

# First-principles LDA+U and GGA+U study of cerium oxides: Dependence on the effective U parameter

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The electronic structure and properties of cerium oxides ( $\text{CeO}_2$  and  $\text{Ce}_2\text{O}_3$ ) have been studied in the framework of the LDA+U and GGA(PW91)+U implementations of density functional theory. The dependence of selected observables of these materials on the effective U parameter has been investigated in detail. The examined properties include lattice constants, bulk moduli, density of states, and formation energies of  $\text{CeO}_2$  and  $\text{Ce}_2\text{O}_3$ . For  $\text{CeO}_2$ , the LDA+U results are in better agreement with experiment than the GGA+U results whereas for the computationally more demanding  $\text{Ce}_2\text{O}_3$  both approaches give comparable accuracy. Furthermore, as expected,  $\text{Ce}_2\text{O}_3$  is much more sensitive to the choice of the U value. Generally, the PW91 functional provides an optimal agreement with experiment at lower U energies than LDA does. In order to achieve a balanced description of both kinds of materials, and also of nonstoichiometric  $\text{CeO}_{2-x}$  phases, an appropriate choice of U is suggested for LDA+U and GGA+U schemes. Nevertheless, an optimum value appears to be property dependent, especially for  $\text{Ce}_2\text{O}_3$ . Optimum U values are found to be, in general, larger than values determined previously in a self-consistent way.

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## I. INTRODUCTION

Cerium dioxide (ceria) is a component of important catalytic applications such as the 3-way car exhaust catalysis,  $\text{SO}_x$  reduction and the water gas shift reaction.<sup>1,2</sup> There is evidence that ceria does not only function as a support for different precious metals. Rather, due to its facile reducibility, ceria can also directly participate in chemical reactions. Its activity is ascribed to the oxygen storage capacity,<sup>1</sup> which takes place according to the formal reaction scheme:  $2\text{Ce(IV)O}_2 \rightarrow \text{Ce}_2\text{(III)O}_3 + 0.5\text{O}_2$ . Thus, the equally accurate theoretical description of pure and mixed Ce(III) and Ce(IV) oxide materials is of primary importance for understanding their functioning and advancement of their practical applications. However, this is not a simple task since the additional electron, which is introduced on the Ce center upon reduction of Ce(IV) to Ce(III), is a strongly correlated *f* electron. Hence, from a computational point of view, a balanced theoretical description of  $\text{CeO}_2$  and  $\text{Ce}_2\text{O}_3$  oxides is not straightforward. The challenge arises when one aims at a unified treatment of both oxidation states as has been addressed recently by a number of theoretical studies of bulk ceria<sup>3–8</sup> and (defective) ceria surfaces.<sup>6,9–14</sup>

In principle, the computational description of the insulating  $\text{CeO}_2$  within conventional density functional theory (DFT) is more or less straightforward due to the unoccupied Ce (4*f*) state. The band gap is still underestimated but this is a well-known deficiency of standard DFT, in particular in the description of transition metal oxides such as NiO.<sup>15–18</sup> Nevertheless, most of the recent DFT calculations yield a description of this material in close accordance with experimental findings, quite independent of the exchange-correlation functionals employed. On the contrary, the  $\text{Ce}_2\text{O}_3$  insulator has been known to be a notorious problem case for electronic structure calculations. From the recently published

work it is evident now that calculations using the standard local density approach (LDA) or generalized gradient approach (GGA) give a wrong metallic ground state for  $\text{Ce}_2\text{O}_3$ . The use of ultrasoft pseudopotentials may give the right insulating solution but it is likely that this is due to a fortuitous error cancellation.<sup>4,5</sup> An accurate calculation demands a modification of the usually employed DFT approaches to account for the strong localization of the Ce *f* electron in the formal Ce oxidation state III.

The shortcomings of standard DFT may be overcome by different approaches, for example by correction of the self-interaction of electrons (self-interaction correction, SIC), which has been used for cerium oxides<sup>19,20</sup> and related systems.<sup>21</sup> A DFT hybrid approach has also been shown to give improved results for the electronic structure of Ce(III) oxide.<sup>7</sup> Another promising way to improve contemporary LDA and GGA approaches is to modify the intra-atomic Coulomb interaction through the LDA+U approach.<sup>22–24</sup> Indeed, this approach allows for a correct treatment of the electronic state of  $\text{Ce}_2\text{O}_3$  as has already been shown by de Fabris *et al.*<sup>4</sup> The physical idea behind the LDA+U or GGA+U schemes comes from the Hubbard Hamiltonian. In the practical implementations, the on-site two-electron integrals, which would appear in Hartree-Fock (or post Hartree-Fock) like treatment, are expressed in terms of two parameters. These are the Hubbard parameter U, which reflects the strength of the on-site Coulomb interaction, and the parameter *J*, which adjusts the strength of the exchange interaction. In the somewhat simplified, yet rotationally invariant method of Dudarev *et al.*<sup>25</sup> these two parameters are combined into a single parameter  $U_{\text{eff}} = U - J$ . This approach can be understood as the introduction of a penalty function which disfavors noninteger occupation numbers of the on-site density matrix. In short, DFT+U correction acts to reduce the one-electron potential locally for the specified orbitals of the

respective atoms (e.g., Ce *f* orbitals), therefore reducing the hybridization with orbitals of the ligands (e.g., O atoms); the  $U_{\text{eff}}=0$  case representing the DFT limit.

