AB INITIO STUDY OF IMPACT OF PRESSURE AND TEMPERATURE ON STABILITY AND POLYMORPHISM OF PdO_2

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INTRODUCTION

- **Palladium** and its **oxides** are important catalysts in many catalytic reactions with diversity of technological applications.
- The only thoroughly scientifically studied and technologically exploited palladium oxide is **PdO**.
- Formation of one **PdO_2** polymorph was observed under elevated hydrostatic pressure and temperature and rutile structure was proposed [1,2].
- We focus on theoretical prediction of stable **PdO_2 polymorphs** and impact of **pressure** and **temperature** on their stability using **Density Functional Theory** modelling**.**
- We model PdO_2 in 19 crystal structures observed for dioxides of transition metals.
- All PdO_2 models were fully optimized at six pressure points: 0, 20, 40, 60, 80 and 100 kbar.

METHODS

- DFT calculations were performed in program VASP[3].
- All models were fully optimized using DFT GGA **PBEsol** functional and hybrid DFT **HSE06** functional. Plane-wave cut-off was set to 700 eV and k-mesh spacing to 0.2 $Å^{-1}$.
- Lattice dynamics was calculated for 2x2x4 supercells using direct phonon method and quasiharmonic approximation as implemented in the program PHONOPY [6].
- Visualization of crystal structures was done in VESTA[4].

CONCLUSIONS

- All 19 PdO_2 models are stable relative to $Pd+O_2$ and 13 structures are stable in respect to PdO in the pressure range 0-100 kbar.
- The lowest-E structure at zero pressure is predicted to be MnO_2 type at hybrid DFT level (VO_2 type at standard DFT).
- Rutile type structure (claimed by experiment) is 10^{th} in energy and dynamically unstable at all pressures, while all models that are energy-preferred over rutile structure are dynamically stable.
- Increase of the electronic temperature via smearing, stabilizes tetragonal rutile type.
- At low temperatures structural transformation from tetragonal to orthorhombic rutile occurs through a B_{1g} soft mode that relaxes the very short d_1(O-O) distance that seems to be the key parameter that drives the phase transition.

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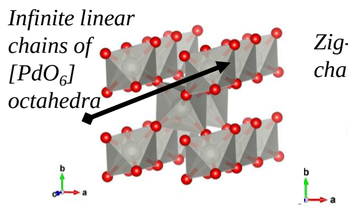
CRYSTAL STRUCTURES OF OPTIMIZED MODELS

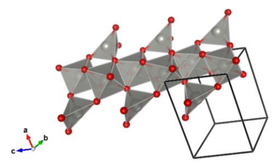
Rutile group



Types: rutile, $CaCl_2$, α-PbO_2, NbO_2

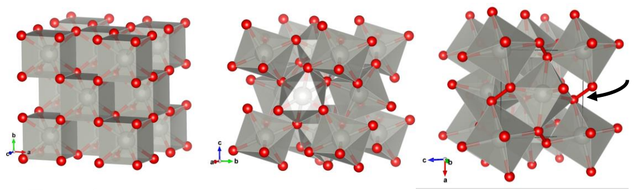
Type: brookite

Complex structure



Type: VO_2 (aP12)

Fluorite group

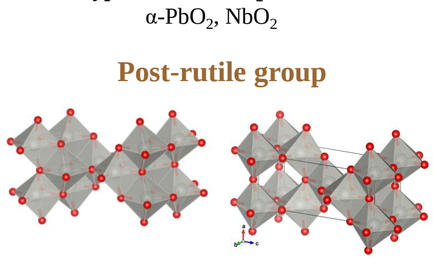


Type: fluorite

Type: PdF_2

Type: pyrite

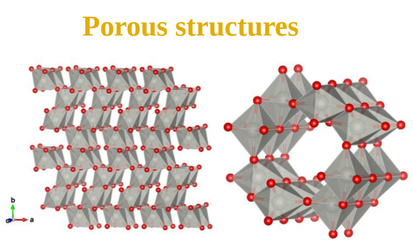
Post-rutile group



Type: VO_2 (HT)

