Institute of Applied Physics and Computational Mathematics

Theoretical investigation of the intrinsic oxygen defects in UO_2 (111) and PuO_2 (111) surfaces

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Speaker: Wenting Lv Time: 2023.06.01

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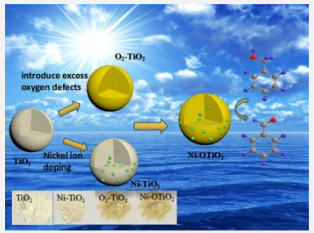
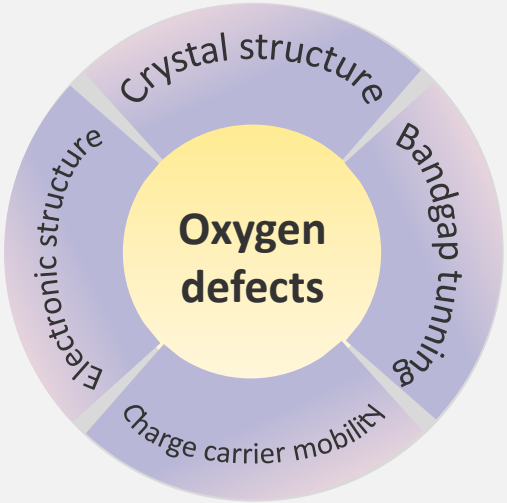
01 Introduction

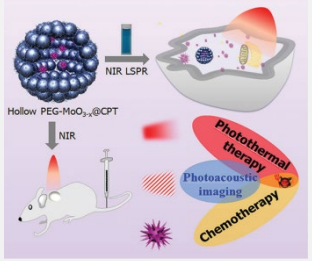
Introduction



Photocatalysis

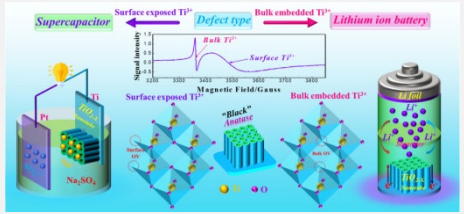
H. She, et al. ACS Sustainable Chem. Eng. 2018





