Covalent versus localized nature of $4f$ electrons in ceria: Resonant angle-resolved photoemission spectroscopy and density functional theory

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We have conducted resonant angle-resolved photoemission spectroscopy of well-defined CeO$_2$(111) and $c$–Ce$_2$O$_3$(111) model surfaces, revealing distinct $f$ contributions in the valence band of the two compounds. In conjunction with density functional theory calculations, we show that the $f$ contribution in CeO$_2$ is of a covalent nature, arising from hybridization with the O 2$p$ bands. In contrast, $c$–Ce$_2$O$_3$ exhibits an almost nondispersive $f$ state at 1.3 eV, which is indicative of almost negligible $c$–$f$ hybridization.

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I. INTRODUCTION

The ground state of CeO$_2$ has been a controversial topic [1–10]. The controversy involves the assignment of the nominally ionic CeO$_2$ as either a mixed valent or a covalent compound, and it arises partially due to the inability to distinguish these electronic configurations using core-level photoelectron spectroscopy, namely that of the Ce 3$d$ level [10]. Strikingly, the ambiguity of the assignment is still prevalent in the scientific literature [11], sustained by a loose usage of the respective terms. By definition, mixed valent compounds contain cations in different oxidation states. The distinguishability of crystal sites occupied by the cations is related to the extent of the mixing between the configurations (typically cation-cation mixing) [12]. This effectively leads to either a highly unusual integral or nonintegral mean oxidation state of the cation [13]. On the other hand, covalent compounds contain only one type of cation site, and they exhibit a nonintegral valence as a consequence of hybridization (typically cation-anion mixing) [14]. In the case of ceria, where there are no crystallographically distinguishable cerium sites in the lattice, the fundamental difference between the two configurations lies in the character of the occupied states. The homogeneous mixed valent ground state would feature a partial occupation of the highly localized atomiclike Ce 4$f$ level [15] through valence fluctuation, while the covalent ground state would exhibit an empty Ce 4$f$ level with the bonding electrons spin-paired with the ligand (specifically the closed O 2$p$ shell) [14]. The two configurations would manifest different responses to electronic perturbations, such as a core hole, an oxygen vacancy, foreign interstitial or substitutional species, adsorbates, or electronic potential in an electrochemical device. The importance of understanding the behavior of the electrons in ceria due to said perturbations is highlighted by recent studies showing gaps in understanding the bonding mechanism and reactivity of ceria [16] and metal oxides in general [17].

Notably, the established mixed valent interpretation of core-level photoemission from ceria [1], based on the semiempirical Gunnarson-Schönhammer theory utilizing a single-impurity Anderson Hamiltonian, has been called into question. Rigorously calculated configuration interaction wave functions for CeO$_2$ and Ce$_2$O$_3$ were used to provide an ab initio theoretical description of core-level photoemission accounting for many-body effects [18–20]. The results show that experimental spectra can be modeled through covalent interaction, revealing possible errors in the former approach.

Motivated by the above-mentioned controversy and the unsatisfactory understanding of photoemission in ceria in general, herein we present the results of a combined angle-resolved photoemission spectroscopy (ARPES) and density functional theory (DFT) study of the 4$f$ electrons in ceria. Leveraging recent advances in in situ preparation of well-defined ceria model surfaces, we directly compare CeO$_2$, a nominal 4$f^0$ compound, and $c$–Ce$_2$O$_3$, a nominal 4$f^1$ compound, and we reveal the covalent nature of the 4$f$ admixture into the O 2$p$ valence band in CeO$_2$ in contrast to the highly localized 4$f$ electrons in $c$–Ce$_2$O$_3$. As a consequence, we show that the resonant photoemission enhancement at the 4$d \rightarrow 4$f absorption threshold in CeO$_2$ does not originate from the occupation of localized 4$f$ states on Ce atoms in the ground state, rather it arises from the covalent character of the O 2$p$ valence band through interatomic effects.

