

The electronic entropy of charged defect formation and its impact on thermochemical redox cycles

Stephan Lany

National Renewable Energy Laboratory, Golden, CO 80401

The ideal material for solar thermochemical water splitting, which has yet to be discovered, must satisfy stringent conditions for the free energy of reduction, including, in particular, a sufficiently large positive contribution from the solid-state entropy. By inverting the commonly used relationship between defect formation energy and defect concentration, it is shown here that charged defect formation causes a large electronic entropy contribution manifesting itself as the temperature dependence of the Fermi level. This result is a general feature of charged defect formation, and motivates new materials design principles for solar thermochemical hydrogen production.

Solar thermochemical hydrogen (STCH) production is one of the most advanced technologies for sustainable fuel generation [1], but further materials design advances are needed for commercial viability [2, 3]. Suitable oxides must satisfy inequalities for the enthalpy and entropy of reduction [4], so that the STCH cycle can proceed under viable conditions for the temperatures and partial pressures. In the prototypical STCH oxide CeO_2 , the entropy contribution has been shown to originate from configurational and vibrational entropies associated with oxygen vacancy defects [5], as well as from a “giant” onsite electronic entropy in the Ce f orbitals [6]. However, most STCH related studies have so far considered only charge-neutral vacancy formation. With special attention to the case of charged defect formation, this work makes a connection between STCH thermodynamics and the calculation of defect equilibria, where the latter are determined from a numerical solution of a thermodynamic detailed balance model. It is shown that charged defect formation generally implies large entropies that depend on the density of states in the conduction band, thereby capturing essentially the same physics as the electronic on-site entropy in lanthanide f orbitals [6]. This finding points towards new design criteria for STCH materials that can be screened for by means of first principles calculations.

In the STCH redox cycle, the thermal reduction (TR) of a metal (M) oxide,



should ideally occur at a temperature $T_{\text{tr}} \leq 1400^\circ\text{C}$ and O_2 partial pressures $p_{\text{O}_2} \geq 10^{-3}$ atm, whereas the gas splitting (GS) reaction



should occur at $T_{\text{gs}} \geq 850^\circ\text{C}$ and at $p_{\text{H}_2} \geq 10^{-1}$ atm [7, 8]. For the oxygen chemical potential, we obtain the corresponding inequalities $\Delta\mu_{\text{O,TR}} \geq -2.46$ eV and $\Delta\mu_{\text{O,GS}} \leq -2.94$ eV, when taking $p_{\text{H}_2\text{O}} = 1$ atm and solving

ideal gas equations [9] using tabulated values [10] for the standard enthalpies and entropies of gaseous O₂, H₂, and H₂O. For these two values of $\Delta\mu_{\text{O}}$, the p_{O_2} and p_{H_2} vs T relationships are shown in Fig. 1. We see that chemical potentials $\Delta\mu_{\text{O}} < -2.46$ eV would result in undesirably high temperatures for the TR step, and that $\Delta\mu_{\text{O}} > -2.94$ eV would result in undesirably low H₂ pressures in the GS step. Thus, in order to reconcile the two conditions, $\Delta\mu_{\text{O}}$ must increase by 0.48 eV over the temperature interval between 850 and 1400°C. The temperature dependence of the O chemical potential $\Delta\mu_{\text{O}}$ can be related to the enthalpy and entropy of reduction, as introduced in ref. [4]. Specifically, considering the free energy of reaction (1), we obtain

$$\begin{aligned}\Delta\mu_{\text{O}}(T) &= -\frac{\partial}{\partial\delta}[\Delta G(\text{M}_x\text{O}_{1-\delta}) - \Delta G(\text{M}_x\text{O})] \\ &\equiv -\frac{\partial}{\partial\delta}[\Delta H_{\text{red}} - T\Delta S_{\text{red}}],\end{aligned}\quad (3)$$

and, hence,

$$\frac{\partial}{\partial T}\Delta\mu_{\text{O}}(T) = \frac{\partial}{\partial\delta}\Delta S^{\text{red}}.\quad (4)$$

Thus, the desirable gain in $\Delta\mu_{\text{O}}$ must result from the entropy of reduction. In ref. [4], it was shown that the required constraints are generally not fulfilled for the reduction/oxidation between ordered stoichiometric phases (e.g. CeO₂/Ce₂O₃). In fact, when neglecting vibrational and magnetic free energies, $\partial\Delta S_{\text{red}}/\partial\delta = 0$ and $\Delta\mu_{\text{O}}(T) = -\partial\Delta H_{\text{red}}/\partial\delta = \text{const}$ for such reactions with no gain in $\Delta\mu_{\text{O}}$ with T . When considering the tabulated thermochemical properties (which include these effects), the resulting entropies are negative for most materials, making the STCH reactions even more unfavorable. Thus, positive solid-state entropies of considerable magnitude are essential for successful STCH materials.

