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Electronic structure of reduced $CeO_2(111)$ surfaces interacting with hydrogen as revealed through electron energy loss spectroscopy in comparison with theoretical investigations

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ABSTRACT

Based on both, ab-initio cluster calculations as well as periodic density functional based loss function calculations, we have assigned the origins of the valence electron excitation regime in electron energy loss spectra of well-ordered ceria films in (111) orientation at various states of reduction as well as after exposing the reduced films to hydrogen from the gas phase (Li et al, Angew. Chem. Int. Ed., 58 (2019) 14686–14693). The explicit calculation of intensity distributions using the dipole approximation allow us to draw conclusions about the nature of oxygen vacancies, which occur upon reduction and how those interact with hydrogen to form hydride species.

The present study also reports a brief discussion of vibrational excitations of hydrogen loaded ceria and corroborates previous interpretations, based on inelastic neutron scattering.

1. Introduction

This paper is dedicated to the memory of the late Earl Ward Plummer (20.10.1940–23.7.2020), who was a pioneer investigating the electronic structure of solid surfaces using mainly electron spectroscopic techniques. While in the early days of the late sixties and seventies, he started to work on metal surfaces (see e.g. Refs. [1–5]), in his latest work he became more and more involved with complex oxide surfaces. (see e. g. Refs [6,7].).

We address in this paper a specific oxide material, namely ceria, connected to the utilization of hydrogen including energy generation.

Recently, ceria-based materials have attracted considerable attention. Ceria (CeO₂) is a versatile material in heterogeneous catalysis because of facile oxidation and reduction of its cerium ions. [8–11] Interaction of hydrogen with metal oxides is intimately involved in many important processes, from H₂ storage to thermal, photo- and electro-catalysis. [9,9,10,11] Ceria (CeO2), widely used as oxidation catalysts, demonstrated its potential as a selective catalyst for alkyne semi-hydrogenation reactions, with hydrogen as reactant [12–18]. The interaction of reduced ceria with hydrogen is complex [19-21], involving homolytic dissociation of H2 at two oxygen sites leading to two hydroxyl (OH) groups [22] and the concomitant reduction of two surface metal cations, or heterolytic dissociation of H2 at metal and oxygen sites. The degree of reduction of ceria essentially determines which of these pathways will be predominantly taken. These processes involve migration of H atoms into the sub-surface region and the bulk to form hydroxyl and hydride (H⁻) species therein. Density functional theory (DFT) calculations showed that on fully oxidized, stoichiometric surfaces of CeO₂(111), the homolytic dissociation of H₂ at two oxygen sites has a higher activation barrier compared to the heterolytic pathway, but the homolytic one is thermodynamically favored. [23-28] Desorption of water is then accompanied by the reduction of ceria and the formation of oxygen vacancies, which strongly affect the H₂-CeO₂ interaction [29,30]. Theoretical calculations indicated that the stability of Ce-H species resulting from heterolytic H₂ dissociation is enhanced on reduced, i.e., O vacancy-containing ceria surfaces [7]. There are several reports on spectroscopic evidence for the formation of Ce-H species upon H₂ dissociation over ceria powder naturally containing oxygen

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vacancies [31,32], as well as reduced single crystal ceria films [33–36]. The presence of oxygen vacancies was found to lead to the penetration of hydrogen into the sub-surface and bulk as hydride species [37].

The present study aims at understanding the electronic structure of those systems, and is based upon the initial observation by Li et al. [38] on the formation of the hydride, which leads to the oxidation of the reduced Ce^{3+} sites to Ce^{4+} , as clearly documented via XPS Ce 3d data. Interestingly, electron energy loss spectra of the valence excitations of fully oxidized and reduced ceria, showed a full recovery of the valence excitation spectra after hydride formation, i.e. oxidation of the reduced ceria through hydride formation. [38] Here we are now documenting our effort to understand this observation based on extended numerical calculations, both ab-initio CI cluster calculations as well as periodic DFT [39-43] calculations using different approaches. Embedded cluster models have been used extensively to study the electronic structure of ionic compounds ranging from transition metal oxides and halides, see, for example de Graff et al. [44], to actinide oxides, see, for example, Gendron and Autschbach [45]. Major concerns in our earlier work has been to use embedded cluster models to study core-level ionization, see Refs [46,47]. and references therein, and core-level excitations, see, for example, Refs. [48,49]. The treatment of valence excitations for CeO₂ requires, as we discuss below, careful treatment of the embedding. The advantage of periodic boundary conditions is that bands or crystal orbitals are functions of the wavevector k complying with the imposed translational periodicity of the crystalline material as well as Bloch's theorem. [50] This is important for the description of bands featuring strong k dependence of the eigenvalue, known as the dispersion relation. It leads to the width of a band. The periodic code employed in the present work uses plane waves together with ab initio pseudo- or effective core potentials as a basis set, which results in basis set superposition free results. However, the disadvantage is a hampered chemical interpretability due to missing local or real-space representation of the orbitals. Thus, besides their ability to employ the entire spectrum of quantum-chemical methods to complex transition metal oxides, ab-initio cluster calculations complement plane-wave-based periodic calculations. This synergy has been exploited in the present work. In light of our findings, we also analyze results of electron energy loss spectra taken in the range of vibrational excitations, in order to provide more evidence for the chemical nature of the hydride species.

2. Experimental

The EELS measurements were carried out in an UHV system consisting of two chambers separated by a gate valve. One of the chambers was equipped with components for sample preparation and characterization: a LEED/AES system (Specs) for surface characterization, a sputter gun for sample cleaning and a metal evaporator (Focus) for cerium deposition. The other chamber contained a HREELS spectrometer (Delta 0.5 manufactured by VSI). Typical pressures were in the low 10^{-10} mbar range (preparation chamber) and the high 10^{-11} mbar range (HREELS chamber).

CeO₂(111) thin films were prepared on Ru(0001) according to a recipe published by Wu et al. [51] The oxygen pressure in the preparation chamber was 1×10^{-6} mbar in all steps. In the first step, 7 Å of cerium were deposited onto Ru(0001) with a (2 × 2) oxygen adsorbate layer while ramping the temperature from 100 K to 670 K with a heating rate of 1 K/s. Following this, cerium was deposited at 670 K until the oxide film thickness was about ~5 nm. Finally, the temperature was increased to ~980 K to order the film.