II. METHODS

ARPES measurements were performed with 110–130 eV $p$-polarized photons on the linear undulator beamline BL-1 at the Hiroshima Synchrotron Radiation Center (HiSOR) at Hiroshima University. The energy and momentum resolution were set at 30 meV and 0.015 Å$^{-1}$, respectively. The experiments were carried out with the sample cooled down to 12 K. Highly ordered epitaxial ceria films exposing the (111) surface of the fluorite lattice were prepared by reactive evaporation of Ce onto Cu(111) single crystal in $5 \times 10^{-5}$ Pa of O$_2$ at a substrate temperature of 250 °C in the preparation chamber connected to the ARPES chamber. The films were around 3 nm thick, which is thick enough to guarantee continuity and mitigation of possible size effects [8,21] while still being...
thin enough to avoid charging during measurements. The stoichiometry of the prepared layers was carefully controlled using a Ce-ceria interfacial reaction [22]. The preparation procedure has been described in detail in Ref. [21]. Briefly, metallic Ce is deposited onto a ceria surface and the sample is heated to 600 °C. The elevated temperature allows oxygen to diffuse through the ceria lattice to the Ce metal overlayer, which then oxidizes and adopts the fluorite structure of the underlying ceria.

Spin-polarized DFT calculations based on the Heyd-Scuseria-Ernzerhof (HSE06) [23] hybrid functional were carried out using the projected augmented wave (PAW) method as implemented in VASP (version 5.3) [24,25]. The (4f,5s,5p,5d,6s) states of Ce and the (2s,2p) states of O were treated as valence states and expanded using a plane-wave basis set up to 400 eV. For bulk CeO2, the lattice constant was optimized on an (11×11×11) Monkhorst-Pack k-point grid to be 5.40 Å, and the O 2p-Ce 4f band gap was calculated to be 3.5 eV, both in close agreement with previous experimental (5.41 Å [26] and 3 eV [3]) and HSE06 results (5.41 Å and 3.3 eV [27]). The equilibrium lattice constant of c–Ce2O3 (bixbyite) was calculated to be 11.20 Å (versus the experimental value of 11.16 Å [28]) with all atoms in the bulk unit cell fully relaxed to below 0.03 eV/Å and the k-space sampled at the Γ point only. The antiferromagnetic state was used, although it was only marginally more stable than the ferromagnetic state. Electronic structures were calculated on a (3×3×3) Monkhorst-Pack k-point grid using the frozen optimized bulk structure. The Ce 4f–5d band gap was calculated to be 2.6 eV (versus the experimental value of 2.4 eV [29]). Core-level electron excitation (4d → 4f) was done using the method of Köhler and Kresse [30] and was applied to all Ce atoms in CeO2 and c–Ce2O3. The bulk oxidation energy for c–Ce2O3 + ½O2 → 2CeO2 was calculated to be −3.12 eV, with available estimates falling between −3.5 and −4.0 eV at ambient temperature [31,32].

III. RESULTS AND DISCUSSION

To elucidate the nature of the ground state of CeO2, we use c–Ce2O3 as a reference 4f4 compound [22]. The advantage of this approach over other prototypical 4f1 compounds that have been previously used for the purpose, such as CeF3 [5], is that it minimizes the influence of structural and chemical variation on the electronic configuration. The Ce sublattice in both CeO2 and c–Ce2O3 is practically identical, the only difference being ordered oxygen vacancies in the O sublattice in c–Ce2O3 [33]. Moreover, we can exploit the isostructural CeO2 ↔ c–Ce2O3 transition and use one sample for both systems, further reducing the extrinsic contributions to our experimental results [21].

Resonant photoemission is a commonly used tool for enhancing the intensity of photoemission features originating from states with low density and for gauging hybridization strength in correlated electron systems, especially the c-f hybridization of cerium compounds [34]. Particularly in ceria, the 4d → 4f resonant transition is routinely used to reveal the occupation of the 4f state, a fingerprint of Ce3+ [35]. However, both CeO2 and c–Ce2O3 exhibit a resonant enhancement at the 4d → 4f photoabsorption threshold (125 and 121 eV for CeO2 and c–Ce2O3, respectively), albeit with different characters. The resonant feature in c–Ce2O3 directly overlaps the direct photoemission 4f peak and has comparable width, while the resonant feature in CeO2 overlaps the top of the O 2p band and is noticeably wider than the 4f photoemission peak in c–Ce2O3. The valence-band photoemission spectra showing the resonant enhancement at the 4d → 4f photoabsorption threshold for CeO2 and c–Ce2O3 are shown in Fig. 1.

