Positron Annihilation Spectroscopy to Characterize Irradiation Induced Vacancy Type Defects in Materials for Nuclear Fission and Fusion

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In nuclear reactors, materials are submitted to irradiations and modification of their macroscopic properties such as swelling or hardening is observed... It is of first importance to understand the origin of these evolutions and how damage at the atomic scale such as vacancy and interstitials type defects can interact with each other or with solutes and impurities to make the microstructure evolved. So the properties of defects have to be determined.

Positron annihilation spectroscopy (**PAS**) is a well-established technique to characterize materials [1]. Due to its positive charge, positron is sensitive to the local variations of the Coulomb potential in solids. As the anti-particle of the electron, both particles can annihilate leading to the emission of gamma rays with energy depending on the momentum of the electron positron annihilated pair. The detection of these gamma rays arises original information on the defects because positron can be trapped and annihilate in localized state such as vacancies. Two different and complementary annihilation characteristics can be measured. Firstly Positron Annihilation Lifetime Spectrometer (**PALS**) allows to measure the *positron lifetime* which depends on the local electron density at the annihilation site. The second characteristic is the momentum distribution of the electron positron annihilated pairs and is obtained by measuring the energy spectrum of the gamma annihilation rays using a Doppler Broadening Spectrometer (**DBS**). Both characteristics give the signature of the defects and allow determining some of their properties such as their nature, concentration, chemical environment... By using slow positron accelerators which produce monokinetic positrons beams with energy varying from 0.1 to 30 keV it is possible to study the depth profile of defects in thin layers from 0.1 to about 5 μm depending on the density of materials with a resolution of the order of $0.1 \times \text{depth}$. ²²Na source based beams [2] or user facilities taking advantages of high positrons flux available around nuclear reactor (FRMII, Garching [3]) or LINAC (as in AIST in Japan [4]) are now available to study defects in materials. PAS has numerous advantages among them, it is non-destructive and can be used for conducting as well as insulating materials crystalline or amorphous. This technique is especially useful to probe vacancy defects in metals for which it is one of the only direct characterization. The annihilation characteristics can be predicted by first principle calculations and these data when available can help to identify defects. Sensitive to the single vacancy, PAS can allow to determine the size of the vacancy clusters up to a maximum of 1 nm approximately in the concentration range from 10^{15} to a few 10^{18} cm^{-3} .

In nuclear science this technique is very powerful to characterize not only damage induced by irradiation but also to determine some fundamental properties of defects that are required for modeling of the microstructural evolution of materials such as formation, migration, agglomeration, interaction with solutes, impurities or transmutation products such as Helium or Hydrogen. PAS has already demonstrated its major role in the study of vacancy defects and material related properties. For example the results obtained by Vehanen et al [6] have had an outmost impact on the knowledge of the role of carbon on vacancy behavior in Fe. They have demonstrated the trapping of vacancy in Carbon Vacancy complexes and the non-localization of C atoms in the center of the vacancy. This attractive interaction and localization has been confirmed by ab initio calculations [7]. It has also to be underlined that positrons can be trapped in precipitates if its affinity for the material of precipitate is higher than the one of the matrix. Nagai et al have demonstrated the complementarity of positron techniques with Atomic Probe Tomography and have recently underlined the effects of matrix damage probed by PAS on the hardening [5].

In this work we will report different results on the determination of the properties of vacancy defects in W and UO₂ using separate effects irradiation experiments coupled to PAS experimental measurements and theoretical data. Recently the self-consistent two components Density Functional Theory has been implemented in PAW approximation and has allowed circumventing the nature of the detected vacancy defects in UO₂ irradiated with electrons or alpha particles [8]. The comparison of the experimental positron lifetime with calculated values show that the Schottky defects made of one uranium vacancy associated to 2 oxygen vacancies seem to be the most detected defects. Due to its properties tungsten has been chosen to cover part of the divertor in ITER and is envisaged for first walls in next tokamak generation such as DEMO. In order to better understand its swelling and embrittlement observed in special irradiation conditions, we use PAS to study the vacancy defects properties in this material. We have first shown the migration and agglomeration of single vacancy in the temperature range from 473 to 600K [9] and its interaction with helium [10]. More recently we have observed the formation of vacancy clusters in self ion irradiated W and the effect of the temperature on the size of these clusters. Today, the development of positron microbeams is very promising. It has already allowed to show the creation of vacancies in region close to the fracture zone of H charging stainless steel [11].

