DE LA RECHERCHE À L'INDUSTRIE

First-Principles LDA+U Modeling of Paramagnetic UO_2 and (U,Pu) Mixed Oxides

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Introduction

- Uranium dioxide UO_2: most widely used nuclear fuel worldwide

- Since the late 90's: first-principles modeling of UO_2 behavior under irradiation
  - DFT (LDA, GGA) – DFT+U – Hybrid functionals – Self Interaction Correction
  - Point defect formation energies
  - Fission product incorporation energies
  - Migration mechanisms and associated activation energies
  - Direct comparison with experiments made possible

- What is MOX?
  - Reference fuel for most 4th generation reactor concepts
  - Uranium Plutonium mixed oxides $(U_{1-y}Pu_y)O_{2\pm x}$, $0.05 \leq y \leq 0.30$
  - Blending of UO_2 and PuO_2 powders

- Goal: study MOX behavior under irradiation

MOX Behavior: Difficulties

- MOX studies not as comprehensive as those of UO_2

- Experimentally:
  - Difficult
  - Expensive

  } Precautions for handling plutonium-based materials
  - Most of experimental studies: thermodynamics and structural characterizations
  - Electronic structure, magnetism, mechanical properties? Scarce

- Theoretically:
  - Important difficulties associated to
    - $(U,Pu)O_2$ solid solution: random positions of plutonium atoms (alloy problem)
    - Strong electron correlations: beyond DFT is required
    - Beyond DFT: metastable states
  - Method validation is made difficult

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MOX Modeling: Methods

- Electronic structure calculations using ABINIT

- Random positions of plutonium atoms: special quasi-random structures (SQS)
  - Supercells that mimic spatial correlation functions of the random alloy
  - 24 atoms
  - MOX 13%: $U_7Pu_1O_{16}$
  - MOX 25%: $U_6Pu_2O_{16}$

- Strong electron correlations: LDA+U approximation

- Metastable states: occupation matrix control (OMC)
  - Occupation matrices (OM's): represent how correlated electrons occupy 5*f* orbitals
  - Ground state (GS) of perfect UO_2 and PuO_2: extract U and Pu GS OM's
  - GS OM's used as input OM's for MOX calculations
  - MOX: local environment of U and Pu different than in UO_2 and PuO_2

SQS+OMC: Validation

- How to validate the SQS+OMC method?
  - Main problem: metastable states
  - Validation of OMC for SQS with no symmetries + both U and Pu
  - Experience on UO_2: no proper treatment = large discrepancies
  - No experimental data on MOX electronic structure, magnetism, mechanical properties, etc.

- Idea: validation on paramagnetic UO_2
  - UO_2 above 30K: Curie-Weiss paramagnetism
  - Disordered local moment approach: random distribution of spin ↑ and spin ↓
  - Modeling paramagnetic UO_2 = modeling alloy $(U^{\uparrow}_{0.5}U^{\downarrow}_{0.5})O_2$
  - Same difficulties as MOX: random distribution (of spins) and metastable states
  - Contrary to MOX, paramagnetic UO_2 well known experimentally

Paramagnetic UO_2

Magnetism	AFM	FM	PM	EXP.
$E-E_{MIN}$ (meV/atom)	1.8	9.5	0.0	
Cell parameters (Å)	5.414	5.418	5.415	5.473
Band-gap (eV)	2.3	1.3	2.4	2.1
Bulk modulus (GPa)	222	227	212	207
C_{11} (GPa)	401	409	385	389
C_{12} (GPa)	132	136	125	119
C_{44} (GPa)	94	96	68	60
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- Significant differences between AFM/FM and PM order (~30% for C_{44})
- Excellent agreement with experimental data and DMFT-HIA