In general, the introduction of the effective parameter  $U_{\text{eff}}$  leads to a drastic improvement in description of reduced ceria.<sup>4,5</sup> However, the specific value of  $U_{\text{eff}}$  remains a matter of debate because its choice strongly influences the calculated observables. From an *ab initio* point of view, it would be desirable to determine this parameter in a self-consistent way, which has been done for CeO<sub>2</sub> with the approach of Cococcioni *et al.*<sup>26</sup> resulting in  $U_{\text{eff}}=2.5\text{--}3.5$  eV and  $U_{\text{eff}}=1.5\text{--}2.0$  eV for the LDA+U and GGA(PBE)+U choices of the exchange-correlation functional, respectively.<sup>4</sup> However, the use of a higher value of  $U_{\text{eff}}$  has yielded better agreement with experiment. Values of  $U_{\text{eff}}=5$  eV and  $U_{\text{eff}}=6.3$  eV for the PW91 (Ref. 13) and PBE (Ref. 6) functionals, respectively, have been suggested. Additionally, the DFT+U approach seems also to be dependent on the specific chosen projector functions.<sup>4</sup> Therefore, a more practically oriented approach consists in taking  $U_{\text{eff}}$  as a sort of empirical parameter and fitting its value to reproduce certain experimental observables much in the same way as it has been done in molecular quantum chemistry for the so-called hybrid functionals<sup>27</sup> but avoiding the introduction of nonlocal exchange and its concomitant computational complications. Although some work in this direction has been published rather recently, i.e., the determination of  $U_{\text{eff}}$  in an empirical way for CeO<sub>2</sub> with the PBE functional,<sup>6</sup> a more systematic study is needed. In particular, Ce<sub>2</sub>O<sub>3</sub> should also be included in the set of benchmarks when probing  $U_{\text{eff}}$ , specially if one is interested in more problematic cases involving Ce(III), such as defective ceria, ceria nanoparticles, and surface redox reactions. Therefore, one may argue that only simultaneous consideration of various properties of CeO<sub>2</sub> and Ce<sub>2</sub>O<sub>3</sub> will allow for a unified treatment of both main oxidation states of ceria, which is especially important for charge transfer chemical reactions involving a transition between Ce(III) and Ce(IV) and playing a fundamental role in the catalytic applications of these materials.<sup>1</sup> Furthermore, from the previous publications the optimal  $U_{\text{eff}}$  parameter seems to be strongly dependent on the particular exchange-correlation chosen but a systematic study of the  $U$  dependence for the common LDA+U and the GGA(PW91)+U functionals in cerium oxides is lacking. This work aims at such a systematic study. We will provide evidence that a semiempirical fitting of the  $U_{\text{eff}}$  parameter will allow for a significant improvement of the cerium oxide properties under investigation, and that the inclusion of Ce<sub>2</sub>O<sub>3</sub> in this study is vital because of its high sensitivity towards a change of the effective on-site Coulomb repulsion.

## II. COMPUTATIONAL METHODS AND MODELS

The density functional calculations were carried out using the plane-wave based Vienna *ab initio* program package (VASP).<sup>28,29</sup> The electron wave functions were described using the projector augmented wave (PAW) method of Blöchl<sup>30</sup> in the implementation of Kresse and Joubert.<sup>31</sup> Plane waves have been included up to an energetic cut off of 415 eV. For

TABLE I. Calculated and experimental lattice parameter  $a_0$  and bulk modulus  $B$  of CeO<sub>2</sub>. Previously reported data are also included for comparison.  $U_{\text{eff}}$  values are specified where applicable.

Method	$U_{\text{eff}}/\text{eV}$	$a_0/\text{\AA}$	$B/\text{GPa}$	Reference
LDA	—	5.39	214.7	3
LDA+U	3.0	5.38	210.7	4
LDA+U	5.0	5.40	213.7	This work
GGA+U	5.0	5.47	192.0	13
GGA	—	5.48	187.8	3
GGA(PBE)+U	1.5	5.48	178.0	4
GGA+U	3.0	5.48	187.0	This work
GGA(PBE)+U	7.0	5.38	202.4	6
HSE	—	5.41	206.1	7
SIC-LSD	—	5.38	—	20
Exp.	—	5.41	204–236	

integration within the Brillouin zone specific  $k$  points were selected using a  $4 \times 4 \times 4$  Monkhorst-Pack grid for CeO<sub>2</sub> and a  $4 \times 4 \times 2$  grid for Ce<sub>2</sub>O<sub>3</sub>. The LDA and PW91 form of the GGA exchange-correlation potentials<sup>32,33</sup> have been used together with their LDA+U and GGA+U variants as implemented in VASP.<sup>34</sup>

We optimized at the LSDA+U ( $U_{\text{eff}}=5$  eV) level the lattice constant ratio  $c_0/a_0$  of the hexagonal unit cell of Ce<sub>2</sub>O<sub>3</sub> (space group  $P\bar{3}m1$ ) to be 1.55, in good agreement with experiment.<sup>35</sup> The  $c_0/a_0$  ratio is not much affected by small changes of structural parameters, therefore it was kept fixed at 1.55 in all calculations. However, it is worth pointing out that calculations of CeO<sub>2</sub> and especially Ce<sub>2</sub>O<sub>3</sub> at small lattice constants and small  $U_{\text{eff}}$  values are quite difficult since the solutions tend to converge into a manifold of electronically excited states which are characterized by only a partial localisation of the Ce *f* electron. Therefore special care was required to get the proper ground state, for example by providing an adequate electronic guess from previous SCF solutions with higher  $U_{\text{eff}}$  and then slowly reducing the  $U_{\text{eff}}$  parameter step by step.

## III. RESULTS AND DISCUSSION

### A. Atomic and electronic structure of CeO<sub>2</sub>

CeO<sub>2</sub> is an insulator featuring cubic  $Fm\bar{3}m$  structure of CaF<sub>2</sub> with the experimentally determined lattice parameter  $a_0 \approx 5.41$  Å [5.406(1) Å (Ref. 36) or 5.411(1) Å (Ref. 37)]. Table I displays the lattice parameter and bulk modulus  $B$  of CeO<sub>2</sub> taken from recent state-of-the-art DFT calculations.<sup>3,4,6,7,13,20</sup> The present  $a_0$  and  $B$  values have been obtained from the corresponding energy minimization at constant volumes and by fitting a Birch-Murnaghan equation of state to the resulting energy-volume data,<sup>39,40</sup> respectively. Other earlier theoretical work on bulk cerium dioxide which is not presented in the table is also available.<sup>9,11,12,41–43</sup> In any case, most of these results, although obtained using different computational approaches, accurately predict the experimental lattice parameter and the experimental bulk