3. Theoretical

3.1. Choice of approximations used in theory

HREELS results are affected by several parameters, such as the crystallinity of films, the kinetic energy of electrons and the geometry of

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the incident electron beam relative to the sample surface. For a comprehensive review of the method and relevant surface science applications, we refer the reader to an article by Rocca and coworkers. [52] Concerning theoretical calculations and their comparison to observed results, awareness of the underlying physical phenomena is of utmost importance, given the complexity of involved scattering processes. Thus, as correctly mentioned in Ref. [52], different levels of approximations used in theoretical approaches can be invoked. There are in general two mechanisms that contribute to the inelastic scattering in HREELS, namely dipole and impact scattering. In dipole scattering, the electric field of incoming electrons and the dynamic dipole moments of a sample interact according to the laws of electrodynamics. To describe this interaction, the electric dipole approximation is commonly applied. This means that a relatively large wavelength associated with the electric field of primary electrons in comparison to interatomic distances in the (crystalline) sample is considered (reflecting the long-range nature of the Coulomb interaction). This in turn implies that oscillations of dynamic sample dipoles are largely in phase, i.e., there is only a small, but non-vanishing momentum transfer parallel to the sample surface. Due to the small momentum transfer, most of the inelastically scattered electrons leave the sample in nearly specular direction. The angular distribution of dipole scattered intensity is given in eq. 1.1 of Ref. [52]. Impact scattering, on the other hand, is due to an energy loss occurring during collisions of the incident electrons with ionic cores of sample atoms. In contrast to dipole scattering its underlying interaction occurs at shorter ranges. Hence, it is not limited to small momentum transfers. Ho, Willis, and Plummer showed that for some of the vibrational modes of H adsorbed on W(100), the angle and energy dependence of the intensity measured with HREELS deviates significantly from the one expected for dipole scattering due to the impact scattering contribution [3]. The theory to describe impact scattering is significantly more demanding due to multiple scattering events and has not been employed in the present work. We note that the scattering mechanism does affect the spectral intensities but not the loss energies. The experiments discussed here were carried out in specular scattering geometry where dipole scattering is most intense. Therefore, we assume that the spectral shapes of the experimental and theoretical EELS spectra are comparable despite the surely existing impact scattering contribution in the experimental data.

3.2. Cluster models and results

For the cluster model, we consider stochiometric oxidized CeO₂ since the crystal structure and bond distances are well established [53] as the fluorite structure with O_h local symmetry for Ce and a Ce-O distance of 2.37 Å. We present results for the largest cluster that we have used to accurately describe the environment of both the central Ce and it nearest neighbor O anions. this cluster is CeO₈Ce₁₂ embedded in a set of point charges to accurately represent the Madelung potential of CeO₂. The logic of the choice of this cluster and its accuracy are described in the SI. In Fig. 1, we show a schematic of the embedded CeO₈Ce₁₂ cluster. We will discuss below the different properties for these clusters.

The wavefunctions are determined by solving Dirac Hartree Fock equations to determine the orbitals for different configurations. For the excited states, we consider excitations from the O orbitals into Ce orbitals. We present here excitations into the localized 4f orbital because the Ce 5d orbitals are delocalized and part of the CeO₂ conduction band. Since the 4f orbital is localized, we are comfortable that we correctly predict the O to 4f excitations. The excited states are formed by exciting an electron from an occupied cluster orbital of g (gerade) symmetry into one of the 4f orbitals. Since a single configuration is not adequate to describe the excited states, we carry out a configuration mixing, or configuration interaction, CI, calculation for the excited WFs; see, for example, Ref. [46] and references therein. We optimize the orbitals for the excited states by removing an electron from one of the O 2p g orbitals for an occupation of 23 electrons in 24 spinors and 1 electron in one of



Fig. 1. A point charge embedded CeO_8Ce_{12} cluster where the central Ce is shown in blue, the 8 O anions in red and the 12 edge Ce atoms in green; only representative embedding point charges are shown in gray.

the 14 4f spinors. This leads to a rather accurate representation of the energies of the CI wavefunctions. The accuracy is measured by considering the calculated band gap as 3.56 eV consistent with our measured band gap of 3.2 eV. In the Supporting Information (SI), we show the convergence of the calculated band gap from values using more approximate WFs and clusters. Calculations of the WFs were carried out with the Dirac program system [54] and the calculations of the dipole intensities were determined with the CLIPS program system [53]. Details are given in the SI.

We consider the relative dipole intensity, Irel, for excitations to Ce 4f from O for the embedded CeO₈Ce₁₂ cluster where the I_{rel} are rigorously calculated taking full account of the differences in the orbitals for ground, initial state and the optimized orbitals for the excited states; see the SI. The calculated intensities are broadened with a Gaussian of 1.00 eV to take account of the broadening of the O 2p band in the crystal. The broadened I_{rel} are rigidly shifted and scaled to match the scaled EELS data at E = 4.27 eV. The scaling of theory and experiment are such that the $I_{rel}\text{, at }E=4.27\text{ eV}$ is $I_{rel}=1.0\text{, in arbitrary units. The shift of the}$ theory is 0.5 eV to match the experimental excitation energies. The leading edges of the shifted and broadened theory and experiment are very similar which gives confidence that the leading peak is correctly described by the O to Ce 4f excitations that we have included in the theory. V. Clearly, we identify the features in the EELS measurement to about 6 eV to arise from excitations to the Ce 4f. The higher energy excitations are to orbitals with Ce 5d character that are not included in our calculation.

3.3. Calculations subject to periodic boundary conditions

We use the Vienna ab initio simulation package, VASP [39,55], employing plane waves together with projector-augmented wave (PAW) pseudopotentials [56,57] as a basis set. These pseudopotentials describe the interaction between the ionic cores and the valence electrons and are distributed via the standard VASP library. We employ the so-called GW variant of these PAW potentials (according to the library's nomenclature), because they describe unoccupied/unbound states at higher energies with optimized scattering properties (for details, see Ref. [58]). GW stands for the first-order term of the perturbation expansion of the self-energy using the single-particle Green's function G and the screened Coulomb interaction W [59]. These potentials are required for calculations of GW quasi-particle shifts [59] and other excited state properties [60]. Herein employed pseudopotentials were generated solving the atomic scalar-relativistic Kohn-Sham-Schrödinger equation employing the Perdew, Burke, and Ernzerhof [61] (PBE) generalized-gradient corrected exchange-correlation (xc) functional. The Ce potential is

based on the $5s^26s^25p^65d^14f^1$ configuration of valence electrons. Each angular momentum channel is described by two projector functions. Oxygen uses $2s^22p^4$ as valence electrons, and hydrogen uses a pseudopotential involving s-, p-, as well as d-type projectors for a $1s^12p3d$ ground state configuration. By virtue of the PAW transformation between all-electron and so-called pseudized orbitals, a potential for H can be constructed that requires a kinetic energy cutoff of 300 eV only.

Compared to conventional density functionals based on the generalized-gradient approximation (GGA), geometric and electronic structure properties of fully oxidized and reduced ceria are more accurately described using the HSE06 [62-64] hybrid functional [40,65]. This also holds for comparison to observed results [40,41]. Besides of their notorious overestimation of lattice parameters [42], GGA functionals also suffer from erroneously delocalizing occupied Ce 4f states (see Refs [66]. and [41], as well as references therein). Thus, we use the HSE06 range-separated hybrid functional for loss function calculations (see below). However, for CeO₂, HSE06 overestimates its fundamental Ce 4f – 5d gap by ca. 1.0 eV. [40]

Structures were obtained by optimizing atomic positions using HSE06 (see SI; Figs. S1, S2, and S7, as well as Fig. 5). These calculations employ a plane wave cutoff of 600 eV for cell optimizations, while optimizations of atomic positions in slab models and calculations of dielectric functions use 450 eV. The employed break criterion for the self-consistent field (SCF) loops is 10^{-5} eV, and a maximal atomic force criterion of 0.04 eV/Å or equivalently 0.00078 E_h/a₀ has been employed to converge structure optimizations. Importantly, all calculations except for stoichiometric or fully oxidized ceria were carried out spin polarized (or unrestricted).