Type: anatase

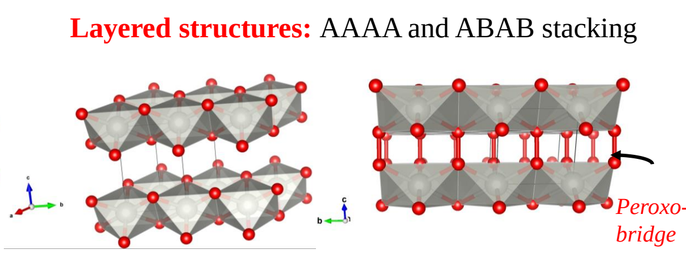
Porous structures



Type: VO_2

Types: MnO_2, $Ni_{0.5}Mn_{1.5}O$

Layered structures: AAAA and ABAB stacking

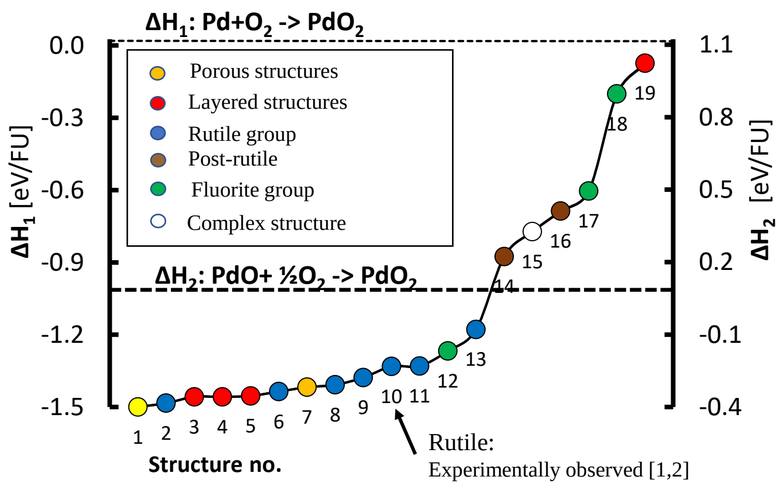


Types: CoO_2, CdI_2, $BaSi_2$

Type: HgO_2

ENTHALPY OF FORMATION

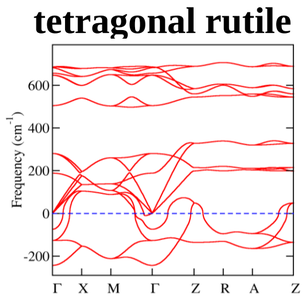
DFT results



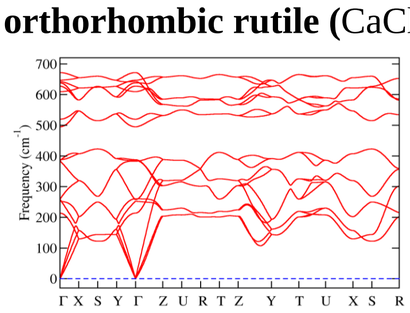
LATTICE DYNAMICS

Phonon dispersion curves (DFT results)

tetragonal rutile

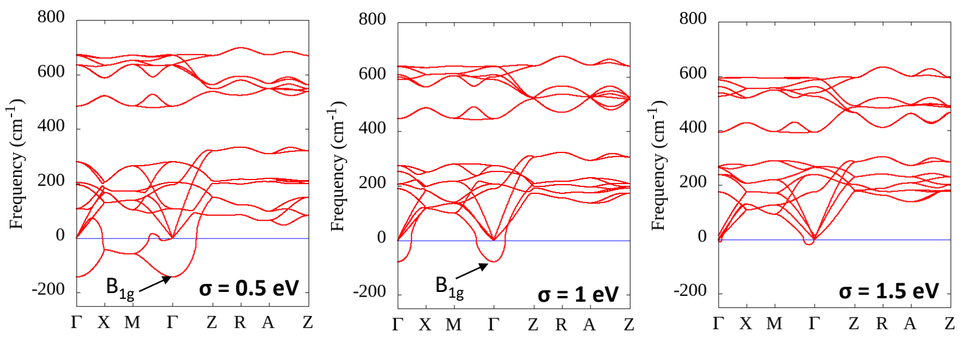


orthorhombic rutile ($CaCl_2$ tp)



- **Tetragonal rutile** is dynamically **unstable** at all pressures.
- **Orthorhombic rutile** predicted to be dynamically **stable**.

