Stabilization of potential superhard RuO$_2$ phases: A theoretical study

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First-principles full-potential linear muffin-tin orbital calculations have been used to study RuO$_2$ in the fluorite (CaF$_2$) and rutile structures. An investigation of the effects of metal and nonmetal alloying, oxygen vacancies, and lattice strain on the phase stabilities and electronic structure has been made. From these theoretical results suggestions on how the cubic phase may be stabilized are made. The pressure induced phase transitions between the rutile, CaCl$_2$, $Pa3$ and fluorite phases and the bulk moduli of several $4d$ and $5d$ transition metal dioxides have also been studied.

I. INTRODUCTION

Transition metal oxides are promising candidates for materials of extreme hardness in different types of applications, e.g., as hard coating materials. It has been suggested that RuO$_2$ and similar isoelectronic materials are particularly promising in this regard. One of the more pertinent parameters of these materials is the intricate structural relationship between four polymorphs, the rutile, CaCl$_2$, $Pa3$, and the fluorite (CaF$_2$) crystal structure, and recently one transformation path between these structures was investigated theoretically.[1] On the theoretical side several other works have addressed the possibility to form hard transition metal oxides.[2] In the latter work the relationship between high hardness and a large bulk modulus[3] was used, and the search for hard materials was simplified to a search for materials with a large bulk modulus. Although this method clearly has limitations, it has a great advantage in reducing the complexity of a theoretical search for hard materials to a much simpler task, especially for first principles calculations where the total energy is calculated, from which the bulk modulus can easily be calculated. In the theoretical works of Ref. 2 it was suggested that in order to optimize the hardness the cubic fluorite structure is desirable for RuO$_2$. This poses a problem since the tetragonal rutile structure is the stable polymorph of the late transition metal oxides.

In this work we elaborate on the structural stabilities of the late transition metal oxides, focusing on the late $4d$ and $5d$ transition metal oxides. In particular we outline different avenues for stabilizing the cubic polymorph of late transition metal oxides, by means of alloying and chemical substitution, both of the nonmetallic atoms and metallic atoms, as well as the influence of vacancy concentration. In order to do this supercells were created and the phase stability of the fluorite structure was calculated from first-principles theory, for different alloy and substitution concentrations. In addition to chemical substitution other ways of stabilizing the cubic structure can be explored. For instance, by growing RuO$_2$ on a carefully chosen substrate, e.g., a cubic substrate, the cubic phase can continue to grow and the fluorite structure may be stabilized in this way. From realistic theoretical calculations suitable substrates may be identified. We have hence also investigated in detail this approach of stabilizing

the fluorite structure, using first principles theory. If the transition metal oxides are grown rather thick, one can ignore the effects of the interface between the substrate and the hard coating oxide. The substrate then only ensures that, via the epitaxial growth, a specific in-plane lattice parameter is adopted in the transition metal dioxide. Provided that epitaxial growth is maintained, this approach should be rather accurate and one can then focus on comparing the phase stability of RuO$_2$ of a rutile phase where the in-plane lattice parameter is dictated by the substrate to the fluorite phase (or a slightly distorted fluorite phase) with the same in-plane lattice parameter. We will describe below suitable choices of in-plane lattice parameters for stabilizing the cubic polymorph of late transition metal dioxides, as given by our first-principles theory.

