

Modelling radiation damage in ceramic materials

J. Mulroue, D. Duffy, A.L. Shluger, S.S. Yardley

Department of Physics and Astronomy, University College London, London, WC1E 6BT

INTRODUCTION

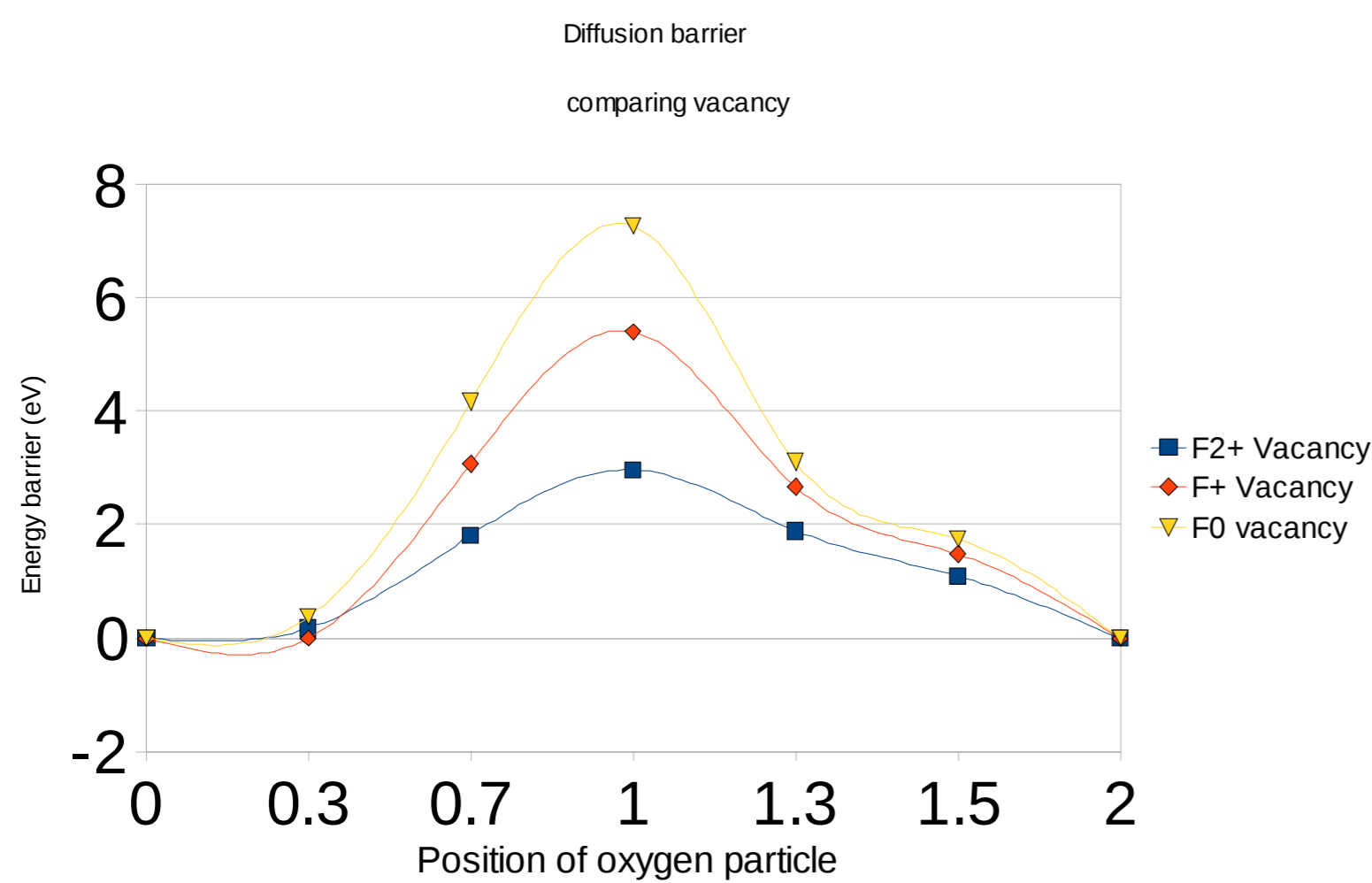
- High level nuclear waste is encapsulated in ceramic materials
- Radiation damage may degrade these materials over geological timescales
- SYNROCs (synthetic rocks) are the current proposed material
- SYNROCs are composed of different crystal structures allowing a variety of the heavy metals found in nuclear waste to be encapsulated.