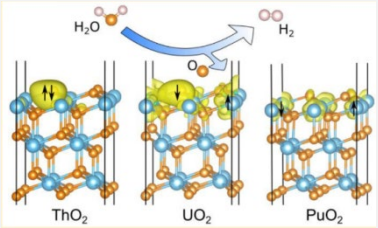
Biomedical application

G. Wang, et al. J. Phys. Chem. C. 2019



Electrocatalysis

J. Chen, et al. J. Energy Chem. 2021

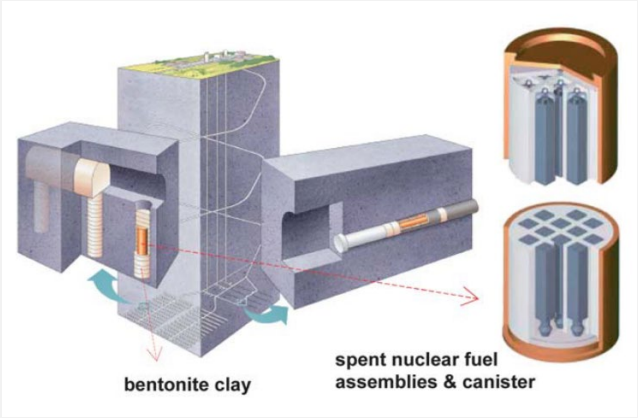


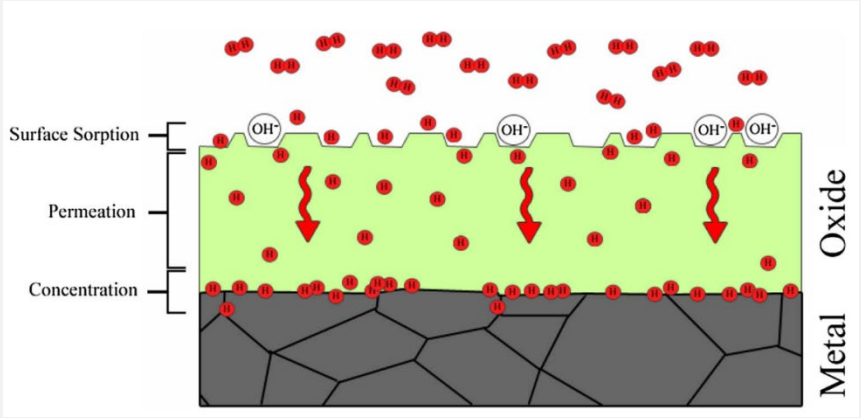
Surface chemistry and corrosion of AnO_2

G. Wang, et al. J. Phys. Chem. C. 2019

Introduction

AnO_2 (An = U, Pu)