II. METHOD AND SETUP

The calculations presented have been made using a full-potential linear muffin-tin orbital method (FP-LMTO) within the local density approximation (LDA) and generalized-gradient approximation (GGA) of density functional theory (DFT).[4,5] The function used for the exchange-correlation in the LDA scheme has been the Hedin-Lundqvist parametrization[6] while for the GGA it was PW-91.[8] In the FP-LMTO method the unit cell is divided into nonoverlapping muffin-tin spheres, inside of which the basis functions are expanded in spherical harmonics up to a cutoff in angular momentum $l_{max}=6$. The basis functions in the interstitial region, outside the muffin-tin spheres, are Neumann or Hankel functions. To speed up convergence each eigenvalue is convoluted with a Gaussian with a width of 20 mRy. Energy convergence in terms of the number of **k** points has also been reached, so that this has a minimal effect when comparing energies of different structures and compounds. When describing the atoms of the crystal the electronic states are divided into core, pseudocore and valence states. For the transition metal atoms the $5s$ and $4d$ states were treated as valence states while the $4p$ and $4s$ states were treated as pseudocore. The pseudocore and valence states were allowed to hybridize in one common energy panel. In the oxygen atom the $1s$ level was treated as core states while the $2s$ and $2p$ levels were treated as valence states, the oxygen basis set
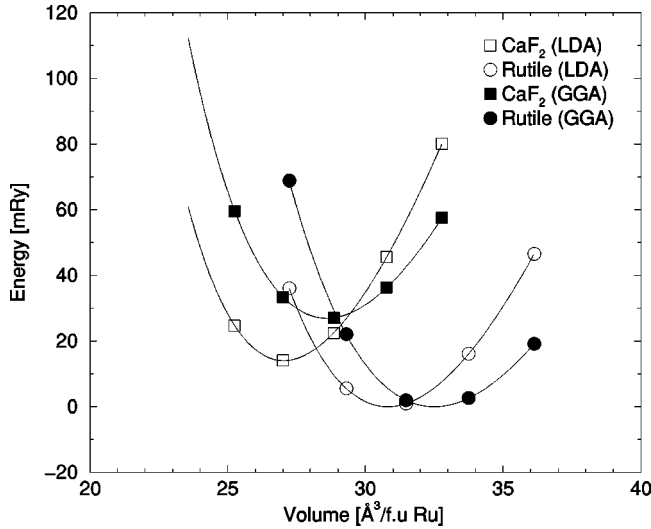
FIG. 1. Energy vs volume for RuO_2 in the fluorite and rutile structures. The equilibrium energy of the rutile phase is taken to be zero. The unfilled/filled symbols denote results from LDA/GGA calculations, respectively.

was extended to include also $3d$ orbitals. In order to find the quilibrium structures and ground-state energies the fluorite and rutile structures were both relaxed in the lattice parameter a and the rutile structure was also relaxed in c. Local relaxations around vacancies and/or substitutions was not taken into account.[7]

III. RELATIVE PHASE STABILITIES AND ELECTRONIC STRUCTURE

The ground-state energy as a function of volume for RuO_2 in the rutile and fluorite phases, within both LDA and GGA, is displayed in Fig. 1. From the energy vs volume curves one can see that the predicted equilibrium volumes are larger when using the GGA than when using the LDA, as is usually the case. The theoretical equilibrium volume for the LDA and GGA calculations (also found in Table I) for the fluorite was 9.00 a.u. (9.09 for GGA) and for the rutile structure it was found to be 8.44 a.u. (8.58 for GGA). This is in good agreement with experimental values of 9.14 a.u. for the fluorite structure and 8.50 a.u. for the rutile structure.[9] The energy difference between the rutile and fluorite phases is also seen to be larger in the GGA calculations.

The electronic structure of MO_2 compounds is governed by a strong hybridization between the M-d and O-p states. The partial densities of electronic states (DOS), evaluated for the stoichiometric (and substoichiometric, to be discussed in a later section) fluorite and rutile phases of RuO_2, are presented in Fig. 2. As is seen in Fig. 2 (bottom), the DOS for the fluorite phase consists of four groups of bands. The two lowest are dominated by O-p states hybridized with Ru-d states, while the two higher lying bands are dominated by the Ru-d states, with a smaller fraction of the oxygen p states. The two lowest groups of bands, the first from -8.5 eV to -5.5 eV and the second from -5.5 to -2 eV, can be considered as the bonding part of the hybridization complex

TABLE I. Experimental and theoretical (LDA and GGA) equilibrium lattice parameters (in a.u.) for the studied compounds and structures.

