Design of atomistic models of the little-known palladium oxide PdO_2

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INTRODUCTION

- **Palladium and its oxides** are important catalyst in many catalytic reactions with diversity of technological applications.
- The only well studied and technologically exploited phase of palladium with oxygen is palladium monoxide PdO.
- One polymorph of palladium dioxide **PdO_2** was also reported. It was obtained in high-p,T synthesis [*Shaplygin*, *1978*], but it is **poorly characterized**.
- Existence of only one PdO_2 polymorph is surprising since at least 5 polymorphs are known for Pt dioxide PtO_2.
- **Our aim** is to **predict** other stable **PdO_2 polymorphs** using Density Functional Theory modelling.

PdO_2 modelled in known MO_2 structures

#	Modelled types
1	VO_2
2	$CaCl_2$
3	CoO_2
4	CdI_2
5	$BaSi_2$
6	$Ni_{0,5}Mn_{1.5}O_4$
7	MnO_2
8	α-PbO_2
9	NbO_2
10	Rutil
11	VO_2 (oF96)
12	PdF_2
13	Brookite
14	Anatase
15	VO_2 (aP12)
16	VO_2 (HT)
17	Fluorit
18	Pyrit
19	HgO_2

- **19** unique structural **types** were taken from ICSD crystallographic database
- DFT **optimization** was performed for the models after **substitution** of the metal atom (M) for Pd: **M→ Pd**
- **Enthalpies of formation** were calculated:
  - in respect to elements:

    $Pd+O_2$ -> PdO_2 **(ΔH_1)**
  - in respect to PdO:

    $PdO + ½O_2$ -> PdO_2 **(ΔH_2)**
- Relative stability at high pressures.
- Dynamical Stability calculations.

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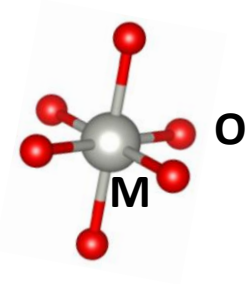
18	Pyrit
19	HgO_2

The modelled structures belong to 6 structural families.

Structural families

- Porous structures
- Layered structures
- Rutile group
- Post-rutiles
- Fluorite group
- Complex structures

- Basic building block in all modelled strucures is octahedron [MO_6]

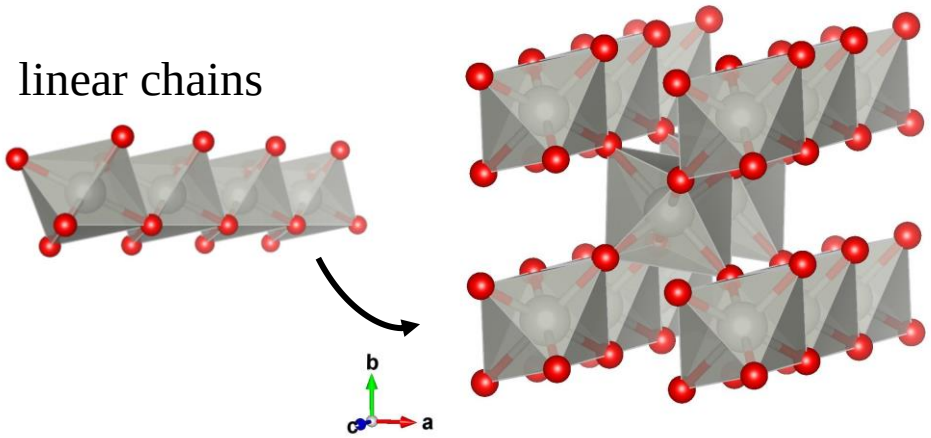


CRYSTAL STRUCTURES

Rutile group

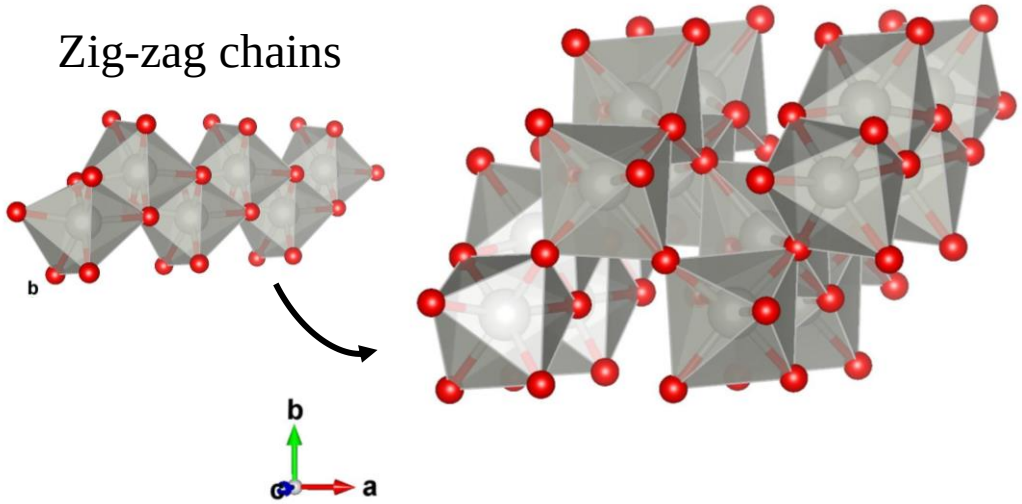
- Formed by infinite chains of edge-shared octahedra.
- The chains are interconnected through corners.

linear chains



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

Zig-zag chains

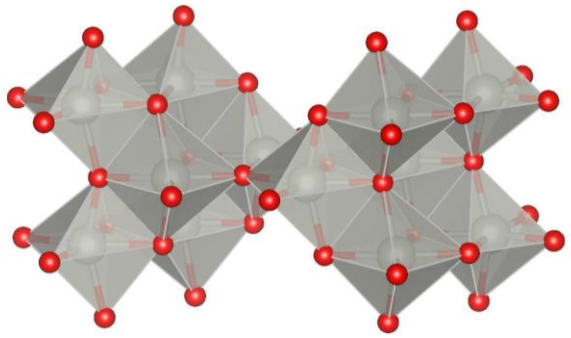


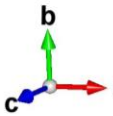
Types: brookite

CRYSTAL STRUCTURES

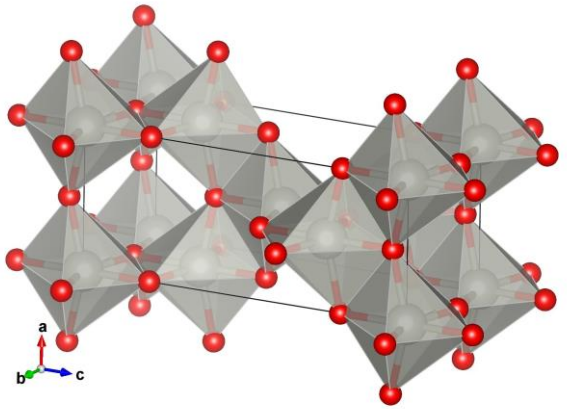
Post-rutile group

- In the post-rutile structures, the rutile-like chains of octahedra share apart from corners, also edges.
- They are known also as compressed rutiles.