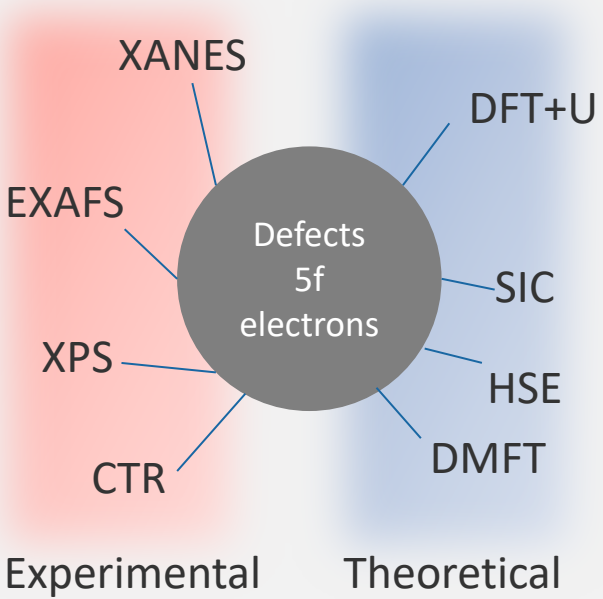
Nuclear fuel

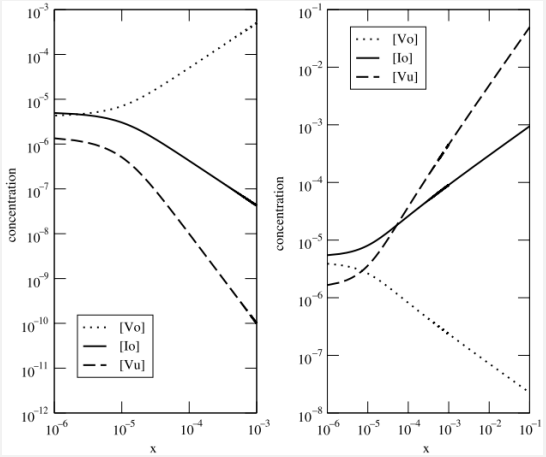
Long-term disposal of the spent fuel

Corrosion of uranium

Passive layer

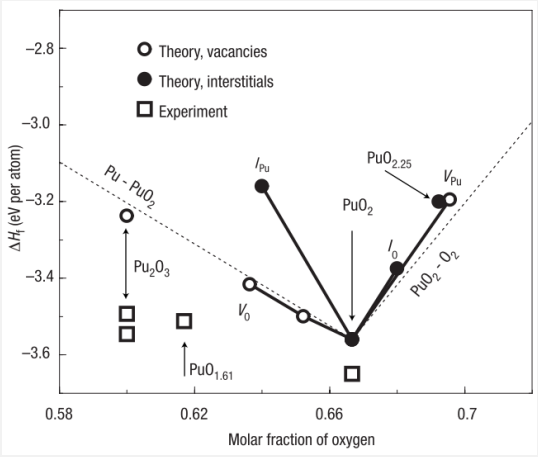
Introduction





UO_{2-x} UO_{2+x}

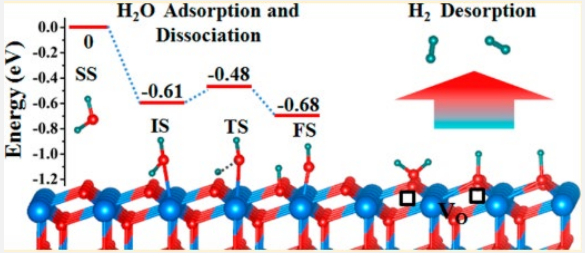
M. Fress, et al. J. Nucl. Mater. 2005

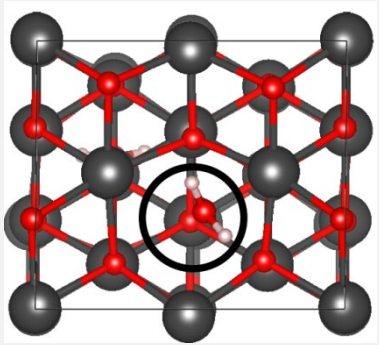


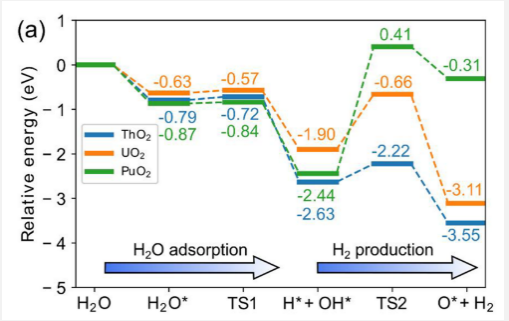
$PuO_{2\pm x}$

P.A. Korzhavyi, et al. Nat. Mater. 2004

Introduction



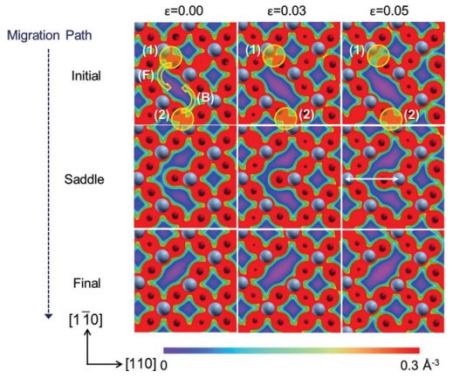




Layer	UO_2	PuO_2	UO_2	PuO_2	UO_2	PuO_2	UO_2	PuO_2	CeO_2
1st	5.92	3.63	6.45	3.35	5.95	2.49	5.21	2.81	1.84
2nd	5.93	3.93	6.14	3.40	6.08	2.54	4.98	2.43	1.76

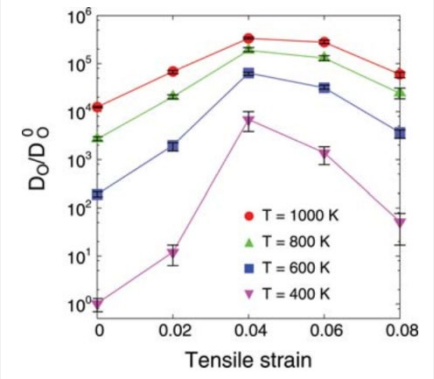
T. Bo, et al. J. Phys. Chem. C 2014 J.P.W. Wellington, et al. J. Phys. Chem. C 2018 G. Wang, et al. J. Phys. Chem. C. 2019 J. Paier, et al. Chem. Rev. 2013

