# Localized and Itinerant States in Lanthanide Oxides United by *GW* @ LDA + *U*

Hong Jiang,[1] Ricardo I. Gomez-Abal,[1] Patrick Rinke,[1,2] and Matthias Scheffler[1,2]
[1]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany*
[2]*University of California at Santa Barbara, Santa Barbara, California 93106, USA*
(Received 22 November 2008; published 24 March 2009)

Many-body perturbation theory in the *GW* approach is applied to lanthanide oxides, using the local-density approximation plus a Hubbard $U$ correction (LDA + $U$) as the starting point. Good agreement between the $G_0W_0$ density of states and experimental spectra is observed for $CeO_2$ and $Ce_2O_3$. Unlike the LDA + $U$ method $G_0W_0$ exhibits only a weak dependence on $U$ in a physically meaningful range of $U$ values. For the whole lanthanide sesquioxide ($Ln_2O_3$) series $G_0W_0$ @ LDA + $U$ reproduces the main features found for the optical experimental band gaps. The relative positions of the occupied and unoccupied $f$ states predicted by $G_0W_0$ confirm the experimental conjecture derived from phenomenological arguments.

DOI: 10.1103/PhysRevLett.102.126403 PACS numbers: 71.10.−w, 71.15.−m, 71.20.−b, 71.27.+a

The accurate first-principles description of the electronic structure of $f$-electron systems, i.e., materials containing lanthanide or actinide elements, is currently regarded as one of the great challenges in condensed matter physics. $f$-electron systems are characterized by the simultaneous presence of itinerant (delocalized) and highly localized $f$ states and interactions between them. Most computational methods are suited only to one type. Density-functional theory (DFT)—currently the standard approach for electronic structure calculations of extended systems—proves to be inadequate for $f$-electron systems in the most commonly applied local-density or generalized gradient approximation (LDA or GGA, respectively). One of the major deficiencies of LDA and GGA is the delocalization (or self-interaction) error [1], which is particularly severe for systems with partially occupied $d$ or $f$ states and can even lead to qualitatively incorrect metallic ground states for many insulating systems. Hybrid functionals [2], on the other hand, partly correct the self-interaction error by incorporating a certain portion of exact exchange, which significantly improves the descriptions of $d$- or $f$-electron systems [3,4]. The dependence on adjustable parameters, however, remains a concern. Conversely, correlation effects that govern the physics of localized $f$ electrons can in principle be treated systematically by dynamical mean field theory (DMFT) [5]. In practice these many-body corrections are only applied locally to an atomic site (e.g., the Anderson impurity model) and the impurity solvers require input parameters (such as the Hubbard $U$) for the interaction strength. Moreover, most existing DMFT schemes are coupled (non-self-consistently) to local or semilocal DFT calculations and the description of the itinerant electrons therefore remains on the level of LDA and GGA.

As a first step towards a systematic *ab initio* understanding of $f$-electron systems, we apply many-body perturbation theory (MBPT) in the *GW* approach to a selected set of lanthanide oxides [$CeO_2$ and $Ln_2O_3$ (Ln = lanthanide series)] [6] in this Letter. These compounds have important technological applications [7–12], in particular, in catalysis, where $CeO_2$-based compounds have attracted considerable interest from both experiment and theory [3,13–20]. Unlike in most previous studies, the *GW* calculations in this work are based on LDA ground state calculations including a Hubbard $U$ correction (henceforth denoted $G_0W_0$ @ LDA + $U$). Our $G_0W_0$ @ LDA + $U$ calculations provide a qualitative understanding of the general trend observed for the band gaps of the $Ln_2O_3$ series and reproduce the characteristic features of the series, in particular, the four dips observed in the experimental curve.

The *GW* approach corresponds to the first-order term of a systematic expansion in MBPT [21] and has become the method of choice for the description of quasiparticle band structures in weakly correlated solids [22]. Through the screened Coulomb interaction $W$ it captures the screening among itinerant electrons while at the same time treating exchange at the exact exchange level (given by the Hartree-Fock expression). The latter should account for a large part of the many-body interactions among localized $d$ or $f$-electrons, as demonstrated recently for $Cu_2O$ and $VO_2$ [23]. In the hierarchy of many-body perturbation theory, strong correlation denotes correlation effects that go beyond exact exchange and the weak correlation regime of *GW*. The good agreement between our *GW* calculations and available experimental data demonstrates that the *GW* method can treat both itinerant *spd* bands and localized $f$ bands accurately for the materials we have considered. Since the screened exchange picture of the *GW* approach captures the essential physics we challenge the classification of these materials as *strongly correlated* [24].