The theory underlying the actual calculation of loss functions is briefly described in the SI. At this point we mention that the present work discusses loss functions computed according to eq. 1 (see e.g. Ref. [67]),

$$I \sim L(\omega) = \frac{Im(\varepsilon_{zz})}{|\varepsilon_{zz} + 1|^2} = -Im\left(\frac{1}{\varepsilon_{zz} + 1}\right) = \frac{Im(\varepsilon_{zz})}{\left(Re(\varepsilon_{zz}) + 1\right)^2 + Im^2(\varepsilon_{zz})}$$
(1)

stating that the loss intensity relates to the imaginary part of the frequency (or energy-dependent) electronic dielectric function, $\varepsilon(\omega)$. Apart from a small life-time broadening used to calculate the linear response function (see SI), all calculations refer to T = 0 K. We relate energy loss mechanisms exclusively to dipole scattering events, which are caused by the long-range Coulomb fields of electronic charges (see also previous section). [52] This work uses ε_{zz} , the relevant component of the dielectric tensor complying with the surface selection rule. [68] The underlying real and imaginary parts of ε have been converged with respect to the number of unoccupied bands such that the resulting loss functions are converged up to an energy loss of ca. 10 eV. Actual calculations employ symmetric surface slab models using four and six O-Ce-O trilayers (TL), with atoms of the innermost TL kept in bulk positions. Integration over Brillouin zones use Monkhorst-Pack [69] k meshes centered at the Γ point. Further details like the actual number of k points, number of occupied, as well as unoccupied bands are summarized in Tab. S8.

To study local minima and transition structures involved in the diffusion of hydrogen in reduced ceria, we employ the PBE+*U* approach. An effective *U* parameter of 4.5 eV along with Dudarev's DFT+*U* approach [70] has been applied to Ce 4f orbitals to take care of local or on-site screening effects among f electrons [71–73]. This is a commonly used and well-tested value for our system of interest [40,71,74]. We use an SCF energy break criterion of 10^{-5} eV and a maximum atomic force criterion of 0.02 eV/Å (= $0.00039 \text{ E}_h/a_0$) is employed to converge structure optimizations. Regarding the slab model used in calculations, we cut from the PBE+*U* optimized bulk cell a (2 × 2) surface unit cell featuring four O-Ce-O TLs and a so-called vacuum gap of 12 Å (normal to the surface). Two oxygen atoms were removed to simulate pronounced reduction of the surface (and one hydrogen atom was added). To

determine transition structures, we apply the improved dimer method [75] and prove their unique imaginary mode connecting initial and final local minima by frequency calculations. These calculations require setting up a (partial) mass-weighted Hessian matrix and employ central differences to differentiate the Hellmann-Feynman gradient along atomic Cartesian coordinates using a step size of 0.015 Å.

We use Grimme's D2 [76] correction for PBE+U energies and therefrom obtained atomic forces to describe otherwise missing long-range dispersion interactions. The employed van-der-Waals C_6 and R_0 parameters for Ce are 20.0 J nm⁶ mol⁻¹ and 1.86 Å, respectively. Because within the D2 approach, these parameters are not available as a default, they were calculated following the procedure described in Ref. [76], and more details are provided in the SI to Ref. [77].

4. Results and discussion

By virtue of electron energy loss spectroscopy (EELS) of valence electron excitations, oxidation of a (reduced) $CeO_{2\cdot x}(111)$ thin film upon exposure to H₂ at 300 K could be shown experimentally. [38] This work studied electronic excitations across the band gap involving loss energies up to 10 eV and systematically compared EEL spectra of the fully oxidized, reduced, as well as re-oxidized ceria films after H₂ exposure. It has been shown that H₂ restores the valence electronic structure to the one of the fully oxidized film. To understand this observation at the atomic as well as electronic structure level, we start with discussing theoretical results, i.e., projected densities of states (pDOS) and computed loss functions (eq. 1) for the fully oxidized and the reduced thin film based on periodic slab models. For comparison reasons, we also discuss pDOS and loss function of a strongly (or fully) reduced ceria bulk cell. A comparison with observed results will be given in the subsequent section.

4.1. Electronic excitations

4.1.1. Electronic structure and loss functions of clean and reduced ceria

Fig. 3a shows the orbitally projected density of states (pDOS) of the pristine or fully oxidized CeO₂(111) surface (see structure model in Fig. S1, left). [41,66] Note that the surface DOS resembles the DOS of the bulk phase (see Fig. S3). Fig. 3c shows a pDOS of the reduced surface having the O vacancy (V_O) in subsurface position (Fig. S1, right), which is predicted by DFT to be thermodynamically more stable than the surface vacancy. [78,79] The pDOS of the (strongly) reduced bulk phase of CeO₂, which was modeled using a fluorite (2 \times 1) super-cell with content [Ce₂O₃], i.e., one V_O per cell, is shown in Fig. 3e. Its structure is shown in Fig. S2 (right). Respective calculated loss functions based on the approach discussed in the previous section are shown in Fig. 3b, d, and f. The changes in the electronic structure of ceria are drastic upon introducing O vacancies (or upon reduction). Whereas in pristine ceria, the highest occupied orbitals are predominantly O 2p (red line) forming the valence band (VB) with a width of ca. 4.2 eV, in reduced ceria the highest occupied orbitals are localized Ce 4f¹ orbitals (dark blue line) located in the O 2p - Ce 4f gap. For pristine ceria, according to HSE06, the O 2p (initial state) – Ce 4f (final state) band gap is ca. 3.2 eV. [40,65] This value is close to the bulk value (see Fig. S3) and agrees excellently with previous EELS results [80] as well as with new EELS data published by Li et al. [38] Upon V₀ formation, occupied 4f¹ defect states are created. These states are very localized or atom-like (see δ -like pDOS at 0 eV in Fig. 3c) and correspond to localized Ce^{3+} ions. Importantly, the remaining Ce³⁺ 4f states are pronouncedly screened, thus less bound by the core potential of the $Ce^{3+}4f^1$ ions and shift towards higher energies between ca. 5.9 and 8.2 eV above the VBM (see also Ref. [81]).

Fig. 3c and e show that Ce 5d orbitals shift slightly downward in energy upon reduction or V_0 formation, although the associated DOS between ca. 4.0 and 6.0 eV is very low. [81] For the pristine case, the O 2p – Ce 5d gap is ca. 7 eV, overestimating the observed value measured by EELS [80], optical spectroscopy [80] and STM [81,82] by ca. 1 eV.

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While for the reduced surface, the gap between highest occupied $4f^1$ and lowest unoccupied 5d orbitals amounts to ca. 2 eV (Fig. 3c; small but noticeable Ce 5d pDOS), for the strongly reduced bulk phase, the 5d orbitals are shifted further downwards in energy and represent the lowest unoccupied orbitals or the conduction band minimum (O 2p - Ce 5d gap ca. 4.3 eV). However, in both cases the low lying 5d DOS is small. Nonetheless, these results suggest that occupation of empty 5d orbitals may be feasible under conditions favoring strong reduction of ceria. Binet et al. conjectured that Ce^{2+} ions may be formed under strong reduction at temperatures of about 600 °C of ceria samples. [81]

Based on our pDOS analyses, the interpretation of the distribution of spectral weight in calculated loss spectra is possible. For the fully oxidized surface, the spectrum onset in Fig. 3b is equal to the O 2p - Ce 4f gap (Fig. 3a). As found in other cases, [83] the RPA or independent response particle function employed to calculate the frequency-dependent dielectric function leads to spectral onsets equaling the gap. Moreover, it is known that inclusion of many-electron or correlation effects (for instance excitons) lead to a slight closure of gaps due to the attractive but screened electrostatic interaction between positively charged holes and negatively charged electrons (see TDHSE06 results shown in Fig. S4 and Refs. [59] and [83]).