Types: VO_2 (HT)

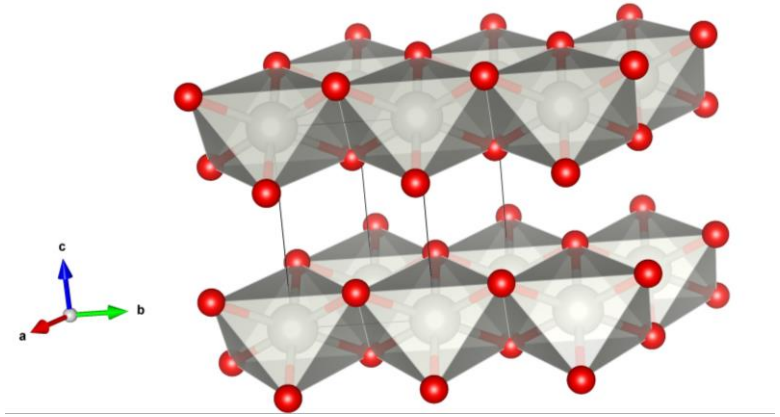


Types: anatase

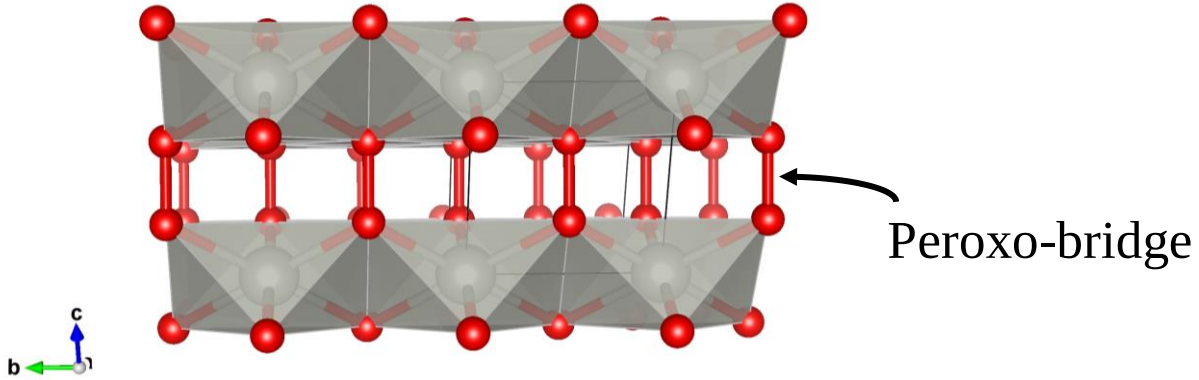
CRYSTAL STRUCTURES

Layered structures

- Formed by layers of octahedra sharing edges.
- Various stackings of layers are possible (AAA or ABAB stacking).
- The layers can be interconnected by peroxo-bridges.