Introduction



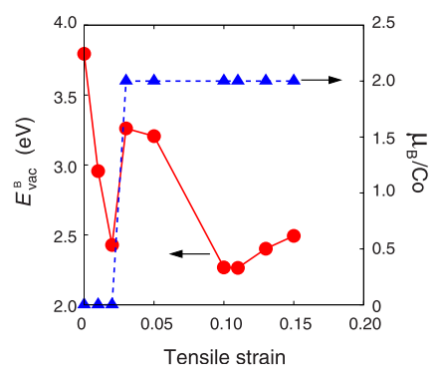
Electric charge density

J. Han, et al. J. Mater. Chem. 2011



oxygen diffusivity

A. Kushima, et al. J. Mater. Chem. 2011



Vacancy formation

A. Kushima, et al. Phys. Rev. B, 2011

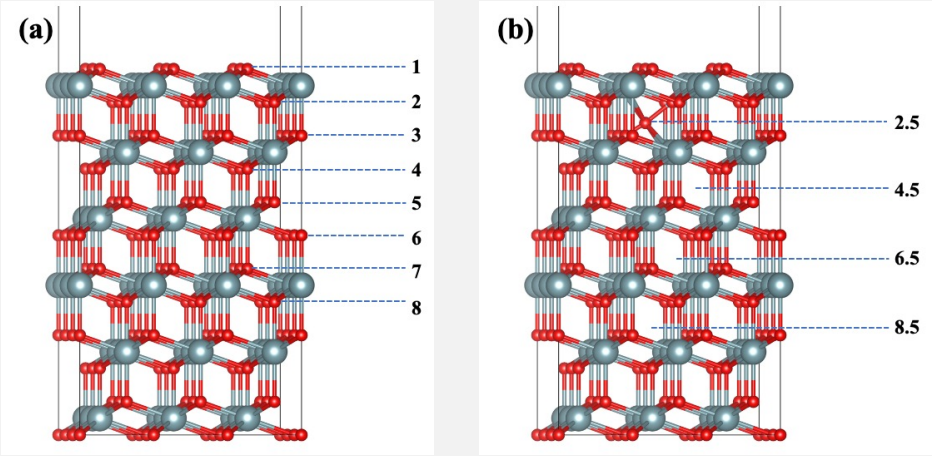
02 Methodology

Methodology

DFT+*U*

U: U = 4.5 eV, J = 0.5 eV

Pu: U = 4.75 eV, J = 0.75 eV



O_v O_i

O_v: Oxygen vacancy O_i: Oxygen interstitial

Larger number means deeper depth from the top surface

Methodology

Thermodynamics

$$E_{Vo}^{f} = E_{slab}^{Vo} - E_{slab}^{ideal} + \mu_O(T,p) + qE_f$$

$$E_{Io}^{f} = E_{slab}^{Io} - E_{slab}^{ideal} - \mu_O(T,p) + qE_f$$

$$\mu_O(T,p) = \mu_O(T,p_0) + \left({}^{1}/_{2}\right)k_B T ln\left({}^{p}/_{p_0}\right)$$

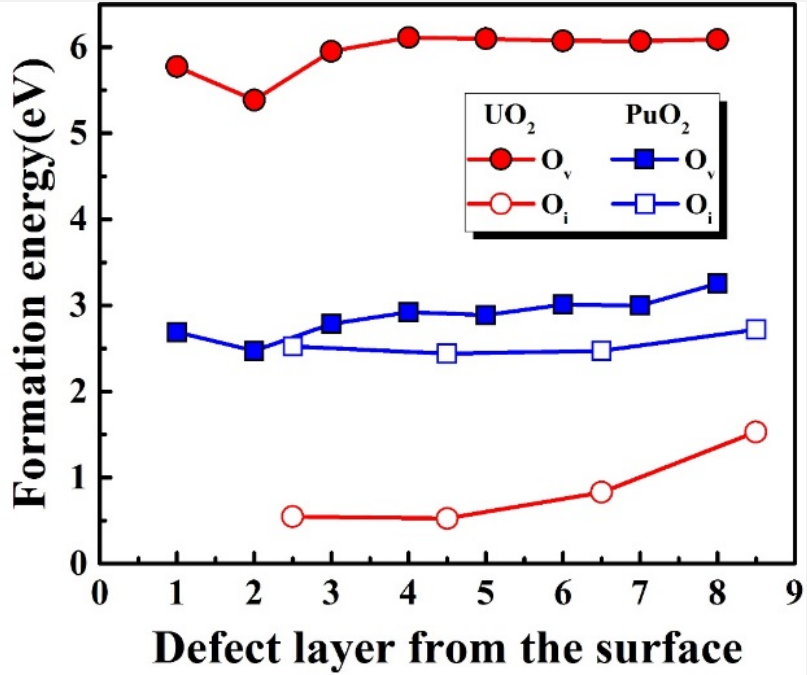
$$\mu_O(T,p_0) = \mu_O(0\ K,p_0) + \left({}^{1}/_{2}\right)\Delta G(T,p_0,O_2)$$