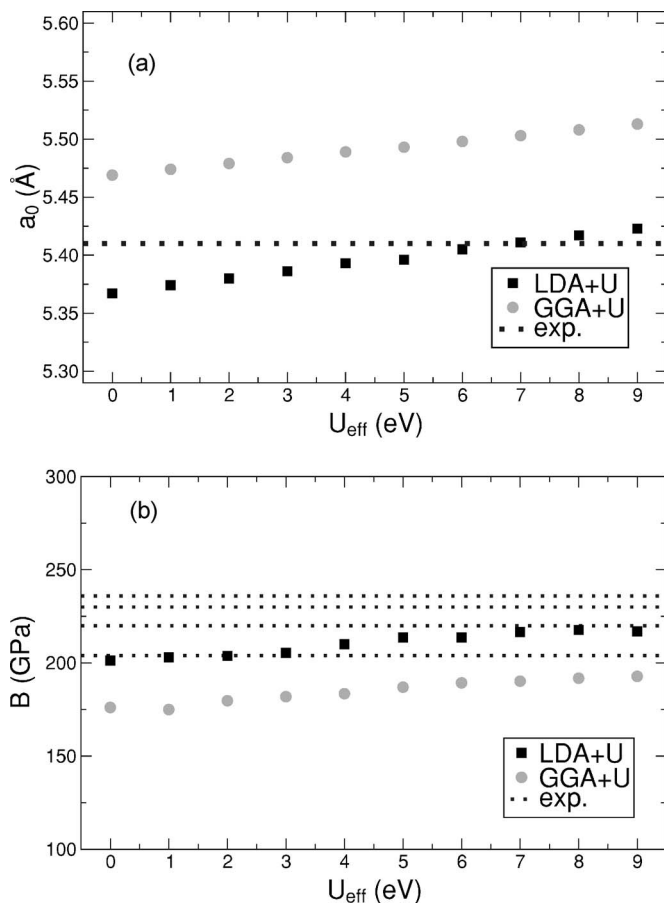


FIG. 1. Dependence of the lattice parameter  $a_0$  (a) and bulk modulus  $B$  (b) of  $\text{CeO}_2$  on  $U_{\text{eff}}$ . Notice that for  $B$  four experimental different values can be found in the literature.

modulus, which varies over a rather broad range of 204 to 236 GPa.<sup>20,36,37,44</sup> Overall, GGA calculations result in a somewhat longer  $a_0$  and a smaller bulk modulus, and thus give a slightly less accurate description of the atomic structure of  $\text{CeO}_2$ . Our lattice parameter values  $a_0$  are 5.40 Å (LDA+U,  $U_{\text{eff}}=5$  eV) and 5.48 Å (GGA+U,  $U_{\text{eff}}=3$  eV), in line with theoretical data cited above. It is also the case for the present bulk modulus values 213.7 GPa (LDA+U) and 187.0 GPa (GGA+U). We note in passing that like the studies of Fabris *et al.*<sup>4</sup> and Hay *et al.*,<sup>7</sup> we could not reproduce with the PBE functional the lattice parameter value reported by Jiang *et al.* as obtained at the PBE level;<sup>6</sup> instead, the value was reproduced by us when using LDA. The structural data of  $\text{CeO}_2$  in Table I seem to be only modestly influenced by the value of  $U_{\text{eff}}$  chosen in the LDA+U or GGA+U calculations. This is more clear in Fig. 1 which displays the dependence of the lattice parameter and bulk modulus for  $U_{\text{eff}} \equiv U - J$  in the range 0–9 eV. There is a steady increase of the lattice parameter with growing  $U_{\text{eff}}$  in combination with both LDA and GGA functionals.  $a_0$  is overestimated already at the purely GGA level ( $U_{\text{eff}}=0$  eV). Thus, introducing  $U_{\text{eff}} > 0$  just makes the deviation from the experiment larger. For the LDA+U scheme the situation is opposite: calculation without  $U_{\text{eff}}$  gives  $a_0$  underestimated by  $\sim 0.03$  Å compared to experiment and for a certain  $U_{\text{eff}}$  value

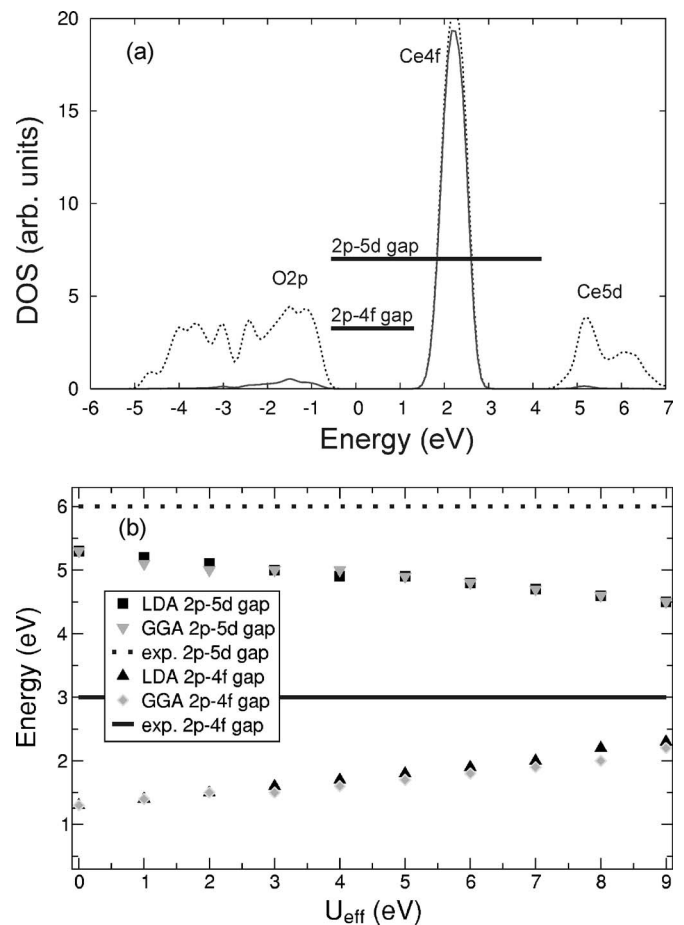


FIG. 2. (a) Density of states (DOS) of  $\text{CeO}_2$  at the LDA+U level ( $U_{\text{eff}}=5$  eV) and (b) dependence of the band gap value  $\text{O}(2p)\text{-Ce}(5d)$  and position of the gap state  $\text{Ce}(4f)$  relative to the top of the  $\text{O}(2p)$  band  $\text{O}(2p)\text{-Ce}(4f)$  on  $U_{\text{eff}}$  for LDA+U and GGA+U calculations.