Types: CoO_2, CdI_2, $BaSi_2$

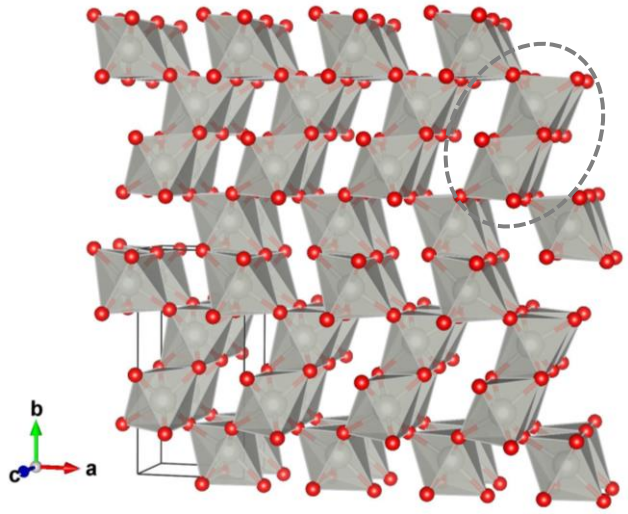


Type: HgO_2

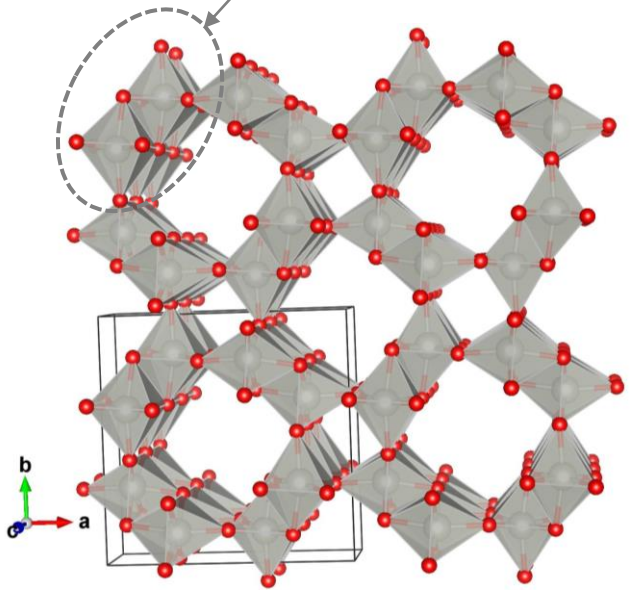
CRYSTAL STRUCTURES

Porous structures

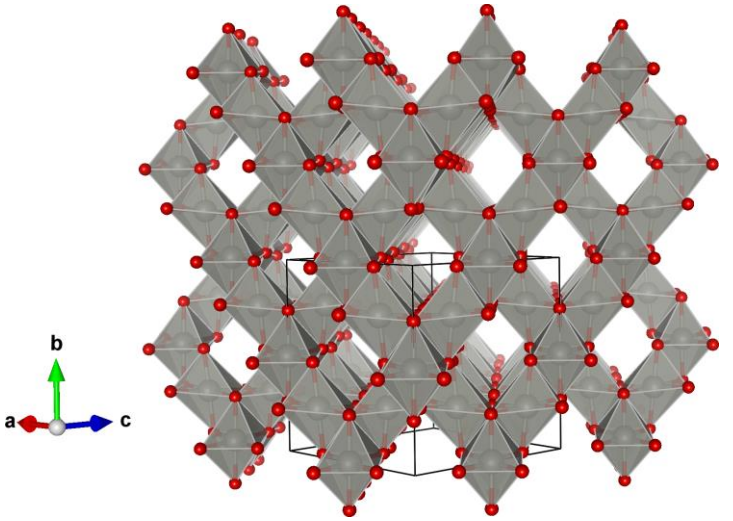
- Characteristic feaure of porous structures is presence of empty channels (1D voids).
- The stuctures are formed by single or double rutile-like chains sharing corners.



Type: VO_2



Type: MnO_2

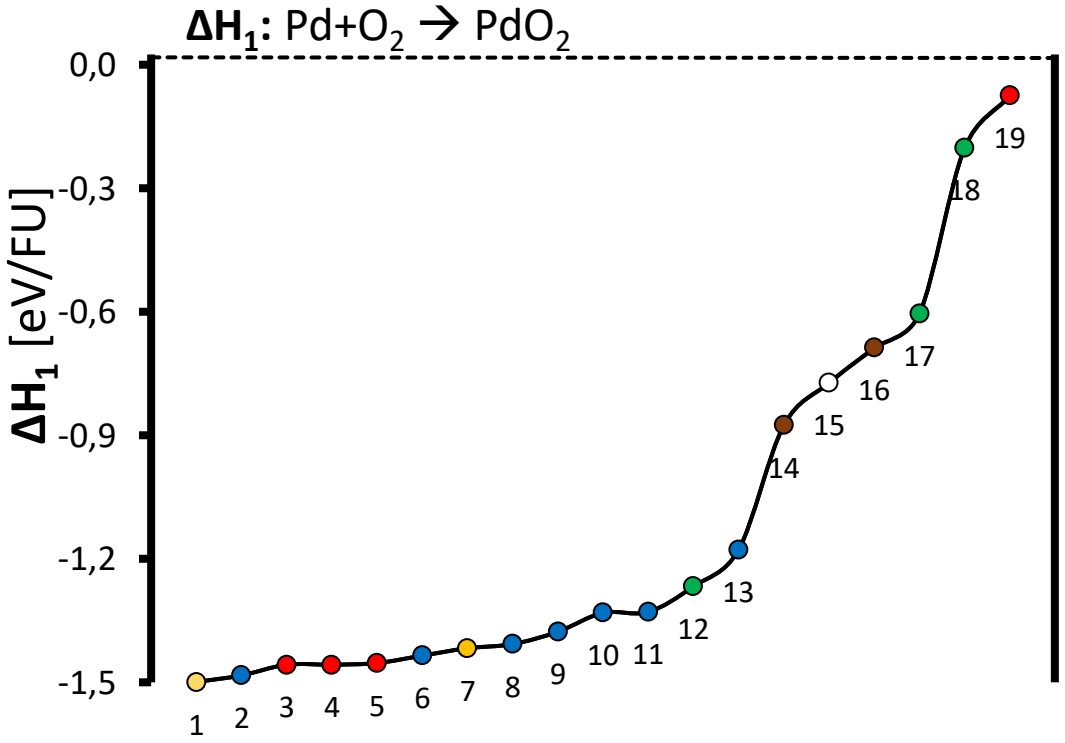


Type: $Ni_{0.5}Mn_{1.5}O$

COMPUTER DETAILS

- All structure models were optimized with DFT functional PBE modified for solids (PBEsol).
- All models were optimized in the pressure range 0-100 kb.
- DFT calculation were performed in program VASP.
- Lattice dynamics was calculated in the program Phonopy.
- Visualization of crystal structures was done in VESTA.

PdO_2: ENTHALPY OF FORMATION



- All models stable in respect to Pd and O_2
- 13 models stable in respect to PdO and O_2
- All structures observed for PtO_2 are stable also for PdO_2
- Rutile structure (#10) is not the ground state
- Lowest-E structure is VO_2 type

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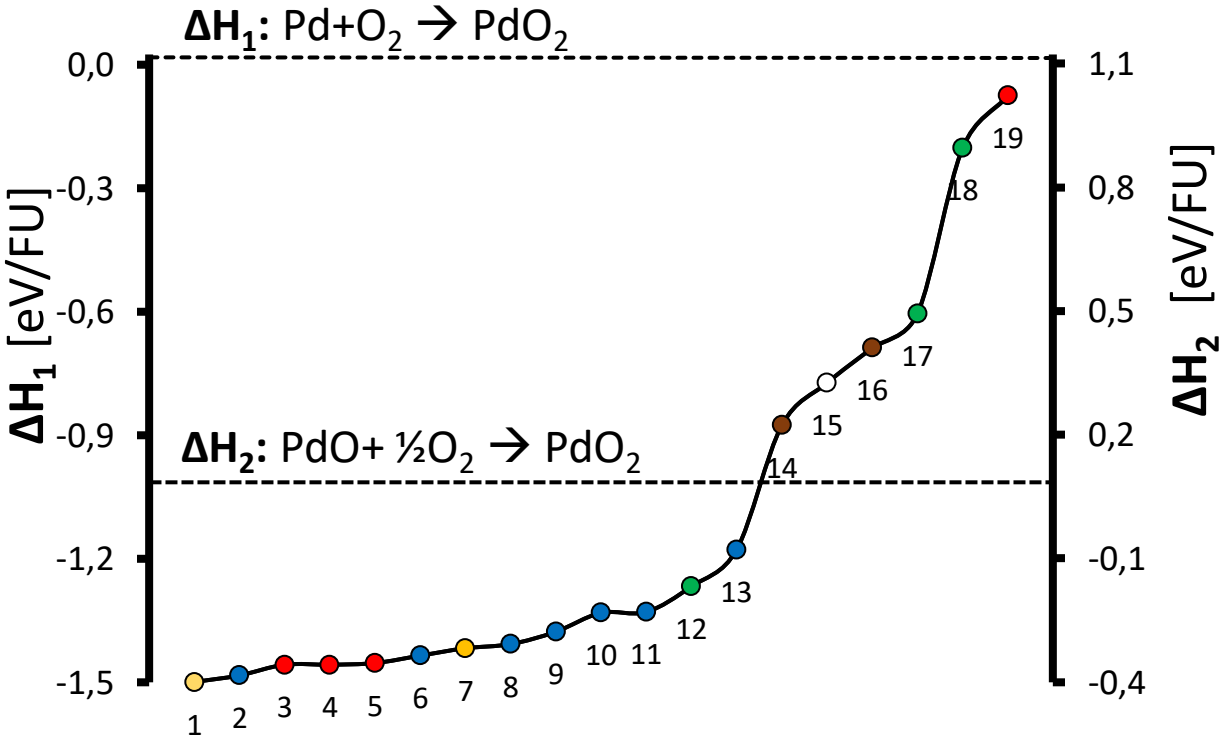