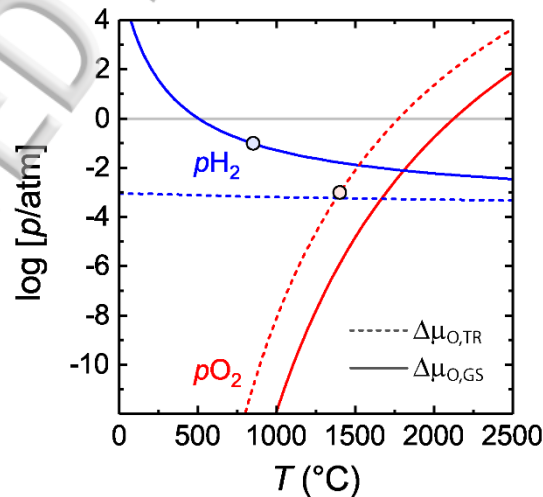


Figure 1. Ideal gas law calculation of p_{O_2} and p_{H_2} vs temperature for two values of the O chemical potential, $\Delta\mu_{\text{O,TR}} = -2.46$ eV and $\Delta\mu_{\text{O,GS}} = -2.94$ eV, corresponding to desirable conditions for the TR and GS steps (dots),

respectively. p_{H_2} is determined from the $\text{H}_2 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{H}_2\text{O}$ equilibrium with $p_{\text{H}_2\text{O}} = 1 \text{ atm}$.

A route towards larger entropies is available via off-stoichiometric reactions resulting from defect formation. In semiconductors or insulators, neutral and charged defects assume an equilibrium that involves also the intrinsic charge carriers, i.e., electrons and holes [11, 12]. The charged species interact with each other through a self-regulation mediated by the Fermi energy E_F [13, 14]. The equilibrium defect concentration follows from minimization of the Gibb's free energy associated with defect formation,

$$\Delta G(x_i, T) = \sum_i x_i \Delta g_i^{\text{ncf}}(T) - T \Delta S^{\text{cf}}(x_i). \quad (5)$$

Here, ΔG is separated into the non-configurational (ncf) contributions and the configurational (cf) entropy ΔS^{cf} . The ncf contributions are proportional to the fractional concentrations $0 \leq x_i \leq 1$, which include both defect (e.g., V_{O}) and non-defect (e.g., O_{O}) site-occupations. The Δg_i^{ncf} are usually taken as the defect formation enthalpy Δh_i , with $\Delta h_i = 0$ for the non-defect sites, but vibrational enthalpy and entropy contributions for each defect [15] can be included in this step (lowercase symbols are used to denote energies per defect, e.g., $\Delta g_i^{\text{ncf}} = \partial / \partial x_i [\Delta G^{\text{ncf}}]$). Minimizing eq. (5) with respect to x_i , subject to the condition $\sum_i x_i - 1 = 0$ via a Lagrange multiplier, and using the regular solution configurational entropy in Stirling's approximation, gives the equilibrium defect concentrations

$$x_i = \frac{\exp(-\Delta h_i/kT)}{\sum_i \exp(-\Delta h_i/kT)}. \quad (6)$$

Taking the O vacancy as example, the defect formation energy can be written as [16]

$$\Delta h^q(\Delta \mu_{\text{O}}, \Delta E_F) = \Delta h_{\text{ref}}^q + \Delta \mu_{\text{O}} + q \Delta E_F. \quad (7)$$

