# Xenon oxides under pressure

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# Xenon oxides

- Xenon is not very reactive at low pressures
- Xenon can be made to form metastable oxides at low pressures which readily decompose
- DFT study by Zhu, Jung, Oganov, Glass, Gatti and Lyakhov [Nature Chem 5, 61 (2013)] considered $XeO_2$, $XeO_3$ and $XeO_4$
- Zhu *et al.* predicted stable xenon oxides above 83 GPa with oxidation states of $+2$, $+4$, $+6$
- No experimental evidence for the formation of xenon oxides at high pressures has been reported

# Questions about xenon oxides

- What are the stable stoichiometries of Xe/O mixtures at high pressures?
- What are the stable structures of xenon oxides?
- What are the oxidation states of xenon atoms in the oxides?
- At what pressure do xenon oxides become thermodynamically stable?
- Metals or insulators?
- Role of Xe $4d$ electrons?

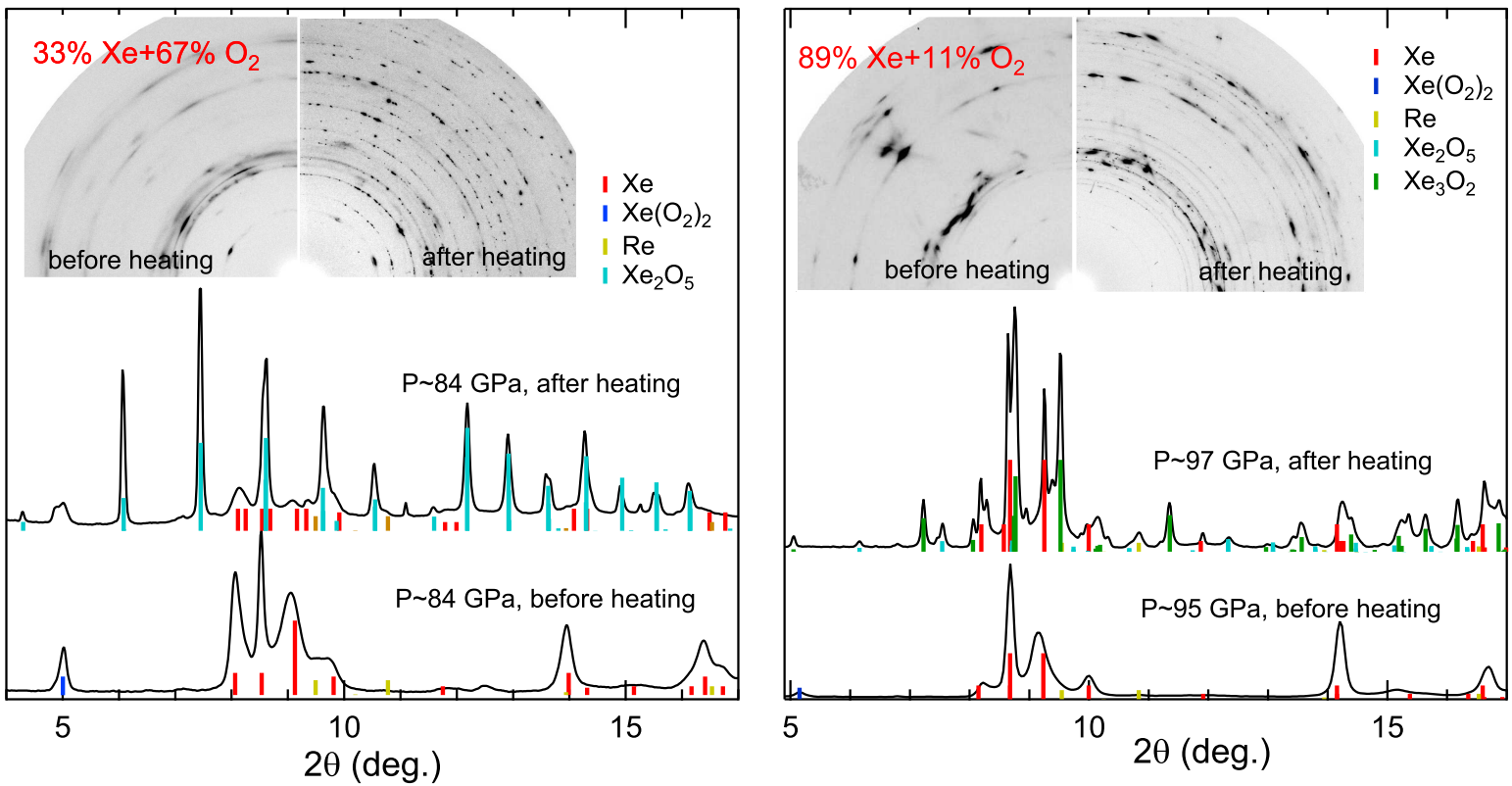
# Methodology

- Diamond anvil cell experiments at ESRF
- Use laser heating to try and synthesise equilibrium phases