Compound	struct	a_{th} (LDA)	a_{th} (GGA)
RuO_2	fluorite	9.00	9.17
	rutile	8.44	8.59
$Ru_{0.75}Tc_{0.25}O_2$	fluorite	9.02	9.19
	rutile	8.46	8.61
$Ru_{0.75}Rh_{0.25}O_2$	fluorite	9.05	9.22
	rutile	8.44	8.59
$Ru_{0.75}Fe_{0.25}O_2$	fluorite	8.90	9.08
	rutile	8.33	8.48
$Ru_{0.75}Mn_{0.25}O_2$	fluorite	8.92	9.09
	rutile	8.34	8.49
$Ru_{0.75}W_{0.25}O_2$	fluorite	9.07	9.23
	rutile	8.50	8.64
$Ru_{0.75}Re_{0.25}O_2$	fluorite	9.04	9.20
	rutile	8.47	8.62
$Ru_{0.75}Os_{0.25}O_2$	fluorite	9.02	9.19
	rutile	8.46	8.61
$Ru_{0.75}Ir_{0.25}O_2$	fluorite	9.07	9.24
	rutile	8.46	8.61
RuN_2	fluorite	9.05	9.20
	rutile	8.48	8.61
$RuO_{1.75}N_{0.25}$	fluorite	9.01	9.19
	rutile	8.44	8.60
RuF_2	fluorite	9.66	9.95
	rutile	8.89	9.19
$RuO_{1.75}F_{0.25}$	fluorite	9.08	9.27
	rutile	8.48	8.63
RuC_2	fluorite	9.20	9.34
	rutile	8.68	8.81
$RuO_{1.75}C_{0.25}$	fluorite	9.05	9.22
	rutile	8.48	8.63
$RuO_{1.75}$	fluorite	8.95	9.13
	rutile	8.40	8.56

formed by the nearest neighbor bonding O-p and Ru-$d_{t_{2g}}$ states, while the unoccupied highest lying bands belong to the corresponding antibonding part. As is discussed in Ref. 2 the fluorite phase RuO_2, analogously to diamond, has an optimal number of valence electrons to occupy the bonding states, while leaving the antibonding states unoccupied. There is also an optimal energy separation between the O-p and metal d states in these compounds to provide strong bonds without having invoking any substantial charge transfer.[2] The small charge transfer from oxygen to the bond between Ru and O indicates a covalent character of the bonding.

The rutile phase of RuO_2 is metallic, in contrast to the fluorite phase, with the Fermi level positioned in a local minimum of the DOS in Fig. 2 (top). In general features, the electronic structure resembles the DOS calculated for the fluorite structure, indicating strong p-d hybridization. The high peak just below E_F originates mainly from the Ru-d
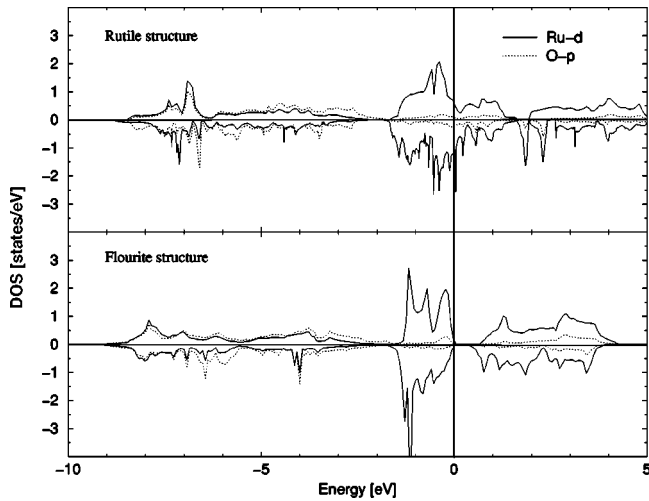
FIG. 2. The density of states for stoichiometric and substoichiometric (mirrored) RuO$_{1.75}$ in the rutile (top) and fluorite (bottom) phases. The Fermi energy is indicated by a solid line.

TABLE II. Bulk moduli B_{theory} and B_{exp} of transition metal dioxides (in GPa).