The *GW* method is typically applied in a perturbative manner (henceforth denoted $G_0W_0$) in which the quasiparticle (QP) energies $\epsilon^{\mathrm{QP}}_{n\mathbf{k}}$ are calculated as a first-order correction to the eigenenergies $\epsilon_{n\mathbf{k}}$ and eigenvectors $\psi_{n\mathbf{k}}$ of a reference single-particle Hamiltonian $\hat{H}_0$

$$\epsilon^{\mathrm{QP}}_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} + \Re\langle\psi_{n\mathbf{k}}|\Sigma^{\mathrm{xc}}(\epsilon^{\mathrm{QP}}_{n\mathbf{k}}) - V^{\mathrm{xc}}|\psi_{n\mathbf{k}}\rangle. \quad (1)$$

 

Here $\Sigma^{xc}$ is the $G_0W_0$ self-energy calculated from the one-particle Green's function $G_0$ and screened Coulomb interaction $W_0$, both evaluated using $\epsilon_{n\mathbf{k}}$ and $\psi_{n\mathbf{k}}$, and $V^{xc}$ is the exchange-correlation potential included in $\hat{H}_0$. For most of the sesquioxides considered in this work LDA and GGA incorrectly predict a metallic ground state. In these cases first-order perturbation theory based on LDA or GGA is not applicable and alternative reference $\hat{H}_0$ have to be employed [25–28]. In this work we use the LDA + $U$ method [29] as the starting point for $G_0W_0$. By adding a site- and orbital-dependent correction $\delta\hat{V}^U$ to the standard LDA single-particle Hamiltonian, LDA + $U$ significantly improves the description of highly localized states, and therefore overcomes the major failure of LDA for these systems. To describe highly localized states accurately, we have implemented an all-electron $G_0W_0$ approach [30] based on the full-potential linearized augmented plane wave method [31].

The LDA + $U$ method is conceptually similar to $GW$. It is, however, *not* a substitute for $GW$ even for localized states: (i) The link between the LDA + $U$ and the $GW$ approximation relies on the assumption that the hybridization between localized and itinerant states can be neglected, which in many cases is not valid; (ii) the $\delta\hat{V}^U$ correction in LDA + $U$ has *direct* effects only on the corresponding localized states; the description of itinerant states remains at the LDA level; and (iii) screening in LDA + $U$ is *static*, while in reality screening is dynamic and has a stronger energy dependence for localized electrons than for itinerant ones. The LDA + $U$ approach by itself is therefore not expected to provide a satisfactory description to the electronic structure of $f$-electron systems.

An advantage of the $G_0W_0$ @ LDA + $U$ approach lies in the fact that the Hubbard $U$ corrections enter self-consistently in the ground state calculation. This becomes important when localized states hybridize with band states. A less appealing aspect of the LDA + $U$ approach concerns the parameter $U$, which, in many cases, is determined by fitting to experimental data. The on-site Coulomb interaction $U$, however, has a well-defined physical meaning, and can be calculated from first-principles (see, e.g., Ref. [32]). In addition we demonstrate below that $G_0W_0$ based on LDA + $U$ is much less sensitive to $U$ than the LDA + $U$ itself. The $G_0W_0$ calculations also remove the problem of the double counting corrections that are not well defined in the LDA + $U$ approach, by subtracting them out as part of $V_{xc}$ in Eq. (1). Despite these advantages the $G_0W_0$ @ LDA + $U$ approach will not be suitable in cases where strong correlation effects become important (e.g., the Kondo resonance), for which many-body interactions that go beyond the $GW$ approach have to be included. This is currently the domain of DMFT, as alluded to in the introduction.