- Characterise xenon oxides using X-ray diffraction (XRD), X-ray absorption, and Raman spectroscopy
- Use *Ab initio random structure searching* (AIRSS) within DFT to identify stable stoichiometries and structures

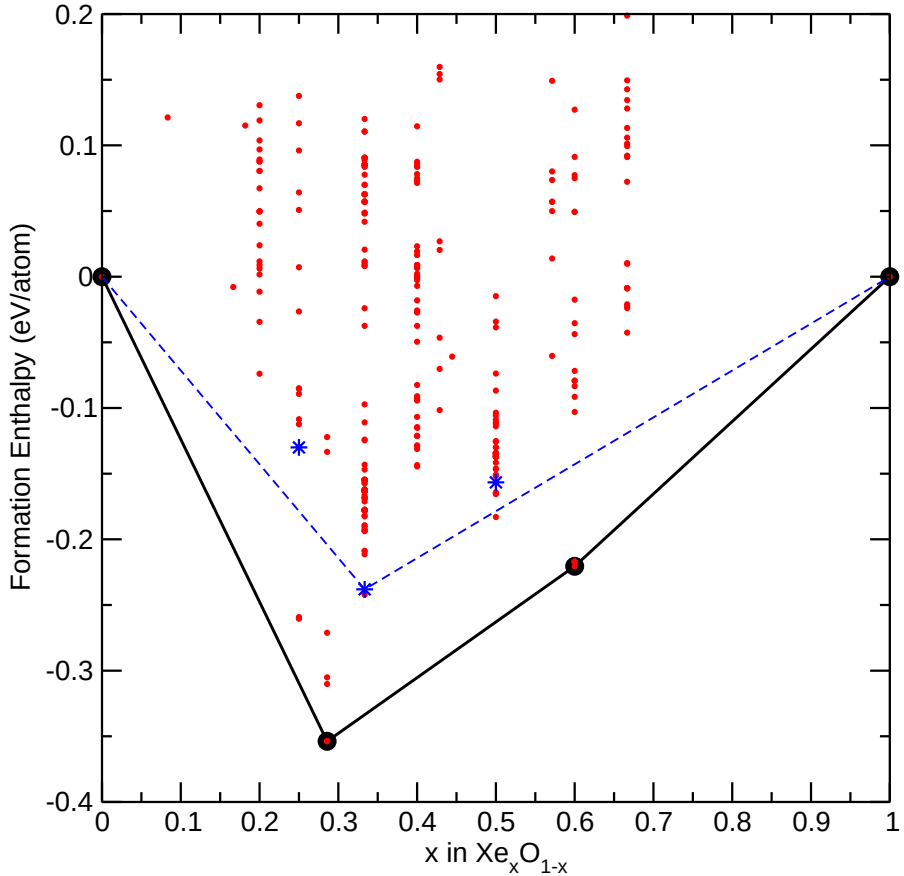
# The "missing xenon" paradox

- Chondrite: a stony meteorite unmodified by melting or differentiation of the parent body
- Xenon depletion of $>90\%$ in the Earth's atmosphere, compared with its abundance in chondritic meteorites
- Possible resolutions of the paradox include:
  Xe could have escaped into space
  Xe could be stored within Earth's mantle
  Xe could be stored within Earth's core
- Solving the paradox will require improved understanding of the high-pressure chemistry of xenon
- We have studied the stability of compounds of xenon with the most abundant element in the Earth's mantle, oxygen

# XRD data


33% Xe+67% O2
before heating
after heating
Xe
Xe(O2)2
Re
Xe2O5
P~84 GPa, after heating
P~84 GPa, before heating
5
10
15
2θ (deg.)
89% Xe+11% O2
before heating
after heating
Xe
Xe(O2)2
Re
Xe2O5
Xe3O2
P~97 GPa, after heating
P~95 GPa, before heating
5
10
15
2θ (deg.)