Paramagnetic MOX 13% Pu

Magnetism	AFM		FM		PM	
$E-E_{MIN}$ (meV/atom)	1.7	1.8	0.0	9.5	3.2	0.0
Cell parameters (Å)	5.410	5.414	5.410	5.418	5.405	5.415
Band-gap (eV)	1.6	2.3	1.1	1.3	1.5	2.4
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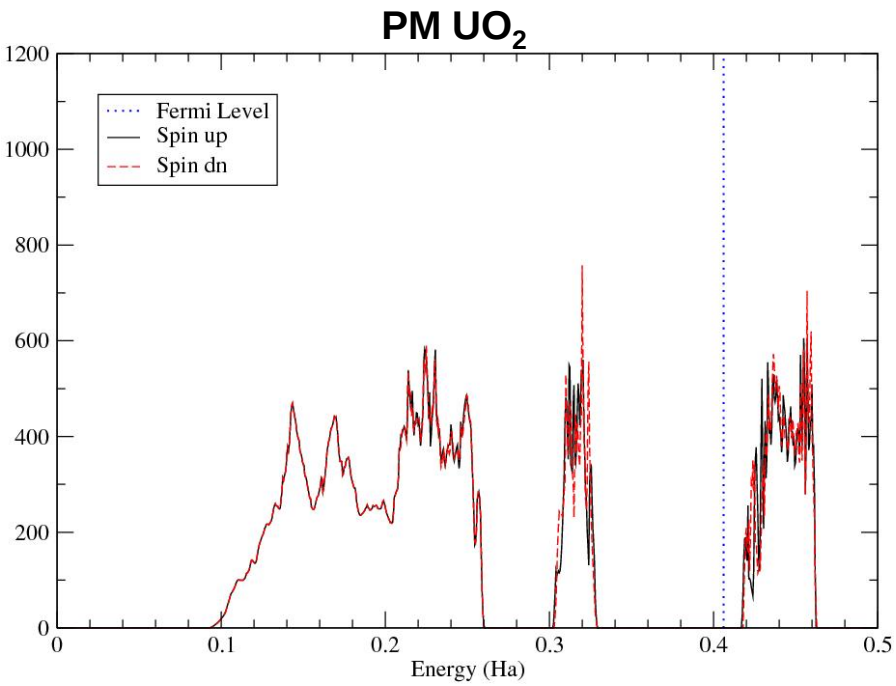
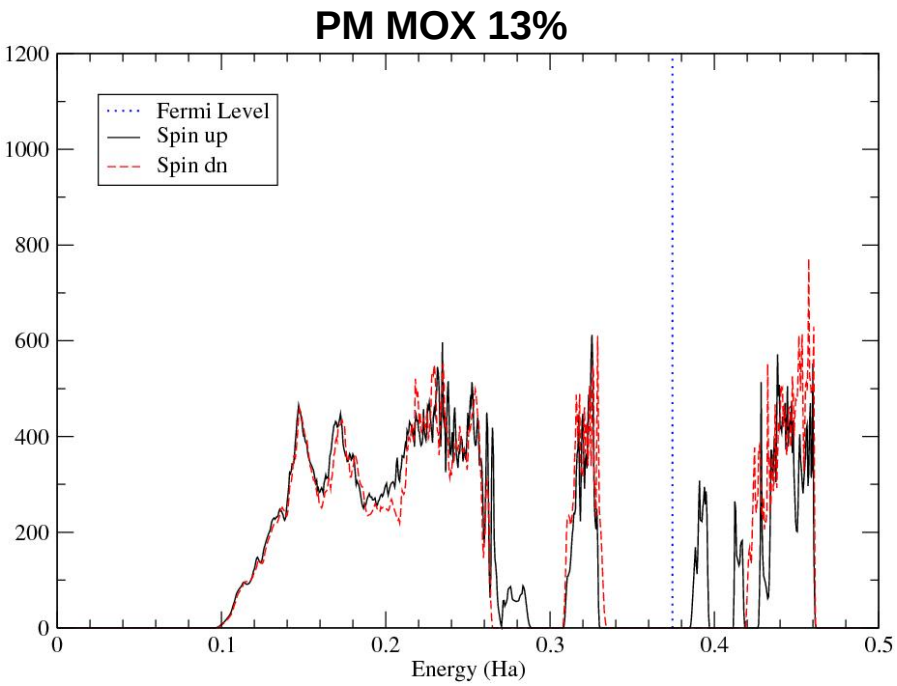
- Mechanical properties not sensitive to AFM or FM order
- Significant differences between AFM/FM and PM order
- Compared to UO_2, addition of 13% Pu impacts GS properties