The resonant enhancement in c–Ce2O3 can be explained by constructive interference of the direct photoemission from the 4f level with an indirect super Coster-Kronig decay of an intermediate 4d94f1 state:

$$\text{4d}^{10}4f^1 + h\nu \rightarrow \text{4d}^94f^2 \rightarrow \text{4d}^{10}4f^0 + e^-,$$

where h\nu and e− stand for an incident photon and a photoelectron, respectively. To interpret the resonant enhancement in CeO2 using the same arguments, one would have to start from an initial configuration with one electron in the 4f
level—a $4d^{10}4f^1 L$ state. This would make CeO$_2$ essentially a $4f^1$ compound in the case of the covalent ground state. Consequently, the assumption of the $4d^{10}4f^1 L$ initial state inevitably leads to the homogeneous mixed valent ground state of CeO$_2$ with a partial occupation of the $4f$ level through mixing between $4f^{10}$ and $4f^1 L$ configurations defined by the integer $4f$ occupation number. However, this description is based on the assumed resonant enhancement process at the $4d \rightarrow 4f$ photoabsorption threshold in CeO$_2$ involving the ground state of the $4f^1 L$ configuration, which is not self-evident. Specifically, the extent of the final-state effects in the resonant photoemission process has not been previously accounted for.

While the occupation of the localized (atomiclike) $4f$ level in the homogeneous mixed valent ground state of ceria is expected to generate a dispersionless photoemission feature, the $p$-bonding mediated itinerant nature of extended covalent states (of $4f$ and $2p$ symmetry) would give rise to an observable dispersion in ARPES. To examine these effects, we have followed the dispersions at the on-resonance for CeO$_2$ and c–Ce$_2$O$_3$ along the $\bar{M}-\bar{\Gamma}-\bar{M}$ direction (in surface Brillouin zone notation).

Figures 2(b) and 2(c) show the on-resonance ARPES image plots for CeO$_2$ and c–Ce$_2$O$_3$, respectively. Compared with the off-resonance ARPES image plot for CeO$_2$ shown in Fig. 2(a), the dispersive features at the binding energy of 3–6 eV are clearly observable. Note that in Fig. 2(b), the Ce $4f$ derived spectral intensity is much enhanced at a binding energy of 3–4 eV where O $2p$ states exist, indicating covalent hybridization between Ce $4f$ and O $2p$. On the other hand, the $4f$ derived spectral feature in c–Ce$_2$O$_3$ at a binding energy of 1.9 eV exhibits no discernible dispersion within the experimental resolution [Fig. 2(c)]. These results indicate different resonant photoemission processes in the two compounds: more specifically, there is no occupation of atomiclike localized $f$ states in the ground state of CeO$_2$.

To further ascertain the covalent hybridization in the valence band of ceria, we have calculated electronic properties in the intermediate states ($4d^{10}4f^1$ for CeO$_2$ and $4d^{10}4f^2$ for c–Ce$_2$O$_3$). The density of states plots are shown in Fig. 1. We find, in agreement with previous DFT studies [36], that the O $2p$ band in the ground state of CeO$_2$ has a small $4f$ and $5d$ admixture at the top and the bottom of the band, respectively. However, this alone cannot be used to abandon the pure ionic bonding picture in ceria (originating from the nominal electron configuration) as the degree of mixing in the calculated partial density of states is comparable to other recognized ionic compounds, such as NaCl [37]. On the other hand, the intermediate state shows an appreciable increase in the $4f$ admixture into the O $2p$ band, to such an extent that the valence band looks covalent in character. It should be noted that the major increase of the $f$ contribution around 5–6 eV is related to the excited $f$ electron of the intermediate state, which will be further discussed below. This behavior is consistent with closed shell screening of the $4d$ core hole by covalent electrons [38]. Appropriately, the response of O $2p$ electrons to a $4d$ core hole in c–Ce$_2$O$_3$ is less significant due to the occupation of the highly localized $4f$ level by two electrons, which can effectively screen the positive charge of the core hole. An interesting aspect of the intermediate $4d^{10}4f^1$
state of CeO$_2$ is that there is no observable gap between the O 2$^p$ pDOS and the 4$f$ pDOS at the Fermi level (Fig. 1).

We examine band-structure calculations along $X$-$\Gamma$-$L$ (in bulk Brillouin zone notation), a straight line close to the experimental setup, for the ground state and the intermediate state of CeO$_2$ [Fig. 3(a)]. Apart from lifting the degeneracy of the 2$p$ bands, it can be seen that as a consequence of the point charge of the core hole, the additional band of the intermediate state appears at 5 eV at $\Gamma$, directly overlapping the O 2$p$ level. It is noteworthy that the excited electron does not occupy highly localized 4$f$ states, but a considerably hybridized one with O 2$p$ character.

