DFT+U COMPUTATIONS OF STRONGLY-CORRELATED SYSTEMS: THE CASE OF PuO_2

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Context

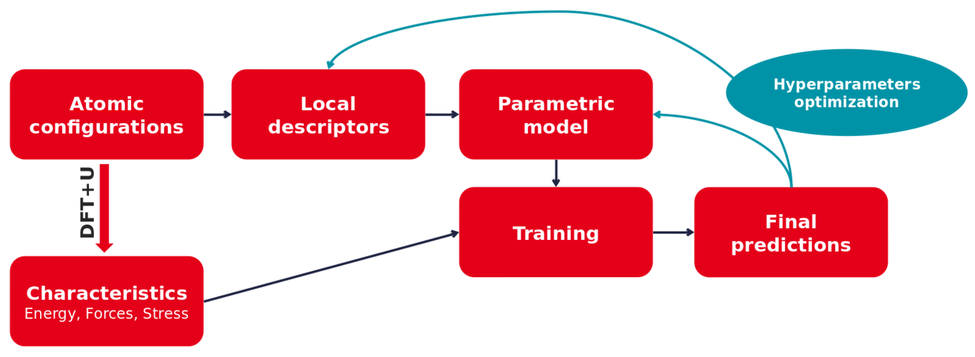
- Mixed oxides (MOX), such as $(U_{1\text{-}x},Pu_x)O_2$, play a key role in the production of nuclear energy. Recycling loop: 10% of France national electricity production, using spent nuclear fuel
- CEA codes modeling fuel behavior in production

ALCYONE (PWR - Pressurized Water Reactor)
GERMINAL (SFR - Sodium-cooled Fast Reactor)

Aim

- Need to improve current models to obtain larger safety margins
- Generate a Machine Learning Interatomic Potential (MLIP)

Accurate: based on DFT
Fast: classic MD
Portable: tailored database



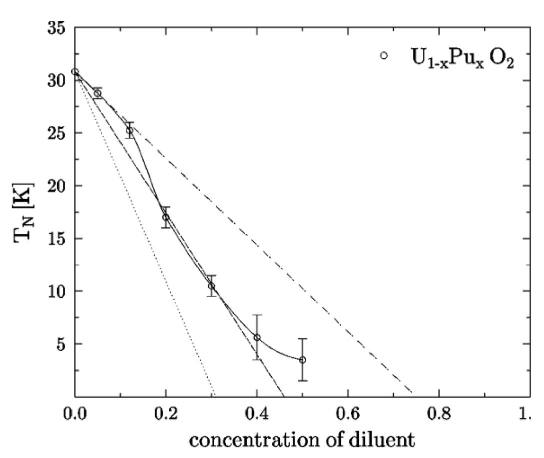
- Eliott Dubois' PhD work: MLIP for UO_2 [3] → **Transfer to PuO_2**

Experiments vs. DFT predictions

Difficulties

Doubts about PuO_2 ground state magnetic phase

- Apparent diamagnetic state at 4K [4], but large temperature-dependent magnetic susceptibility may indicate AFM structure, as seen in $Th_{1\text{-}x}Pu_xO_2$ [5] and $U_{1\text{-}x}Pu_xO_2$ [6]
- Small Néel's temperature (transition to paramagnetism) [6]



Néel temperatures as a function of Pu content (figure from [6])

<5K for $(U_{0.5},Pu_{0.5})O_2$

Difficult to obtain experimental results because of **radioactive decay**, and **inhomogeneity** of the samples

DFT setup

- **PBEsol** xc functional
- Hubbard corrections: **DFT+U**
  (U,J)=(6,0) eV: **match** band gap and lattice parameter [1]
- Noncollinear magnetism + Spin Orbit Coupling (SOC)
- No Occupation Matrix Procedure (OMC) [2]
  Hope SOC is enough to prevent metastability in the electronic landscape…