Our results based on cluster models discussed in previous sections clearly showed that the excitations falling in the energy range between onset of the gap (ca. 3.2 eV) and ca. 6 eV (see Fig. 2) are exclusively due to O 2p - Ce 4f transitions. Likewise, we show using periodic calculations that the main features of electronic (valence) excitations in fully oxidized ceria are already well described allowing excitations only into the first few (energy degenerate) unoccupied bands. These empty bands have a high, not to say exclusive, 4f character. Fig. S5 shows the imaginary part of the HSE06 dielectric function relating to the optical absorption spectrum. [84] The spectrum onset and its overall distribution of spectral weight are correctly described including only the four lowest unoccupied bands featuring large 4f character. Based on these cluster as well as periodic results, one can conclude that the spectrum of the partially reduced surface, still showing noticeable intensity in the energy interval between 4 and 6 eV results from O 2p - Ce 4f transitions. In contrast, this characteristic energy interval does not show significant intensity for the strongly reduced bulk phase, as shown in Fig. 3f. In analogy to the comparisons between pDOS and loss functions for the clean (Fig. 3a and b) and partially reduced surfaces (Fig. 3c and d), it is suggested that O 2p - Ce 4f transitions will occur at much higher energies, as indicated by the large 6.2 eV O 2p - Ce 4f⁰ gap shown in Fig. 3e. In consequence, there is noticeable intensity only beyond this value for the energy loss (Fig. 3f). However, as the unoccupied Ce 5d states are also available for excitations, substantial admixture of Ce 5d states in those higher lying 5d states cannot be excluded (see also previous section on cluster results).

4.1.2. Hydrogen in reduced ceria

This work focuses on understanding the experimentally observed (re-)oxidation of reduced CeO_{2-x}(111) applying—for surface science investigations—high H₂ pressures of 10 mbar. In the following, we compare the observed EELS data with calculated loss functions, $L(\omega)$ (eq. 1). To get an idea, how the theoretical approaches described above perform in comparison with experiment, we start with discussing features of the fully oxidized and the reduced CeO₂(111) surfaces first. These systems represent our benchmarks to assess the underlying electronic structure approaches.

Fig. 4a shows the calculated loss function for the fully oxidized or stoichiometric $CeO_2(111)$ surface (red line), and Fig. 4b (blue line) shows corresponding EELS results. Note that all calculated loss functions shown in Fig. 4 have been shifted by 0.5 eV towards lower energies to align them with observed data. We discussed in the previous section that this is expected and in part related to missing some of the electronic correlation effects within the RPA approximation. [85] As already discussed in the seminal work by Pfau and Schierbaum [80] using EELS and



Fig. 2. Plot of the theoretical I_{rel} broadened by a 1.0 eV Gaussian compared to the experimental EELS. The shifted theory and experiment are scaled to have the same intensity at E = 4.27 eV; see text.



Fig. 3. Left: Projected electronic densities of states of fully oxidized $CeO_2(111)$ (a), reduced $CeO_2(111)$ with O vacancy in subsurface position (c), and strongly reduced CeO_2 bulk (e). Orbital energy of 0 eV corresponds to the VBM. Right: Corresponding calculated loss functions (b, d, f) according to Eq. (1).

optical spectroscopy, the dominant broad feature with a maximum cross section at ca. 4.5 eV relates to O 2p – Ce 4f transitions. Our ab-initio cluster calculations, the pDOS analysis of the CeO₂ loss function (Fig. 3a and b), as well as calculating $Im(\varepsilon)$ using a stepwise increased number of unoccupied bands of 4f character (Fig. S5) confirms their findings. Indeed, the maximum of the loss function behaves like the known parabolic progression of the (empty) Ce 4f density of states. The calculated loss function shown in Fig. 4a agrees with the observed spectrum. There is no observed intensity at energy losses below the optical gap of ca. 3.2 eV, which is accurately described using the HSE06 hybrid functional. [86] The computed intensity reaches its maximum at ca. 4.7 eV, relating to the increase in the (unoccupied) Ce 4f DOS. Beyond that energy loss, intensity decreases monotonically up to ca. 6.5 eV. Beyond that value, a broader shoulder evolves. It is fair to state that

these features are well described by the RPA loss function. Based on Fig. S6, results shown in Fig. 4a are converged up to an energy loss of at least 10 eV.

Results for the reduced $\text{CeO}_{2.x}(111)$ surface are displayed in Fig. 4c (red line, theory) and 4d (blue line, experiment). Again, computed results agree well with observation. As discussed in the previous section, reduction or oxygen vacancy formation leads to formation of Ce^{3+} 4f¹ gap states. Because one electro-neutral O atom is removed from the lattice, there are two electrons of O^{2-} left behind that localize in the energetically readily accessible Ce 4f⁰ orbitals, thereby creating two Ce^{3+} ions (also referred to as small polarons). [41,66,87] These Ce^{3+} ions can be easily projected (see Fig. 3c). Note that the sharp 4f¹ peak of the pDOS at ca. 2.6 eV (up-spin) corresponds to the Ce^{3+} ion in subsurface position, while the lower lying and broader, i.e., less localized

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Fig. 4. Left: Comparison of computed loss functions and observed EELS data for stoichiometric $CeO_2(111)$ (a and b), reduced $CeO_2(111)$ (c and d), and reduced $CeO_2(111)$ exposed to 10 mbar of H₂ at room temperature (e and f). Computed data are shifted by 0.5 eV towards lower energy losses to align with observed spectra (see text). The EELS spectra were recorded with 25 eV electrons in specular geometry with a scattering angle of 70°, i.e. 35° between the surface normal and incoming/outgoing beams. Right: LEED patterns ($E_{electron} = 67 \text{ eV}$) corresponding to the marked EELS spectra.



Fig. 5. Structure or slab model of O-deficient CeO₂(111), re-oxidized by two H atoms and featuring a (2 × 2) periodicity. The model consists of six O-Ce-O trilayers. Its content is $[Ce_{24}O_{47}H_2]$. See main text for details. Color code. Ce⁴⁺ is blue, O is red, H is white.