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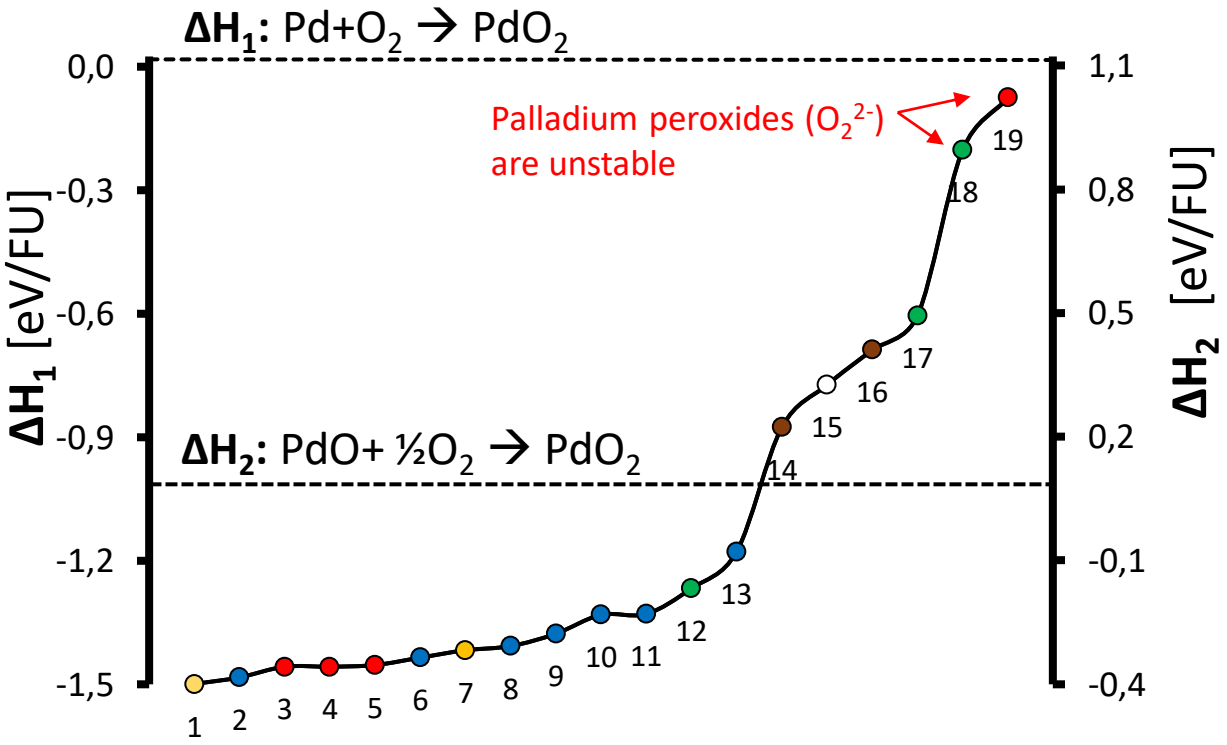

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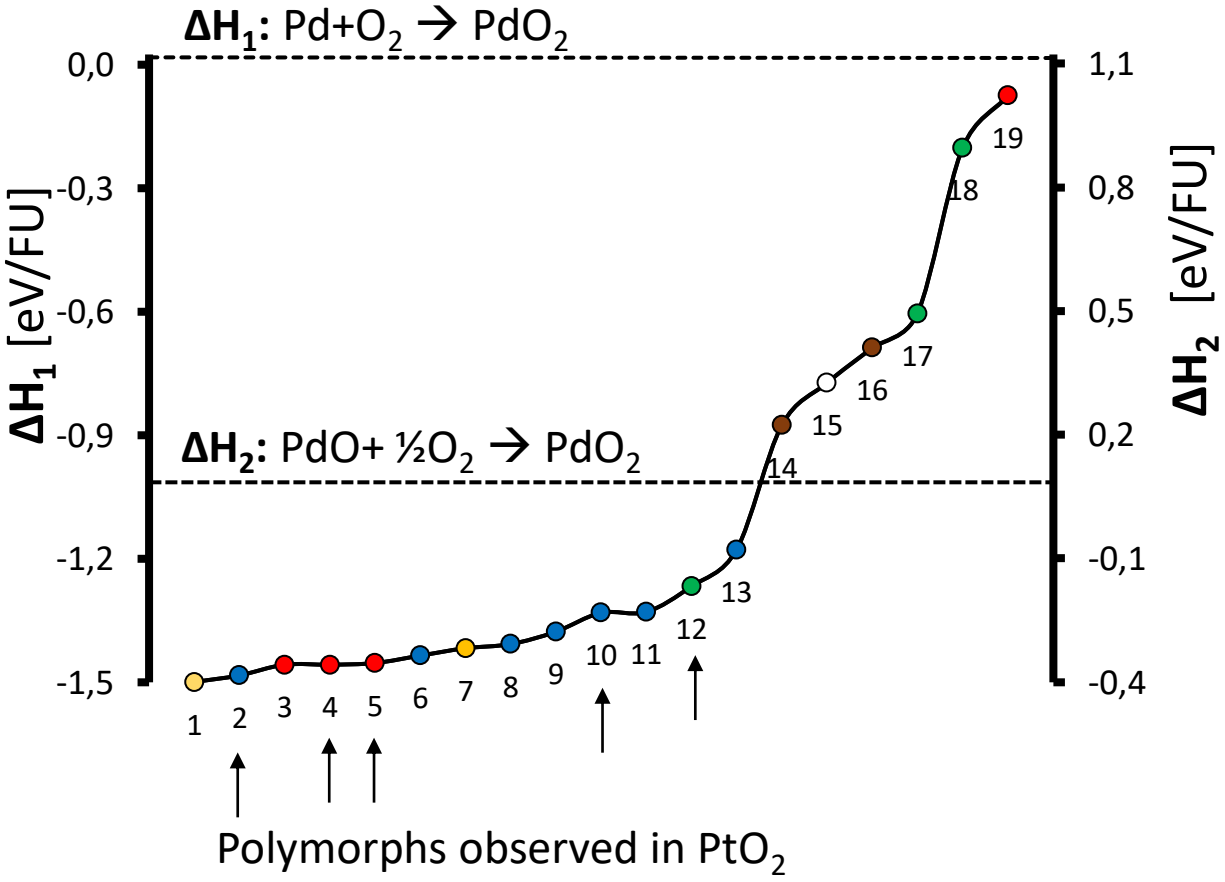