Fig. 1 : Positron Lifetime in electron and alpha irradiated UO₂ and positron isodensities in Uranium vacancy and complexes with oxygen vacancy as calculated in self-consistent 2 components Density Functional Theory [8]

References

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- [3] <https://www.frm2.tum.de/en/the-neutron-source/secondary-sources-for-neutrons-and-positrons/positron-source/>
- [4] https://unit.aist.go.jp/rima/xr-pos/group_detail/facilities/facilities.html
- [5] A. Kuramoto et al., "Microstructural changes in a Russian-type reactor weld material after neutron irradiation, post-irradiation annealing and re-irradiation studied by atom probe tomography and positron annihilation spectroscopy", Acta Materialia 61, 5236 (2013).
- [6] A. Vehanen et al., "Vacancies and carbon impurities in α -Fe- electron irradiation", Phys. Rev. B 25, 762, (1982).
- [7] C. Barouh et al., "Interaction between vacancies and interstitial solutes (C, N, and O) in α -Fe: From electronic structure to thermodynamics", Phys. Rev. B 90, 054112 (2014).
- [8] J. Wiktor et al., "Coupled experimental and DFT plus U investigation of positron lifetimes in UO₂", Phys. Rev. B 90, 184101 (2014).
- [9] P. E. Lhuillier et al., "Positron annihilation studies on the nature and thermal behaviour of irradiation induced defects in tungsten", Physica Status Solidi C 6, 2329 (2009).
- [10] P. E. Lhuillier et al., "Helium retention and early stages of helium-vacancy complexes formation in low energy helium-implanted tungsten", JNM 433, 305 (2013).
- [11] N. Oshima et al., "Rapid three-dimensional imaging of defect distributions using a high-intensity positron microbeam", Appl. Phys. Lett. 94, 194104 (2009).

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CEMHTI Facilities for the study of irradiation in Materials

Cyclotron

Light ions : H^+, D^+, α

- Energy = 10 - 45 MeV
- Temperatures -120° to 1200°C DIAMANT
- Neutrons flux $\Rightarrow$ a few 10^{11} neutron/cm²/s

DIAMANT
Radiolysis, corrosion

RAMAN / Irradiation / HT

Feb. – Oct. 2014 :
Now running

Pelletron **New**

Positrons

Na22, Slow positron beam (0.5-25 keV)

- vacancy defects

– **Light ions** : $H^+, D^+, {}^3\text{He}, \alpha$

- Energies = 0.5 - 3 MeV
- Temperatures -130°C to 1200°C

Positron e^+ = antiparticle of electron (opposite charge, same mass)

Positron Annihilation Spectroscopy is based on 2 **properties of positron**

- ✓ In dense solids annihilation leads to emission of 2 γ : $E = 511 \text{ keV} \pm \Delta E$
- ✓ **Trapping** in vacancy defects

⇒ Electronic Structure of solids
 Probe for **vacancy defects** (negative or neutral) and **free volumes**

^{22}Na : fast positrons

$T_{1/2} = 2.6$ ans,

Thick samples

Slow positron beam: monokinetic slow positrons (0.5-25 keV)

Thin layers

$$\Delta E = cP_L/2$$

P_L : $e^- e^+$ pair
momentum

**Momentum distribution of
electron- positron annihilated pairs**

Annihilation line at 511 keV

$$DE = cP_L/2$$

P_L : $e^- e^+$ pair momentum

Momentum distribution of electron- positron annihilated pairs

Comparison of theoretical and experimental annihilation probability densities

valence

electrons 3s
and 3p
dominate

High momentum : **core** electrons

Experimental Spectra in SiC without vacancies

S_L, W_L

Annihilation characteristics
in **Lattice** (without defects)