Here, q is the charge state of the defect (e.g., $q = 0$ or $q = +2$ for V_{O}), and ΔE_F is the Fermi energy relative to a reference (ref), usually taken as the valence band maximum. For the atomic reservoir, the reference is the zero-temperature enthalpy, e.g., $\Delta \mu_{\text{O}} = \mu_{\text{O}} - \frac{1}{2}E(\text{O}_2)$. The defect equilibrium is then obtained by a self-consistent solution of eqs. (6) and (7) under the condition of overall charge balance between charged defects and electronic carriers [13, 17]. For a given Fermi level, the electron and hole concentrations are determined by, e.g. for the case of electrons,

$$n_e(T) = \int_{E_{\text{cbm}}}^{\infty} D_{\text{cb}}(E) f_{\text{FD}}(E, T) dE, \quad (8)$$

where f_{FD} is the Fermi-Dirac distribution, E_{cbm} is the energy of the conduction band minimum (cbm) and D_{cb} is the conduction band density of states (DOS), which is here approximated by using a DOS effective mass [18].

For a given material, all input parameters required for solving the defect equilibrium can be calculated from first principles, i.e., the defect formation energies Δh_{ref}^q (which are T -independent constants), the band gap energy E_g , and the effective masses m_e^* and m_h^* . For the purpose of the present work, however, we invert the problem and determine the formation energy Δh^q for V_{O}^q as a function of the O off-stoichiometry δ [cf. eq. (1)] for a range of temperatures T . In practice, this is done by numerically searching

within the self-consistent loop for a formation energy that results in the targeted value for δ . From eq. (7), we then obtain the temperature dependence of the O chemical potential,

$$\frac{\partial}{\partial T} \Delta\mu_{\text{O}}(T) = \frac{\partial}{\partial T} [\Delta h^q(T) - q\Delta E_F(T)], \quad (9)$$

thereby gaining access to information about the requirements for the STCH reactions discussed above. On the other hand, we can consider the minimum condition of eq. (5) for the defect equilibrium, $\partial/\partial\delta [\Delta G(\delta, T)] = 0$, then substitute Δh^q from eq. (7) for Δg_i^{ncf} , and take the T partial derivative, yielding

$$\frac{\partial}{\partial T} \Delta\mu_{\text{O}}(T) = \frac{\partial}{\partial\delta} \Delta S^{\text{cf}}(\delta) - q \frac{\partial}{\partial T} \Delta E_F(T). \quad (10)$$

The first term on the rhs of eq. (10) is simply the differential configurational entropy, which is widely recognized as important factor for meeting the STCH conditions [5, 19]. If vibrational entropy is included in Δg_i^{ncf} , it will contribute here a corresponding additional term. The last term in eq. (10), i.e., the temperature derivative of the Fermi level, enters as the electronic contribution to the entropy of reduction, and it is the consequence of charged defect formation. Within the detailed balance model, the charged defect formation energy [eqs. (7)] is coupled via the Fermi level to the Fermi Dirac distribution [cf. eq. (8)], which is the statistical origin of the electronic entropy as it describes the thermal occupation of the conduction band density of states. Further, by comparing eqs. (9) and (10), we see that the temperature derivative of the enthalpy is equal to the configurational entropy. Thus, it is worth mentioning that the approximate T independence of ΔH_{red} in case of stoichiometric redox reaction does not apply to off-stoichiometric (defect mediated) reactions.