around 6.7 eV  $a_0$  matches the experimental value. As indicated in Fig. 1(b), the bulk modulus value is also steadily increasing with increasing  $U_{\text{eff}}$  but this observable is even less affected by the latter parameter. Note that calculation of the bulk modulus using the stress tensor, i.e., a pressure versus volume fit instead of energy versus volume fit we referred so far, gave slightly less precise (lower) bulk modulus due to the so-called Pulay stress which arises from incompleteness of the plane wave basis set with respect to changes of the volume.<sup>45</sup> To conclude [Fig. 1(b)], the LDA functional provides a better agreement with experiment than the GGA one does: the LDA bulk modulus values lie basically at all  $U_{\text{eff}}$  considered within the experimental range of 204–236 GPa.

Concerning the electronic structure of  $\text{CeO}_2$ , a  $\text{O}(2p)\text{-Ce}(5d)$  band gap of  $\sim 5$  eV is predicted at both LDA+U and GGA+U levels (Fig. 2); the dependence on  $U_{\text{eff}}$  used is noticeable but not very large. The consequence is that the calculated values are always slightly smaller than the measured one at 6 eV.<sup>46</sup> Figure 2(a) shows the density of states (DOS) obtained at the LDA+U level ( $U_{\text{eff}}=5$  eV). Important features in the DOS are the  $\text{O}(2p)\text{-Ce}(5d)$  band gap and the empty  $\text{Ce}(4f)$  state in the gap above the  $\text{O}(2p)$  band.

TABLE II. Calculated and experimental lattice parameter  $a_0$  and bulk modulus  $B$  of  $\text{Ce}_2\text{O}_3$ . Previously reported data are also included for comparison.  $U_{\text{eff}}$  values are specified where applicable.

Method	$U_{\text{eff}}/\text{eV}$	$a_0/\text{\AA}$	$B/\text{GPa}$	Reference
LDA+U	3.0	3.84	150.9	4
LDA+U	5.0	3.85	144.7	This work
GGA(PBE)+U	1.5	3.94	131.3	4
GGA+U	3.0	3.92	128.5	This work
HSE	—	3.86	—	7
SIC-LSD	—	3.85	—	19
Exp.	—	3.89	—	35

Figure 2(b) displays changes in the band gap with altered  $U_{\text{eff}}$ . As the on-site Coulomb repulsion ( $U_{\text{eff}}$ ) increases, the overall band gap decreases, from 5.3 eV to 4.6 eV, for both density functional approaches. However, the gap between the  $\text{O}(2p)$  band and the empty  $\text{Ce}(4f)$  state increases concomitantly, from 1.3 eV to 2.3 eV. Because experimentally the  $\text{Ce}(4f)$  state lies  $\sim 3$  eV above the  $\text{O}(2p)$  band, a better agreement with experiment would require a large  $U_{\text{eff}}$  value, which, on the other hand, leads to more significant underestimation of the  $\text{O}(2p)$ - $\text{Ce}(5d)$  band gap. Another consequence of higher values  $U_{\text{eff}}$  (not shown here) is a slightly reduced width of the  $\text{Ce}(4f)$  peak, which reflects stronger localization.

The conclusion to be drawn from this systematic study is that an additional Hubbard-type on-site electron interaction only modestly influences the structural properties of  $\text{CeO}_2$ . For different  $U_{\text{eff}}$  values under scrutiny deviations from experiment still lie within the accuracy usually achieved with standard LDA and GGA approaches. The influence of  $U_{\text{eff}}$  on the DOS is basically restricted to the *empty f* band and, thus, does not qualitatively change the electronic distribution. Generally speaking,  $\text{CeO}_2$  can be handled fairly well within contemporary density functional methods and quite independently of the particular approach chosen. This is also evident from Table I and the numerous theoretical publications on cerium dioxide cited above.

### B. Atomic and electronic structure of $\text{Ce}_2\text{O}_3$

$\text{Ce}_2\text{O}_3$  is an insulating oxide of the hexagonal sesquioxide A-type ( $P\bar{3}m1$ ) with a lattice parameter  $a_0=3.888$  Å and a ratio of  $c_0/a_0=1.56$ .<sup>35</sup> It is characterized by an antiferromagnetic ground state with an *effective* magnetic moment  $\mu_{\text{eff}}=2.17$   $\mu_B/\text{mol}$ .<sup>35</sup> The presently calculated  $a_0$  values for bulk  $\text{Ce}_2\text{O}_3$  are shown in Table II together with the data from recently communicated DFT computations. Other earlier approaches to compute  $\text{Ce}_2\text{O}_3$  also exist, but either they do not consider explicitly on-site Coulomb repulsion<sup>11,12</sup> and hence result in an incorrect description of the electronic structure, or they treat  $\text{Ce}_2\text{O}_3$  by incorporating the *f* electron inside the core.<sup>3</sup> However, to account for the localized *f* electron of the formal  $\text{Ce}^{3+}$  ion and at the same time to properly represent the  $\text{Ce}^{4+}$  analog an explicit consideration of the on-site Coulomb interaction is unavoidable.<sup>4,5</sup> Recently, it has been sug-