# Convex hull at 83 GPa




Structures on the convex hull are stable against decomposition

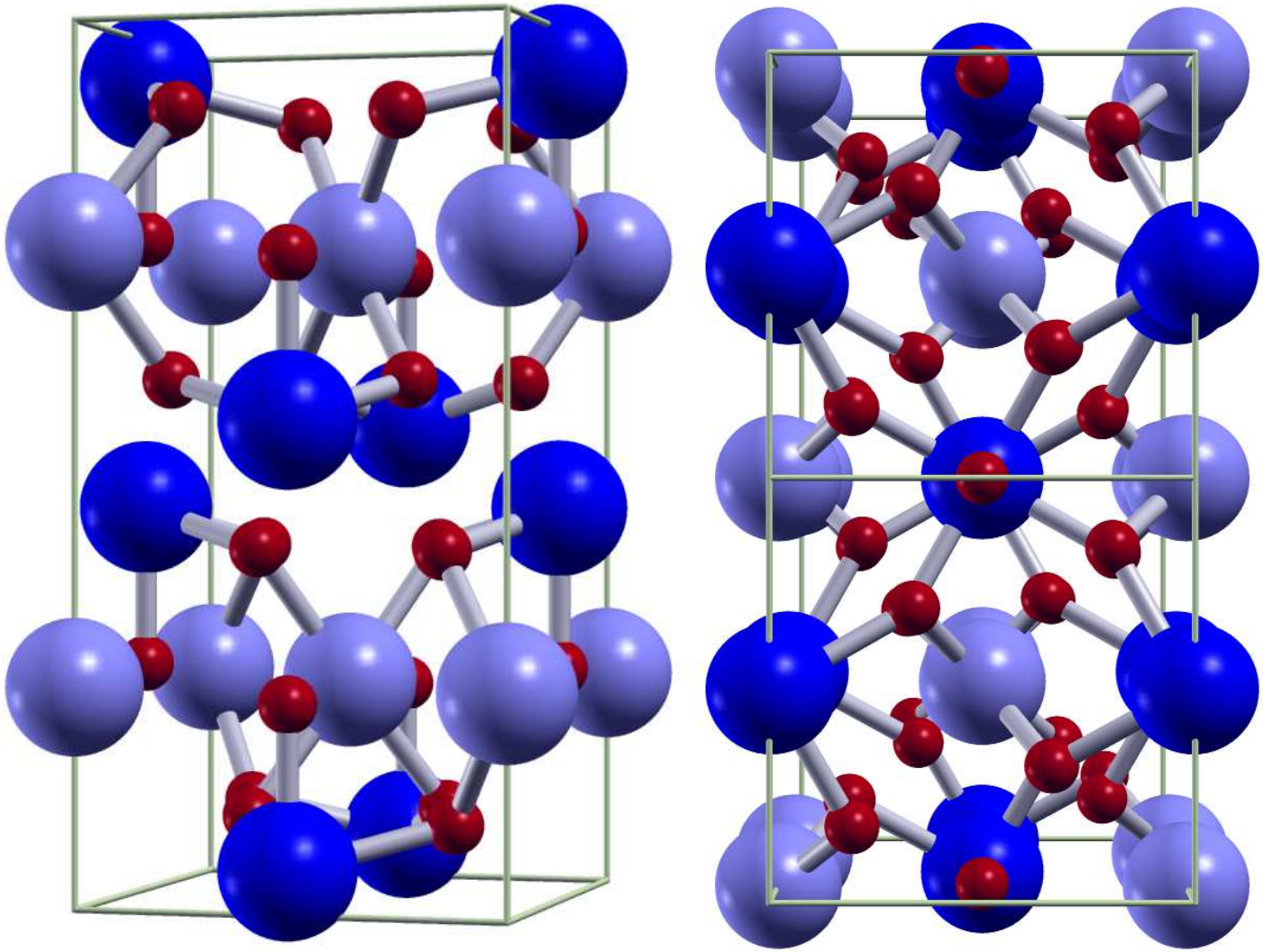
Structures above the convex hull are unstable to decomposition