Figure 1 shows the density of states (DOS) of $CeO_2$ and $Ce_2O_3$ calculated from LDA, LDA + $U$, and $G_0W_0$ @ LDA + $U$ (with $U = 5.4$ eV [33]) together with the experimental spectra. The $G_0W_0$ density of states for $CeO_2$ agrees well with the experimental data from direct (XPS) and inverse (BIS) photoemission spectroscopy or x-ray absorption spectroscopy (XAS). In $CeO_2$, the empty $f$ states introduce a sharp peak in the fundamental band gap formed between the O-2$p$ valence and Ce-5$d$ conduction band. The most important quantities here are therefore the $p$-$f$ and $p$-$d$ gaps. For the latter the $G_0W_0$ value of 6.1 eV is in good agreement with the experimental one of 6.0 eV. The $p$-$f$ gap, however, cannot be unambiguously determined from XPS-BIS or other available measurements (See, e.g., Ref. [18] and references therein). As expected, LDA underestimates both gaps, but the $p$-$d$ gap is only slightly smaller than in experiment (5.5 vs 6.0 eV), whereas LDA + $U$ decreases it to 5.1 eV. We also note that our $G_0W_0$ @ LDA + $U$ DOS for $CeO_2$ is very close to that obtained from the recently proposed self-consistent $GW$ method [34].

More intriguing features are observed for $Ce_2O_3$. As expected, the on-site Hubbard correction in the LDA + $U$ splits the single $f$ peak in LDA to occupied and unoccupied $f$ bands (denoted as $f^{occ}$ and $f^{un}$, respectively), the former falling within the $p$-$d$ gap and the latter overlapping with the conduction bands. The $p$-$d$ gap is nearly the same as in LDA, but the $p$-$f^{occ}$ splitting is greatly reduced. Applying the $G_0W_0$ corrections to the LDA + $U$ ground state, we observe two remarkable features: (i) the O-2$p$ band is pushed to lower energy with respect to the $f^{occ}$ band, and (ii) the $f^{un}$-band shifts up in energy away from the conduction band edge increasing the splitting between the $f^{occ}$ and $f^{un}$ bands at the same time.

The $G_0W_0$ and the experimental spectrum in Fig. 1 are aligned at the upper valence band edge and not the Fermi level since this is not well defined at the 0 K at which the calculations are performed. We again find the $f^{un}$ peak to be in good agreement with the BIS data. The position of the $f^{occ}$ peak, however, differs by approximately 1 eV. With respect to the band gap the comparison with experiment is aggravated by the limited experimental resolution. Taking the difference between the conduction band edge and the upper edge of the XPS-XAS $f^{occ}$ peak gives a band gap that is consistent with the optical band gap of ~2.4 eV [8,35]

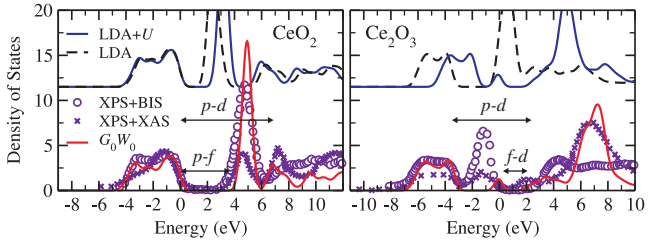


FIG. 1 (color online). The DOS of $CeO_2$ (left) and $Ce_2O_3$ (right) from LDA, LDA + $U$ and $G_0W_0$ @ LDA + $U$ with $U = 5.4$ eV are compared to experimental data (XPS + BIS and XPS + XAS) [38]. The LDA and LDA + $U$ curves have been offset vertically for clarity.

and the $G_0W_0$ gap of 2.0 eV. If one instead references against the peak center of the $f^{occ}$ states, the experimental band gap of $Ce_2O_3$ would be larger than 3 eV. Further experimental evidence is clearly needed to determine the actual value.

Figure 2 illustrates the influence of $U$ on the LDA + $U$ and $G_0W_0$ @ LDA + $U$ calculations for the examples of $CeO_2$ and $Ce_2O_3$. Since the $f$ states are essentially empty in $CeO_2$, the effect of $U$ is relatively weak: For $U = 0$ to 8 eV, the $p$-$f$ and $p$-$d$ gaps from LDA + $U$ change only by approximately 1.0 and 0.5 eV, respectively, and become nearly constant in $G_0W_0$. The situation is more complex in $Ce_2O_3$. In LDA + $U$, the $f$-$d$ gap depends sensitively on $U$ and varies by nearly 3 eV, but the $p$-$d$ gap remains almost unaffected. In contrast, both the $f$-$d$ and the $p$-$d$ gap exhibit a slight $U$ dependence in $G_0W_0$, changing by 1.2 and 0.6 eV over the full $U$ range explored here. Most importantly, however, the $U$ dependence reduces to only approximately 0.3 eV in the range of "physically meaningful" values of $U$ (~5–7 eV [18,19]), which is already in the range of experimental error bars. We note in passing that the relatively weak dependence on $U$ has also recently been reported by Kioupakis *et al.*, who applied a similar approach to solid hydrogen [36]. In addition, Fig. 2 shows that within LDA + $U$ one could obtain an apparently more accurate $p$-$f$ (in $CeO_2$) and $f$-$d$ (in $Ce_2O_3$) gap by using a significantly larger $U$, which, however, would not improve the description of itinerant states including, in particular, the $p$-$d$ gap.