Experimental Spectra in SiC with and without vacancies

S_L, W_L

Annihilation characteristics
in **Lattice** (without defects)

Experimental Spectra in SiC with and without vacancies

S_L, W_L

Annihilation characteristics
in **Lattice** (without defects)

Vacancies

$\rightarrow W \searrow, S \nearrow$

S = annihilation fraction of $e^- e^+$ with low
momentum,

$$S = A_S / A_T$$

W = annihilation fraction of $e^- e^+$ with high
momentum,

$$W = W_L + W_R = (A_{WL} + A_{WR}) / A_T$$

Experimental Spectra in SiC with and without vacancies

S_L, W_L

Annihilation characteristics
in **Lattice** (without defects)

Vacancies

$\rightarrow W \searrow, S \nearrow$

S = annihilation fraction of $e^- e^+$ with low
momentum,

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W = annihilation fraction of $e^- e^+$ with high
momentum,

$$W = W_L + W_R = (A_{WL} + A_{WR}) / A_T$$

$V_N : N \nearrow \Rightarrow S, R \nearrow, W \searrow$

PALS with PLEPS
in Munich

Positron lifetime

$$\tau = (\pi r_0^2 c n_{e-}^*)^{-1}$$

r_0 : electron radius

c : light velocity

n_{e-}^* : Local electronic density

Lifetime spectrum

$$S(t) = BG + R(t) \circ P(t)$$

$P(t)$: prob. for positron to annihilate at time t

$$P(t) = \sum_i I_i \exp(-t/\tau_i), \quad \text{with } \sum_i I_i = 1$$

$\tau_i = 1/\lambda_i$: lifetime component i and its intensity I_i

2 lifetime components $\rightarrow$ at least 2 annihilation states

$\rightarrow \tau_2$ long component = $\tau_{\text{vacancy defect}}$

Theory (DFT) [1]

Specific lifetime for each type of defects

Lacunae V_N : $N \nearrow \Rightarrow \tau \nearrow$

Use separate effects experiments combining irradiations in different conditions and PAS (and other techniques) measurements and calculations to characterize vacancy defects in materials:

- ✓ Nature
- ✓ Interactions with impurities
- ✓ Migration

In W and UO_2

Vacancy defects in W : Single vacancies properties and V-clusters

Dpa and He, H induced in material for fusion

- ✓ ITER, DEMO : steps in the development of fusion energy production
- ✓ Fusion reaction $^2\text{H} + ^3\text{H} \rightarrow ^4\text{He}(3,5 \text{ MeV}) + n(14.1 \text{ MeV})$
- ✓ W divertor, first walls?

dpa : displacements per atom

ITER Tokamak

Change the microstructure and chemical composition
Evolution of thermal, electrical, mechanical properties of materials

W for FW or divertor

Damage dose max in 3 years = 12dpa

[He]max in 3 years = 20-30 appm

He/damage = 1.6-2.5 appm/dpa

-- W = predominant recoil

- Large energy distribution (up to 300 keV) mean value at 3.3 keV

Macroscopic properties: Irradiations with neutrons

Vacancy defects ?

➤ Swelling in W irradiated with neutrons ($E > 0.1 \text{ MeV}$), $5.5 \times 10^{26} \text{ n.m}^2$ (9.5dpa) [1]

[1] J.Motolich et al., Scripta Metallurgica, 8 (1974) 837-842; [2] V. Barabash, G. Federici, M. Rödiger, L.L. Snead, C.H. Wu, Journal of Nuclear Materials, 283-287, Part 1 (2000) 138-146.