Blue: Structures of Zhu *et al.* recalculated at high accuracy

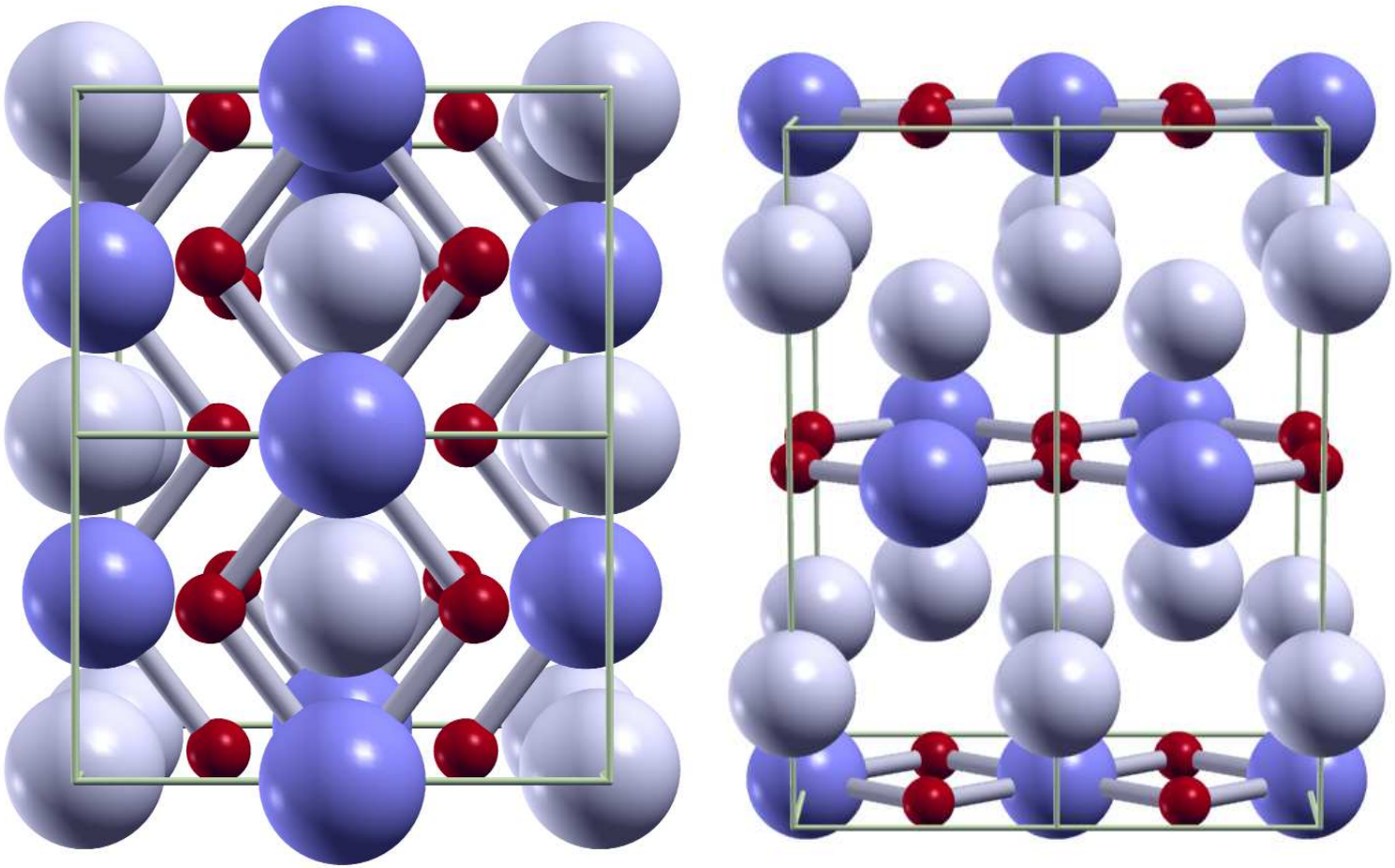
# Combining theory and experiment

- The $Xe_2O_5$ phase was discovered in XRD experiments and identified using AIRSS
- The $Xe_3O_2$ phase was predicted using AIRSS and subsequently verified by XRD experiments
- Fruitful "dialogue" between theory and experiment

