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Formation energies of rutile metal dioxides using density functional theory

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We apply standard density functional theory at the generalized gradient approximation (GGA) level to study the stability of rutile metal oxides. It is well known that standard GGA exchange and correlation in some cases is not sufficient to address reduction and oxidation reactions. Especially the formation energy of the oxygen molecule and the electron self-interaction for localized *d* and *f* electrons are known shortcomings. In this paper we show that despite the known problems, it is possible to calculate the stability of a wide range of rutile oxides MO_2, with M being Pt, Ru, Ir, Os, Pb, Re, Mn, Se, Ge, Ti, Cr, Nb, W, Mo, and V, using the electrochemical series as reference. The mean absolute error of the formation energy is 0.29 eV using the revised Perdew-Burke-Ernzerhof (PBE) GGA functional. We believe that the reason for the success is due to the reference level being H_2 and H_2O and not O_2 and due to a more accurate description of exchange for this particular GGA functional compared to PBE. Furthermore, we would expect the self-interaction problem to be largest for the most localized *d* orbitals; that means the late 3*d* metals and since Co, Fe, Ni, and Cu do not form rutile oxides they are not included in this study. We show that the variations in formation energy can be understood in terms of a previously suggested model separating the formation energy into a metal deformation contribution and an oxygen binding contribution. The latter is found to scale with the filling of the *d* band.

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I. INTRODUCTION

Bulk oxides are important in oxidation and reduction reactions, playing a key role in many technological and environmental processes such as corrosion, combustion, metal refining, electrochemical energy conversion and storage, photosynthesis, and photocatalysis.[1] Rutile metal dioxides are particularly well studied. Electron, neutron, and x-ray diffraction experiments have detected a large number of transition-metal dioxides to possess very stable β' rutile crystal phases.[2–19] In addition, some theoretical studies, at different levels of theory, have confirmed the structural results of the experiments, showing enhanced stability of the rutile phase for most metal dioxides.[20–23]

Rutile oxides are interesting in connection with electrochemical and photoelectrochemical water splitting,[24–27] and recently the surface redox processes on, e.g., RuO_2 and TiO_2 have been treated using density functional theory (DFT).[28,29] The question remains whether standard DFT-generalized gradient approximation (GGA) (Refs. 30 and 31) calculations have sufficient accuracy. It has for instance been shown that for a series of (nonrutile) transition-metal oxides the standard GGA treatment of exchange and correlation is not sufficient to describe redox processes.[32–37]

In the present study we compare DFT-GGA calculations of formation energies with experimental values obtained from electrochemical series[38–40] for a large number of rutile metal dioxides MO_2, with M being Pt, Ru, Ir, Os, Pb, Re, Mn, Se, Ge, Ti, Cr, Nb, W, Mo, and V, in order to assess the accuracy of such calculations. All these metal oxides are known to form in the rutile structure; however, for some (e.g., Pt) the rutile structure is not the most stable phase. We show that for these oxides it is possible to accurately calculate the electrochemical stability with a mean absolute error (MAE) of 0.29 eV, using the revised Perdew-Burke-Ernzerhof (PBE) (RPBE) GGA functional.[31] We find that, in agreement with experiments, the formation energies decrease with increasing number of *d* electrons in the metal. We show that this trend may be understood based on a simple model first proposed by Gelatt, Jr. *et al.*,[41] where the formation energy is decomposed into two contributions: (i) the energy required to expand the metal lattice of the metal bulk and (ii) the bond energy gained by introducing oxygen into the deformed metal lattice, following the dioxide stoichiometry.

II. METHOD

The plane-wave pseudopotential DFT code DACAPO (Refs. 31 and 42) has been used for the calculation of all the total energies in this study. The bulk structures have been modeled by using periodically repeated unit cells in a supercell geometry to create the crystal conditions. All atom coordinates and lattice vectors are fully relaxed for each structure using the quasi-Newton minimization scheme[43] until the maximum force component is found to be smaller than 0.05 eV/Å. The metal dioxides have been treated in their rutilelike structure, while the most stable crystal phase was chosen for each pure metal bulk except Mn (modeled as pure bcc). The ion-electron interaction is described by using ultrasoft pseudopotentials,[44] and the Kohn-Sham (KS) one-electron valence states are expanded in a basis of plane waves with kinetic energy below 350 eV; a density cutoff of 500 eV is used. The Brillouin zone of all the systems is sampled with an $(8\times8\times8)$ Monkhorst-Pack grid. The convergence of the total energy with respect to the cutoff energies and the **k** points set is confirmed. Exchange and correlation effects are described using the RPBE-GGA functional[31] and the self-consistent RPBE density is determined by iterative diagonalization of the KS Hamiltonian, Fermi population of the KS states ($k_BT=0.1$ eV), and Pulay mixing of the resulting electronic density.[45] All total energies have been extrapolated to $k_BT=0$ eV. Spin polarization effects are included in the reported results for the dioxides in which naturally magnetized metals are present.