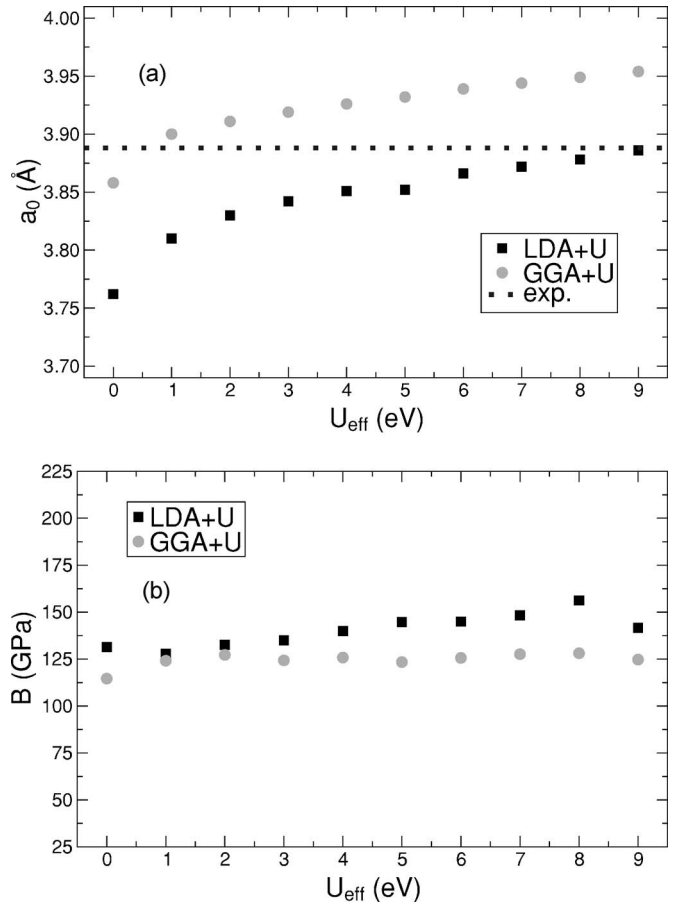


FIG. 3. Dependence of the lattice parameter  $a_0$  (a) and bulk modulus  $B$  (b) of  $\text{Ce}_2\text{O}_3$  on  $U_{\text{eff}}$ .

gested that a DFT hybrid approach with the Heyd-Scuseria-Ernzerhof (HSE) functional might serve as an alternative to accurately describe reduced ceria.<sup>7</sup>

Let us now turn to the lattice parameter  $a_0$  of  $\text{Ce}_2\text{O}_3$  as predicted by the different DFT approaches (Table II). Very similarly to results discussed for  $\text{CeO}_2$  in Secs. III A, LDA slightly underestimates  $a_0$  whereas GGA exhibits the opposite trend and overestimates it. The lattice parameter and the bulk modulus of  $\text{Ce}_2\text{O}_3$  as a function of  $U_{\text{eff}}$  are explicitly shown in Fig. 3. Introducing  $U$  into the LDA methods results in an increase of  $a_0$  so that eventually LDA+U may predict the experimental lattice constant. However, since the GGA predicted  $a_0$  is already too big, introduction of  $U$  into the GGA potential leads to an even worse estimate. To the best of our knowledge, the bulk modulus of  $\text{Ce}_2\text{O}_3$  has not been measured so far, but in analogy to the calculated trends reported above for  $\text{CeO}_2$  one may expect a value around 150 GPa.

Overall, the effect of  $U_{\text{eff}}$  is similar to what is found for  $\text{CeO}_2$ , but, and this is a crucial point, the observables of  $\text{Ce}_2\text{O}_3$  are much more affected by variation of  $U_{\text{eff}}$  than those of the nonmagnetic  $\text{CeO}_2$ . For  $U_{\text{eff}}$  increasing from 0 to 9 eV, the lattice constant of  $\text{Ce}_2\text{O}_3$  varies over a range of 0.12 Å and the bulk modulus changes over more than 40 GPa, compared to the corresponding variations of 0.06 Å and 20 GPa for  $\text{CeO}_2$ . These data clearly demonstrate the



importance of including in the determination of  $U_{\text{eff}}$  also  $\text{Ce}_2\text{O}_3$  as a substance considerably more sensitive to this parameter. Note that the unsteadiness of the bulk modulus [Fig. 3(b)], especially for small values of  $U_{\text{eff}}$ , is due to the fact that it is not possible to get a well-balanced energy versus volume curve in the area of small volumes where electronic solutions with localised  $f$  electrons could not be found. However, this is not a problem for the lattice parameter as for its determination only a few values around the minimum of the energy versus volume curve are needed.

It is important to mention that the just discussed observables are computed for the ground state of  $\text{Ce}_2\text{O}_3$ , which we found to be insulating and *antiferromagnetic*, and which lies 25 meV (LDA+U,  $U_{\text{eff}}=5$  eV) and 24 meV (GGA+U,  $U_{\text{eff}}=3$  eV) below the insulating *ferromagnetic* state. In a simple mapping approach<sup>47–51</sup> this gives a Heisenberg exchange coupling constant  $J \approx -50$  meV. Unfortunately it is very difficult to assess the accuracy of this prediction since, to the best of our knowledge, no experimentally determined  $J$  value for  $\text{Ce}_2\text{O}_3$  has been reported. The presently computed value is significantly larger than the coupling constant of  $-6$  meV predicted by Hay *et al.*<sup>7</sup> using the HSE hybrid functional. In any case it is worth pointing out that LDA and GGA approaches tend to overestimate the Heisenberg exchange effective parameter<sup>49</sup> and hybrid functionals exhibit very strong dependence on the amount of Fock exchange.<sup>52</sup> One may also argue that the LDA+U or GGA+U values also depend on the choice of the  $U_{\text{eff}}$  parameter. We have investigated the variation of  $J$  with respect to  $U_{\text{eff}}$  and found that this is rather small, within the range of a few meV. Moreover, a rather stable value of  $J \approx -50$  meV is predicted for  $U_{\text{eff}}$  in the 4–5 eV range for the LDA+U and in the 2–3 eV range for the GGA+U, respectively. The low influence of the effective on-site Coulomb repulsion on the Heisenberg exchange coupling can be rationalized by the fact, that in the LDA+U approach only one-center two-electron interactions are modified. This contrasts with the behavior of hybrid density functional approaches where a modification of the exchange potential strongly influences the electron interactions between different centers.<sup>49–52</sup> Further studies dealing with the interplay between  $U_{\text{eff}}$  and the exchange coupling for other systems than ceria are in preparation.