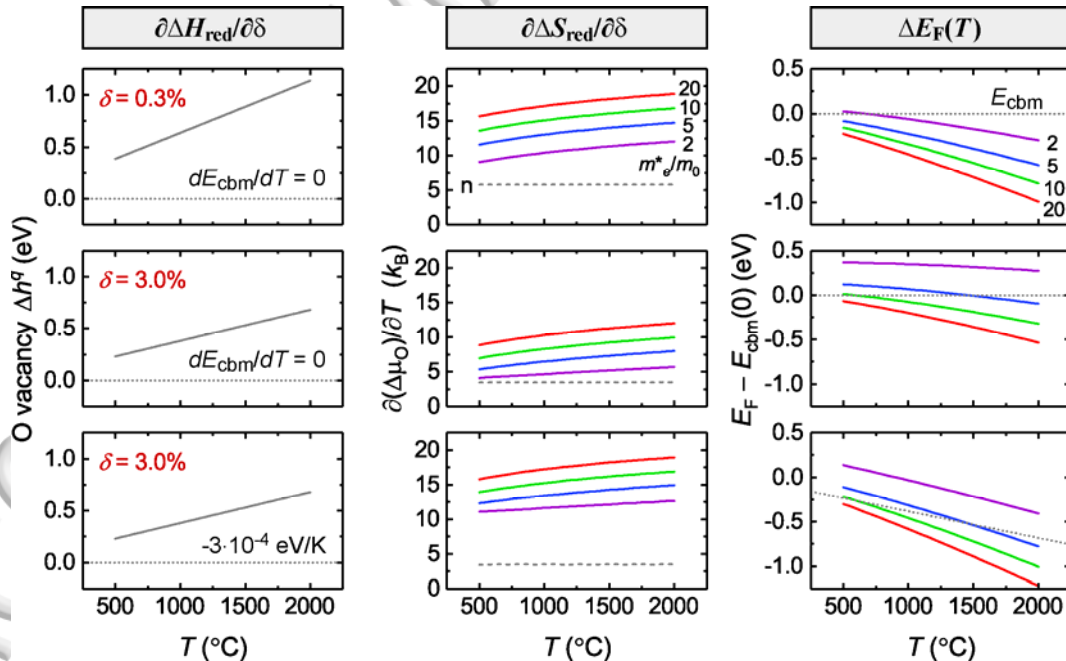


Figure 2. (Left column) The enthalpy of reduction $\partial H_{\text{red}}/\partial T$ required to establish an O off-stoichiometry of $\delta = 0.3\%$ and 3.0% , as a function of the temperature T . (Center column) The entropy of reduction $\partial S_{\text{red}}/\partial T$, for the case of neutral (n) O vacancies V_{O}^0 (dashed line),

and that of charged V_{O}^{+2} defects (solid lines) for various values of the conduction band effective mass. (Right column) The Fermi level relative to the conduction band minimum (E_{cbm}). In the upper and middle rows, E_{cbm} was taken as T independent, whereas in the bottom row, a linear T dependence was assumed with $dE_{cbm}/dT = -3 \cdot 10^{-4}$ eV/K.

Considering that the temperature derivative of the O chemical potential equals the differential entropy of reduction $\partial\Delta S_{red}/\partial\delta$ (cf. eq. (4)), the desired gain of $\Delta\mu_o$ of 0.48 eV over 550°C (cf. Fig. 1) can be expressed as an average entropy of about $10 k_B$. Since the regular solution entropy $\partial\Delta S^{cf}/\partial\delta$ varies between, say, $6.9 k_B$ for $\delta = 0.1\%$ and $2.9 k_B$ for $\delta = 5.0\%$, it is clear that configurational entropy alone is insufficient. The electronic entropy contribution due to charged defect formation therefore deserves special attention. So far, materials discovery strategies for STCH based of high throughput calculation have been limited to the case of charge neutral O vacancies [20, 21].

Figure 2 shows the results of numerical defect equilibria calculations, assuming an O site density of $5 \times 10^{22} \text{ cm}^{-3}$. The enthalpy of reduction $\partial\Delta H_{red}/\partial\delta$ for a given off-stoichiometry δ simply follows eq. (6), irrespective of the question whether the O vacancies form as charge neutral ($q = 0$) or fully charged ($q = +2$) defects. More interestingly, the entropy of reduction $\partial\Delta S_{red}/\partial\delta = \partial\Delta\mu_o/\partial T$ increases dramatically in case of charged defects, when compared to the purely configurational entropy obtained for the neutral defects. This increase is a result of the temperature dependence of E_F [cf. eq. (9)], and the amount of the increase depends on δ and the conduction band effective mass. To elucidate this dependence, $\Delta E_F(T)$ is shown in the right column of Fig. 2. In case of the smaller off-stoichiometry $\delta = 0.3\%$, the Fermi energies remain mostly inside the band gap for effective masses $m_e^*/m_0 \geq 2$ (with m_0 being the rest mass of the electron). With increasing T , E_F must move to lower energies deeper in the gap, such that the negative charge due to the electron density $n_e(T)$ [eq. (8)] remains equal to the positive charge due to V_{O}^{+2} defects. The larger m_e^* , the more pronounced this shift, and, hence, the larger the contribution to the entropy of reduction.