Compound	Structure	B_{theory}	B_{exp}
RuO$_2$	rutile	297	270
	fluorite	345	399
	$Pa3$	339	
RuO$_{1.75}$	rutile	224	
	flourite	256	
RhO$_2$	rutile	249	
	fluorite	303	
TcO$_2$	rutile	290	
	fluorite	327	
OsO$_2$	rutile	271	
	fluorite	392	
IrO$_2$	rutile	266	
	fluorite	319	
ReO$_2$	rutile	256	
	fluorite	305	
ReRhO$_4$	rutile	255	
	fluorite	325	

states, whereas the lower broad peaks lie in the range of predominantly oxygen p states. There is a qualitative agreement of the calculated DOS in Fig. 2 with the experimental XPS spectra measured for RuO$_2$ (Ref. 10) and good agreement with previous theoretical calculations.[2,11]

IV. BULK MODULI FOR 4d AND 5d TRANSITION METAL OXIDES

The bulk moduli for a range of 4d and 5d MO$_2$ were evaluated for both the rutile and fluorite phases. To do this the calculated total energy E as a function of volume V was fitted to analytical parameterizations for the equation of state, such as the Murnaghan and more recently proposed universal[12] bonding equations. The universal bonding equation has given almost the same $E(V)$ curves and bulk moduli for all compounds studied. The bulk moduli B (calculated within LDA) are listed in Table II. The effect of the spin-orbit coupling, included in the Hamiltonian, appeared to be almost negligible for the calculated bulk moduli, even for 5d transition metal dioxides.

As can be seen in Table II, changing from Ru to Os increases the bulk modulus for the fluorite phase of the dioxide. Substituting Ru (or Os) in the dioxides with a d element from another group leads to larger equilibrium volumes and smaller bulk moduli. For later transition metals, Rh and Ir in MO$_2$, the antibonding states are getting filled leading, in turn, to weaker bonds. When going to lower transition metals, Tc and Re in MO$_2$, the unfilling of the nonbonding d_{e_g} states has but little effect on the bonding properties. However, a high value of DOS at the Fermi energy indicates that the fluorite structure is probably unstable for TcO$_2$ and ReO$_2$, due to Jahn-Teller or Pierls-like distortions. Other studies have found that for the early 4d and 5d dioxides the bonds are of more ionic character.[13]

In addition to studying MO$_2$ compounds, similar calculations were performed for a pseudo-binary dioxide with rutilelike ground state structure, namely, ReRhO$_4$.[14] The cor-

responding bulk moduli are given in Table II, and appeared to be slightly lower than for isovalent RuO$_2$ and OsO$_2$ compounds both in the rutile and fluorite phases.

For the corresponding phases of the isovalent compound OsO$_2$, the electronic structure (DOS) was found to be very similar to that of RuO$_2$, displayed in Fig. 2. In general features the electronic structure is also reproduced qualitatively for other dioxides RhO$_2$, IrO$_2$, TcO$_2$, and ReO$_2$.

V. PRESSURE INDUCED PHASE TRANSITIONS

In addition to identifying potential hard transition metal dioxides, we have carried out calculations for several different crystal structures of RuO$_2$ such as stishovite (rutile), CaCl$_2$, α-PbO$_2$ ($Pnc2$), $Pa3$, and fluorite, which have been considered by various workers.[15] We have performed total energy minimizations to find the equilibrium structure of these phases and the results from these calculations are presented in Figs. 3 and 4. As the first transition from rutile to CaCl$_2$ is of second order, the total energy of rutile and CaCl$_2$ is almost the same. In Table III we list the various transition pressures in RuO$_2$ reported experimentally and calculated theoretically here. Our calculated transition pressure for the rutile to CaCl$_2$ phase is around 5 GPa and for the CaCl$_2$ phase to the $Pa3$ phase the transition pressure is around 9 GPa.