It has long been recognized that, although many properties of rare-earth compounds exhibit a monotonic behavior across the lanthanide series, some show a striking variation. For example the optical band gaps of rare-earth sesquioxides [8] shown in Fig. 3 exhibit clear dips for Ce, Eu, Tb, and Yb, which appear to be unaffected by structural variation across the series. In Fig. 3 the optical gaps of the $Ln_2O_3$ series [35] are compared to LDA + $U$, $G_0W_0$ @ LDA + $U$ and previous self-interaction corrected LDA (SIC-LDA) results [10]. Since $U$ is the effective $e$-$e$ interaction among $f$ electrons screened by $spd$ states, which are very similar in all $Ln_2O_3$ compounds, we expect $U$ to be only weakly dependent on the number of localized $f$ electrons, and therefore use a constant $U = 5.4$ eV for the whole series. Compounds denoted by filled circles in Fig. 3 crystallize preferentially in the hexagonal structure, for which all calculations have been performed. Starting from $Sm_2O_3$ (denoted by open circles), the most stable phase at room temperature is cubic bixbyite, but the middle members can also exist in the monoclinic phase [9].

As can be seen from Fig. 3 all the essential features in the experimental curve are reproduced by the $G_0W_0$ calculations including the four dips and the behavior in between. Even the quantitative agreement is good for most compounds. In addition our first-principles calculations provide easy access to the character of each peak in the DOS and thus the character of the band gap, which is schematically shown in the upper part of Fig. 3. In $La_2O_3$ (empty $f$ shell) the band gap is formed between the O-2$p$ valence and the La-5$d$ conduction band. As the occupation of the $f$ states increases, both $f^{occ}$ and $f^{un}$ continuously move downward in energy and the band gap evolves from $p$-$d$ via $f$-$d$ to $p$-$f$. This process repeats itself in the second part of the series (starting from $Gd_2O_3$) where the spin-up $f$ states have become fully occupied (and lie deep below the O-2$p$ states) and the spin-down $f$ states move downward in energy with increasing occupation.

The character of the band gap across the series agrees well with the experimental conjecture derived from phenomenological arguments [7,8,37]. This is not the case in SIC-LDA and LDA + $U$. Not only does LDA + $U$ underestimate the band gaps of most $Ln_2O_3$ compounds, it also only shows a weak minimum at $Tb_2O_3$ and fails to reproduce the plateau between $Ho_2O_3$, $Er_2O_3$, and $Tm_2O_3$.

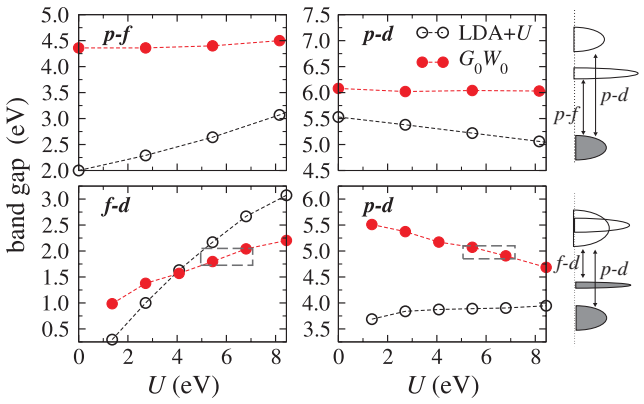


FIG. 2 (color online). Band gaps of $CeO_2$ ($p$-$f$ and $p$-$d$, upper row) and $Ce_2O_3$ ($f$-$d$ and $p$-$d$, lower row) from LDA + $U$ and $G_0W_0$ @ LDA + $U$ as a function of $U$. The dashed rectangles in the lower panel indicate the range of physically meaningful values of $U$ (see text).