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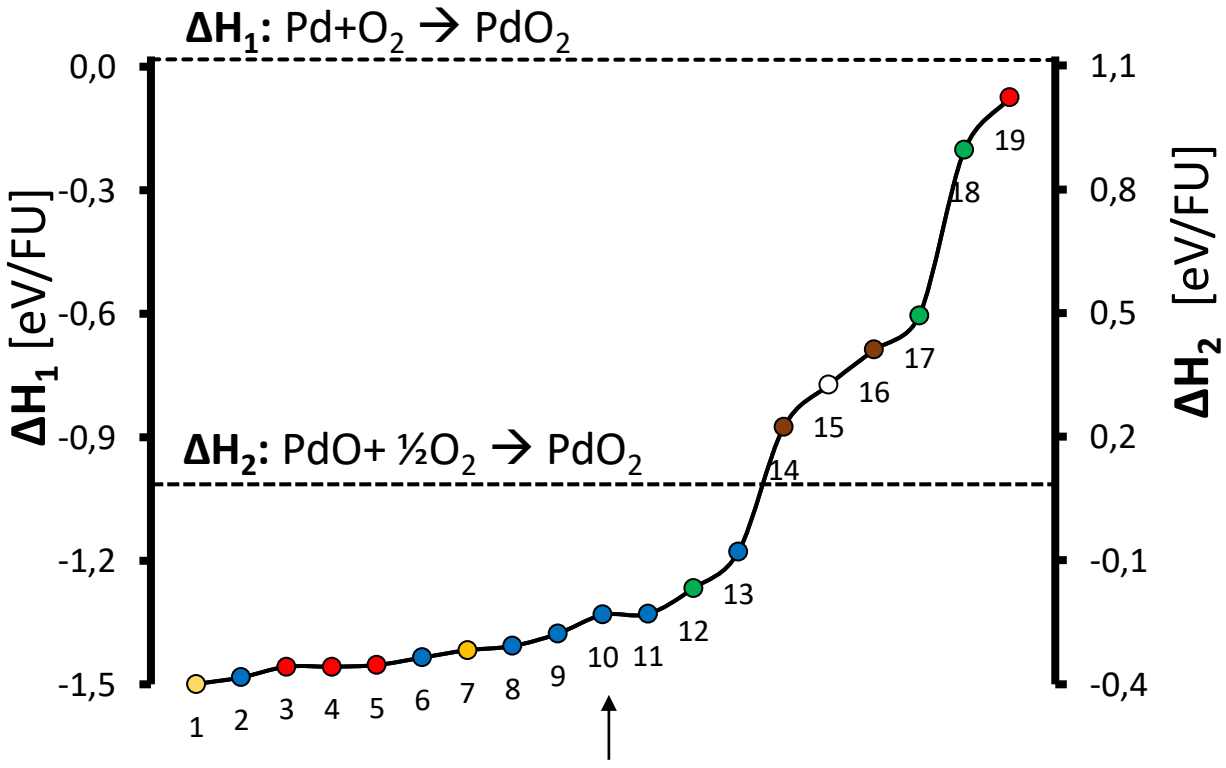
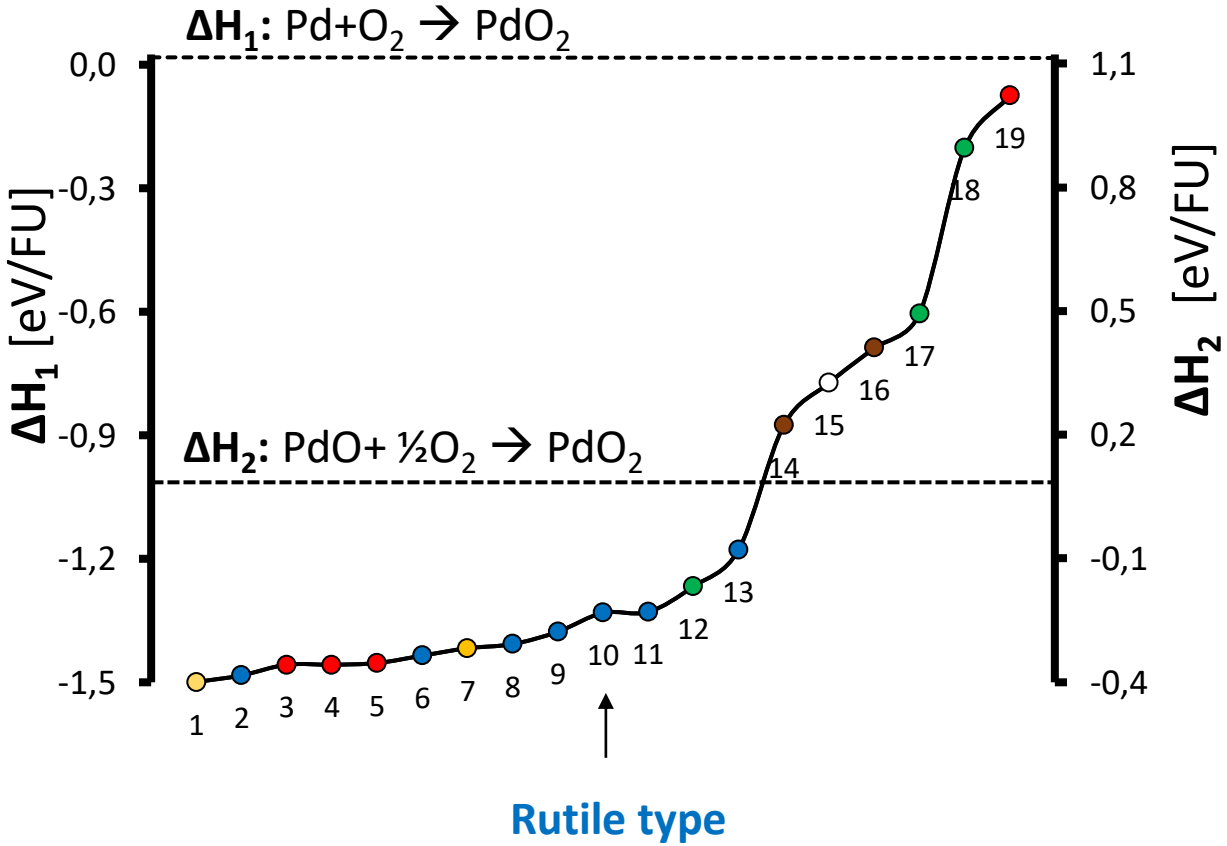