With respect to the electronic structure of  $\text{Ce}_2\text{O}_3$ , the major effect of  $U_{\text{eff}}$  in the LDA+U and GGA+U approaches is to force the localisation of the  $4f$  electron within the band gap. As a result, this material becomes to be properly described as insulating instead of metallic as has been discussed in detail by other groups.<sup>4,5</sup> In the following we will focus on the changes that occur to the DOS when the on-site Coulomb interaction is modified via  $U_{\text{eff}}$ .

Figure 4 displays the DOS plot of  $\text{Ce}_2\text{O}_3$  as well as change of the position of the  $\text{O}(2p)$  band relative to the  $\text{Ce}(4f)$  state  $\text{O}(2p)\text{-Ce}(4f)$  and the bottom of the  $\text{Ce}(5d)$  band  $\text{O}(2p)\text{-Ce}(5d)$ ; the  $U_{\text{eff}}$  dependence of the gaps  $\text{O}(2p)\text{-Ce}(4f)$  and  $\text{O}(2p)\text{-Ce}(5d)$  [Fig. 4(b)] is shown for both LDA+U and GGA+U results. For  $U_{\text{eff}}=1$  eV (not shown), the  $\text{Ce}(4f)$  gap state still mixes with the  $\text{Ce}(5d)$  empty band and gives only a small gap. For stronger on-site repulsion imposed one gets larger band gap values although

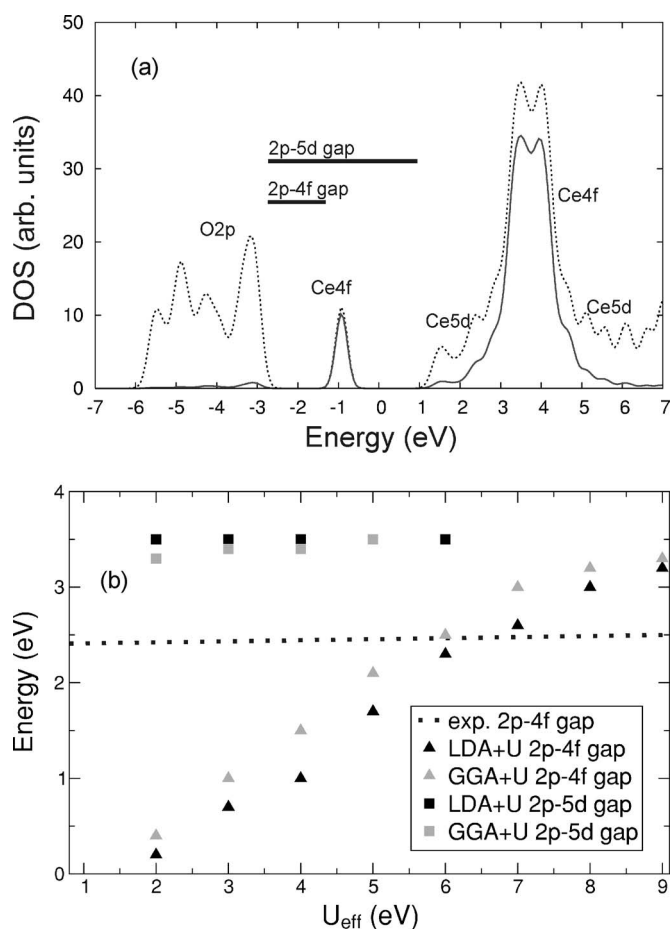


FIG. 4. (a) Density of states (DOS) of  $\text{Ce}_2\text{O}_3$  (dashed line) and partial DOS of the  $\text{Ce}(4f)$  state (solid line) at the LDA+U level ( $U_{\text{eff}}=5$  eV) and (b) dependence of the band gap value  $\text{O}(2p)\text{-Ce}(5d)$  and position of the gap state  $\text{Ce}(4f)$  relative to the top of the  $\text{O}(2p)$  band  $\text{O}(2p)\text{-Ce}(4f)$  on  $U_{\text{eff}}$  for LDA+U and GGA+U calculations.

the  $\text{O}(2p)\text{-Ce}(5d)$  splitting stays nearly constant. The  $\text{Ce}(4f)$  gap state however moves towards the conduction band until it eventually overlaps the  $\text{Ce}(5d)$  band. For an intermediate value of  $U_{\text{eff}}=5$  eV, the LDA+U method places the  $\text{Ce}(4f)$  state approximately 1.7 eV above the  $\text{O}(2p)$  valence band, compared to 2.4 eV measured experimentally.<sup>53</sup> The GGA+U scheme predicts a somewhat bigger gap  $\text{O}(2p)\text{-Ce}(4f)$  of 2.1 eV for  $U_{\text{eff}}=5$  eV.

Thus, the electronic structure of  $\text{Ce}_2\text{O}_3$  is obviously strongly dependent on  $U_{\text{eff}}$ : a small change on this parameter causes a substantial effect, especially when compared to the modest effect of  $U_{\text{eff}}$  on the electronic structure of  $\text{CeO}_2$ . The effect becomes dramatic indeed for the magnetic moment as clearly evidenced on Fig. 5, which displays the change of the magnetic moment of  $\text{Ce}_2\text{O}_3$  per Ce atom as a function of  $U_{\text{eff}}$ . Unless the on-site Coulomb interaction is explicitly taken into account, the magnetic moment per Ce center in the antiferromagnetic ground state solution almost vanishes and the electronic structure becomes metallic. The experimental value of the *effective* magnetic moment ( $\mu_{\text{eff}}=2.17\mu_B/\text{mol}$ ) (Ref. 35) is indicative of one  $f$  electron per Ce site within the unit cell containing two Ce atoms. In the calculation only