AIMS

- To investigate radiation damage in zirconolite, a component of SYNROC
- To assess the role of electronic excitations on the evolution of radiation damage within ceramic materials, using MgO as a model oxide
 - Excited electrons and holes may get trapped at vacancies and interstitials and affect migration barriers

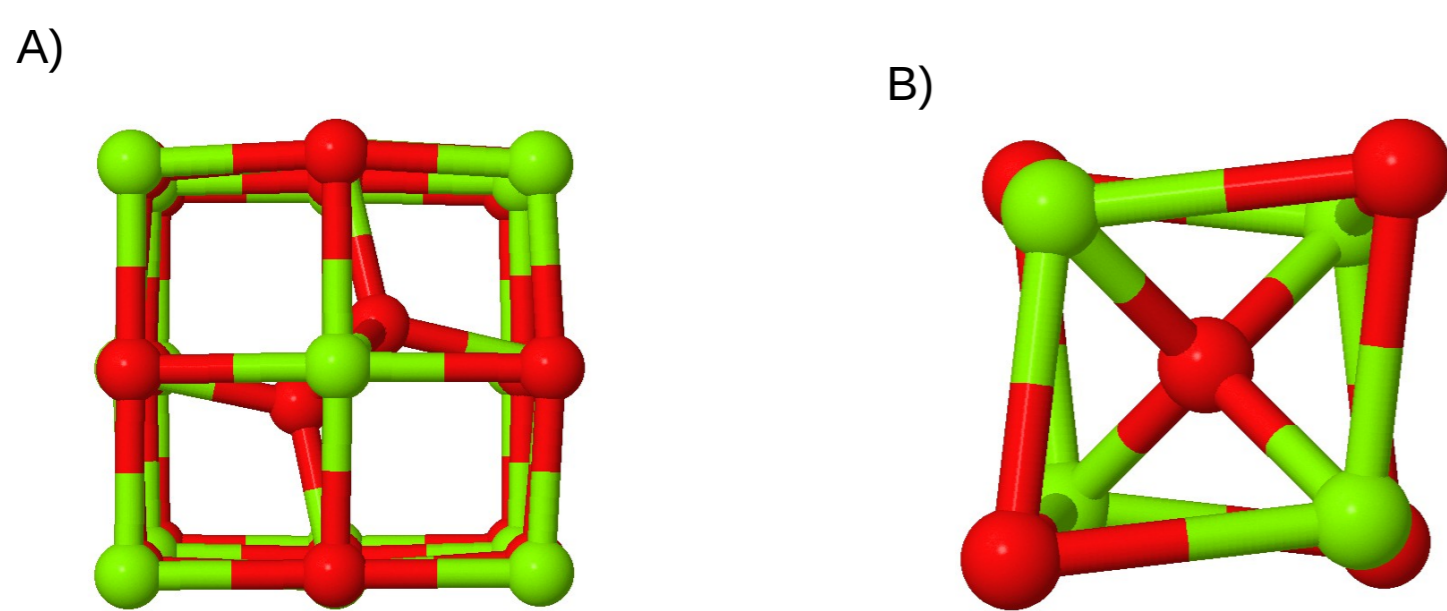
Magnesium Oxide

- MgO (fcc structure) has been extensively studied both theoretically and experimentally
- O vacancy has 3 charge states (F^{2+} , F^+ , F^0)
- The ionisation potentials of the oxygen vacancies have been calculated using B3LYP with 6-31G basis set
 - $F^0 \rightarrow F^+$ vacancy is 2.56 eV
 - $F^+ \rightarrow F^{2+}$ vacancy is 4.26 eV
- Barrier calculated for the diffusion of oxygen vacancies (F^0 , F^+ and F^{2+}) are shown below