4f¹ peak of the pDOS corresponds to the Ce³⁺ ion in the surface O-Ce-O TL. The broadening of this gap state can be understood by inspection of the atomic structure of the surface. While the Ce^{3+} 4f¹ in subsurface position is 7-fold coordinated featuring Ce-O bond distances between 2.35 and 2.61 Å, the $Ce^{3+} 4f^1$ in the surface layer is only 4-fold coordinated with Ce-O bond distances ranging between 2.12 and 2.26 Å. Thus "compression effects" due to for instance electrostatic interactions or Pauli repulsion imposed by surrounding O²⁻ ions are less effective in the surface layer, leading to a larger intercell overlap, particularly so taking the employed, small (1×1) surface unit cell into account. These findings suggest that Ce³⁺ ions in subsurface position are less stable compared with Ce³⁺ ions located in surface layers. On passing, we note that structures involving antiferromagnetic and ferromagnetic orientations of (local) magnetic moments of the two Ce³⁺ 4f¹ ions are very close in energy (within few tens of meV) and are thus not discerned in the present work. [78]

The role of the crystal field affecting the energy of Ce $4f^1$ gap states has been thoroughly studied using STM. [82,88] Two effects will contribute. First, the creation of Ce³⁺ ions, for instance upon V₀ formation, induces pronounced lattice relaxation changing the local geometric structure of O-Ce-O surface layers. [89] Second, and more important, due to the undercoordination of Ce ions around the O vacancy, a modified crystal field will result inducing splitting of the $4f^1$ orbital energies. This has been detected by STM, where characteristic protrusions have been found. For example, STM detected a bright but less abundant triple protrusion and an abundant paired protrusion with one faint site. Together with theory, this could be understood based on different localization patterns of the excess electrons around the O vacancy. The position of the Ce³⁺ ion pair is reflected in these characteristic defect patterns observed in empty-state STM images, which arise from the bright appearance of Ce⁴⁺ 4f⁰ ions next to the defect while the

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Ce³⁺ 4f¹ remain dark. Both findings could show that at least one excess electron localizes in a Ce ion that is not adjacent to the O vacancy. [88]

Returning to the discussion of the loss data of the reduced CeO₂(111) surface shown in Fig. 4c and d and comparing them to results of the fully oxidized system (Fig. 4a and b), it is apparent that there are two major differences: i) there is obvious intensity in the gap region between 0 and 3.2 eV, and ii) there is monotonically growing intensity in the region beyond ca. 5.5 eV until a plateau at ca. 7.0-7.5 eV is reached. To understand these spectral features, we refer to the corresponding pDOS displayed in Fig. 3c. Based on the lowest energy differences between unoccupied and occupied Ce 4f orbitals, the loss intensity in the gap is assigned to transitions between these states. For a partially reduced surface, still empty 4f⁰ conduction states exist, which originate from Ce⁴⁺ ions at an energy ca. 3.2 eV beyond the O 2p VB edge. These bands have a width of ca. 1.2 eV like in the stoichiometric surface. However, for the reduced surface, a second block of 4f⁰ orbitals occurs at ca. 5.5–6.0 eV beyond the O 2p VB maximum (Fig. 3c). Coincident with this range of energy loss, the intensity starts to increase again. Note that the theoretical calculations on the partially reduced $CeO_{2,x}(111)$ surface refers to an O vacancy concentration of 1 monolayer (ML), i.e. the subsurface O layer is missing (see Fig. S1, right). The real degree of reduction in the ceria film is unknown. [38]

It is educating to compare the partially reduced case with the fully reduced ceria. Its corresponding pDOS, as well as its loss function are shown in Fig. 3e and f, respectively. In this case, all Ce ions are Ce³⁺ 4f¹ and no empty 4f⁰ DOS located in the energy range between ca. 3.5-5 eV above the O 2p VB maximum survives. Instead, all remaining Ce 4f⁰ orbitals are efficiently screened and shift to higher energies at ca. 6.2 eV above the O 2p VB maximum. Therefore, no O 2p – Ce 4f charge transfer excitations in the range of energy loss between ca. 4 and 6 eV typical of the stoichiometric case occur, and—disregarding the low energy intensity at 1–2 eV—the calculated loss function features only low intensity in this region. Obvious intensity occurs only in the region beyond the O 2p – Ce 4f gap of 6.2 eV. Based on these comparisons, one can conclude that the reduced ceria film has been partially reduced and not fully reduced, but we repeat that the real degree of reduction is unknown. [38]

After having understood the EELS spectra of the fully oxidized and the reduced CeO_{2-x}(111) films, we discuss the effect of H₂ incorporated into the ceria lattice. Computed loss functions, $L(\omega)$, are shown in Fig. 4e as well as in Fig. S7, and the observed EELS data are displayed in Fig. 4f. The structure model underlying the theoretical result is displayed in Fig. 5. In Fig. S7 corresponding structure models are shown next to the loss function. Computed results agree with observation for energy losses typical of O 2p - Ce 4f transitions discussed above for stoichiometric ceria. However, they are distinct with respect to the energy loss intensity in the gap at ca. 2 eV. To understand this gap state, obviously related to hydrogen, we refer to the orbital projected DOS shown in Fig. S8. Note that the DOS has been normalized to the number of CeO₂ units per cell. The loss functions (Fig. S7) as well as the densities of states (Fig. S8) reflect the same trend. The lower the amount of hydrogen per cell, or in other words the more CeO₂ in the cell, the lower the computed intensity of the gap state.

We recapitulate relevant findings of Ref. [34], which are related to the present work. First, after exposure of reduced ceria films to H₂ (or D₂) at 10 mbar, the amount of detected surface hydroxyls was minor. Second, H₂ has been incorporated in deeper layers of the CeO_{2-x}(111) film as found based on nuclear reaction analysis (NRA) depth profiling. We reiterate that per O vacancy two Ce³⁺ 4f¹ ions are formed. Therefore, for complete reoxidation, i.e., transfer of the two 4f¹ electrons into the potential H 1s acceptor states, two H atoms per O vacancy are needed. Our models were created such that one of the H atoms sits at the vacant site, and the second H atom sits in a neighboring void site. In other words, the first H species substitutes or replaces an O ion. After optimizing the atomic positions, the distance between these H species is ca. 2.78 Å in each of these structures. The projection techniques

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implemented into the VASP code enables one to check for the presence or absence of occupied Ce³⁺ 4f¹ electrons easily. This is detected by projecting occupied orbitals or bands into on-site 4f spherical harmonics. For Ce³⁺ 4f¹ ions, this results in a (spin-only) magnetic moment of ca. 0.9 μ_B /Ce(III) (see also Ref. [90]) and corresponds to one electron in either up or down spin orientation per Ce³⁺ ion. In all our theoretically studied H₂/CeO_{2-x}(111) structure models containing one oxygen vacancy and two hydrogen atoms, no Ce³⁺ 4f¹ ions were left in the crystal lattice after optimization, suggesting thermodynamically favored formation of hydride, H⁻, species.

To show where the excess electrons have gone, we projected the characteristic gap state's partial charge density shown in Fig. 6a (same as in panel 3 of Figs. S7 and S8) and plotted the associated iso-contour surface at 0.01 $bohr^{-3}$ (Fig. 6b). Based on our analysis, one finds, that after successful optimization of the electronic and ionic structure, none of the occupied Ce 4f¹ orbitals of reduced ceria (with one O vacancy) survives. Instead, the two electrons left behind after creation of an O vacancy [78,81] occupy H 1s orbitals, symmetrically in terms of up and down spin degrees of freedom. The charge or electron density corresponding to the gap state shown in dark green can be easily projected, too. The resulting density integrated over the entire cell volume is equal to 2.00. This proofs that the H species, shown in Fig. 6b with a corresponding iso-contour surface (yellow) at 0.01 bohr⁻³, is an H⁻ or hydride ion. This very H ion is located at a so-called interstitial site above one O ion, the above-mentioned "void site" next to the vacancy. Similarly, the H^{-} ion without iso-contour surface also features a spin-symmetric $1s^{2}$ pDOS shown in light green, but due to higher stability (see below), it is shifted into the O 2p valence band. Hence, not surprising, there is apparent overlap between H 1s and O 2p orbitals, when the H ion is located at the oxygen vacancy or, equivalently, when it substitutes an O^{2-} ion.