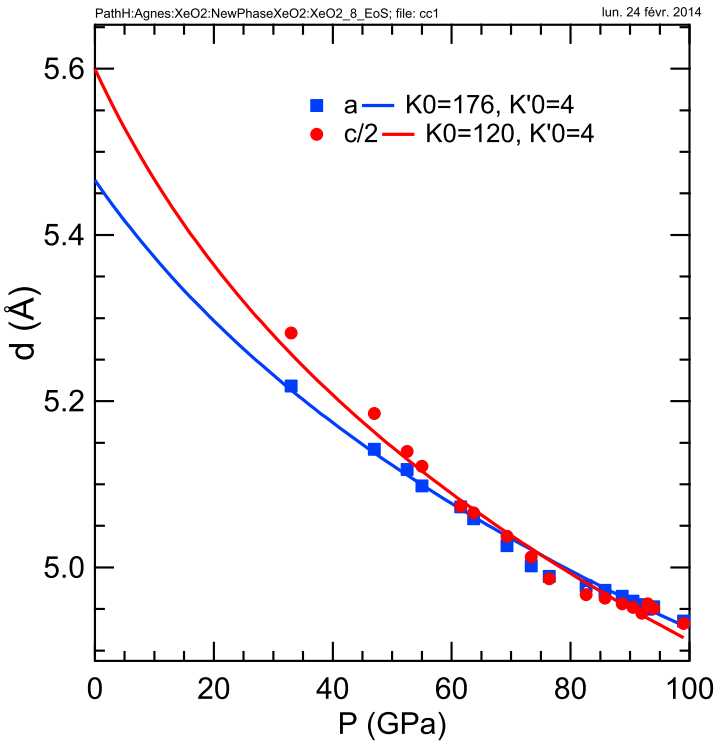
# Structure of $Xe_2O_5$ with $+4$ and $+6$ xenon atoms



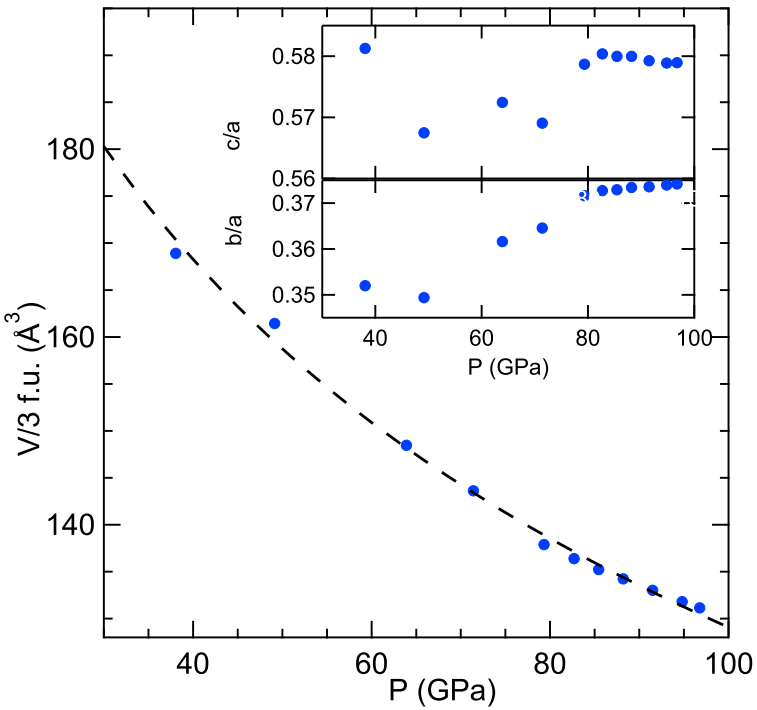
# Structure of $Xe_3O_2$ with 0 and $+4$ xenon atoms