Virgin samples : thin foils (150 μ m), 7*7 mm², annealed at 1600°C/1h/Vacuum

Implantation to induce defects

³He 800keV

Fluence de 10¹³ à 5.10¹⁶cm⁻²

Study of defects in the
Track region with PAS

Fluence	Estimated Damage (dpa) ^[SRIM] 0 to 700 nm
10 ¹⁴	2.5×10 ⁻⁴
10 ¹⁵	2.5×10 ⁻³
10 ¹⁶	0.025
5×10 ¹⁶	0.13

PAS ; Positron Annihilation Spectroscopy

Virgin sample annealed 1600°C/1h/vacuum

^3He 800 keV implantation, Fluence from 10^{13} to $5 \times 10^{16} \text{ cm}^{-2}$ (VDG Orléans)

One single type of defect V

A Debelle, MF Barthe et al., J. Nucl. Mat., 376 (2008) 216-221

Virgin sample : annealed 1500°C/1h/ArH₂

³He 800 keV irradiation

Fluence from 10¹⁴ to 5x10¹⁶ cm⁻²

➡ One single type of defect

- [1] A Debelle , MF Barthe et al, JNM.376 (2008) 216; [2] T. Troev, E. Popov, et al, NIMB 267, (2009), 335; [3] P.E. Lhuillier, MF Barthe et al., PSS ,C6, (2009), 2329, [4] C.Becquart,et al JNM 403, Issues 1-3, 2010, 75-88

Virgin sample : annealed 1500°C/1h/ArH₂

³He 800 keV irradiation

Fluence from 10¹⁴ to 5x10¹⁶ cm⁻²

➡ One single type of defect

Positron Lifetime In agreement with calculations

$\tau = 200 \pm 0.4 \text{ ps}$ $I = 98 \pm 0.2\%$, [3] $\tau_{V\text{Calc}} = 200 \text{ ps}$ [2]

Single vacancy (V)

Virgin sample : annealed 1500°C/1h/ArH₂

³He 800 keV irradiation

Fluence from 10¹⁴ to 5x10¹⁶ cm⁻²

Single vacancy (V)

Trapping in one trap = 2 annihilation states

- Lattice, S_L and τ_L = 110ps
- Single Vacancy V, S_V

Trapping rate, K_V = C_V · μ_V

μ_V trapping specific coefficient,

$$\mu_V = 4 \pm 2 \times 10^{14} \text{ s}^{-1} [1]$$

$$C_V = \frac{\lambda_L}{\mu_V} \frac{A_{norm}}{1 - A_{norm}}$$

$$A_{norm} = S_{norm}, S_{norm} = S/S_L$$

[1] PE Lhuillier Thesis CEMHTI 2010,

Trapping in one trap = 2 annihilation states

- Lattice, S_L and $\tau_L = 110\text{ps}$
- Single Vacancy V , S_V

PAS Experimental data
 SRIM
 Marlowe

Trapping rate, $K_V = C_V \cdot \mu_V$
 μ_V trapping specific coefficient,
 $\mu_V = 4 \pm 2 \times 10^{14} \text{ s}^{-1}$ [1]

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$$A_{norm} = S_{norm}, S_{norm} = S/S_L$$

[1] PE Lhuillier Thesis CEMHTI 2010, [2] A De Backer, C Becquart, C. Domain, MF Barthe, JNM 429 (2012) 78–91, [3] C.Becquart, et al JNM 403, Issues 1-3, 2010, 75-88

LAKIMOCA (C. Domain EdF) [3]

PAS Experimental data
 SRIM
 Marlowe

Marlowe

[1] PE Lhuillier Thesis CEMHTI 2010, [2] A De Backer, C Becquart, C. Domain, MF Barthe, JNM 429 (2012) 78–91, [3] C.Becquart, et al JNM 403, Issues 1-3, 2010, 75-88

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PAS Experimental data
 SRIM
 Marlowe
 Okmc, mono-vac

[1] PE Lhuillier Thesis CEMHTI 2010, [2] A De Backer, C Becquart, C. Domain, MF Barthe, JNM 429 (2012) 78–91, [3] C.Becquart, et al JNM 403, Issues 1-3, 2010, 75-88

LAKIMOCA (C. Domain EdF) [3]