We define the calculated formation energy of the rutile metal dioxides as the reaction energies of the following reaction:

$$M(\text{bulk}) + 2H_2O(\text{l}) \rightarrow MO_2(\text{bulk}) + 2H_2(\text{g}), \qquad (1)$$

where M is the metal forming the dioxide, H_2 is in the gas phase, and H_2O is in liquid phase. The calculated formation energies for the rutilelike metal dioxides are obtained by evaluating free-energy differences between the subsystems involved in reaction (1) as the following:

$$\Delta G_{\text{form}} = G[MO_2(\text{bulk})] + 2G[H_2(g)] - \{G[M(\text{bulk})] + 2G[H_2O(\text{l})]\}, \qquad (2)$$

where G is the free energy of each subsystem involved in reaction (1). The general procedure for calculating the free energy has been presented previously in Ref. 46. For bulk crystals we neglect the entropy (S) and zero-point energy (ZPE) effects.[47] These quantities have been estimated from vibrational analyses for some representative pure metals and metal oxides involved in this study (Ru/RuO_2 and Ir/IrO_2), yielding differences between total DFT and Gibbs free energies below 0.1 eV and below 0.02 eV for the reaction given in Eq. (1) (at room temperature). We include the gas-phase entropy for H_2 and ZPE for H_2 and H_2O. We get the free energy of liquid water by calculating gas-phase H_2O and applying the entropy at the gas/liquid equilibrium pressure (0.035 bar).[48]

We get the experimental change in free energy by considering the related electrochemical reaction

$$MO_2(\text{bulk}) + 4H^+ + 4e^- \leftrightarrow M(\text{bulk}) + 2H_2O(\text{l}). \qquad (3)$$

ΔG for this reaction is $-4eU$, with U being the standard potential vs the normal hydrogen electrode. The experimental values for ΔG_{form} [Eq. (2)] can then either be taken directly from the equilibrium potential of reaction (3) listed in electrochemical series[38–40] or via the dissolution potential

$$M(\text{bulk}) \leftrightarrow M^{n+} + ne^-, \qquad (4)$$

and

$$MO_2(\text{bulk}) + 4H^+ + (4-n)e^- \leftrightarrow M^{n+} + 2H_2O(\text{l}). \qquad (5)$$

Thereby we can obtain the experimental free energy of reaction (1), which can be directly compared to the values calculated theoretically using Eq. (2).

III. RESULTS AND DISCUSSION

Figure 1 shows the calculated ΔG_{form} for a series of rutile metal dioxides as a function of the experimental values extracted from the electrochemical series.[38–40] Two sets of data points are shown: one corresponding to experimental results extracted from Refs. 38 and 39 and other extracted from Ref. 40. The MAE is 0.29 eV. The *one-to-one* correspondence between the DFT-RPBE results and experiments may be surprising, considering the known shortcomings of standard GGAs. Part of this problem is related to describe the oxygen molecule correctly, which is reflected in the calculated formation energy. The deviation from experiment in the reaction $O_2 \rightarrow 2O$ is 1.01 eV for PBE and 0.60 eV for RPBE (Ref. 49); on the contrary, errors on formation energies of H_2O and H_2 are known to be much lower. The deviation introduced in the water formation enthalpy via the reaction

$$2O + 2H_2 \rightarrow 2H_2O \qquad (6)$$

is 0.56 eV for PBE and −0.14 eV for RPBE.[49] Therefore, the poor DFT description of the O_2 molecule is totally avoided using the electrochemical formation energy described above, which means using H_2O rather than O_2 as the reference for oxygen on the calculation of the heat of formation.