$$\mu_O(T,p_0) = \left({}^{1}/_{2}\right)[H(T,p_0,O_2) - H(0\ K,p_0,O_2)] - \left({}^{1}/_{2}\right)T[S(T,p_0,O_2) - S(0\ K,p_0,O_2)]$$

T(K)	μ_O(eV)	T(K)	μ_O(eV)
298.15	-0.272	900	-0.974
300	-0.274	1000	-1.010
400	-0.383	1100	-1.227
500	-0.495	1200	-1.356
600	-0.611	1300	-1.486
700	-0.730	1400	-1.618
800	-0.851	1500	-1.751

03 Results and discussion

Formation stability of oxygen defects



Formation energies

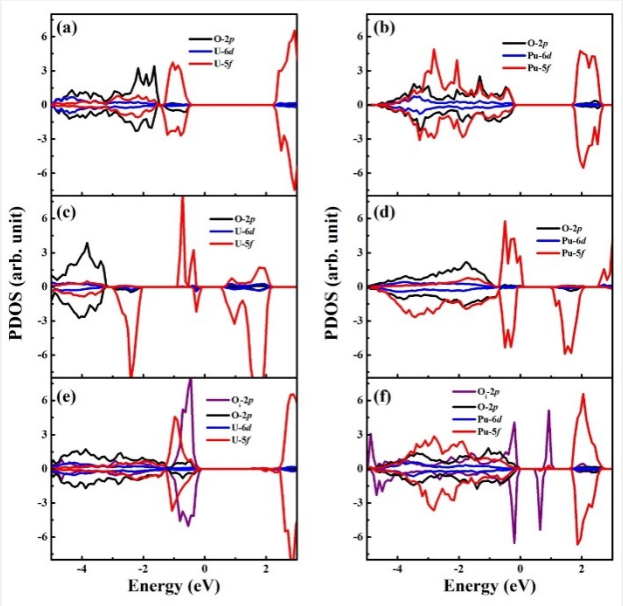
- O_i is more easily formed than O_v in UO_2, while the possibility of forming O_v and O_i is similar in PuO_2
- O_v is most likely to form in the second O atomic layer for both UO_2 and PuO_2
- The formation energy of O_v gradually tends to be flat. The formation energy of O_i changes slightly with the surface depth.