For the larger off-stoichiometry $\delta = 3.0\%$ and the corresponding larger defect charge, E_F stays close to or even above E_{cbm} , and exhibits a smaller temperature dependence and correspondingly smaller entropies. So far, we have, however, not considered that the band gap is temperature dependent. A lowering of the conduction band edge E_{cbm} with temperature will further reduce the Fermi energy that produces [via eq. (8)] the electron density required for charge balance, and therefore contribute to $\partial\Delta S_{red}/\partial\delta$. Temperature coefficients of the band gap energy in the order of $dE_g/dT = -5 \cdot 10^{-4}$ eV/K are common for oxides [22]. The contribution dE_{cbm}/dT from the conduction band may be difficult to determine experimentally, but is readily accessible in first principles calculations [23]. Taking $dE_{cbm}/dT = -3 \cdot 10^{-4}$ eV/K as an example, we see in Fig. 2 that reduction entropies in excess of $10 k_B$ should be attainable, provided that the O vacancies do form in the +2 charged state instead of the charge-neutral state. At this point, it is useful to recall that O vacancies often form deep negative-U centers in main group oxides [17, 24], whereas in transition metal oxides, such as TiO_2 [18], or similarly in CeO_2 [25], electrons can often form a localized small polaron state that is bound to the vacancy. In either case, the localized, deep states can be expected to be relatively independent on perturbations like temperature or pressure [26], compared to the band gap and band edge energies. Therefore, the condition of charged vacancy

formation is likely to be fulfilled if the temperature dependent Fermi energy remains below the defect level of the vacancy. For the example shown in Fig. 2, this would be the case if the V_O defect level lies above about $E_{\text{cbm}}(0) - 0.4$ eV for the larger values of m_e^* . If the defect level lies lower, E_F will drop below the defect level towards the lower end of the temperature interval between T_{GS} and T_{TR} , causing a corresponding reduction of the entropy $\partial\Delta S_{\text{red}}/\partial\delta$ due to neutral vacancy formation.

It is notable that CeO_2 fulfills the criteria discussed here rather well: The $p\text{O}_2$ dependence of the stoichiometry determined from thermogravimetric experiments shows that vacancies form in a doubly charged state [19]. A recent first principles calculation [25] reported V_O defect levels within less than 0.5 eV from the energy of the conduction band minimum at low temperature, which is consistent with the experimental observations. CeO_2 has also a large conduction band density of states due to the localized Ce-4f orbitals [27], with $m_e^*/m_0 \approx 20$. Thus, the fact that this prototypical STCH material in retrospect fulfills the criteria for entropy gain through charged defect formation suggests that considering the possibility of charged defect formation is an important next step in the search and design of novel STCH oxides.

In conclusion, the temperature dependence of the O chemical potential was calculated from a materials-agnostic defect equilibrium model, and related to the entropy of reduction in thermochemical redox cycles. The detailed balance condition in this model couples the defect formation and the electronic free energy, i.e., the Fermi level, thereby incorporating the electronic entropy. It was shown that a large “giant” electronic entropy is not exclusive to f-orbital elements, but occurs quite generally for the case of *charged* defect formation. In addition to the commonly used neutral defect formation energy, the present finding suggests new screening criteria for STCH materials that can be addressed by first principles calculations, i.e., the defect level of the O vacancy, the conduction band effective mass, and the temperature dependence of the conduction band minimum.

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[1] N.P. Siegel, J.E. Miller, I. Ermanoski, R.B. Diver, E.B. Stechel, Factors affecting the efficiency of solar driven metal oxide thermochemical cycles. *Industrial & Engineering Chemistry Research* 52, 3276 (2013).

[2] J.E. Miller, A.H. McDaniel, M.D. Allendorf, Considerations in the Design of Materials for Solar-Driven Fuel Production Using Metal-Oxide Thermochemical Cycles. *Advanced Energy Materials*, 4, 1300469 (2014).

[3] R.J. Carrillo, J.R. Scheffe, Advances and trends in redox materials for solar thermochemical fuel production. *Solar Energy* 156, 3 (2017).

[4] B. Meredig, C. Wolverton, First-principles thermodynamic framework for the evaluation of thermochemical H_2O or CO_2 splitting materials. *Physical Review B* 80, 245119 (2009).

[5] C.B. Gopal, A. van de Walle, Ab initio thermodynamics of intrinsic oxygen vacancies in ceria. *Physical Review B* 86, 134117 (2012).

