Density Functional Theory for fission products transport in UO₂

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Context & objectives

- Define fission products behaviour in nuclear UO₂ fuel on the basis of analysis of electronic structure calculations to characterize the nature of chemical bonding for understanding origin of binding strength to interpret incorporation and migration energies values calculated for Fission Products (FPs), from orbitals consideration, charge transfer, distribution of surrounding oxygen atoms and crystal field effects.

Objectives:

- To assess FP behaviour in order to determine preferential diffusion mechanisms principally for stoichiometry and over-stoichiometry where oxygen clustering is dominant.
- Being able to provide semi-empirical potentials for Molecular Dynamics deduced from specificities of chemical bonding obtained from ab-initio calculations.

Introductive considerations

- Previous results:
  - Stabilisation of excess oxygen interstitials by formation of oxygen clustering in quadri-interstitial and cuboctahedron geometry was demonstrated in over-stoichiometry.
  - Uranium atom diffusion at over-stoichiometry is activated by the presence of oxygen interstitials clusters that stabilize uranium in saddle point position.

- Ab-initio calculations are performed on
  - A 144 atoms size supercell is required to treat large clustering defects.
  - Using the pseudo-potentials method (PAW) in GGA-U approximation.
  - No Hubbard potential was used for fission products.

Uranium bonding characterization in oxide

- Characteristics of Density of States curves in Uranium-oxygen bonding:
  - Characteristics peaks of Sigma and n type bonding between s, p, d and f orbitals of uranium with s and p orbitals of oxygen (hybridization) in valence bands.
  - Intense peak of localized non-bonding orbitals at the Fermi level corresponding to no overlapping f uranium occupied-orbitals.

- Electrons depletion for the basis of orbitals toward the corner of the cube, i.e. 2sg/2p=2 by which charge transfer occurs.
- Charge increasing for the basis of orbitals toward the face of the cube, i.e. 2sg m=3, m=2 and 1sg/m=1, m=0

Modification of oxygen atoms distribution

- Two cases are explored in regards of the DOS:
  - For Uranium in Schottky defect, DOS suggests:
    - Occupation of non-bonding localised upper orbitals corresponding to some d and f uranium directional lobes pointing in direction of oxygen vacancies.
    - A lowest charge transfer between uranium and oxygen orbitals due to lower overlapping between orbitals confirmed by Bader charge calculation for perfect crystal (+2.56 e) and in Schottky configuration (+1.86 e).
  - For uranium in quadri-interstitial, DOS suggests:
    - Oxygen interstitial atoms when placed in direction of lobes of f and d uranium orbitals of initially non-bonding orbitals of perfect fluorde structure have for effect to create sigma bond that stabilises structure. The more orbitals overlapping, the more charge transfers (+2.56 e) in perfect crystal against +2.86 e in quadri) which makes localized states to disappear.

About behavior of incorporated fission products

- Investigation of fission products DOS for Schottky and quadri-interstitial defects:

  - Caesium, Barium and Neodymium:
    - No localized states whatever the defect type.
    - Very low modification of the Bader charge: Charge transfer is unaffected by the distribution of surrounding oxygen atoms.

  - Uranium, Zirconium and Molybdenum:
    - Localized orbitals from at least one defect type.
    - Variation of the Bader charge in function of oxygen distribution and oxygen number surrounding PF atom (variable charge).

Migration energies

- Incorporation energy increases linearly with charge transfer except when crystal field is dominant.

- Crystal field generated by oxygen ligands on occupied d orbitals of molybdenum atoms induces repulsive effects which increase incorporation energy.

- Lowest impact of crystal field on uranium orbitals due to the lowest radial extent of f wavefunctions.

Conclusions

- Localised states at Fermi level in the DOS for element with d and/or f type orbitals are at the origin of the difference in energy observed both between incorporation energies of defects studied, but also between initial and saddle point along FP diffusion path.

- Oxygen atoms in excess in interstitial position aim at suppress localised states at the benefit of sigma type bonding, having for effect to stabilise binding energy.

- For s spherical orbitals case, no significant impact on the role played by oxygen interstitials is highlighted from DFT calculations due to systematic hybridization of s orbitals with oxygen surrounding atoms, preventing thus formation of localised states.