Electronic properties

ideal

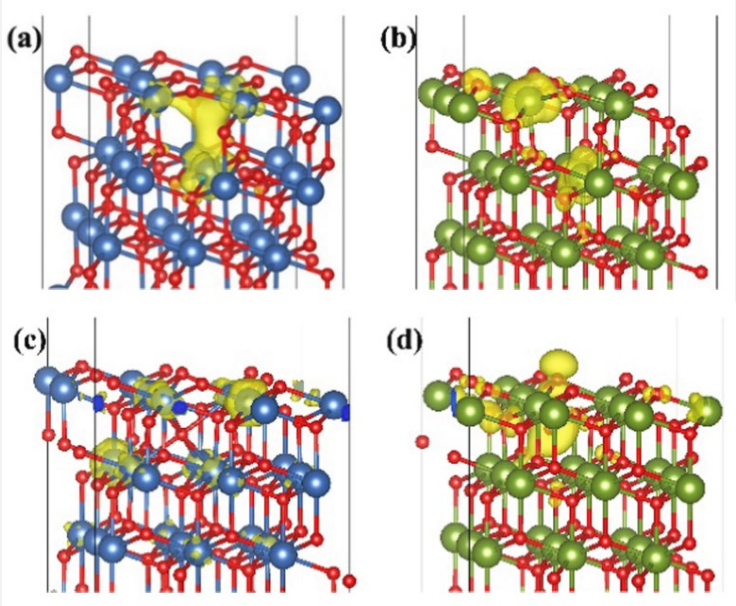
O_v

O_i



UO_2 PuO_2

PDOS

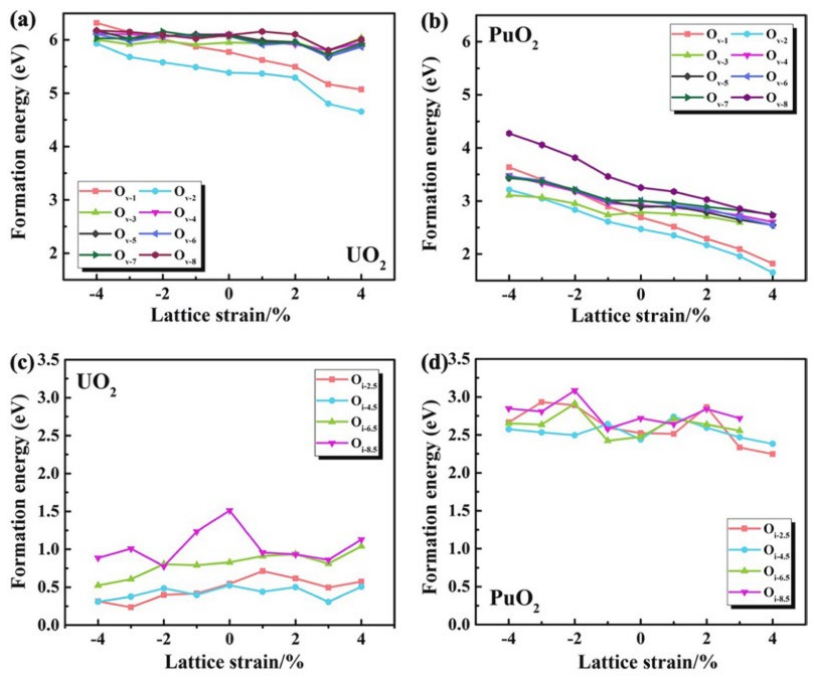


UO_2 PuO_2

CD

- ✓ O_v defect states appear in the band gap of both UO_2 and PuO_2.
- ✓ Compared to plutonium, uranium in UO_2 is more prone to bond with additional oxygen atoms