The interaction of molecular hydrogen (H2) with the (111) surface of ceria has been theoretically studied by many workers. [13,27,34,91,92] In the present work, we focus on the interaction of hydrogen with the reduced surface. In addition, we want to understand how H species migrate from surface layers into deeper, bulk-like layers. Thus, we determined various local minima and calculated the activation barrier for H⁻ migrating into an oxygen vacancy in nearest-neighbor position. We repeat that our slab models contain two oxygen vacancies to model the reduced surface. Corresponding structures are shown in Figs. 7 and 8. Structure M1 (Fig. 7), i.e. a H⁻ ion at the oxygen vacancy site in the surface layer and a subsurface oxygen vacancy (red, dashed circle in Fig. 7) represents the reference energy in these energy profiles. Note that also the thermodynamically more favorable structure M2 is shown. The latter structure represents the hydroxylated surface, which is by 0.46 eV more stable than structure M1. It is important to notice that formation of OH groups starting from a fully oxidized or stoichiometric surface has been found to be a very stable state with a reaction energy of ca. 2.2 eV (for low coverage). [13,34] Our results show that reduced CeO₂(111) surfaces favor the formation of OH groups less, because this reaction comes along with creation of additional Ce³⁺ ions. Hence, hydroxylation reduces the surface further, in turn causing pronounced relaxation as well as strain effects. [78] Therefore, competing alternative reaction channels, such as the formation of hydride species, will be opened. We repeat (see above) that the formation of an H⁻ ion is indirectly detected by re-oxidation of a Ce^{3+} (4f¹) ion to a Ce^{4+} (4f⁰) ion. Indeed, after successful optimization of structure M1, one counts three instead of the (expected) four Ce³⁺ ions in the surface unit cell by virtue of projected local spin magnetic moments of ca. 0.9 μ_B/Ce^{3+} . H₂ dissociation into surface hydride species may spontaneously happen at strongly undercoordinated Ce³⁺ ions for H₂ molecules colliding with Ce³⁺ in a side-on position, which was found by initializing structure optimizations in appropriate starting geometries. Apparently, the favorable overlap between the $4f^1$ orbital of Ce^{3+} and the antibonding σ_u MO of H_2 triggers instantaneous electron transfer causing dissociation of the molecule. Thus, depending on conditions, strongly reduced surfaces do not



Fig. 6. Projected density of states (pDOS) of re-oxidized ceria (111) with two H atoms (a). Note that the gap state shown in dark green corresponds to a largely localized electron density (see text for details). Structure model showing these H atoms (b), as well as an iso-contour surface at 0.01 bohr⁻³ corresponding to the electron density of the gap state shown in a). Color code: Ce is blue, O is red, H is white.



Fig. 7. Reaction energy profile (eV) for H migration from the surface layer into subsurface and deeper layers in CeO_{2-x}(111). Note that a (2 × 2) cell has been used containing two oxygen vacancies ($^{1}/_{2}$ ML vacancy concentration) and one H atom. The oxygen vacancy is marked with a red, dashed circle. The energy zero refers to structure **M1**, i.e. H⁻ in the surface oxygen vacancy together with a neighboring vacancy in subsurface position. Ce⁴⁺ is shown in light blue, Ce³⁺ is dark blue, oxygen is red, and hydrogen is white.



Fig. 8. Local minima for H⁻ in CeO_{2-x}(111) in deep subsurface and bulk layers. Relative energies (eV) refer to structure M1 (see Fig. 7). Same color code as in Fig. 7.

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necessarily form OH groups upon exposure to hydrogen. Instead, strongly reduced ceria surfaces can be re-oxidized under formation of H^- species. Due to attractive electrostatic interactions (see below), H species involved in the electron transfer to H^- , optimize spontaneously into surface oxygen vacancy sites.

Structures M3 and M4 show two alternative intermediates for H⁻ migration into the bulk phase of (partially) reduced ceria. M3 refers to the surface oxygen vacancy with an H⁻ in subsurface position. This structure is by 0.45 eV less stable than the surface hydride (M1) and is by 0.74 eV less stable than structure M4, accommodating both the hydride and the oxygen vacancy in the subsurface layer. Importantly, M4 is 0.29 eV more stable than the surface hydride M1, which represents a thermodynamic driving force for the H⁻ ion to diffuse into the subsurface position. Although, we have not determined a connecting transition structure, we believe that M3 can be easily bypassed via a concerted mechanism involving simultaneous refilling of the surface oxygen vacancy upon downward migration of the hydride. Such a refilling of surface oxygen vacancies proceeding with a moderate activation barrier of ca. 0.44 eV has been found by Hu and coworkers to understand oxvgen vacancy migration in the $CeO_2(111)$ surface. [37] The crucial point is that upon reduction of CeO₂(111), i.e. oxygen vacancy as well as Ce³⁺ formation, the surface undergoes large structure relaxation involving (depending on the degree of reduction) a decrease of the coordination number of individual subsurface O²⁻ ions from 4 to (at least) 3. Hu coined it as the exchange mechanism between surface oxygen vacancies and subsurface O²⁻ ions. Note that the average bond distance between Ce^{4+} and O^{2-} in pristine $CeO_2(111)$ is ca. 2.38 Å, while this distance increases to ca. 2.65 Å for the $Ce^{3+}-O^{2-}$ bond in partially reduced ceria.

By virtue of this exchange mechanism involving undercoordinated O^{2-} ions, structure M5 can be formed. This structure refers to a subsurface H- ion (in the second oxygen layer) and a neighboring oxygen vacancy in the next deeper, i.e. the third oxygen layer. Importantly, this structure is as stable as the surface hydride (M1). In a next step, the hydride ion may migrate to fill the neighboring oxygen vacancy, going slightly downhill in energy by 0.07 eV (structure M6). The activation barrier involved in this direct pathway, where H⁻ passes through two Ce cations (structure TS1) is 0.35 eV. The hydride in the transition structure is 2-fold coordinated by Ce^{4+} ions, while it is 4-fold coordinated (same as the O²⁻ ions) when it occupies a deeper subsurface or bulk-like oxygen vacancy. Upon checking local 4f occupations of Ce ions in transition structure TS1, we found that slight delocalization of 4f spin density occurs leading to partial recreation of a fourth $Ce^{3+} 4f^{1}$ ion. This partial re-occupation of Ce 4f orbitals likely contributes to the barrier height, because it incurs lattice relaxation effects.

Fig. 8 displays representative structures of the H⁻ ion and the oxygen vacancy located in deeper, bulk-like layers (M7, M8) as well as in the bulk phase (M9, M10). Structure M7 represents the situation accommodating the oxygen vacancy as well as the H⁻ ion in the third oxygen layer counted from the topmost or terminating oxygen layer. This structure is thermally accessible being 0.39 eV less stable than M1. However, accommodating the oxygen vacancy one layer deeper requires 0.54 eV. Hence the structure is noticeably less stable than M7 and substantially less stable than the surface hydride, M1 (+0.93 eV). Finally, we calculated structures M9, with H⁻ replacing a O²⁻ ion in the bulk as well as containing a subsurface oxygen vacancy, and M10, where both H⁻ and the vacancy are in bulk layers. Remarkably, structure M9 is substantially more stable than M1 (surface hydride), representing a fairly re-oxidized surface. In stark contrast, M10 is thermally out of reach (with respect to M1) because it is ca. 1.6 eV less stable.