- O^0 and O^{2-} interstitials were investigated

- O^0 formed a dumbbell interstitial
- O^{2-} relaxed to the centre of the cube

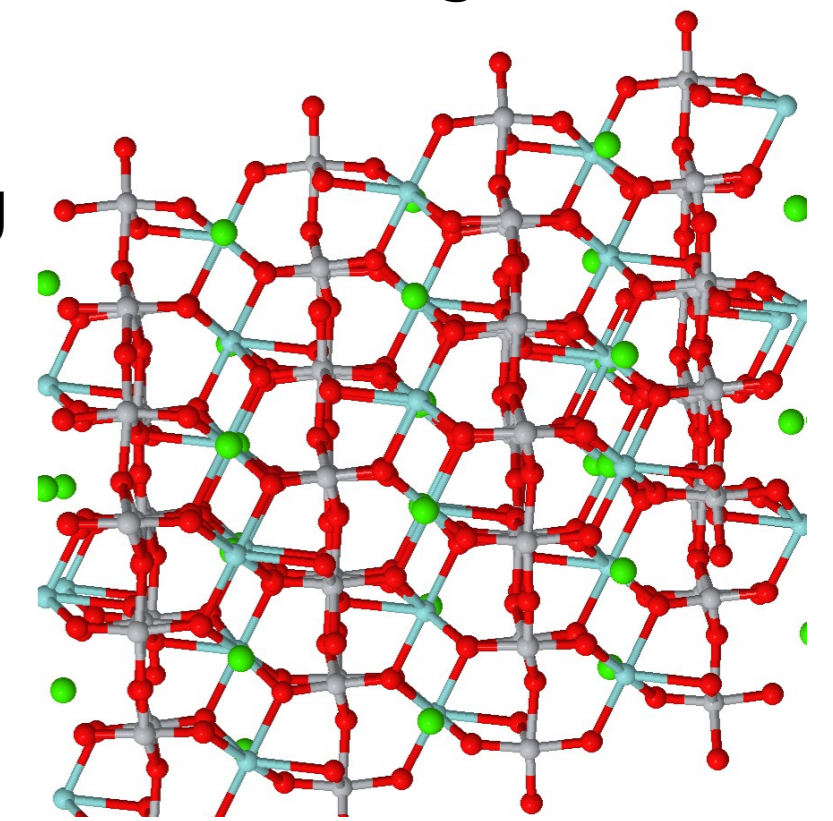


Relaxed configurations of the oxygen interstitials in MgO.
A) O^0 interstitial B) O^{2-} interstitial

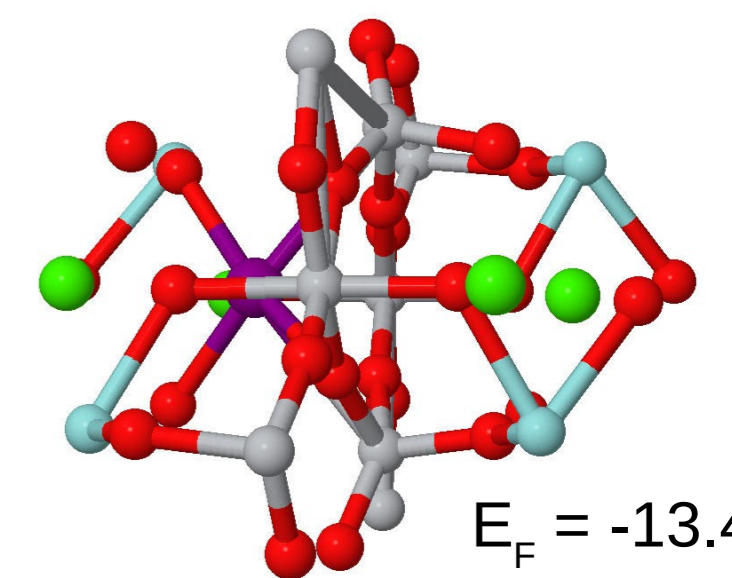
Zirconolite

- Zirconolite is able to accommodate U and Pu into its structure.
- The compound has a monoclinic structure, built up from titanium polyhedra with layers of alternating calcium and zirconium ions
- The intrinsic point defects of zirconolite were studied using empirical potentials (Veiller *et al.*)

Zirconolite Vacancy	Vacancy E_F (eV)	Frenkel defect (eV)
Ca	20.82	7.33
Zr	75.83	9.72
Ti 1	92.97	7.91
Ti 2	98.58	13.53
Ti 3	99.63	14.57
O 1	17.17	2.23
O 2	20.14	5.20
O 3	17.18	2.23
O 4	17.18	2.24
O 5	19.22	4.28
O 6	17.52	2.58
O 7	17.18	2.24