The enhancement of the spectral intensity at the top of the O 2$p$ band [Fig. 2(b)] suggests that the top of the O 2$p$ state coupled with the 4$f$ state plays a major role in the screening response to the core-hole potential. We further rationalize this observation by examining the calculated Kohn-Sham wave functions of the valence bands of the intermediate state of CeO$_2$. The analysis reveals a distinct difference between the three topmost [Figs. 3(b) and 3(c)] and three bottommost [Fig. 3(e)] O 2$p$ bands. While the bottom three bands are localized solely on the O atoms, the three topmost bands are partially localized over the Ce atoms in the intermediate state. The shapes of the orbitals suggest $p$ character on the O atoms and $f$ character on the Ce atoms. The band closest to the Fermi energy has the strongest $f$ character [a minute $f$ character from the band corresponding to Fig. 3(b)] has been present on the Ce atoms in the ground state—not shown]. Thus, by participating in the screening of the 4$d$ hole on the Ce atom, the top three electrons play a significant role in the Auger decay process of the Ce 4$d^0$ 4$f^1$ excited state compared with the rest of the O 2$p$ electrons. This is effected by their $f$ character, the proximity in energy, and the wave-function overlap with the 4$f^1$ electron [Fig. 3(d)] positively influencing the Coulomb matrix elements, making the Auger decay process with the respective electrons much more probable.

Taking into account the experimental and theoretical findings, the resonant photoemission process in CeO$_2$, with a 4$f^0$ configuration in the ground state and partial covalent bonding character, can be rationalized as a core-level interatomic effect. In contrast to the intra-atomic single-atom resonant photoemission, the electrons participating in the indirect photoemission channel of the resonant process in CeO$_2$ are primarily associated with two atoms—Ce and O. Specifically, we see an enhancement of the intensity of the photoemission from the top of the O 2$p$ band in ceria due to core-level absorption at the 4$d$ $\rightarrow$ 4$f$ threshold of Ce. This process is known as an intermediate type of multilayer resonant photoemission [39]. We can thus describe the resonant photoemission in CeO$_2$ as an interference of the following two processes:

1. Ce 4$d^{10}$ 4$f^0$ O 2$p^6$ + \hbar\nu \rightarrow Ce 4$d^{10}$ 4$f^1$ O 2$p^5$ + $e^-$.
2. Ce 4$d^{10}$ 4$f^0$ O 2$p^6$ + \hbar\nu \rightarrow Ce 4$d^9$ 4$f^1$ O 2$p^6$ \rightarrow Ce 4$d^{10}$ 4$f^0$ O 2$p^5$ + $e^-$.

Now it is clear that the resonance enhancement at the $4d$ $\rightarrow$ 4$f$ threshold for Ce$^{4+}$ and Ce$^{3+}$ atoms is of a profoundly different nature. Since the resonant enhancement of the $f$ derived spectral feature from Ce$^{4+}$ atoms is caused by interatomic effects, it is likely to be sensitive to perturbations such as oxygen vacancies, adsorbates, foreign substitutional and interstitial species, etc. On the other hand, the resonant process for Ce$^{3+}$ atoms is less influenced by the perturbations because it is an intra-atomic transition. This requires reexamination of the widely used formula for derivation of stoichiometry of various ceria-based materials from the ratio of resonant enhancement of Ce$^{4+}$ and Ce$^{3+}$ photoemission [40–44]. Given the widespread use of the method, the observation of the interatomic effects in the resonance photoemission in ceria calls for further study evaluating the validity of the direct proportion between the intensity of the resonant feature and the density of Ce$^{4+}$ atoms with respect to the electronic perturbations in their vicinity.

**IV. CONCLUSION**

We have presented the results of a combined experimental and theoretical study of the electronic structure of CeO$_2$. We find that there are no occupied localized $f$ states in the ground state of CeO$_2$. Instead, we demonstrate that the $f$ contribution in CeO$_2$ is of a coherent nature, arising from
hybridization with the \( \text{O} 2p \) bands. This is in contrast to the nondispersive \( 4f \) state at 1.9 eV in \( \text{c-CeO}_2 \), where the \( \text{O} 2p \) bands shift to higher binding energy, reducing mixing with the \( 4f \) states at the top. We show that, as a consequence of the covalent hybridization, the resonant photoemission process in \( \text{Ce}_2\text{O}_3 \) involves interatomic core-hole screening, which is in contrast to the intra-atomic process in \( \text{Ce}_2\text{O}_3 \). We suggest that the different nature of the two processes should be taken into account when interpreting resonant photoemission experiments from ceria and other covalent materials.

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