Rutile type
(observed in experiment)

- All models stable in respect to Pd and O_2
- 13 models stable in respect to PdO and O_2
- All structures observed for PtO_2 are stable also for PdO_2
- Experimentally observed rutile structure (#10) is not the ground state
- Lowest-E structure is VO_2 type

PdO_2: ENTHALPY OF FORMATION



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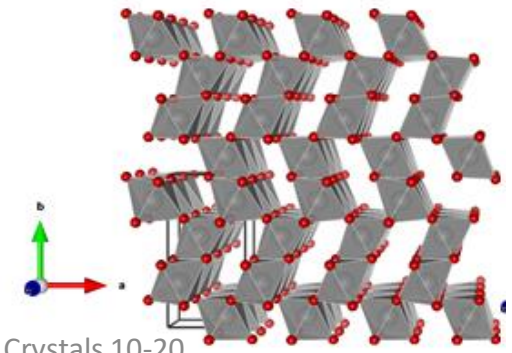
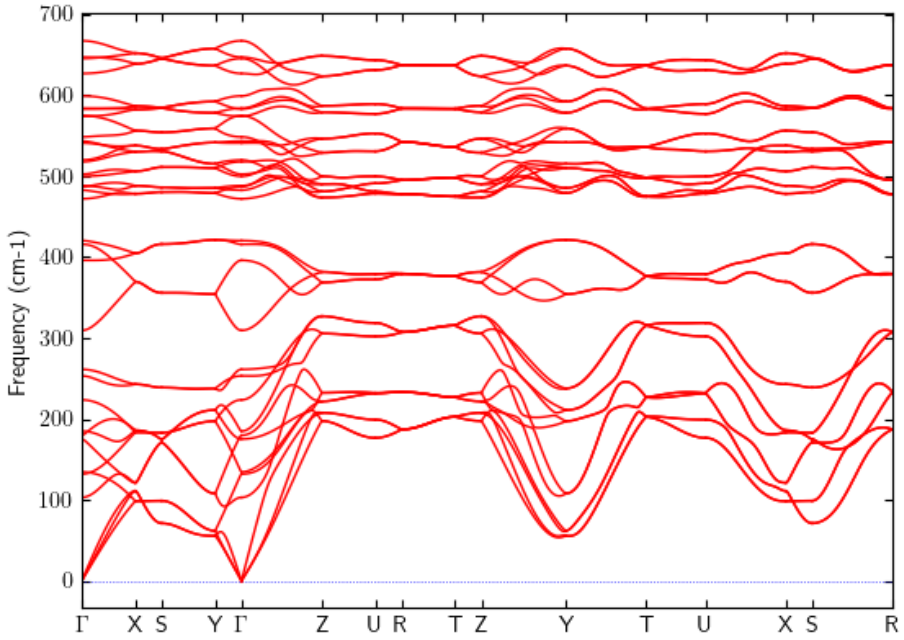


VO_2 type
(ground state)

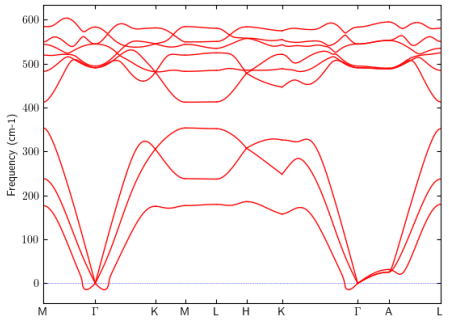
PdO_2: DYNAMICAL STABILITY

Phonon dispersion curves of PdO_2 in VO_2 type (dynamically stable)

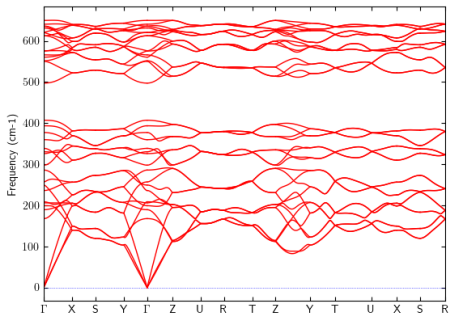


- We have calculated impact of atomic vibrations on crystal stability by calculation of phonon dispersion curves.
- Positive (real) values of energies indicate dynamical stability.
- Negative (imaginary) values of energies indicate dynamical instability.
- **All PdO_2 models** that are stable in respect to PdO are also **dynamically stable**.
- Only **rutile** structure is dynamically **unstable**.
  - **Possible reasons:**
    - Failure of DFT method,
    - different structure observed in experiment.