We learn from these calculations, that upon H⁻ diffusion into deeper layers, the "re-generated" vacancies may be refilled by lower lying, undercoordinated O²⁻ ions. This is shown by the strongly exothermic reaction energy of -0.54 eV starting from a surface oxygen vacancy (**M3**) and involving H⁻ migrating into a subsurface vacancy. This energy helps to accomplish the refilling of near-surface O vacancies by bulk O²⁻ ions. In addition, there is a strong thermodynamic preference to replace O²⁻ ions by H^- ions in (deep) bulk-like layers [93] and to accommodate the remaining oxygen vacancies in near-surface positions. Overall, this represents a driving force to reinstall a close-to healed or stoichiometric material.

These results on the thermodynamic stabilities and kinetic barriers of H⁻ ions in reduced ceria, supporting H⁻ migration into deeper, bulk-like layers, allow us to infer that the "gap-state-less" EELS (Fig. 4f) refers to H⁻ ions in the bulk, thus out of the detection limit of EELS. As described in a previous section, detection in specular geometry leads to EELS spectra dominated by dipole scattering with a somewhat smaller impact scattering contribution. Impact scattering is a local mechanism and requires a direct contact between the electrons and the scattering centers. The inelastic mean free path is about 5 Å for a kinetic energy of 25 eV (see Fig. 1.1 in Ref. [52]) Considering that the electrons also have to escape from the sample leads us to the conclusion that impact scattering is essentially limited to the topmost two layers. According to Persson [94] the interaction distance for the dipole scattering mechanism can be computed as $d = v/\omega$ with v being the electron speed and ω the angular frequency corresponding to the loss energy ($E_{loss}=\hbar\omega$). From the given experimental parameters, a distance of d = 1 nm results for the spectra shown in Fig. 4. We note that the equation has been derived for a situation where the electrons and the scattering centers are separated by vacuum. In the present case the hydrogen atoms are below the surface, which will probably result in a reduction of the distance d due to the interaction of the external electric field with CeO2 electrons.

4.1.3. Electrostatic analysis

In order to understand the origin for the energetic preference of the $Ce^{4+}(4f^{0})H^{-}$ configuration over the $Ce^{3+}(4f^{1})H^{0}$ configuration, we have carried out an electrostatic analysis with a cluster of Ce4HO18 to represent the environment of the H atom in the environment of reduced ceria. The positions of these atoms are taken from the slab model optimization of the geometry of a H atom in a bulk position in reduced CeO₂. The H atom is in a distorted tetrahedral coordination of four Ce atoms; three of the Ce atoms have a distance of d(Ce-H) = 2.39 Å and the fourth has a somewhat shorter distance of d(Ce-H) = 2.31 Å. The 18 O atoms include the nearest neighbors of the four Ce atoms. A schematic representation of the Ce₄HO₁₈ cluster is given in Fig. 9. In our purely electrostatic model, we assigned point charges to each of the atoms. In a second model which takes account of the electronic structure, we continued to treat the O anions as point charges, but we determined the energies of the different configurations where the Ce and H electrons were included in the wavefunctions, WFs.

For the purely electrostatic model, the point charges were assigned as follows. For the Ce⁴⁺H⁻ configuration where Q = -2 for the O atoms, Q = -1 for the H atom and Q = +4 for all the 4 Ce atoms. For the Ce³⁺H⁰ configuration, the O atoms are still Q = -2, the H atom is Q = 0, three of the Ce atoms have Q = +4, and one has a charge of Q = +3 The +3 charge



Fig. 9. Cluster model used to examine the electrostatic stability of the $Ce^{4+}(f^0)$ H⁻ configuration versus $Ce^{3+}(f^1)H^0$ configuration. Color code: Ce ions are shown in blue, O ions are red, and H is shown in white.

is placed on the Ce atom which gives the lowest, negative, electrostatic energy for the Ce³⁺H⁰ and most favors this configuration, although the difference of the total electrostatic energy is quite small, 1.2 eV. The electrostatic energy is calculated neglecting the self-interactions of the O anions since this is the same for both configurations. The configuration with Ce⁴⁺H⁻ has a lower electrostatic energy than the Ce³⁺H⁰ by 43.4 eV indicating that it is favored. However, the purely electrostatic terms neglect the cost of ionizing Ce³⁺ to Ce⁴⁺, which is 36.9 eV [95], and the gain of the H electron affinity of 0.75 eV [96]; this leads to a correction of 35.2 eV to the electrostatic energy. Thus, in this point charge model, the configuration Ce⁴⁺H⁻ is favored by 7.2 eV, a huge energy advantage.

To investigate how the point charge model would be modified by treating the atoms as having electrons rather than entirely as point charges, we have including the Ce and H electrons into the calculation, but we still treat the O anions as point charges. This neglects the influence of covalent mixing between the Ce cations and the O anions, but it does allow modification of the orbitals for the different Ce occupations including formation of covalent mixing between the Ce and the H. For the Ce, we have used a pseudo-potential for the 28 core electrons. [97] The relativistic calculations for the WFs are performed with the Dirac program system [54]. The occupations for the closed shell $Ce^{4+}H^{-}$ are straight forward with 106 electrons in 53 orbitals. The Mulliken population analysis assigns 1.75 electrons to H and 0.06 electrons of 4f character to the 4 Ce atoms. Given the quantitative limitations for the assignments of charge with a Mulliken population analysis, see for example Bagus et al. [98] and references therein, this is fully consistent with $Ce^{4+}H^{-}$ modified by covalent mixing of H(1 s) with Ce valence orbitals. For the Ce³⁺H⁰ configuration, there are 104 electrons in closed shell orbitals and two electrons in singly occupied orbitals; the orbital variation is for the average of the configurations. The WFs are determined as complete orbit space configuration interaction WFs. This is necessary to obtain WFs that have the correct angular momentum coupling, which in the nonrelativistic limit is the singlet-triplet splitting of the two open shell electrons. The two open shell orbitals are strongly localized on the H atom and the Ce atom which gave the lowest electrostatic energy as a plus three ions in the electrostatic calculation. The splitting of the relativistic multiplets arising from the slightly symmetry broken triplet and singlet states is very small, 0.018 eV. The separation of the $Ce^{4+}H^{-}$ and the average of the $Ce^{3+}H^{0}$ configurations is 4.4 eV with the Ce⁴⁺H⁻ favored. While the orbital variation lowers the relative stability of the Ce⁴⁺H⁻ configuration from the pure electrostatic model, this configuration is clearly energetically preferred by a large energy. The origin of the energetic stability of this configuration is the electrostatics of the ionic interactions somewhat modified by the orbital optimization for the different configurations.

4.2. Vibrational properties

The role of the reduced ceria surface versus its bulk phase in the formation (and possible reaction) of hydride species has been studied recently. [99] This work employed infra-red absorption spectroscopy (IRAS) to study hydride species in well-defined reduced ceria films and diffuse reflectance infra-red Fourier transform spectroscopy (DRIFTS) for powder samples. Recent work by Wu et al. carried out inelastic neutron scattering (INS) in order to detect the Ce-H vibration. [33] The present work employs HREELS to provide direct evidence for hydride species.