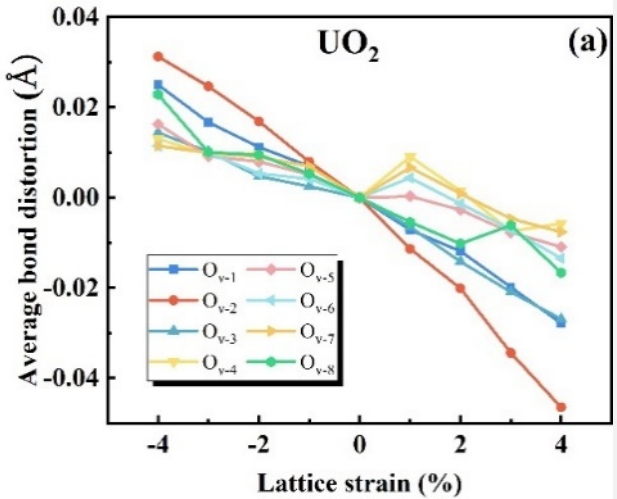
Strain effect

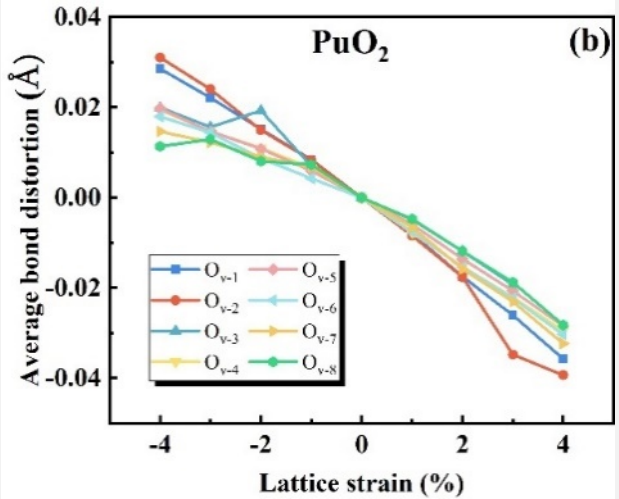


Variations of formation energy with lattice strain

- Stretching strain promote the formation of O_v, while compressive strain inhibit O_v
- Lattice strain has no regular influence on the formation energy of O_i