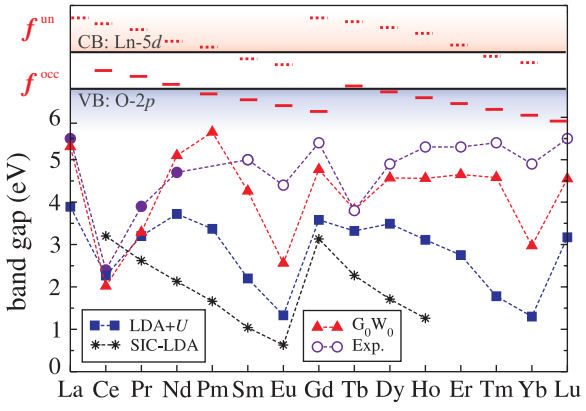


FIG. 3 (color online). Band gaps of the $Ln_2O_3$ series from LDA + $U$ and $G_0W_0$ ($U = 5.4$ eV) are compared to SIC-LDA results [10] and experimental optical gaps [8]. The schematic in the upper part of the figure illustrates the position of the $f^{occ}$ and $f^{un}$ states extracted from the $G_0W_0$ @ LDA + $U$ calculations in relation to the valence and conduction band edge (VB and CB).

The remaining quantitative differences between the $G_0W_0$ and experimental curve (especially for the later members of the series) could be due to several factors: (i) the experimental error bar, sample quality and instrumental resolution are not known [8]; (ii) to exclude the influence of excitonic effects the $G_0W_0$ results should be compared to photoemission (both direct and inverse) spectra, which are unfortunately not available for most members of the $Ln_2O_3$ series; (iii) spin-orbit and multiplet effects are not taken into account in our calculations; and (iv) our $G_0W_0$ calculations are performed for the hexagonal structure, but the later members of the $Ln_2O_3$ series (after Ln = Sm) crystallize in the monoclinic or cubic bixbyite structure [6]. Further investigations of these issues will be addressed in the future.

We close this Letter with some remarks about strong correlation. A system is often commonly (but by no means satisfactorily) classified as strongly correlated if DMFT provides an improved description over LDA and it is therefore interesting to compare $G_0W_0$ @ LDA + $U$ and LDA + DMFT [5]. Both methods add dynamic (i.e., energy dependent) effects to the LDA + $U$ Hamiltonian. LDA + DMFT is based on an underlying picture of *localized states*, in which higher order correlation effects among the localized states can be easily incorporated. However, delocalized states (e.g., *spd* states in $f$-electron systems) are still treated at the LDA level. In contrast, $G_0W_0$ based on LDA + $U$ improves upon LDA + $U$ in the band picture and both localized and itinerant states are treated at the same level (i.e., $G_0W_0$). For $Ce_2O_3$ this can be directly quantified by comparing the $G_0W_0$ @ LDA + $U$ density of states with that from recent LDA + DMFT calculations by Pourovskii *et. al.* [20]. The $f$ states are described in a similar manner, but the $p$-$d$ gap in LDA + DMFT amounts to only ~3.5 eV, which is significantly smaller than the experimental (~5.5 eV) and the $G_0W_0$ @ LDA + $U$ (~ 5.1 eV) value. For many open $d$- or $f$-shell compounds it can therefore be expected that the $GW$ approach can provide a consistent and accurate treatment for both localized and itinerant states and it will be illuminating to see when many-body effects beyond the $G_0W_0$ approximation become significant.

We acknowledge fruitful discussions with Xinzheng Li, Xinguo Ren, and Kris Delaney, and the Nanoquanta Network of Excellence (NMP4-CT-2004-500198) for financial support.