PBEsol+U+SOC+3k

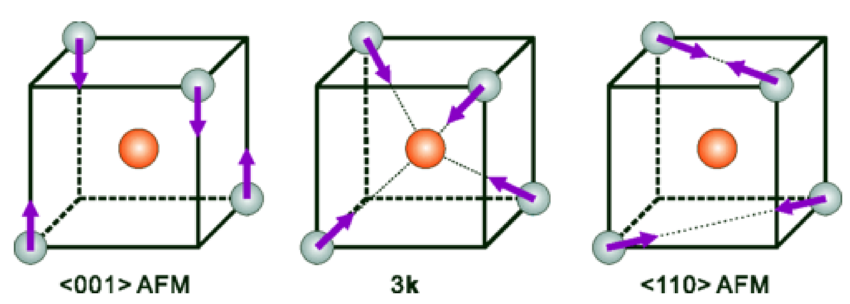
FCC [Fm$\bar{3}$m (225) space group] AFM 3k stable phase [1]
→ Same as in UO_2, about 1eV/F.U. difference with diamagnetic structure

Computational details

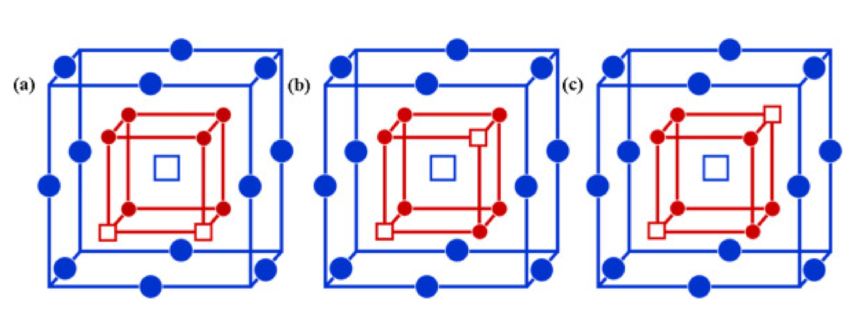
Pu ($5f^5 6s^2 6p^6 6d^1 7s^2$) ; O ($1s^2 2s^2 2p^2$)
Liechtenstein scheme, E_{cut}= 600eV, $2^3/4^3$ k-points
AFM 3k initial magnetic state with $4\mu_B$ per Pu atom

	ABINIT	VASP
Version	10.0.9	6.4.3
Convergence	TOLVRS=10^{-1}	DIFFE=10^{-4}

Benchmark on $(U,Pu)O_2$ system
ABINIT: 1500h CPUs — 560 MPI/no OMP
VASP: 157h CPUs for DIFFE=3×10^{-5} — 112 MPI/no OMP



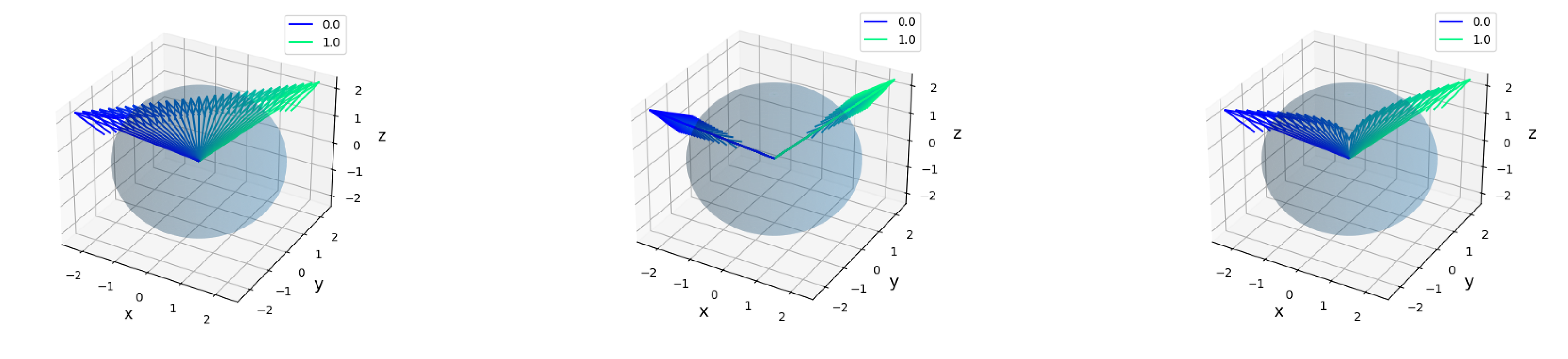
Dudarev *et al*, Parametrization of LSDA+U for noncollinear magnetic configurations: Multipolar magnetism in UO_2. *Phys.Rev.Mater., 2019*