- [6] S.S. Naghavi, A.A. Emery, H.A. Hansen, F. Zhou, V. Ozolins, C. Wolverton, Giant onsite electronic entropy enhances the performance of ceria for water splitting. *Nature communications* 8, 285 (2017).
- [7] R. Perret, Solar Thermochemical Hydrogen Production Research (STCH): Thermochemical Cycle Selection and Investment Priority, Sandia Report (U.S. Department of Commerce, Springfield, 2011).
- [8] Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy (EERE), Fuel Cell Technologies Office Annual FOA, Funding Opportunity Announcement (FOA) Number: DE-FOA-0001647
- [9] J. Osorio-Guillén, S. Lany, S. Barabash, A. Zunger, *Phys. Rev. Lett.* 96, 107203 (2006).
- [10] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney, and R.L. Nutall, *J. Phys. Chem. Ref. Data* 11, Suppl. 2 (1982).
- [11] F.A. Kröger, *The Chemistry of Imperfect Crystals* (2nd ed., North-Holland, Amsterdam, 1974).
- [12] D.B. Laks, C.G. van de Walle, G.F. Neumark, P.E. Blöchl, S.T. Pandelides, Native defects and self-compensation in ZnSe, *Phys. Rev. B* 45, 10965 (1992).
- [13] S.B. Zhang, J.E. Northrup, Chemical potential dependence of defect formation energies in GaAs: Application to Ga self-diffusion, *Phys. Rev. Lett.* 67, 2339 (1991).
- [14] A. Zunger, Practical doping principles, *Appl. Phys. Lett.* 83, 57 (2003).
- [15] A. Lindman, P. Erhart, G. Wahnström, Implications of the band gap problem on oxidation and hydration in acceptor-doped barium zirconate. *Physical Review B* 91, 245114 (2015).
- [16] H. Peng, D.O. Scanlon, V. Stevanovic, J. Vidal, G.W. Watson, S. Lany, Convergence of density and hybrid functional defect calculations for compound semiconductors. *Physical Review B* 88, 115201 (2013).
- [17] S. Lany, A. Zunger, Dopability, intrinsic conductivity, and nonstoichiometry of transparent conducting oxides. *Physical Review Letters* 98, 045501 (2007).
- [18] S. Lany, Semiconducting transition metal oxides. *Journal of Physics: Condensed Matter* 27, 283203 (2015).
- [19] R.J. Panlener, R.N. Blumenthal, J.E. Garnier, A thermodynamic study of nonstoichiometric cerium dioxide. *Journal of Physics and Chemistry of Solids* 36, 1213 (1975),
- [20] A.M. Deml, V. Stevanović, C.L. Muhich, C.B. Musgrave, R. O'Hayre, Oxide enthalpy of formation and band gap energy as accurate descriptors of oxygen vacancy formation energetics. *Energy & Environmental Science* 7, 1996 (2014).
- [21] A.A. Emery, J.E. Saal, S. Kirklin, V.I. Hegde, C. Wolverton, High-throughput computational screening of perovskites for thermochemical water splitting applications. *Chemistry of Materials* 28, 5621 (2016).
- [22] F.J. Manjón, M. Mollar, M.A. Hernández-Fenollosa, B. Mari, R. Lauck, M. Cardona, Effect of isotopic mass on the photoluminescence spectra of zinc oxide. *Solid state communications* 128, 35 (2003).
- [23] A. Franceschetti, First-principles calculations of the temperature dependence of the band gap of Si nanocrystals. *Physical Review B* 76, 161301 (2007).
- [24] S. Lany, A. Zunger, Anion vacancies as a source of persistent photoconductivity in II-VI and chalcopyrite semiconductors. *Physical Review B* 72, 035215 (2005).
- [25] L. Sun, X. Huang, L. Wang, A. Janotti, Disentangling the role of small polarons and oxygen vacancies in CeO₂. *Physical Review B* 95, 245101 (2017).
- [26] S.Y. Ren, J.D. Dow, D.J. Wolford, Pressure dependence of deep levels in GaAs. *Physical Review B* 25, 7661 (1982).
- [27] J.L.F. da Silva, M.V. Ganduglia-Pirovano, J. Sauer, V. Bayer, and G. Kresse, Hybrid functionals applied to rare-earth oxides: The example of ceria, *Phys. Rev. B* 75, 045121 (2007).

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