Fig. 10 compares an CeO₂(111) HREELS spectrum with an INS (inelastic neutron scattering) spectrum of CeO₂ powder (from Ref. [33]). Both samples were exposed to hydrogen at conditions noted in the caption. The intense feature in the HREELS spectrum, Fig. 10a, which has been cut off at the top is due to the CeO₂(111) Fuchs-Kliewer phonon centered at ~550 cm⁻¹. [19] The other features are related to the presence of hydrogen. We note that there is hydrogen related intensity in the HREELS spectrum while this is not the case for the EELS spectrum f in Fig. 4. We attribute this to the larger dipole detection distance which





Fig. 10. Vibrational data of CeO₂ exposed to H₂. (a) HREELS spectrum of CeO₂(111) exposed to 10 mbar of H₂ at 300 K for 15 min. The spectrum was recorded in specular geometry using electrons with a kinetic energy of 6 eV. In order to remove multiple loss intensities related to the intense Fuchs-Kliewer polariton at ~550 cm⁻¹, the spectrum was subjected to a Fourier deconvolution process as described by Cox et al. [100] (b) INS (inelastic neutron scattering) spectrum of CeO₂ powder exposed to 1 bar of H₂ for 2 h at 623 K. The spectrum was reproduced from Fig. 4c in Ref. [33].

is d = 7.5 nm in the case of the HREELS spectrum while for the EELS we have d = 1 nm (see discussion above). Thus, HREELS 'looks' deeper into the oxide and may detect the hydrogen.

To approach the problem systematically, we follow work published in Ref. [99] and examine the vibrational properties of H⁻ located near the surface of $CeO_{2-x}(111)$ and compare it to the properties of bulk hydride species. Table 1 and Fig. 11 summarize these essential results. On the left-hand-side, the normal mode of H⁻ in subsurface position is drawn using orange arrows. Importantly, and confirming results discussed in Ref. [99], only a mode parallel to the surface is found. According to the surface selection rule, the mode with a vibrational energy of 1104 cm⁻¹ or 137 meV cannot be detected using either IRAS or HREELS. Results are distinct for the bulk hydride, which are shown on the right-hand-side of the same Figure. The arrows indicate that the mode features a pronounced component parallel to [111], i.e. normal to the metal substrate. Therefore, this mode with the vibrational energy of 1090 cm⁻¹ or 135 meV can be detected. A second mode with a vibrational wavenumber of 940 cm⁻¹ was also found. However, this mode has only normal coordinates oriented (purely) parallel to the surface and is hence not detectable. The remaining modes fall into the energy range of Fuchs-Kliewer phonons.

Note that we carefully examined whether anharmonicity or masscoupling effects had an impact on our quantitative results. We tested for anharmonic effects using potential energy plots along the relevant normal coordinate and found only very minor deviations from the second order or parabolic behavior. Also, coupling effects were found to be

Table 1

Vibrational energies (cm^{-1}) of hydride in an O vacancy in subsurface position (see Fig. 11, lhs) and in the O vacancy in the bulk phase (Fig. 11, rhs). Orientation of mode relative to substrate is given in parenthesis.

	H in O _{sub} vacancy	H in bulk O vacancy
Mode		
1	1104 ()	1090 (⊥)
2	785 ()	940 ()
3	780 (⊥)	830 (⊥)

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Fig. 11. Left: Vibrational mode of a H⁻ ion substituting an O²⁻ ion in subsurface position. The normal coordinates of the mode featuring the highest vibrational energy is indicated by orange arrows. Right: Vibration of two H⁻ ions in re-oxidized ceria bulk phase. Normal coordinates are displayed by orange arrows. Note that different lengths indicate distinct amplitudes. H⁻ on the lhs substitutes an O²⁻ ion, i.e., it is located at the O vacancy, tetrahedrally coordinated to (four) Ce⁴⁺ ions. The H⁻ ion on the rhs sits in a void site next to it (d(H-H) =2.78 Å). Same color code as in Fig. 5.

minor based on our frequency analysis involving stepwise increased partial Hessian matrices, corresponding to more and more O as well as Ce ions included in force constant calculations. Although one could have expected effects induced by coupling to the O lattice, this finding is reasonable as the hydride species has a low mass compared to the heavy O and Ce sublattices.

Comparing theory with the observed results shown in Fig. 10, one finds that indeed a vibrational band located at ca. 1000 cm^{-1} has been found both in HREELS as well as independently in the INS experiment. By virtue of the calculated wavenumbers (Table 1), we assign this observed band to a hydride species located at the O vacancy site. Because of its high stability, it is reasonable that O vacancy sites will be predominantly occupied by hydride ions, but they might also occupy other, less stable, void sites. In this case, the calculated frequency is 930 cm⁻¹ and the mode has a purely normal component with respect to the metal substrate. Note that there are indeed two distinct bands at ca. 1100 and 920 cm⁻¹ in the HREELS spectrum shown in Fig. 10a. These computational results agree well with observation.

5. Summary and conclusions

We have presented a detailed theoretical analysis of the electronic structure of ceria, including stoichiometric ceria, ceria containing oxygen vacancies, as well as ceria with hydrogen atoms occupying oxygen vacancies. The properties of those materials, as measured previously by electron energy loss spectra taken on well-ordered ceria films grown on Ru(0001) in the regime of valence excitation, are compared with intensity distributions calculated on the basis of dipole excitations using cluster calculations as well as loss function calculations using periodic models of the material. Based on a cluster calculation a definite assignment of excitations in stoichiometric ceria to transitions from occupied oxygen 2p derived bands to the empty Ce-4f states at the valence edge is achieved. Since the excitations into the Ce-5d states have not been considered for the dipole intensity calculations, the missing intensity at higher excitation energies may be easily understood. This is also consistent with the corresponding loss function calculations on periodic models. Concerning the loss function calculations on periodic models for ceria with oxygen vacancies, the weak intensities observed at lower excitation energies within the band gap region of stoichiometric ceria assigned to transitions between occupied and unoccupied Ce-4f states and the modified signal intensity distributions in the range of O 2p-Ce 4f/5d transitions are well reproduced by the calculations. Upon introduction of hydrogen into the oxygen vacancies, a clear dependence of intensity distributions on whether a surface or near surface oxygen vacancy or a bulk vacancy is filled with hydrogen is observed. The comparison with experiment indicates that the hydrogen must be located well below the surface. Only then approaches the calculated loss-function-based intensity distribution the almost complete recovery of the distribution observed in stoichiometric ceria, indicating a screening of the hydrogen induced features in the band gap region by the ceria layers above the hydrogen filled oxygen vacancies. In other words, upon increasing the hydrogen pressure at the corresponding temperature, the hydrogen, together with the vacancy, it resides in, migrates to layers deeper in the bulk. In order to identify the chemical nature of the hydrogen within the oxygen vacancy a model study is presented, clearly indicating that the hydrogen, indeed, is a hydride with a fully transferred electron.

Such conclusions had been claimed in earlier publications studying the vibrational properties of hydrogen in ceria using inelastic neutron scattering and infrared spectroscopy. Here we show HREELS spectra of the samples studied with respect to electronic excitations in the region of vibrational states, which are compared with published data and clearly indicating consistency with the previously drawn conclusions.

In summary the present study provides a full picture of the valence electronic and vibrational properties of stoichiometric, reduced and hydrogen containing ceria clearly corroborating the formation of a hydride.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.elspec.2021.147088.

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