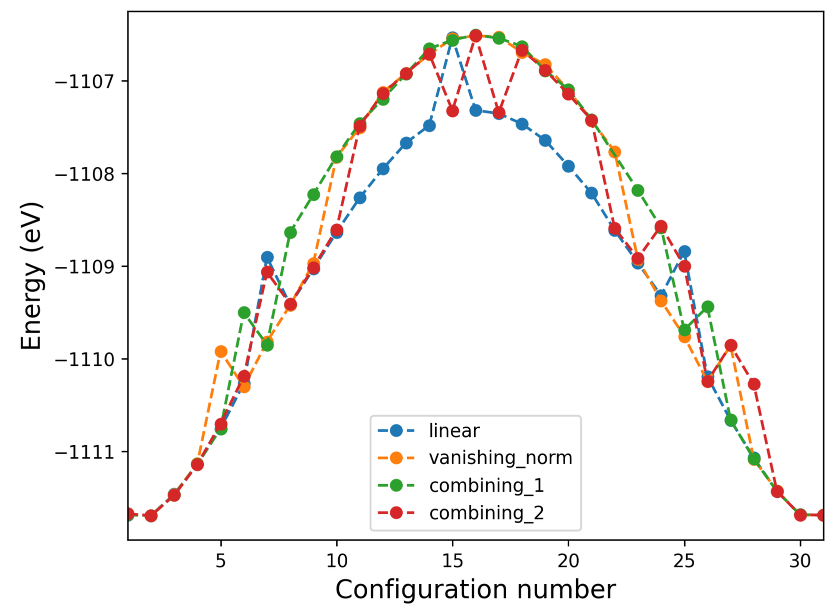
Bounded Schottky Defects of types 1/2/3
Singh *et al.* A first principles investigation of defect energetics and diffusion in actinide dioxides. *Journal of Nuclear Materials, 2024*

BSD3 defect NEB

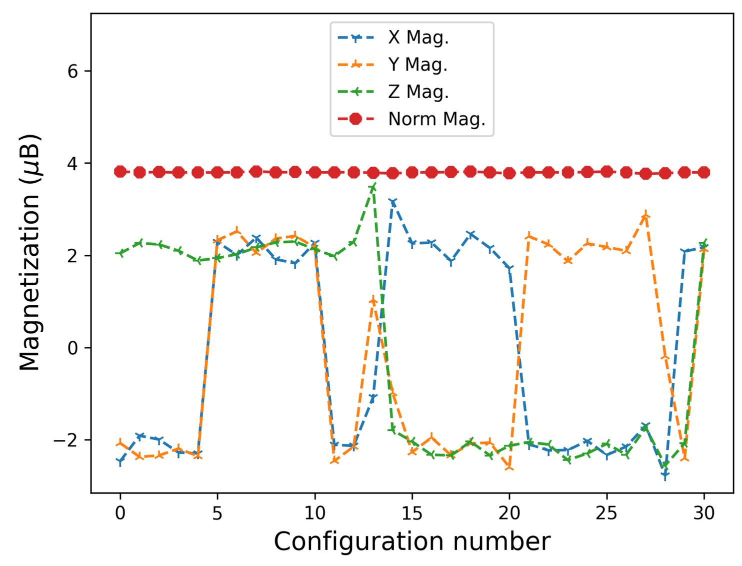
Predict the impact of **defect migrations**: diffusion path of one Pu atom between stable fcc sites (magnetism change between --+ and +++)