Paramagnetic MOX 13% Pu





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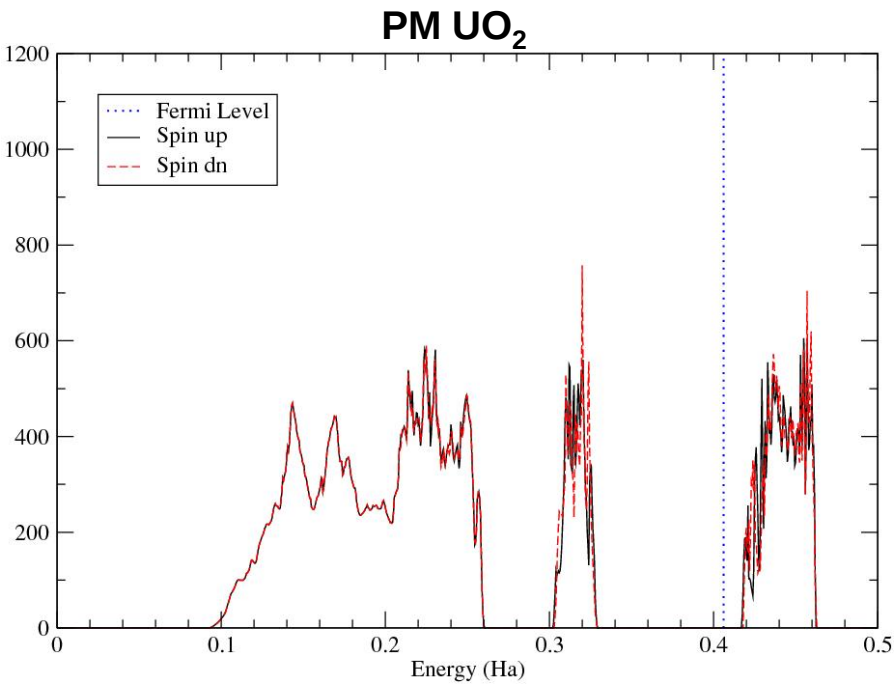