Strain effect

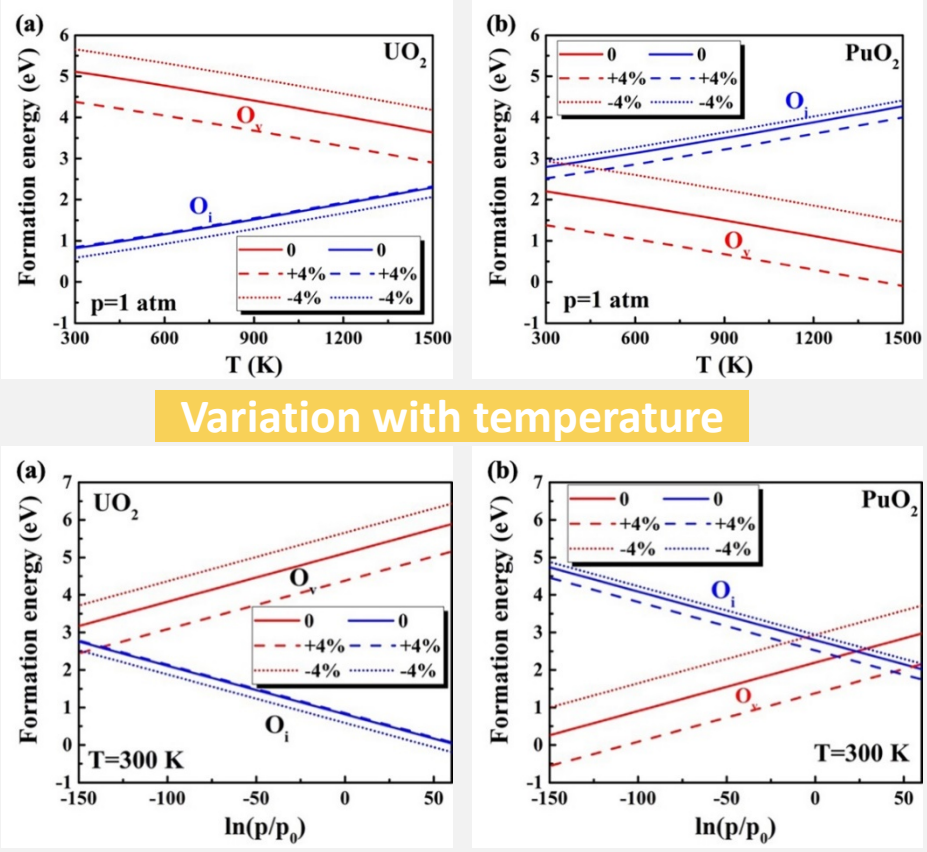




Bond distortion

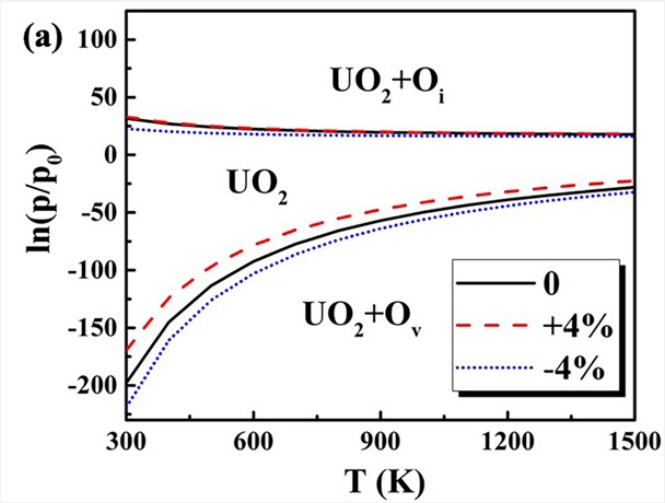
- **Stretching and compressive strain promote the U(Pu)-O bond distortions for O_v in UO_2 (111) and PuO_2 (111)**
- **The variation of the bond distortion induced by lattice strain of Ov in UO_2 (111) changes gently compared with the surface layers**

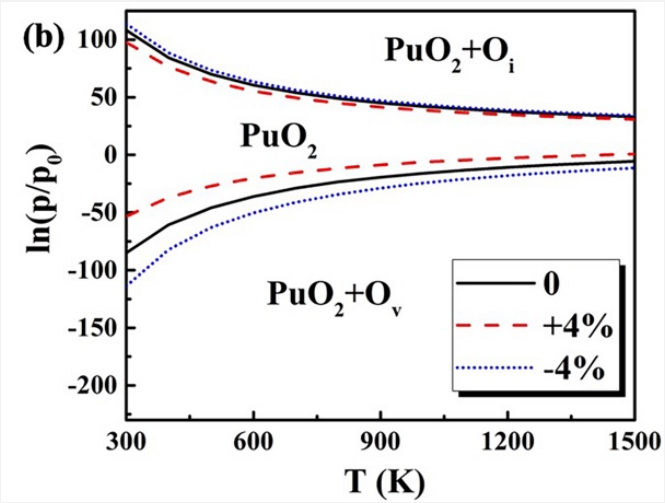
Thermodynamic phase diagram



- The formation energy of O_v decreases with temperature, while the formation energy of O_i increase with temperature.
- The formation energies of O_v increase with the pressure, while the formation energies of O_i decrease with increasing pressure
- Stretching strain reduces the formation energy of vacancy, while compressive strain increases it, and formation of Oi is less affected by strain.
- Oi is easier to form in in UO_2 in the considering temperature and pressure range

Thermodynamic phase diagram





Phase diagram of formation of oxygen defects with different lattice strain

- **Low oxygen partial pressure encourages the formation of vacancy, while high oxygen partial pressure facilitates the formation of interstitials**
- **Stretching strain enlarges the vacancy region and contracts the stable structure phase region, while compressive strain contracts the vacancy phase region and enlarges the stable structure region.**

04 Conclusions

Conclusions

Structural stability

The formation of O_i is much easier than O_v in UO_2, while the formations of O_i and O_v have similar chances in PuO_2. O_v prefer to form on the sub-surface layer for both UO_2 and PuO_2. Comparatively, the formation of O_i is insensitive to the incorporation depth.

Electronic characters

An O_v introduces a defect state in the band gap of UO_2 and PuO_2. For Oi, its electronic states hybridize with neighboring uranium atoms and results in negligible changes in the band structure of UO_2. Comparatively an O_i introduces a deep-level defect state in the band gap of PuO_2.

Strain response

Stretching strain reduces the formation energy of vacancy, while compressive strain increases it. Lattice strain has little effect on interstitial oxygen. This strain effect is mainly contributed by the local structural distortion, rather than the electronic hybridization.

Thermodynamic phase diagram

The strain-modulated formation energy phase diagrams of the oxygen defects have been established over a wide range of temperature and pressure, providing the potential strategy for controlling the type and concentration of intrinsic oxygen defects in UO_2 and PuO_2

Thank you for your listening!