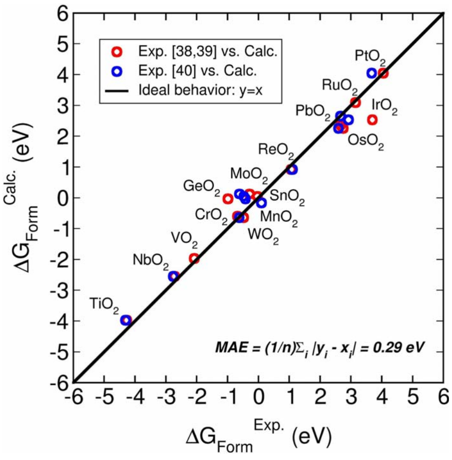

FIG. 1. (Color online) Calculated formation energies of various representative rutile metal dioxides as a function of the experimental values extracted from the electrochemical series (Refs. 38–40). The zero free-energy reference has been taken as the total energy of the metal oxide bulks.

Another important point is that the values for the formation energies range from around −4 eV for TiO_2 to around 4 eV for PtO_2. This ~8 eV span provides a wide span of energies, making the comparison to experiment looks very good. Investigations in a narrow energy window will in some cases give wrong trends. We test that the findings are robust concerning the choice of GGA-exchange functional by comparing the RPBE with PBE.[30] The RPBE functional appears to have a more accurate inclusion of exchange than PBE, which is important to get reliable adsorption energies.[50,51] We find that while the trends are conserved, PBE systematically overestimates the formation energies by around ~ −0.8 eV. This justifies our choice for the inclusion of the exchange effects (see Table I).

Having established that our DFT calculations give a good representation of the trends on the formation energies, we now turn to the question of the origin of the variation in the heats of oxide formation from one transition metal to the next. The model proposed by Gelatt, Jr. *et al.*[41] to describe the bonding in 4*d* transition-metal compounds in the NaCl structure provides a good starting point. In this model the formation energy is decomposed into two contributions. First, the bulk metal lattice is deformed to the lattice adopted by the metal atoms in the oxide. The deformation energy is

TABLE I. From left to right: experimental formation energies obtained from different sources and PBE and RPBE formation energies for all rutile metal dioxides studied in the present work (all in eV). Beside each oxide label we show references of experiments justifying the existence and stability of the corresponding rutile phase. As superscripts in the experimental values, direct (d) and indirect (i) mean values are extracted from Eq. (3) or from Eqs. (4) and (5), respectively. Only experimental values have been considered from Refs. 38–40.

Rutile system	Reference	ΔG_{form} [a]	ΔG_{form} [b]	$\Delta G_{\text{form}}^{\text{PBE}}$	$\Delta G_{\text{form}}^{\text{RPBE}}$
TiO_2	2	-4.26^{i}	-4.30^{d}	−4.83	−3.97
NbO_2	3 and 4	-2.72^{i}	-2.76^{d}	−3.36	−2.55
VO_2	5	-2.08^{i}		−2.76	−1.97
GeO_2	6 and 7	-0.98^{i}	-0.42^{d}	−0.87	−0.03
CrO_2	8	-0.68^{i}		−1.44	−0.60
WO_2	4 and 9	-0.48^{i}	-0.62^{d}	−1.45	−0.64
MoO_2	4 and 10	-0.29^{i}	-0.61^{d}	−0.29	0.13
SnO_2	5, 11, and 12	-0.03^{i}	-0.47^{d}	−0.75	0.05
MnO_2	13	0.10^{i}	0.10^{i}	−0.87	−0.16
ReO_2	14	1.06^{i}	1.10^{d}	0.05	0.93
PbO_2	15	2.49^{i}	2.66^{i}	1.78	2.65
OsO_2	16	2.75^{i}	2.60^{d}	1.40	2.26
RuO_2	7 and 17	3.15^{i}		2.36	3.10
IrO_2	7, 17, and 18	3.70^{i}	2.92^{d}	1.68	2.53
PtO_2	19	4.05^{i}	3.68^{d}	3.26	4.05

[a] References 38 and 39.