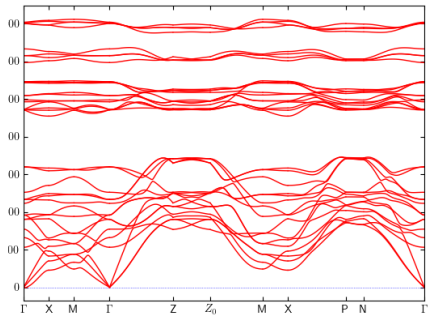
PdO_2: DYNAMICAL STABILITY



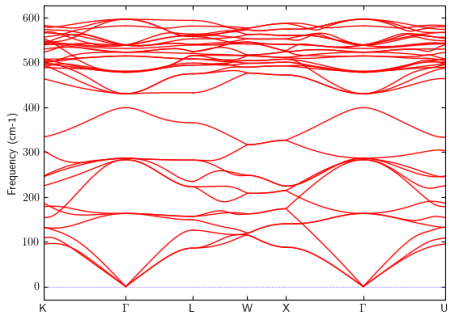
$BaSi_2$



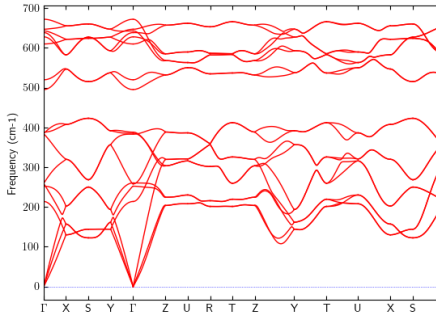
α-PbO_2



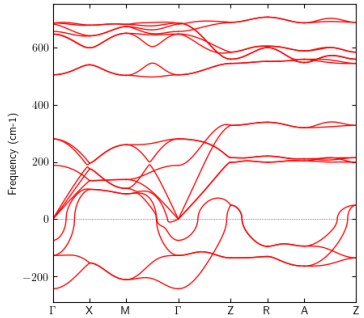
MnO_2



$Ni_{0.5}Mn_{1.5}O_4$



$CaCl_2$



rutile

- We have calculated impact of atomic vibrations on crystal stability by calculation of phonon dispersion curves.
- Positive (real) values of energies indicate dynamical stability.
- Negative (imaginary) values of energies indicate dynamical instability.

All PdO_2 models that are stable in respect to PdO are also **dynamically stable**.

Only **rutile** structure, which was reported experimentaly is dynamically **unstable**.

- **Possible reasons:**
  - Failure of DFT method,
  - different structure observed in experiment.

PdO_2: LATTICE PARAMETERS

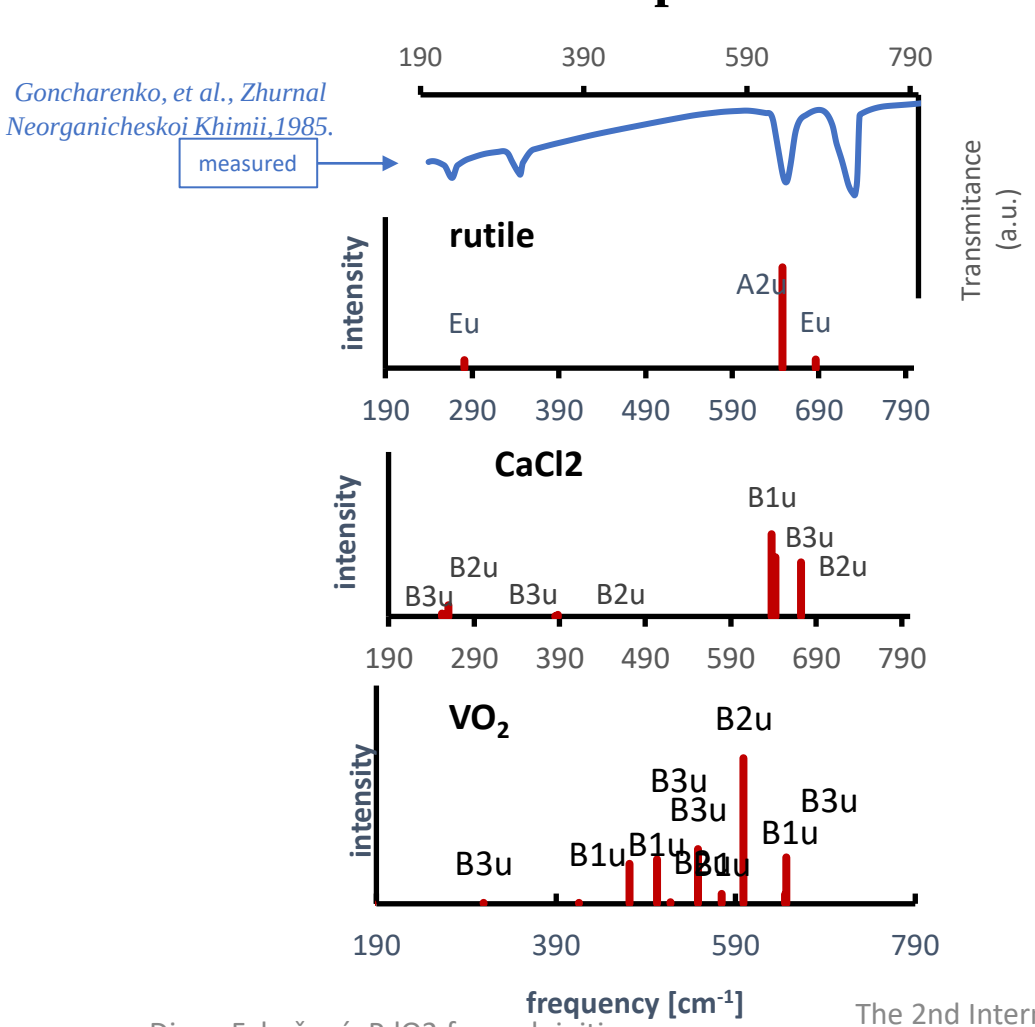
Calculated lattice parameters for the lowest-energy polymorphs