# Cell parameters

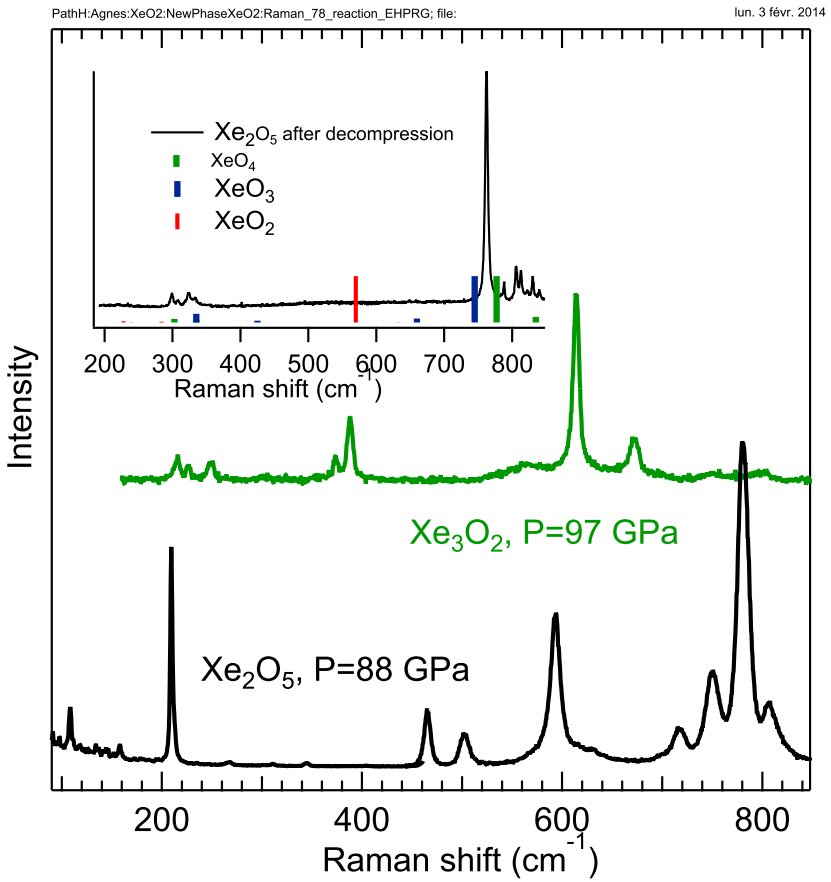



$Xe_2O_5$

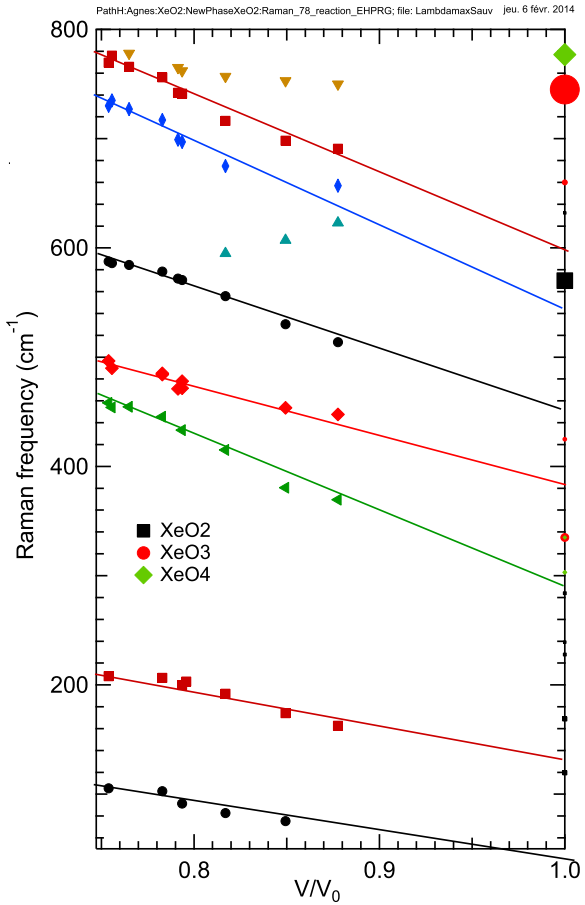



$Xe_3O_2$

# Raman Data

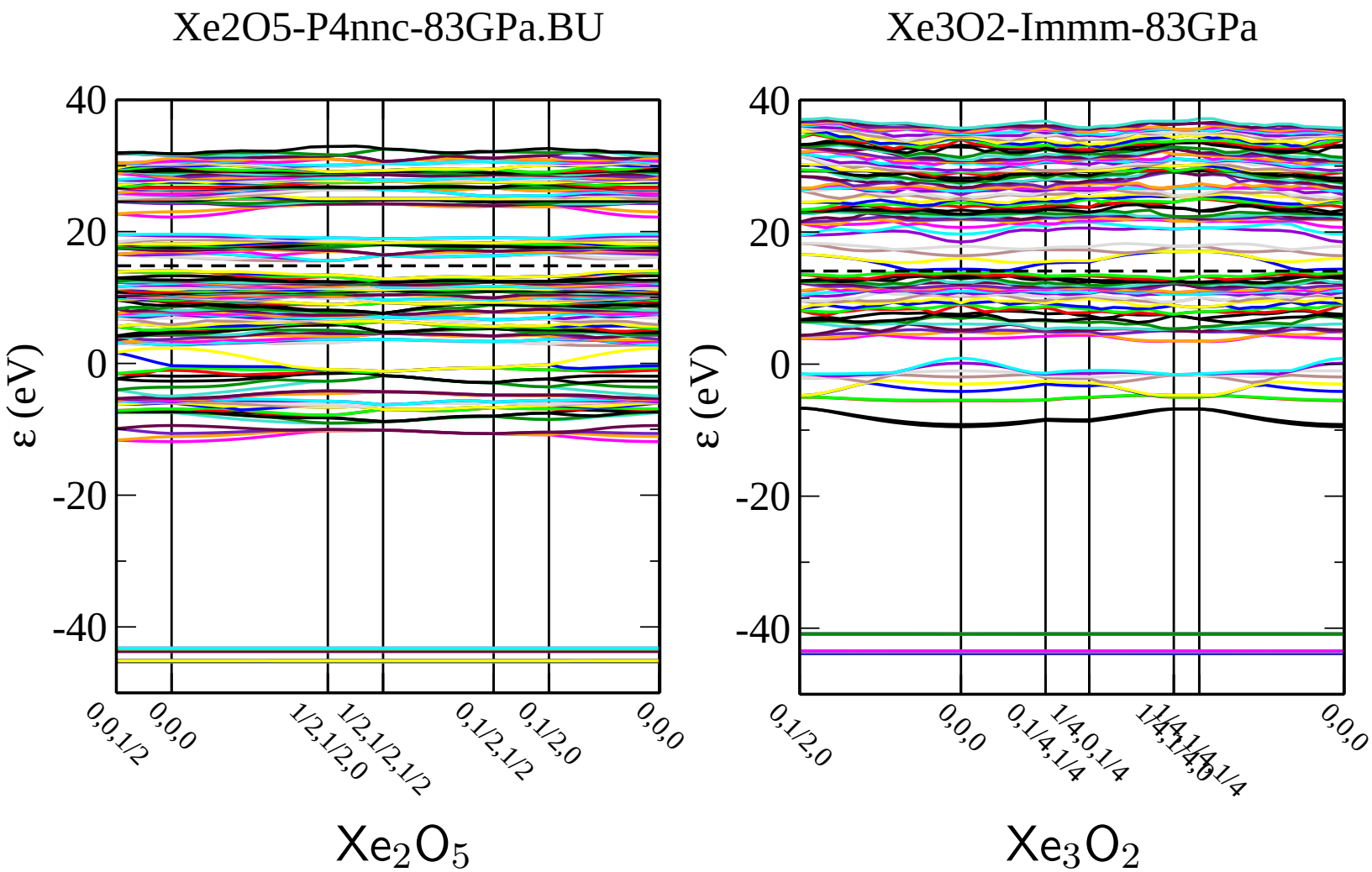



$Xe_2O_5$ and $Xe_3O_2$




$Xe_2O_5$

# Bandstructures of $Xe_2O_5$ and $Xe_3O_2$ at 83 GPa



# Influence of the Xe $4d$ electrons

- Xe $4d$ orbitals lie 45 eV below the HOMO and 30 eV below the bottom of the $sp$ bands
- Surely they contribute very little to the bonding and they can be replaced by the pseudopotential?

# Influence of the Xe $4d$ electrons

- The Xe $4d$ orbitals have a strong influence on the energies of structures
- Surely they contribute very little to the bonding and they can be replaced by the pseudopotential?

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