[b] Reference 40.

defined as $G_{\text{deform}}=E_{\text{bulk}}^{\text{expanded}}-E_{\text{bulk}}^{\text{pure}}$, where $E_{\text{bulk}}^{\text{expanded}}$ is the energy per metal atom of the rutile bulk structure without oxygen atoms and $E_{\text{bulk}}^{\text{pure}}$ is the energy per metal atom in the pure metal bulk crystal. This contribution is the energy required to deform the metal lattice from the bulk structure toward the metal lattice in the rutile structure and is expected to be some positive fraction of the cohesive energy. Second, oxygen is introduced into the expanded metal lattice. This results in hybridization between metal d states and oxygen $2p$ states and contributes with a bonding energy $G_{\text{bond}}=G_{\text{deform}}-G_{\text{form}}$, where $G_{\text{form}}=\Delta G_{\text{form}}$ is given by Eq. (2).

When moving through the d series, the d band of the transition metals in each dioxide shifts down in energy, which may affect slightly the hybridization. However, the resulting density of states may often be well described by shifting the bands formed from the hybridization in order to accommodate more electrons into the bands as the number of d electrons is increased through the nd series. The bonding energy thus increases when bonding states are being filled and decreases when antibonding states are being filled.

The octahedral ligand field in the rutile dioxides splits the metal d states into t_{2g} and e_g bands. Based on ligand-field theory, we expect the metal t_{2g} states to be nonbonding or antibonding and the metal e_g states to be clearly antibonding.[52] The bonding orbitals from the nd-O $2p$ hybridization have high O $2p$ character, and they are always filled for the rutile dioxides. Therefore, as the number of d electrons increases, the new d electrons are always added to the antibonding t_{2g} states. Figure 2 shows the formation energy and, separately, its metal bulk deformation and bonding energy contributions, for some representative rutile $4d$ oxides. It is noticeable that the main trend in the formation energies is well captured by the bonding energy alone, meanwhile the deformation energy is rather invariant independently of the transition metal. The bonding energy G_{bond} decreases linearly with the number of d electrons, which suggests a single antibonding band is filled. In accordance with ligand-field theory, the projected density of states shows this band having high t_{2g} character.

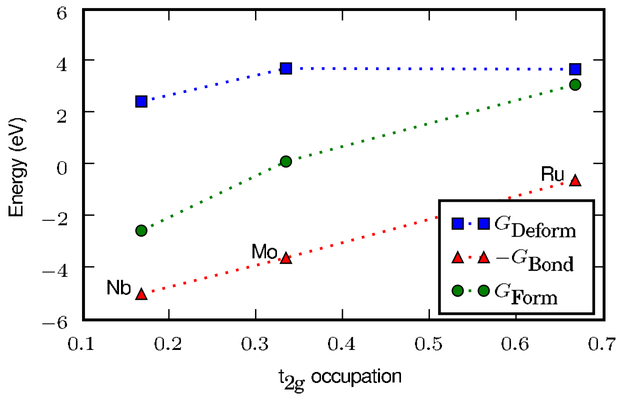

FIG. 2. (Color online) The formation energy, the metal bulk deformation energy, and the bonding energy in the expanded metal lattice as functions of the filling of the metal t_{2g} band for some representative rutile $4d$ metal dioxides (Nb, Mo, and Ru). The variation in formation energy is clearly dominated by the oxygen binding energy.

IV. SUMMARY AND CONCLUSIONS

We have calculated the formation energy of a large number of rutile metal oxides by using the RPBE-GGA functional, comparing the results to experimental values obtained from the electrochemical series. We find that the MAE is 0.29 eV, which is surprisingly low given the well-known limitations of standard DFT-GGA. To explain this we point at a number of points. First, using water (the natural source of oxygen in an electrochemical experiment) as the reference, we avoid calculations of the oxygen molecule. Second, the late $3d$ metals are not included in this study since they do not form rutile oxides. We expect that problems due to self-interaction are largest for those. Finally, the RPBE exchange is more accurate than PBE and Perdew-Wang 91 (PW91) for this kind of problem. We note however that trends are conserved using the PBE exchange. We show that the trends in formation energies can be understood within a simple model originally proposed by Gelatt, Jr. *et al.* The formation energy is split into two contributions: one from the deformation of the metal and one from the binding between metal and oxygen atoms. The latter is the larger of the two, and the variations can be understood by the degree of d-band electrons filling the antibonding t_{2g} orbital.

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