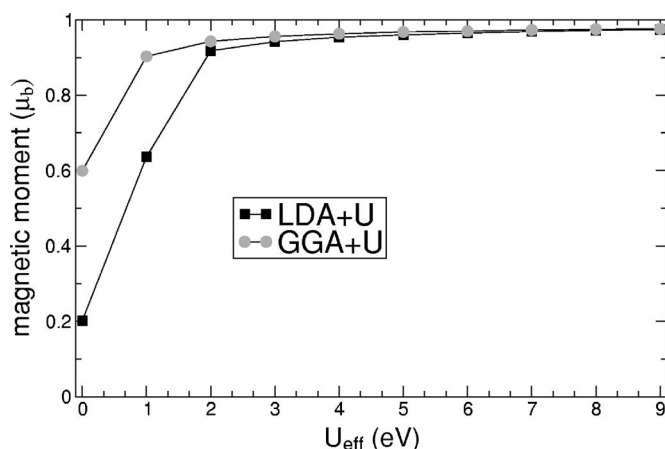


FIG. 5. Dependence of the magnetic moment per Ce atom in the antiferromagnetic spin state of  $\text{Ce}_2\text{O}_3$  with respect to the  $U_{\text{eff}}$  parameter.

magnetic contributions arising from the spin of the  $f$  electrons are accounted for. So, deviations from the experimental value of the magnetic moment have to be expected. The computed values are obtained by projecting the PAW wave function for each spin onto spherical harmonics. At low  $U_{\text{eff}}$  values, the  $f$  electron still exhibits some itinerant character, unveiled by a fractional magnetic moment, whereas at  $U_{\text{eff}} \approx 3$  eV the electron is nearly completely localised in both LDA+U and GGA+U calculations and the magnetic moment approaches unity. For the GGA functional, the localisation of the  $f$  electron occurs at lower values of  $U_{\text{eff}}$ , suggesting that in general a lower value for  $U_{\text{eff}}$  is sufficient. This effect might have been expected, because in principle electron correlation is treated in a more accurate way within the GGA than within LDA.

### C. Reaction energies

In addition to the dependence of geometric and electronic structure observables on  $U_{\text{eff}}$  we have also investigated the effect of this parameter on selected reaction energies involving ceria. First, we computed the formation energies of  $\text{CeO}_2$  and  $\text{Ce}_2\text{O}_3$  at zero pressure and zero temperature (see Fig. 6). The corresponding experimental values are  $-11.29$  eV ( $\text{CeO}_2$ ) and  $-18.63$  eV ( $\text{Ce}_2\text{O}_3$ ).<sup>54,55</sup> To correctly evaluate these energies it is necessary to consider the  $\gamma$  modification of fcc Ce at different values of  $U_{\text{eff}}$ .<sup>56</sup> (The results for bulk Ce are not reported here but are available from the authors upon request.) The reliability of the LSDA+U and the GGA+U schemes for fcc  $\gamma$  cerium have been established by Shick *et al.*<sup>57</sup> The minimum appearing in both curves is an artifact because for LDA+U with  $U_{\text{eff}} < 3$  eV and GGA+U with  $U_{\text{eff}} < 2$  eV, the electron solutions for the  $\gamma$ -Ce reference collapsed to the high pressure solution for  $\alpha$ -Ce with itinerant  $f$  electrons. It was therefore not possible to get the correct stable electronic solution for  $\gamma$ -Ce at these points. For sake of consistency one should then only consider reaction energies starting from  $U_{\text{eff}} = 3$  eV or  $U_{\text{eff}} = 2$  eV for the LDA+U and GGA+U methods, respectively.

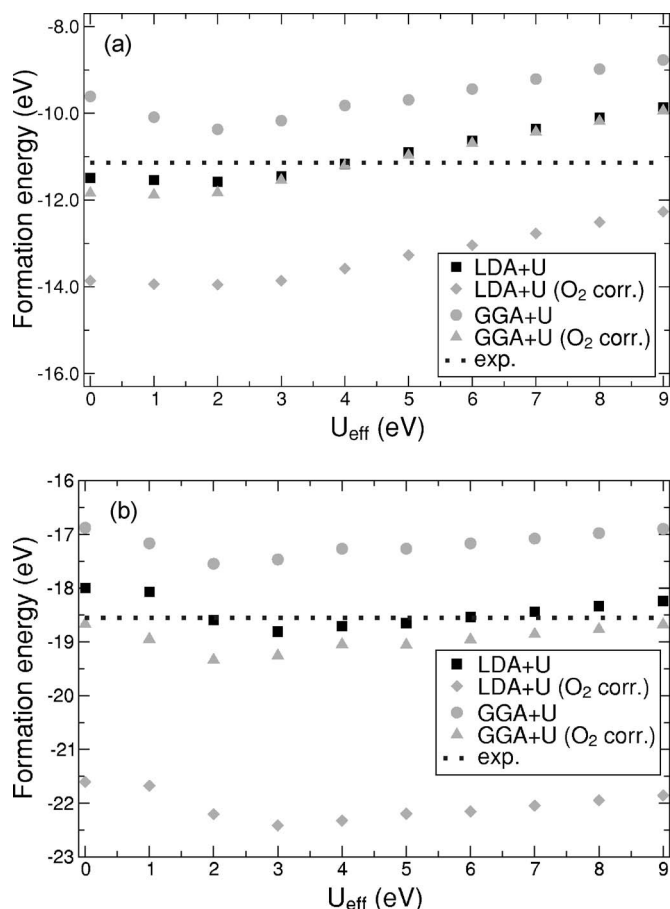


FIG. 6. Dependence of the formation energies of (a)  $\text{CeO}_2: \text{Ce} + \text{O}_2 \rightarrow \text{CeO}_2$  and (b)  $\text{Ce}_2\text{O}_3: 2\text{Ce} + 1.5\text{O}_2 \rightarrow \text{Ce}_2\text{O}_3$  on the  $U_{\text{eff}}$  parameter.