The calculated transition pressures for these phase transitions are in good agreement with the recent experimental data.[16] We have also explored the stability of the α-PbO$_2$ ($Pnc2$) type phase in RuO$_2$. We found that this phase is not stable in the studied pressure range, whereas a transition from CaCl$_2$ to α-PbO$_2$ ($Pnc2$) has been experimentally observed in SiO$_2$ and it has previously been calculated theoretically.[17] Our calculations here also support the stability of $Pa3$ phase as compared to fluorite (CaF$_2$) phase,
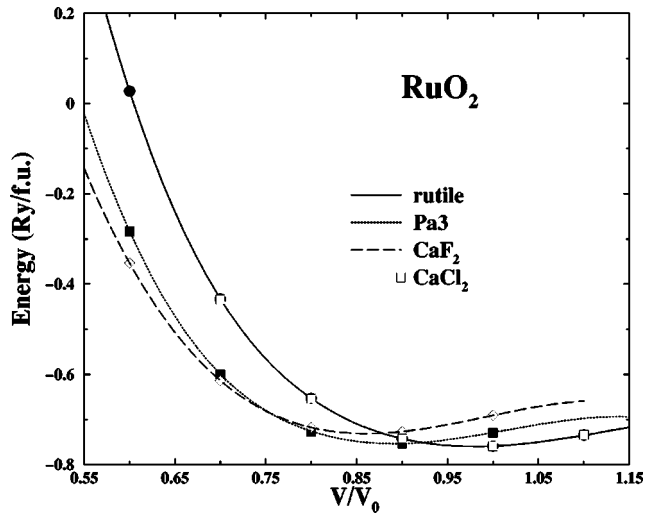
FIG. 3. The calculated total energies of the rutile, $Pa3$ and fluorite type crystal structures for RuO_2 as a function of volume (V/V_0, where V_0 is experimental equilibrium volume).

which has been experimentally reported by Haines *et al.*[18] We predict that a further compression of $Pa3$ type RuO_2 will lead to a phase transition to the fluorite (fluorite) type of structure. Our calculated pressure for this phase transition is around 65 GPa.

VI. EFFECTS OF IMPERFECTIONS ON THE RELATIVE PHASE STABILITIES

One of the primary objectives of this theoretical study of RuO_2, and its sister compounds, has been to find a way of stabilizing the fluorite phase with respect to the rutile phase. One way to stabilize different phases may be to alloy the compound. The effect of metal and nonmetal substitutional impurities and vacancies, on the relative phase stability of the two phases has therefore been investigated. In order to do
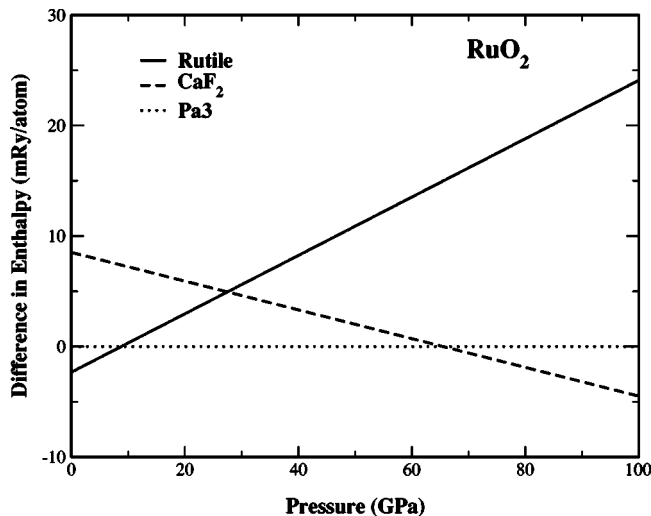

FIG. 4. The calculated differences in enthalpy between the rutile (solid line), $Pa3$ (dotted line), and fluorite (dashed line) type crystal structures for RuO_2 as a function of pressure (in GPa).

TABLE III. Theoretical and experimental transition pressures in RuO2.

	rutile-$CaCl_2$	$CaCl_2$-$Pa3$	$Pa3$-CaF_2
Theory [GPa]	5.0	9.0	65
Exp. [GPa]	6.0	13.0	

this supercells containing four ruthenium atoms and eight oxygen atoms were created. All these substitutional systems were relaxed in volume in order to find the equilibrium volume for RuO_2 with 25% metal and 12.5% non-metal substitution. Local relaxations around the substitutions was not taken into account.[7] The equilibrium volumes are tabulated in Table I, and the calculated changes in relative phase stabilities are found in Table IV.

A. Metal substitutional impurities

Several possible metal substitutions are conceivable and in the investigation the effect of metal substitutional impurities was studied by substituting one of the Ru atoms in the 12 atom supercell by a range of $3d$ (Mn and Fe), $4d$ (Tc and Rh) and $5d$ (W, Re, Os, and Ir) metal atoms. The metal substitutional atoms were always treated as being paramagnetic.