Species	Em (eV)
mono-SIA (1I)	0.013
mono-v (1v)	1.66

PAS Experimental data

SRIM

Marlowe

Okmc, mono-vac

[1] PE Lhuillier Thesis CEMHTI 2010, [2] A De Backer, C Becquart, C. Domain, MF Barthe, JNM 429 (2012) 78–91, [3] C.Becquart, et al JNM 403, Issues 1-3, 2010, 75-88

Virgin sample : annealed 1500°C/1h/ArH₂

³He 800 keV irradiation

Fluence from 10¹⁴ to 5x10¹⁶ cm⁻²

One single type of defect

Single vacancy (V)

Annealing

Virgin sample : annealed 1500°C/1h/ArH₂

³He 800 keV irradiation

Fluence from 10¹⁴ to 5x10¹⁶ cm⁻²

➡ One single type of defect
Single vacancy (V)

V-clusters
V_N with N>30 [2]

At 873K Positron Annihilation Lifetime Spectrometry with PLEPS [3]

Mean lifetime	1 st component		2 nd component	
τ_m (ps)	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)
331	176	54	458	45

V migration, 473-623K
 $E_m(V) = 1.66$ eV [4]

[1] A Debelle, MF Barthe et al, JNM.376 (2008) 216; [2] T. Troev, E. Popov, et al, NIMB 267, (2009), 335; [3] P.E. Lhuillier, MF Barthe et al., PSS, C6, (2009), 2329, [4] C.Becquart, et al JNM 403, Issues 1-3, 2010, 75-88

Vacancy defects in self ions irradiated W :

Positron annihilation spectroscopy
Transmission electron microscopy

Saclay

Orsay

Experiments done at JANNUS (Joint Accelerators for Nanoscience and Nuclear Simulation), France

Irradiation **W 20 MeV** in bulk : post-mortem characterizations

Irradiation **W 1.2 MeV** in thin foils: in situ and post-mortem characterizations

PAS, **TEM**

20 MeV W irradiation: low dpa

V-clusters (small 3D V-cluster+ V-loops) are created **even at low dpa**

W irradiated 1.2 MeV W ions at 0.017 dpa at RT

Image 1 : over focused image, cavities appear black surrounded by a white halo

Image 2 : under focused image, cavities appear white surrounded by a black halo

V-clusters (small 3D V-cluster+ V-loops) are created **even at low dpa**
 Size and/or concentration of vacancy clusters increases with dpa
 Saturation from 1 dpa

Annealing in vacuum : effect of dpa

Annealing in vacuum : effect of dpa

^3He 800 keV irradiations

V migration, $\sim 573\text{K}$
 $E_m(\text{V}) = 1.66 \text{ eV}$ [4]

- $\forall$ dpa clustering occurs in the same temperature range as for single vacancies
- ➔ mainly due to V migration and agglomeration on small clusters

Vacancy defects in UO_2 :

XRD, lattice parameter changes, [1,2,3]

RBS/C in Xe and He implanted UO_2 [4]

Thermal properties in $(\text{U,Pu})\text{O}_2$ samples, [5]

[1] J.H.Davies et al, JNM 41 (1971), 143., [2] Weber W.J, JNM 114 (1983), 213 [3] N.Nakae, JNM 80 (1979), 314-322 , [4] F. Garrido et al. NIM B 266 (2008) 2842–2847, [5] D. Staicu, T. Wiss et al. JNM 397 (2010) 8–18

XRD, lattice parameter changes, [1,2,3]

Indirect information about primary defects
No direct observation of vacancy defects

Thermal properties in $(\text{U,Pu})\text{O}_2$ samples, [5]

[1] J.H.Davies et al, JNM 41 (1971), 143., [2] Weber W.J, JNM 114 (1983), 213 [3] N.Nakae, JNM 80 (1979), 314-322 , [4] F. Garrido et al. NIM B 266 (2008) 2842–2847, [5] D. Staicu, T. Wiss et al. JNM 397 (2010) 8–18

Fluorine structure

Vacancy defects in irradiated UO_2

- (fast) Positron Lifetime,
- Self-consistent Two Component DFT calculations of positron lifetime