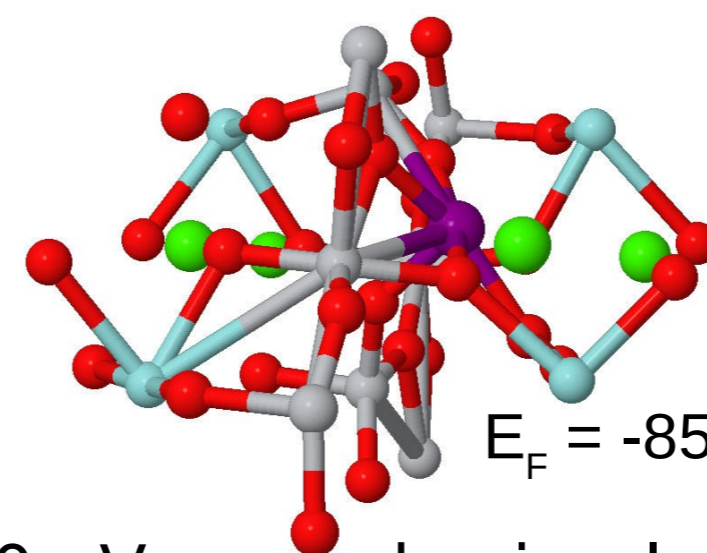
Ca interstitial



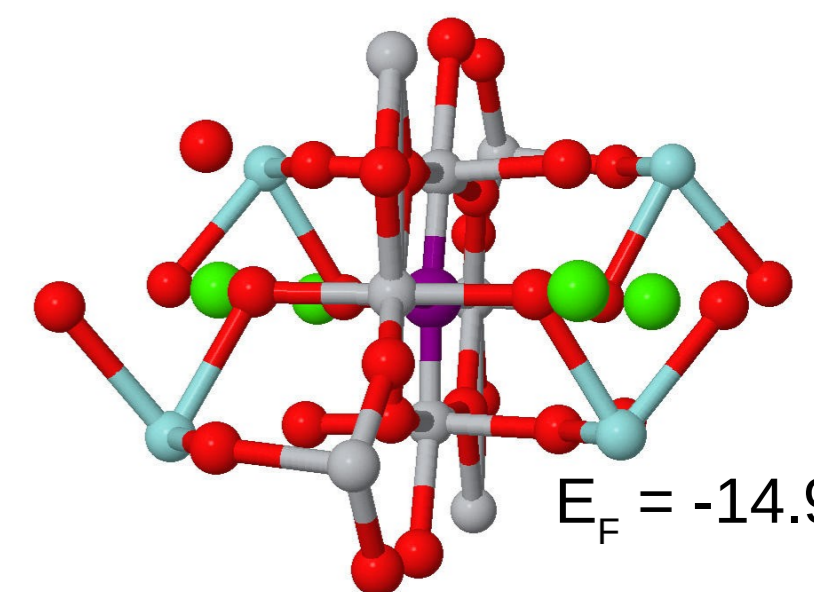
$E_F = -13.49$ eV

O interstitial

Ti interstitial



$E_F = -85.57$ eV

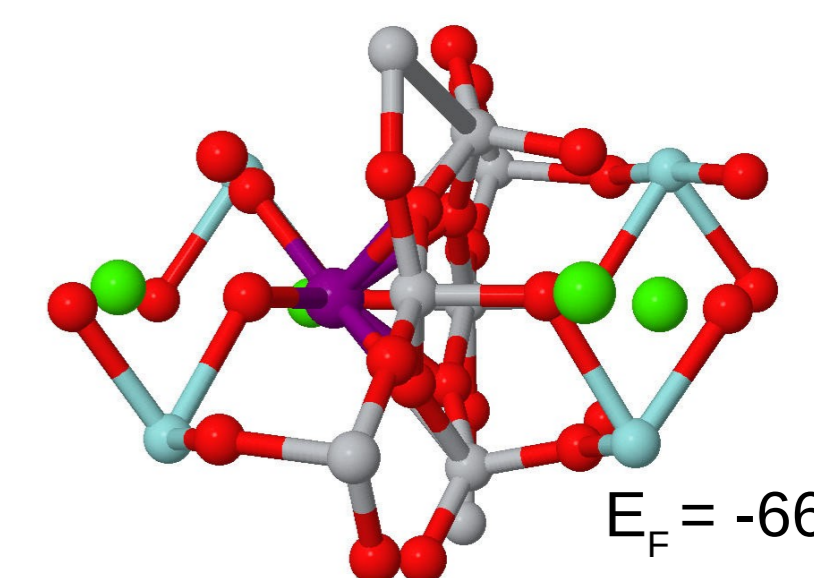


$E_F = -14.94$ eV

Zr interstitial

- 100 eV cascade simulations (10 ps) were run in zirconolite.
- A variety of PKA ions and directions were selected and the peak and residual damage (number of defects) are tabulated below.

Ion	Damage	a	b	c
Ca	Peak	54	36	42
	Residual	18	24	22
Zr	Peak	74	74	52
	Residual	40	60	24
Ti	Peak	40	38	44
	Residual	24	0	24
O	Peak	40	42	28
	Residual	32	32	26



$E_F = -66.11$ eV

Residual damage from the 100 eV Zr cascade with the PKA directed along the (010) direction

Conclusions

- The charge state of the oxygen defects in MgO has a large effect on their properties
 - The stable configuration of the O interstitial
 - The diffusion barrier for O vacancies
- The 5 coordinated Ti (Ti 3) has the highest Frenkel defect energy in zirconolite (1 eV higher than the 6 coordinated Ti), while the lowest is the 3 coordinated oxygen (O1).
- Zr cascades cause the largest amount of residual damage in zirconolite, due to the size of the ion.

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