No.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	
TYPE	VO_2	$CaCl_2$	CoO_2	CdI_2	$BaSi_2$	$Ni_{0.5}Mn_{1.5}O_4$	MnO_2	α-PbO_2	NbO_2	rutile	rutile experiment
SPGR	Pnma	Pnnm	C2/m	$P6_3mc$	P-3m1	Fd-3m	I4/m	Pbcn	I41/a	$P4_2/mnm$	
a [Å]	4.573	4.503	5.283	3.051	3.05	8.559	10.017	4.487	17,998 4,500	4.495	**4.483**
b [Å]	9.311	4.447	3.05	3.051	3.05	8.559	10.017	5.448	17,998 4,500	4.495	**4.483**
c [Å]	3.054	3.095	5.74	8.913	4.419	8.559	3.075	5,072 2,536	6,228 3,114	3.158	**3.101**
β [°]			128.1								
V [Å³]/Z	32.5	31	36.4	35.9	35.6	39.2	38.6	31	31.5	31.9	**31.6**
Z	4	2	2	2	1	16	8	4	32	2	**2**

- Calculated lattice parameters of the rutile structure compare well with the measured values.
- **$CaCl_2$ type** has also lattice parameters comparable to experimental values.
- All other models have quite distinct lattice parameters.
- $CaCl_2$ type is in fact **orthorhombic rutile,** which differs only slightly from the ideal tetragonal rutile lattice.
- So the question arises if the orthorhombic rutile could be the experimentally observed structure instead of the tetragonal one.

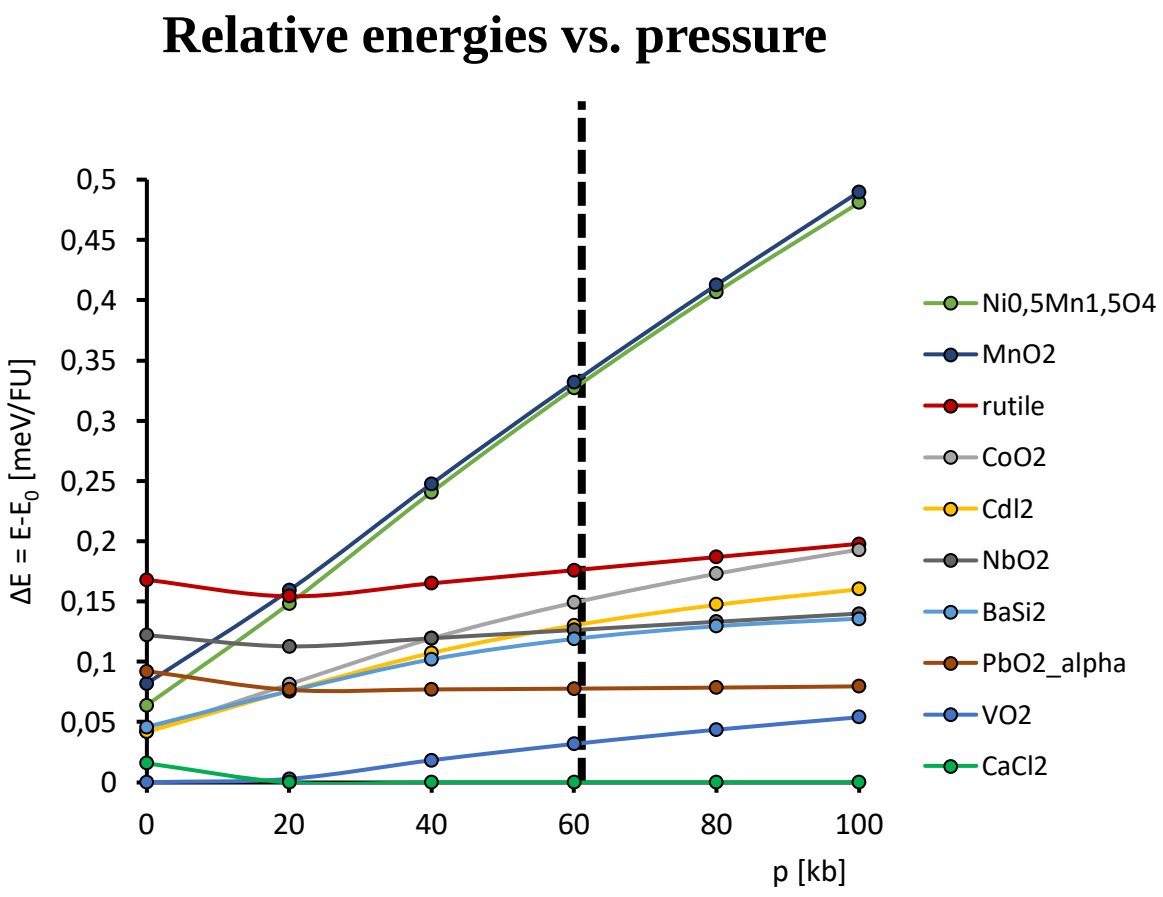
Shaplygin et al., Zhurnal Neorganicheskoi Khimii, 23, 884 (1978).

PdO_2: LATTICE PARAMETERS



- Here we show the calculated Infrared spectra for the tetragonal and orthorhombic rutile ($CaCl_2$) and VO_2 type together with the experimental one.
- Calculated frequencies and intensities for both rutile and $CaCl_2$ type structure correlate well with the experiment.
- Calculated IR spectrum for the ground states VO_2 type structure does not correlate with the measured spectrum.

PdO_2: HIGH PRESSURES



- Since the only known polymorph was obtained at high pressures, we have optimized the 10 lowest-E models under various **hydrostatic pressures up to 100 kb**.
- The plot shows relative energies of the models in function of pressure.
- Orthorhombic rutile ($CaCl_2$) becomes the ground state above 20 kb.
- The high-pressure calculations predict **formation of orthorhombic rutile** structural type under pressure.
- On the other hand, tetragonal rutile becomes even more unstable under pressure and remains also dynamically unstable.

PdO_2: SUMMARY

- We have modelled PdO_2 in 19 structural types observed for MO_2 oxides.
- All models are stable relative to Pd + O_2.
- 13 structures are stable in respect to well-known PdO.
- Tetragonal rutile (claimed in experiment) is only 10^{th} lowest in energy.
- All models accept tetragonal rutile are dynamically stable.
- The ground state structure at low pressure is VO_2 type structure and at high pressures orthorhombic rutile.
- Measured PdO_2 structure and IR spectrum could be interpreted based on orthorhombic variant of rutile.
- Overall we predict rich polymorphism for PdO_2 compound comparable to PtO_2.

ACKNOWLEDGEMENTS

- **The European Regional Development Fund**, Research and Innovation Operational Programme, for project No. ITMS2014+: 313011W085;

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- **The Slovak Research and Development Agency**, grant No. APVV-18-0168;

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Thank you for your attention ☺