The results, the changes in relative phase stabilities, from these substitutions as a function of valence electron concentration for the different 25% substitutional transition metal impurities are shown in Fig. 5 and collected in Table IV. The results for both LDA and GGA calculations are shown, the trends being mostly consistent using both methods. Almost no change in the relative phase stabilities is found when Ru ($4d$) atoms are substituted for isoelectronic Fe ($3d$) or Os

TABLE IV. The energy difference ΔE (in mRy/f.u.) between the fluorite and the rutile structure for all the compounds studied.

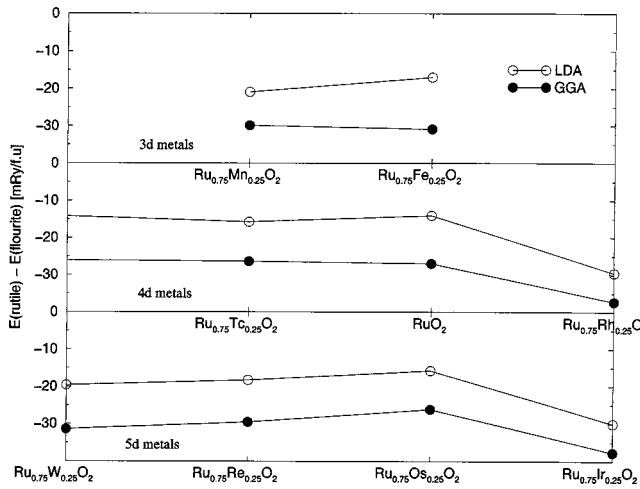| Compound	ΔE (LDA)	ΔE (GGA)
RuO_2	−14.0	−27.0
RhO_2	−39.8	−45.1
TcO_2	−11.0	−25.3
$Ru_{0.75}Tc_{0.25}O_2$	−15.7	−26.3
$Ru_{0.75}Rh_{0.25}O_2$	−29.6	−37.3
$Ru_{0.75}Mn_{0.25}O_2$	−20.94	−29.8
$Ru_{0.75}Fe_{0.25}O_2$	−17.0	−30.8
$Ru_{0.75}W_{0.25}O_2$	−19.6	−31.4
$Ru_{0.75}Re_{0.25}O_2$	−18.2	−29.6
$Ru_{0.75}Os_{0.25}O_2$	−15.7	−26.1
$Ru_{0.75}Ir_{0.25}O_2$	−30.1	−37.7
$RuO_{1.75}$	+6.7	+3.9
RuC_2	+15.2	−1.1
$RuO_{1.75}C_{0.25}$	−16.3	−27.1
RuN_2	−6.5	−20.6
$RuO_{1.75}N_{0.25}$	−17.3	−27.3
RuF_2	−47.0	−57.0
$RuO_{1.75}F_{0.25}$	−25.0	−28.8

FIG. 5. Energy difference between the rutile and fluorite structures as a function of valence electron concentration for 25% for 3d, 4d, and 5d transition metal substitutional impurities. The energy of the fluorite phase is taken to be zero. Filled/unfilled symbols represent results form GGA/LDA calculations.
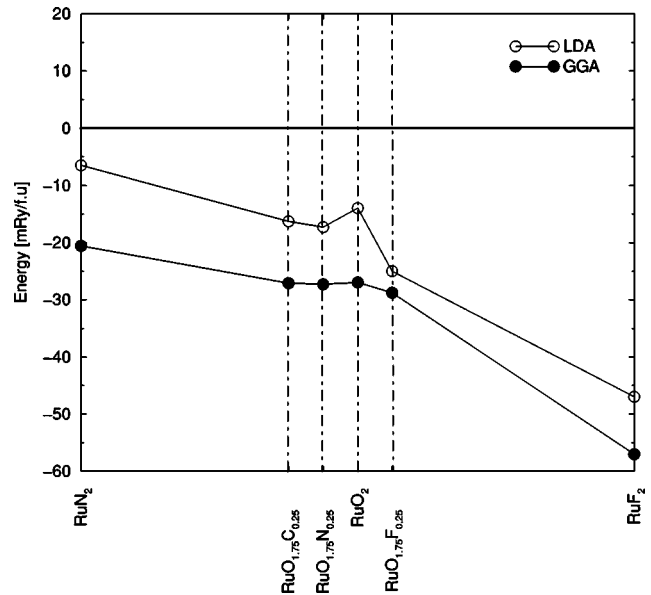

FIG. 6. Energy difference between the rutile and fluorite structures as a function of valence electron concentration for 25 and 100% nonmetal substitutional impurities. The energy of the fluorite phase is taken to be zero. Filled/unfilled symbols represent results form GGA/LDA calculations.