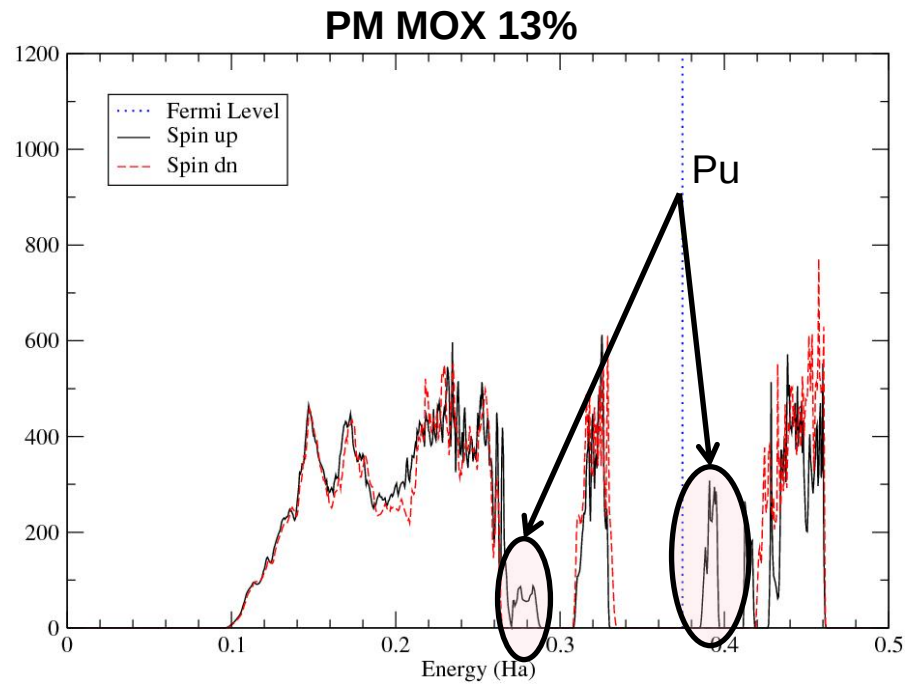

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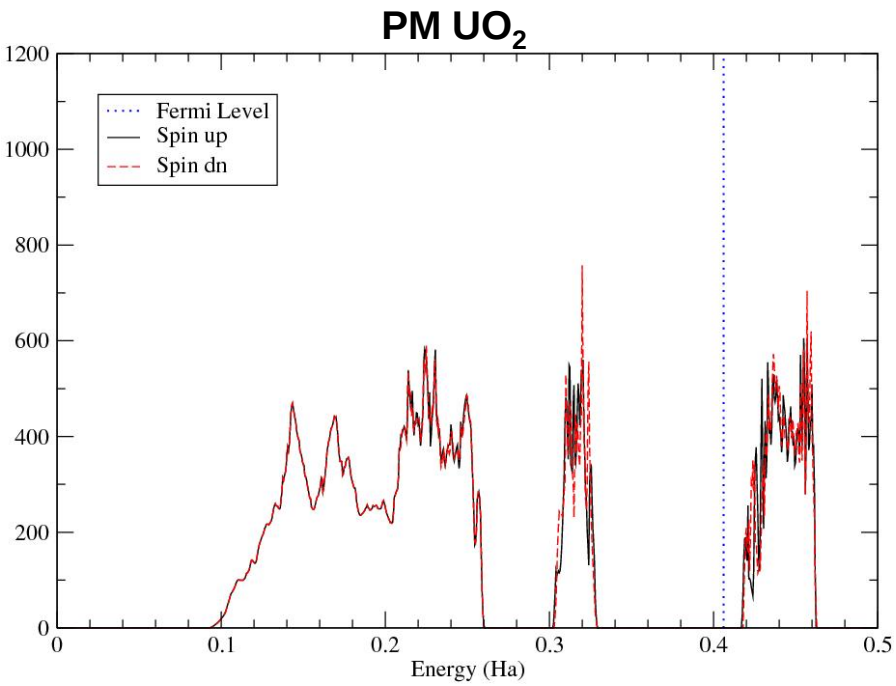

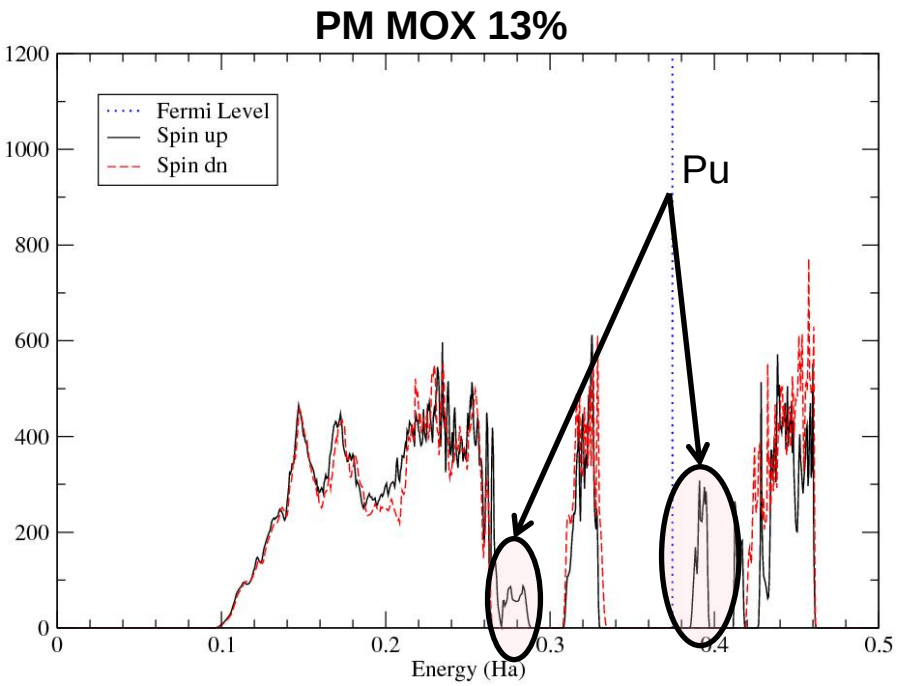

- Additional Pu levels above E_F: band-gap decreased
- Further increase in Pu content (MOX 25%): no significant change in GS properties

Conclusion

- SQS+OMC:
  - SQS for random distribution of spins and of Pu atoms
  - OMC for metastable states inherent to DFT+U
- Paramagnetic UO_2:
  - Found more stable than AFM and FM UO_2
  - GS properties in excellent agreement with experiments and DMFT-HIA
  - PM order: significantly impacts GS properties, compared to AFM and FM orders
  - Validation of SQS+OMC
- Paramagnetic MOX 13% and 25%
  - Additional Pu levels above Fermi level: band gap significantly decreased
  - GS properties are affected by 13% Pu (overall increase in mechanical properties)
  - Increasing Pu content has no significant impact on GS properties (below 30%)
- FM MOX found more stable than AFM and PM MOX
  - Initial electronic structure for Pu: PuO_2 is assumed AFM
  - PuO_2 experimentally non magnetic