Sample	Density (%)	Dopant		Integrated dose before thermal treatment		Annealing	
		Nature	Conc. (wt.%)	(α g ⁻¹)	(dpa)	T (K)	Time (h)
UO ₂ _target	95	–	–	0	0	1973	24
UO ₂ G1_1373	95			1.5×10^{11}		1373	5
UO ₂ G1_1673	95			1.5×10^{11}		1673	4
UO ₂ G1_1773	95			1.5×10^{11}		1773	4
B1d/B3d	95	²³⁹ Pu	0.2	10^{15}	2×10^{-4}	None	
B1d_1373/B3d_1373	95	²³⁹ Pu	0.2	10^{15}	2×10^{-4}	1373	6
GIGONDAS	96	²³⁹ Pu	27	1.2×10^{18}	0.3	None	

Table 3
Positron lifetime components in UO₂ and doped UO₂.

Sample	Mean lifetime (ps)	Lifetime component					
		τ_1 (ps)	I_1 (%)	τ_2	I_2	τ_3	I_3
UO ₂ _target	179.9 ± 2	179.9 ± 2	100				
UO ₂ G1_1373	192.8 ± 2	183 ± 2	85	230	14.7	2195 ± 430	0.3
UO ₂ G1_1673	178.1 ± 1	177.3 ± 2	98.5	230	1.5		
UO ₂ G1_1773	169.2 ± 0.3 ^a	169.2 ± 0.3	100				
B1d/B3d	240.3 ± 2	204.5 ± 7	69.5	313 ± 19	30.4	3176 ± 2056	0.1
B1d_1373/B3d_1373	219.6 ± 1	200 ± 2	93.76	446.5 ± 55	5.8	1798	0.3
Gigondas	352.6 ± 1	222.4 ± 14	41.3	340.6 ± 14	54.9	1916 ± 43	3.9

^a ²²NaCl source deposited on aluminum foil.

DEN/DTCD/SECM/LMPA CEA Marcoule

Irradiations α 45 MeV (2×10^{-4} dpa), 1 MeV and 2.5 MeV electrons
Positron Annihilation Spectroscopy (Fast Positrons), 300K Lifetime

M F Barthe, et al Phys. Stat. Solidi C 4 3627-3632
2007

Irradiations α 45 MeV, 1 MeV and 2.5 MeV electrons

Positron Annihilation Spectroscopy (Fast Positrons), 300K Lifetime

$$\tau_V = 307 \pm 4 \text{ ps}$$

No vacancy defects are detected for 1 MeV e- irradiation

Vacancy defects detected if 2.5 MeV e- irradiation

Displacement of U if $E(e^-) > 2$ MeV

V_U , or complexes $V_U 2V_O$

M F Barthe, et al Phys. Stat. Solidi C 4 3627-3632 **2007**

Calculations in the **ABINIT** code (Two Components DFT) [1]

Self consistent scheme PSN² with gradient correction GC for the enhancement factor g

*Defects were fully relaxed

Relaxation of defects due to positron localization = iterations

DEN/DEC/SESC/LLCC

Calculations in the **ABINIT code** (Two Components DFT) [1]

Self consistent scheme PSN² with gradient correction GC for the enhancement factor g
DFT(GGA, PBE)+ U formalism³ to treat the **5f** electrons
 Defects were fully relaxed

	Charge	Lifetime PSN+GC (ps)
Lattice		167
V_O	0	199
V_O	2-	195
V_U	0	304
V_U	4-	293
V_U+V_O	0	306
V_U+V_O	2-	301
$V_U+2V_O(100)$	0	304
$V_U+2V_O(110)$	0	313
$V_U+2V_O(111)$	0	316
$2V_U$	0	318
$2V_U$	8-	289
$2V_U+2V_O$	0	339
$2V_U+2V_O$	4-	319
$2V_U+4V_O$	0	329
$2V_U+4V_O$	2-	365

Exp ~170 ps

Reduction of the lifetime with increase of the charge

Due to relaxation for V_U
 4- :+10% outward
 0: +13% outward

Schottky defects

DEN/DEC/SESC/LLCC

- 1 J Wiktor, M. Bertolus, G. Jomard, MF Barthe et al, Phys Rev B 90, 184101 (2014)
 2 M. J. Puska, A. P. Seitsonen, and R. M. Nieminen, Phys. Rev. B 52, 10947 (1995). 3 S. Dudarev, D. Manh, and A. Sutton, Philos. Mag. Part B 75, 613 (1997).