(5d) atoms. It is also found that substituting for metal atoms with smaller or large number of valence electrons are all found to make the rutile phase more stable versus the fluorite phase (GGA perhaps indicating a small stabilization of the fluorite phase from substitution of Mn/Tc). The trends in 3d, 4d, and 5d metals are found to follow each other.

B. Nonmetal substitutional impurities

Also for the nonmetal atoms several substitutions are possible and we chose to study the effect of the elements nearest to oxygen in the periodic table; carbon, nitrogen, and fluorine. The changes in the relative phase stabilities for the different substitutions are shown in Fig. 6 and tabulated in Table IV. It is seen from these calculations that substitution with F lead to increased stabilization of the rutile phase. Small substitutions with N or C both lead to small relative stabilizations of the rutile phase, while increased substitution leads to a stabilization of the fluorite phase. It can be noted that the trends are consistent when comparing the result from LDA with those from GGA.

C. Oxygen vacancies

The effect of nonmetal vacancies on the electronic structure and properties of transition metal compounds can often be significant.[19] Therefore we have studied the effect of vacancies on the relative phase stability by removing one of the oxygen atoms in the 12 atom supercell, thus creating RuO$_{1.75}$ with 12.5% vacancies. The relative energy difference between the two phases is changed to +3.9 mRy (+6.7 mRy for LDA results), showing a stabilization of the fluorite phase when vacancies are introduced.

In Fig. 2 the density of states (DOS) is displayed for substoichiometric (and stoichiometric) RuO$_{1.75}$ in the rutile

and fluorite phases. By contrasting the DOS of the stoichiometric and substoichiometric phases one can identify that the occupied part of the electronic structure is not greatly changed, except for a slight upward shift expected from simple band filling arguments, when vacancies are introduced. So-called vacancy peaks common to other transition metal compounds,[20] often situated in regions of low DOS, are seen in the unoccupied DOS at around 1.7 and 2.3 eV for the rutile phase and at around 0.7 eV for the fluorite phase. These vacancy peaks are of metallic Ru-d character and, from previous studies by ourselves of related systems,[20] can be attributed to metal-metal d bonds through the vacancy sites.

VII. THE EFFECT OF LATTICE STRAIN ON THE RELATIVE PHASE STABILITIES

Another way of stabilizing the different structures is to strain the lattice (for example, by judicious choice of substrate) of the RuO$_2$ phases. In Fig. 7 the total energies of the rutile and fluorite phases are shown as a function of lattice parameter. In order to stabilize the growth of the rutile phase on a strained lattice parameter a lattice spacing a must be found where the energies of the fluorite phase is lower than that of the rutile phase. From inspection of Fig. 7 one finds that this happens at a lattice parameter a equal to, or larger than, 8.8 a.u. (9.0 a.u. for GGA results). Also taking into account the extra degree of freedom in the rutile structure, which may relax in c/a, only shifts the predicted turnover point to slightly larger lattice parameters (data not shown).
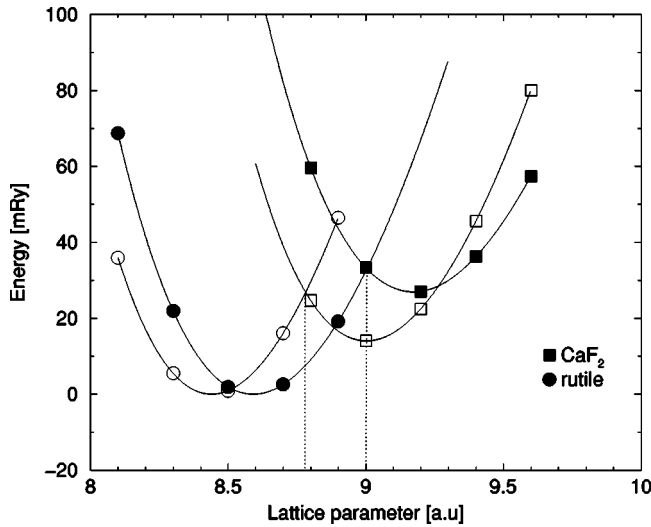
FIG. 7. The energy as function of lattice parameter a for the rutile and fluorite structures of RuO_2. Filled/unfilled symbols show GGA/LDA results, respectively. The lattice parameter at which the fluorite phase becomes the most stable is indicated by dotted lines for GGA/LDA results.