Thus, for  $\text{CeO}_2$  and  $\text{Ce}_2\text{O}_3$  the LDA+U and GGA+U formation energy rises gradually upon increasing  $U_{\text{eff}}$ , the reaction is predicted to become less exothermic. Since LDA is well known to overestimate binding energies  $\Delta E$  in molecular systems [e.g.,  $\Delta E(\text{O}_2, \text{LDA}) = -7.53$  eV compared to  $\Delta E(\text{O}_2, \text{exp}) = -5.2$  eV],<sup>54</sup> the calculated formation energy has been empirically corrected for this effect by shifting the energy of  $\text{O}_2$  so as to give the experimental binding energy, this is to assume  $E(\text{O}_2, \text{DFT, corr}) = \Delta E(\text{O}_2, \text{exp}) - 2E(^3\text{O}, \text{DFT})$ . In the case of LDA+U this did lead to a severe worsening of the reaction energies, whereas for GGA+U, which also shows overbinding [ $\Delta E(\text{O}_2, \text{GGA}) = -6.31$  eV], a significant improvement is obtained (Fig. 6). For both the LDA and the GGA functionals, intermediate values of  $U_{\text{eff}}$  of about 3–5 eV seem to be advisable, whereas the LDA energies appear to profit from a fortuitous error cancellation. Formation energies for  $\text{CeO}_2$  and  $\text{Ce}_2\text{O}_3$  have also been calculated by Fabris *et al.* to be  $-11.33$  eV and  $-18.49$  eV for LDA+U ( $U_{\text{eff}} = 3$  eV) which are close to the present LDA+U values and to experiment. However, the present uncorrected GGA+U reported in Fig. 6 and by Fabris *et al.*<sup>4</sup> GGA(PBE)+U values with  $U_{\text{eff}} = 1.5$  eV of  $-9.2$  eV and  $-16.78$  eV exhibit a substantial deviation from experiment.

The dependence of the transformation reaction energy  $2\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3 + 0.5\text{O}_2$  on  $U_{\text{eff}}$  is presented in Fig. 7. Inter-

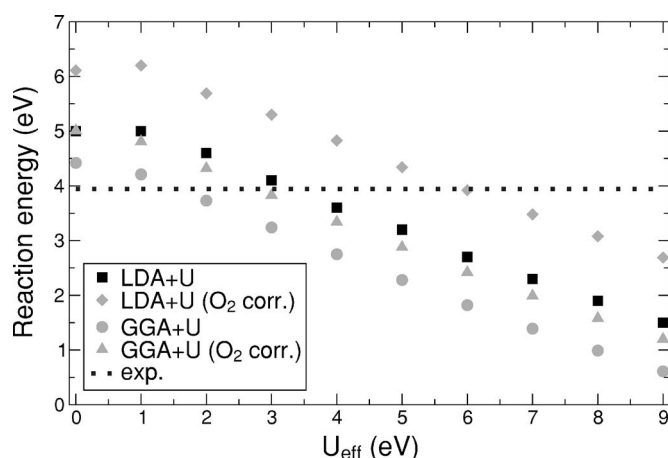


FIG. 7. Dependence of the  $2\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3 + 0.5\text{O}_2$  reaction energy on  $U_{\text{eff}}$ .

mediate values of 2–4 eV seem to give the best agreement with the experimental value of 3.94 eV.<sup>54</sup> Again, for the GGA functional lower values than for LDA seem appropriate. The corrected GGA values lead to an improvement of reaction energies as it was the case for the formation energies. The corresponding results of Fabris *et al.* are 4.04 eV for LDA+U ( $U_{\text{eff}}=3$  eV) and 1.64 eV for GGA(PBE)+U ( $U_{\text{eff}}=1.5$  eV).<sup>4</sup> The agreement with present data, 4.1 eV (LDA,  $U_{\text{eff}}=3$  eV) and 3.7 eV (GGA,  $U_{\text{eff}}=2$  eV), respectively, is acceptable, taking into account that different GGA functionals have been used in both studies.

#### IV. CONCLUSIONS

The bulk cerium oxides  $\text{CeO}_2$  and  $\text{Ce}_2\text{O}_3$  have been studied by means of periodic density functional calculations including explicitly the Hubbard on-site Coulomb repulsion  $U_{\text{eff}}$  parameter. The impact of this parameter on several structural and electronic observables of both materials has been investigated in a systematic way. It is found that the optimal value of  $U_{\text{eff}}$  is considerably dependent on the property under examination, and the sensitivity towards  $U_{\text{eff}}$  is especially high for properties of  $\text{Ce}_2\text{O}_3$ . Overall, the scheme GGA(PW91) reveals an acceptable agreement with experiment at lower energies of  $U_{\text{eff}}$  than LDA does; this is partly due to the more accurate treatment of correlation effects within the GGA potential. Structural properties such as lattice constants and bulk modulus are somewhat better rep-

resented by the LDA+U method for  $\text{CeO}_2$ . Regarding  $\text{Ce}_2\text{O}_3$  electronic structure, both LDA+U and GGA+U results show a similarly good accuracy. Interestingly, for the calculated reaction energies LDA+U scheme appears to perform better, although presumably taking benefit of error cancellation. The GGA(PW91)+U estimated reaction energies involving the molecular oxygen total energy may be improved by the correction as indicated above.

A well balanced choice of  $U_{\text{eff}}$  is proposed to be at 5–6 eV for the LDA+U calculations and at 2–3 eV for the GGA+U ones. An important conclusion is that, in order to correctly reproduce the experimental observables, the Coulomb on-site repulsion has to be increased compared to the one determined in a self-consistent way (2.5–3.5 eV for LDA+U and 1.5–2.0 eV for GGA+U), although the physical reason for this remains unclear. We would like to point out that self-consistency on  $U_{\text{eff}}$ , albeit a convenient conceptual procedure, is not supported from any fundamental theorem. In addition, it is well possible that screening effects due to other electrons are slightly overemphasized in the DFT+U approaches.

Finally, it should be mentioned that even if this work is based on purely Ce(IV) or purely Ce(III) materials, the present conclusions are expected to be valid for other related materials of a mixed valence character, simultaneously containing Ce ions in the two oxidations states, such as defective ceria surfaces or nanosized ceria particles. In this sense, the suggested choice of an optimal  $U_{\text{eff}}$  parameter based on comparison to a large enough set of experimental data validates a promising and efficient way to study these systems within the DFT+U formalism.

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