 ($a = 0.1$) to 0.944 ($a = 0.25$) in table 2.

In stark contrast, the flat band is absent in the band structure of the $\alpha$ phase, indicating that the occupied 4f bands of the $\alpha$ phase hybridize more strongly with the spd bands than those of the $\gamma$ phase. The large dispersion of the bands in the $\alpha$ phase suggests that the 4f electronic states are more delocalized compared to those in the $\gamma$ phase. The results provide further microscopic details for the peak below the Fermi level shown in figure 3, and are consistent with the difference of the magnetic property in the two phases as listed in table 1. In conclusion, the computed band structures point out the substantial differences of the occupied 4f electrons in the two phases at zero temperature.

3.5. Electron density analysis
In order to further clarify the different roles played by the 4f electrons in the $\alpha$ and $\gamma$ phases of Ce, we perform an analysis of the electron density in figure 5. The equilibrium lattice constants in table 1 are employed for different $a$ values and phases. Figures 5(a) and (b) illustrate the band-decomposed electron density differences between $a = 0.1$ and 0.25 for the $\alpha$ and $\gamma$ phases, respectively. By using the band-decomposed analysis for a single band, we obtain contributions from different angular momentum channels. The flat bands from the two phases marked with green arrows in figure 4 are chosen. Interestingly, we find that the differences of the band-decomposed electron density for the two phases possess distinct shapes. Compared to the data listed in table 2, we find the sphere shape in figure 5(a) origins from the fact that the contributions from the seven 4f orbitals in the $\alpha$ phase increase comparably as $a$ decreases from 0.25 to 0.1. As explained above, in the $\gamma$ phase, the electron density difference is mainly contributed by the
Figure 4. Band structures of the $\alpha$ and $\gamma$ phases of Ce calculated by using the PBE0 functional with the mixing parameter $a = 0.1$ and 0.25.

Figure 5. Band-decomposed electron density differences between $a = 0.1$ and $a = 0.25$ for (a) the $\alpha$ phase and (b) the $\gamma$ phase of Ce. The density difference is projected onto the [100] plane; the [010] and [001] planes are equivalent. The red dot depicts the Ce atom. (c) Charge difference as computed from the PBE0 and PBE calculations for the $\alpha$ phase (black) and the $\gamma$ phase (red) with $a = 0.1, 0.25$ and 0.4. The dashed lines present the cubic spline extrapolation of the solid lines to $a = 0$. (d) Charge difference $\Delta Q$ between PBE and PBE0 results. The solid and dashed lines respectively correspond to $\Delta Q$ of the $\alpha$ phase and the $\gamma$ phase. Different values of $a$ including 0.1, 0.25 and 0.4 are chosen.

4f $xyz$ orbital, resulting in a shape that is close to the electron density of the $xyz$ orbital, as illustrated in figure 5(b).

For in-depth analysis of the spatial electron density differences caused by the 4f electrons, we define the charge difference from electron densities from PBE and PBE0 calculations

$$\Delta Q = \int |\rho(r)_{\text{PBE0}} - \rho(r)_{\text{PBE}}| 4\pi r^2 \, dr,$$

where $\rho(r)_{\text{PBE0}}$ and $\rho(r)_{\text{PBE}}$ denote the radial functions of the ground-state electron density as obtained from the PBE0 and PBE exchange–correlation functionals, respectively. The radius cutoff is chosen as half of the distance from Ce to its nearest neighboring atom. The charge difference $\Delta Q$ with respect to the mixing parameter $a$ in both phases is shown in figure 5(c) and the following points can be addressed.

First, the $\Delta Q$ of the $\alpha$ phase increases linearly with $a$, which is consistent with the reduction of the 4f electron number listed in table 1, suggesting that the $\Delta Q$ of the $\alpha$ phase is mainly caused by the more delocalized 4f electrons. Second, because the 4f electron number in the $\gamma$ phase is almost unchanged with respect to $a$ (table 1), the increased $\Delta Q$ of $\gamma$ phase implies that the electron density is redistributed around the Ce atoms within the cutoff radius. Third, by using the cubic spline extrapolation of the charge difference...
to $a = 0$, we find $\Delta Q$ is close to zero in the $\alpha$ phase but about 0.241 in the $\gamma$ phase, which indicates that the use of hybrid functional leads to an abrupt change of charge in the $\gamma$ phase.

In figure 5(d), the angular part of electron density is integrated out in order to plot the charge difference along the radial $r$,

$$\Delta Q(r) = (\rho(r)_{PBE0} - \rho(r)_{PBE}) 4\pi r^2 \, dr. \tag{4}$$

Here $a = 0.1$, 0.25, and 0.4 for both phases of Ce are utilized. In general, we find that the signs of $\Delta Q(r)$ are opposite in the two phases and conclude the following points. First, when the hybrid functional is applied to the $\gamma$ phase, $\Delta Q$ is mainly contributed by the charge transfer from the outer region to the inner region around the Ce ion, and the effect becomes more significant as $a$ increases from 0.1 to 0.4. In other words, the electron density becomes more localized in the $\gamma$ phase when $a$ becomes larger. Second, in stark contrast, $\Delta Q$ for the $\alpha$ phase is reduced in the inner region and increases in the outer region, which is consistent with the reduced number of 4f electrons shown in table 1. Moreover, the effect is more substantial as $a$ increases from 0.1 to 0.4, suggesting that the electron density becomes more delocalized in the $\alpha$ phase when $a$ becomes larger. Third, the $\Delta Q(r)$ for the $\gamma$ phase is substantially larger than that of the $\alpha$ phase, implying that the hybrid functional affects the electronic properties of the $\gamma$ phase more than those in the $\alpha$ phase.

4. Conclusions

We have performed a thorough DFT study of the $\alpha$ and $\gamma$ phases of Ce using the PBE0 and HSE06 hybrid functionals, where variable fractions of the exact exchange ($a = 0.05–0.4$) were chosen to be mixed in the hybrid functionals. We systematically studied a variety of structural and electronic properties of Ce including cohesive energies, bulk moduli, magnetic moments, and 4f electron numbers. By comparing these properties to the available experimental data, we observed a small portion of exact exchange close to 0.1 yielded an accurate description for the two phases. In particular, the energy ordering between the $\alpha$ and $\gamma$ phase can be accurately determined. In order to elucidate the effects of exact exchange on the description of the 4f electron in the $\alpha$ and $\gamma$ phases, we further analyzed the DOS, PDOS, band structures and electron densities of the two phases with different $a$ values. The exact exchange was found to substantially affect the $\gamma$ phase by localizing the 4f electrons, while it delocalized the 4f electrons in the $\alpha$ phase. In particular, the exact exchange imposed greater effects on the description of the 4f electron in the $\gamma$ phase than in the $\alpha$ phase. Our results provided new support for the Mott transition scenario that the localization/delocalization of the 4f electron plays an important role in the isostructural transition. However, the contribution of the KVC model cannot be ruled out due to the lack of the entropy contribution in the zero temperature ground state DFT calculations. In this regard, our work inherently suggested that the Mott scenario is the most plausible model at zero temperature.

In conclusion, our work demonstrated that for strongly screening materials such as metals, it is reasonable to use a small portion of nonlocal exchange in hybrid functionals to describe the structural and electronic properties of Ce. This work provided new clues for the theoretical investigation of the 4f electrons by using an appropriate fraction of exact exchange in hybrid functional calculations. In future works, it might be interesting to explore the usage of the double-hybrid functionals or calculate larger-size systems via machine learning techniques. In addition, combing DFT with molecular dynamics may be an effective tool to tackle the temperature effects on the isostructural phase transition of Ce.

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