The result of this part of our study is the, at first inspection counterintuitive, conclusion that one should stabilize the high-pressure fluorite phase by growth on a lattice with a larger lattice parameter than that of the equilibrium, lower pressure, rutile structure. This comes about since the volume per atom for the fluorite is still smaller than that for the rutile phase even at a slightly larger lattice parameter; the flourite phase has a higher density than the rutile phase at equal lattice parameters. When searching for suitable substrates on which to grow cubic RuO_2 one should search for substrates with lattice parameters equal to whole integer multiples of the lattice parameter range suggested here. One should also take into account that substrates with an fcc-lattice may also be suitable if the parameter is an integer multiple of $\sqrt{2}$ times the lattice parameter range suggested here.

VIII. CONCLUSIONS

Throughout our study we have compared GGA and LDA results with experimental data. As is usual we find that GGA results in somewhat larger lattice constants than LDA (around 0.15 a.u.). For the flourite phase GGA agrees better with experiment whereas for the rutile phase LDA and GGA are approximately equally accurate. In both phases the calculations reproduce experimental data within a few percent. As regards the energy difference between the two studied polymorphs GGA gives around 10 mRy larger difference but in all studied systems the two approximations gives consistent results as regards structural stability (except RuC_2—see Table IV). Our results hence suggest that there is no need to incorporate corrections to the density functional, e.g., trying to take into account Hubbard type interactions,[21,22] and that LDA and GGA calculations are a good starting point to understand this type of materials. One can speculate that the

reason for the observed difference in phase stability from LDA and GGA, reflects the fact that the density in the more open rutile phase has larger variations, from low to high values, compared to the density of the more close packed flourite phase. Hence, one may argue that gradient effects shoud be larger for the rutile structure.

Finally, the results of this study of the phase stabilities and pressure induced phase transitions in RuO_2 can be summarized by five points.

(i) The effect of lattice strain on the relative phase stabilities was studied and a range of lattice parameters for possible substrates, favorable for growth of the cubic fluorite RuO_2 phase is suggested. It is predicted that growth of RuO_2 on a substrate with an in-plane lattice parameter larger than 9.0 a.u. will lead to a stabilization of the fluorite phase. It is thus found that one should stabilize the high-pressure fluorite phase by growing it on a lattice with a larger lattice parameter than the lattice parameter of the equilibrium rutile structure.

(ii) The relative phase stability of the fluorite (CaF_2) and rutile phases in RuO_2 have been studied. The effect of metal and nonmetal substitutions as well as substoichiometry were taken into account. It was found that none of the metal substitutions studied lead to a stabilization of the fluorite phase. Small substitutions with nonmetal carbon, nitrogen, or fluorine stabilize the rutile phase. The effect of larger carbon or nitrogen substitutions, together with nonstoichiometry was seen to be an increased stabilization of the fluorite phase. Even though substoichiometry is also shown to decrease the bulk modulus this might be a fruitful way of stabilizing the flourite structure.

(iii) The electronic structure of stoichiometric and substoichiometric RuO_2 in the rutile and the fluorite phases is reported.

(iv) The bulk moduli have been calculated for several $4d$ and $5d$ transition metal oxides. The highest bulk modulus predicted is that of OsO_2, isovalent to RuO_2.

(v) The pressure induced phase transitions in RuO_2 were studied and the theoretical transition pressures agree well with experiment. The calculations support the stability of the $Pa3$ phase previously reported in experiment.[18]

By combinations of the trends in structural stabilities from metal and nonmetal substitutional impurities, oxygen vacancies, pressure transitions and lattice strains shown here, many possible avenues for the realization of superhard transition metal dioxides presents themselves that should merit experimental activity.

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