[1] A. J. Cohen *et al.*, Science **321**, 792 (2008).
[2] A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).
[3] J. L. F. Da Silva *et al.*, Phys. Rev. B **75**, 045121 (2007).
[4] K. N. Kudin *et al.*, Phys. Rev. Lett. **89**, 266402 (2002).
[5] G. Kotliar *et al.*, Rev. Mod. Phys. **78**, 865 (2006).
[6] We consider $CeO_2$ in the cubic fluorite structure, and $Ln_2O_3$ in the hexagonal ($A$-type) structure with antiferromagnetic ordering. Experimental lattice constants are used for $CeO_2$ and the light oxides ($Ln_2O_3$, Ln = La-Nd); for the heavy lanthanides (after Ln = Pm), we use lattice constants obtained by extrapolation from those of the light $Ln_2O_3$.
[7] H. B. Lal and K. Gaur, J. Mater. Sci. **23**, 919 (1988).
[8] A. V. Prokofiev *et al.*, J. Alloys Compd. **242**, 41 (1996).
[9] G. Adachi and N. Imanaka, Chem. Rev. **98**, 1479 (1998).
[10] L. Petit *et al.*, Phys. Rev. B **72**, 205118 (2005).
[11] N. Singh *et al.*, J. Appl. Phys. **100**, 083525 (2006).
[12] *Rare Earth Oxides Thin Films*, edited by M. Fanciulli and G. Scarel, Topics in Appl. Physics Vol. 106 (Springer, Berlin, 2007).
[13] A. Trovarelli, *Catalysis by Ceria and Related Materials* (Imperial College Press, London, 2002).
[14] E. Wuilloud *et al.*, Phys. Rev. Lett. **53**, 202 (1984).
[15] F. Marabelli and P. Wachter, Phys. Rev. B **36**, 1238 (1987).
[16] D. R. Mullins *et al.*, Surf. Sci. **409**, 307 (1998).
[17] N. V. Skorodumova *et al.*, Phys. Rev. B **64**, 115108 (2001).
[18] C. W. M. Castleton *et al.*, J. Chem. Phys. **127**, 244704 (2007).
[19] S. Fabris *et al.*, Phys. Rev. B **72**, 237102 (2005).
[20] L. V. Pourovskii *et al.*, Phys. Rev. B **76**, 235101 (2007).
[21] L. Hedin, Phys. Rev. **139**, A796 (1965).
[22] F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61**, 237 (1998); G. Onida *et al.*, Rev. Mod. Phys. **74**, 601 (2002).
[23] M. Gatti *et al.*, Phys. Rev. Lett. **99**, 266402 (2007); F. Bruneval *et al.*, Phys. Rev. Lett. **97**, 267601 (2006).
[24] W. Luo *et al.*, Phys. Rev. Lett. **99**, 036402 (2007).
[25] P. Rinke *et al.*, Phys. Status Solidi B **245**, 929 (2008); P. Rinke *et al.*, New J. Phys. **7**, 126 (2005).
[26] M. van Schilfgaarde *et al.*, Phys. Rev. B **74**, 245125 (2006).
[27] F. Bruneval *et al.*, Phys. Rev. B **74**, 045102 (2006).
[28] M. Shishkin *et al.*, Phys. Rev. Lett. **99**, 246403 (2007).
[29] V. I. Anisimov *et al.*, Phys. Rev. B **48**, 16 929 (1993); V. I. Anisimov *et al.*, J. Phys. Condens. Matter **9**, 767 (1997).
[30] R. Gomez-Abal *et al.*, Phys. Rev. Lett. **101**, 106404 (2008).
[31] P. Blaha *et al.*, *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Techn. Universität Wien, Austria, 2001).
[32] V. I. Anisimov and O. Gunnarsson, Phys. Rev. B **43**, 7570 (1991); M. Cococcioni and S. de Gironcoli, Phys. Rev. B **71**, 035105 (2005).
[33] $U$ is chosen based on a physical estimate without any fitting; further details will be reported elsewhere.
[34] M. van Schilfgaarde *et al.*, Phys. Rev. Lett. **96**, 226402 (2006).
[35] The band gap obtained from optical absorption experiment differs from the fundamental gap, to which the $GW$ band gap should be compared, by electron-hole interaction effects [22], whose size is not known at present for lanthanide oxides.
[36] E. Kioupakis *et al.*, Phys. Rev. B **77**, 155114 (2008).
[37] E. van der Kolk and P. Dorenbos, Chem. Mater. **18**, 3458 (2006).
[38] The XPS + BIS data for $CeO_2$ and $Ce_2O_3$ have been extracted from Refs. [14,39], respectively, and the XPS + XAS data from Ref. [16]. Fermi energy (the valence band maximum for insulating states) is taken as zero.
[39] J. W. Allen, J. Magn. Magn. Mater. **47–48**, 168 (1985).