Linear — Vanishing norm — Combining the two

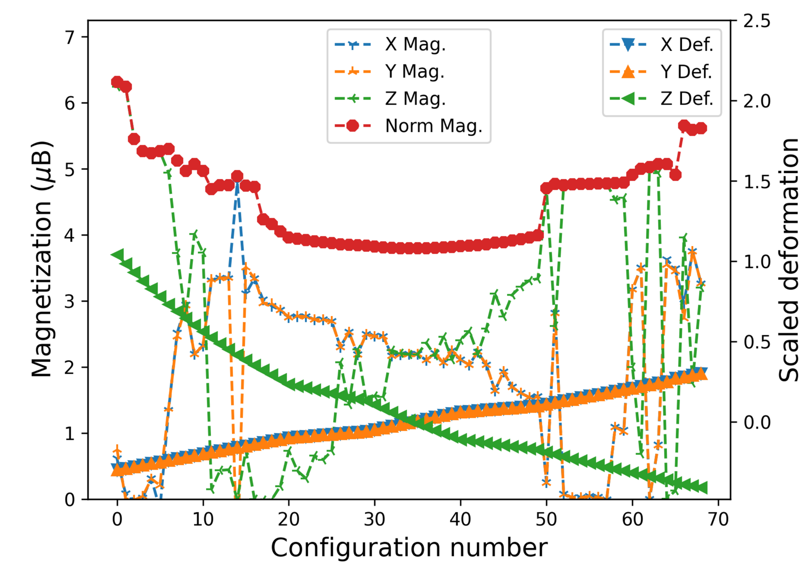


Metastability between diamagnetic and AFM 3k paths

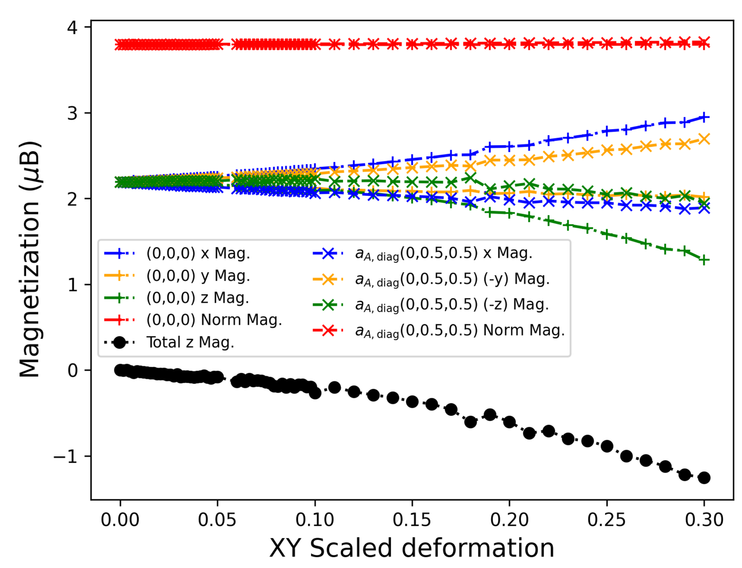


Stable magnetic norm but various magnetic configurations

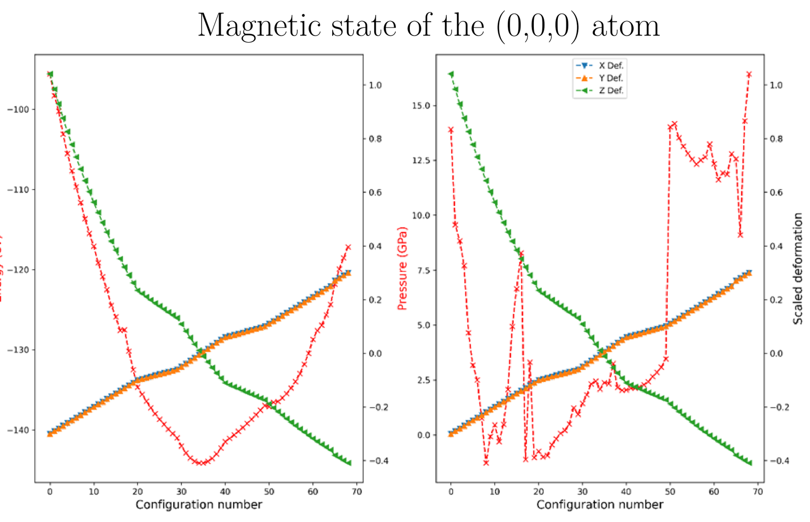
Elasticity



Magnetic state of the (0,0,0) atom

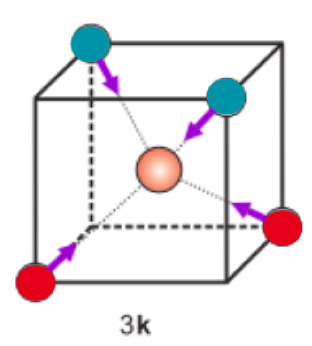


Spontaneous magnetization

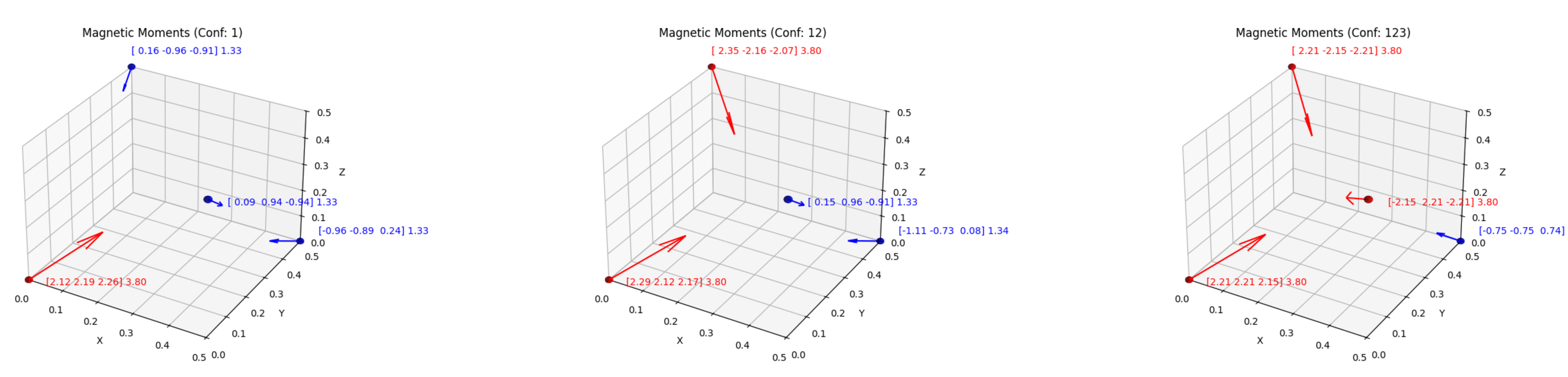


Jump of observable values matching magnetic transitions

Coupling of magnetic components between blue and red Pu pairs



(U,Pu)O₂ systems



3k for **Pu**, **2k** for **U** or **3k** with small magnetic norm

Conclusion and perspectives

- Lack of experimental data
- DFT setup is complex and computations are costly, convergence is difficult
- Magnetic state changes with deformations: need to extract homogeneous data for the MLIP training

Mixed oxydes are even harder

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[1] Pegg, *et al.* Hidden magnetic order in plutonium dioxide nuclear fuel, *Phys. Chem. Chem. Phys., 2018*

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[3] Dubois, Utilisation des méthodes de machine learning pour la description des oxydes mixtes à l'échelle atomique, *Aix-Marseille Université, 2024*

[4] Raphael and Lallement, Susceptibilité magnétique de PuO_2, *Solid State Communications*

[5] Candela *et al.* Magnetic susceptibilities of uranium (IV) and plutonium (IV) ions in cubic fields, *The Journal of Chemical Physics, 1959*

[6] Kolberg *et al.* Magnetic susceptibility and spin-lattice interactions in $U_{1-x}Pu_xO_2$ single crystals, *Phys. Rev. B, 2002*

[7] Dudarev *et al.* Parametrization of LSDA + U for noncollinear magnetic configurations: Multipolar magnetism in UO_2, *Phys. Rev. Mater., 2019*

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