EFFECT OF TEMPERATURE via smearing of Fermi surface

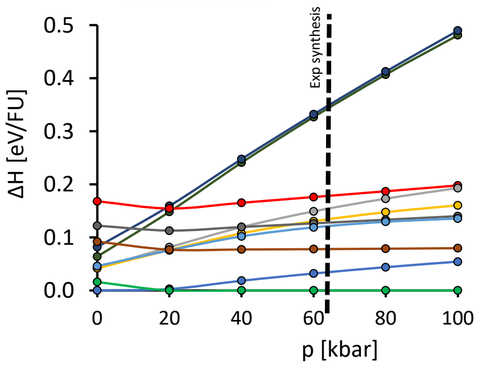


- The increasing Gaussian occupancy smearing width σ (0.02-1.6 eV) in standard DFT method dramatically affects lattice dynamics of PdO_2 in rutile type structure.
- For **σ ≥ 1.5 eV** the **tetragonal rutile** type structure becomes stable.
- For **σ < 1.5 eV** rutile type PdO_2 becomes unstable in respect to B_{1g} mode that lowers the tetragonal symmetry to **orthorhombic rutile**.

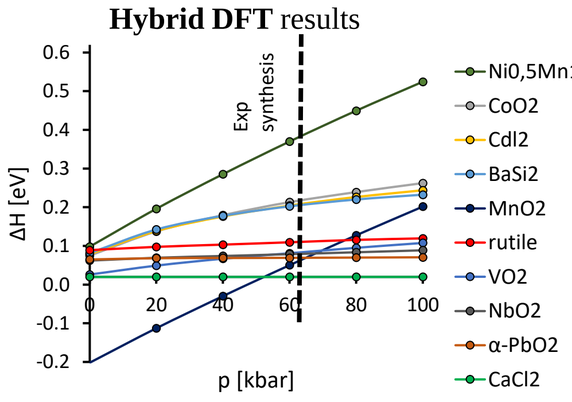
HIGH PRESSURE REGIME

Relative enthalpies vs. pressure

DFT results



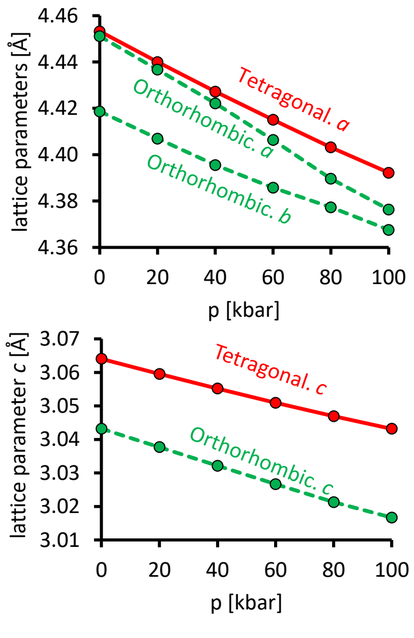
Hybrid DFT results



- **At zero pressure,** the lowest energy type is **VO_2** in **DFT**, while the **hybrid DFT** method predicts that the energetically preferred type is **MnO_2**.
- Both standard and hybrid DFT predict **orthorhombic rutile** type structure to be preferred **at elevated pressure** above 20 kbar (DFT) and 50 kbar (hybrid DFT).
- In both methods, **tetragonal rutile** structure is **disfavoured** at all pressures.

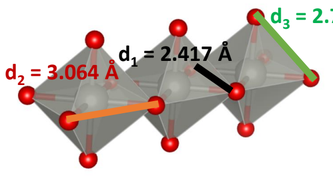
Rutile structures: geometry analysis (hybrid DFT results)

Lattice parameters vs. pressure

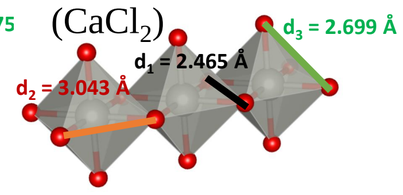


Interatomic O…O distances

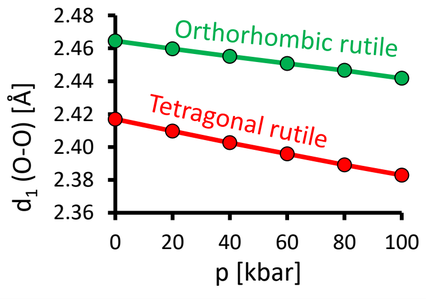
Tetragonal rutile



Orthorhombic rutile ($CaCl_2$)



Change of d_1 (O-O) length under pressure



- In the tetragonal rutile type structure, the d_1(O-O) distance is considerably shorter than the typical distance between O^{2-} anions (2.8 Å).
- Orthorhombic distortion relaxes the very short d_1(O-O) distance.
- The d_1(O-O) length remains longer in the orthorhombic rutile than in tetragonal rutile at all pressures up to 100 kbar.
- The relaxation of the d_1(O-O) distance seems to be the key parameter that drives the phase transition from the tetragonal to the orthorhombic rutil type structure in PdO_2 at low temperatures.