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Exp .

Long lifetime $\sim 310 \pm 10$ ps

UO₂ (set G, sintered polished and annealed 1700°C/24h/ArH₂) irr alpha 45 MeV 2x10¹⁶ cm⁻²
Measurement in ultra vacuum as a function of temperature

Model with 3 Traps : negative ions IN, V₁⁻, et V₂

$\tau_{IN}=170$ ps and $\tau_{V^-} = \tau_{V_2} = 310$ ps

Cv2(cm ⁻³)	μ_{v1}
6,50E+19	1,00E+15

>30 times more neutral vacancies than negatively charged ones

Cv-(cm ⁻³)	$\mu_0 r$	$\mu_0 2$	Er(eV)	Vr(s ⁻¹)
2.0E+18	3,40E+16	4,00E+16	1,00E-02	1,00E+11

C _{IN} (cm ⁻³)	$\mu_0(IN)$	E _{IN} (eV)
1,00E+19	4,20E+16	3,00E-01

High binding energy
at Rydberg state of negative ions

short lifetime is constant
Trapping saturation

Formation energies of defects in stoichiometric UO_2 [1]

In the undoped UO_2 V_O should be **positive**, hence not detected by PAS

V_U and $V_U + V_O$ defects should be **negative**, while the $V_U + 2V_O$ should be **neutral**.

DEN/DEC/SESC/LLCC

Close to stoichiometry, $I_O^{2-}, V_O^{2+}, V_U^{4-}$ DFT LDA+U [2]

[1] J Wiktor, M. Bertolus, G. Jomard, MF Barthe et al, Phys Rev B 90, 184101 (2014), [2] J P Crocombette Phys Rev B **85**, 144101 (2012)

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$V_U+2V_O(100)$	0	304
$V_U+2V_O(110)$	0	313
$V_U+2V_O(111)$	0	316
$2V_U$	0	318
$2V_U$	8-	289
$2V_U+2V_O$	0	339
$2V_U+2V_O$	4-	319
$2V_U+4V_O$	0	329
$2V_U+4V_O$	2-	365

V_U and V_U-V_O are negatively charged
close to the middle of the bandgap in
close stoichiometric UO_2

Exp .
Long lifetime $\sim 310 \pm 10$ ps
Vacancy defects

$2V_U$ is 8- close to the middle of the
bandgap in close stoichiometric UO_2

We propose

Neutral vacancy defects which are preponderant = Schottky defects

Negatively charged vacancy defects = a mixing of $(V_U-V_O)^{2-}$, $(2V_U-2V_O)^{4-}$

Positron annihilation spectroscopy

- Vacancy defects properties (nature, migration, agglomeration...) concentration
 - From single vacancy to V-clusters
- Thin layers (damage region with HI) / thick samples (electron or high energy LI)
- DFT Calculations of annihilation characteristics
- Complementarity of Lifetime and Doppler
- Complementarity with TEM

In tungsten

- Light ions : single vacancies
 - ✓ from T in the range 473-623K: migration and clustering
- Heavy ions
 - ✓ at RT or lower temperature
 - low dpa : V-clusters (3D small voids +V-loops) + single vacancies
 - high dpa : V-clusters with larger size + single vacancies
 - >423K clustering due to migration of single vacancies and with V-loops as precursors?
- He Plasma
 - nV-mHe complexes close to the surface

In UO₂

- Identification of the dominant vacancy defect detected : Schottky defect $V_U + 2V_O$

Thank to

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Thank You for your kind attention