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 0.1xdepth. \textsuperscript{22}Na 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].

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In this work we will report different results on the determination of the properties of vacancy defects in W and UO$_2$ 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 circumcising the nature of the detected vacancy defects in UO$_2$ 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 UO$_2$ 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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CEMHTI Facilities for the study of irradiation in Materials

**Particles beams:**
* Irradiations, and chemical and structural characterization

**Light ions:** $H^+$, $D^+$, $\alpha$
- Energy = $10 - 45$ MeV
- Temperatures -120° to 1200°C DIAMANT
- Neutrons flux $\Rightarrow$ a few $10^{11}$ neutron/cm²/s

**Positrons**
- Na22, Slow positron beam (0.5-25 keV)
  - vacancy defects

**Cyclotron**

**Diamant**

**Pelletron** New

**Pelletron**
- Light ions: $H^+$, $D^+$, $^3$He, $\alpha$
  - Energies = 0.5 - 3 MeV
  - Temperatures -130°C to 1200°C

**Radiolysis, corrosion**

**Creep (PSI)**
Positron Annihilation Spectroscopy

Positron Annihilation Spectroscopy is based on 2 properties of positron:
- In dense solids annihilation leads to emission of $2 \gamma : E = 511 \text{ keV} \pm \Delta E$
- Trapping in vacancy defects

Electronic Structure of solids
Probe for vacancy defects (negative or neutral) and free volumes
Positron Source (1): $^{22}\text{Na}$

$^{22}\text{Na}$: fast positrons

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

$E_{\text{max}} (\beta^+) = 0.54$ MeV

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

Moderator $10^{-4}$ to $10^{-5}$
Energy filter
Source $^{22}\text{Na}$
Positrons ($\sim 3$ eV)

Surface
Annihilation $e^+$
Sample bulk

Positron implantation profile in W

$e^-$ Energy
- 5 keV
- 10 keV
- 12 keV
- 15 keV
- 20 keV
- 25 keV

Thick samples

Thin layers

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Doppler broadening spectrometry

Momentum distribution of electron-positron annihilated pairs

$\Delta E = cP_L/2$

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

Sample

$\gamma$ 511 keV $\pm \Delta E$

511 keV

Ge coincidence

Annihilation line at 511 keV

counts

$\Delta E \# \text{momentum}$

511 keV

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Doppler broadening spectrometry

Momentum distribution of electron- positron annihilated pairs

\[ DE = cP_L/2 \]

\( P_L \): e- e+ pair momentum

Annihilation line at 511 keV
Comparison of theoretical and experimental annihilation probability densities

Valence electrons 3s and 3p dominate.

High momentum: core electrons.
Doppler broadening

Experimental Spectra in SiC **without** vacancies

Epitaxial layer 6H-SiC, \( n = 10^{17} \, \text{cm}^{-3}, 4 \, \mu\text{m} \)

\[ S_L, W_L \]

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

Experimental Spectra in SiC with and without vacancies

$S_L, W_L$

Annihilation characteristics in Lattice (without defects)
Doppler broadening

Experimental Spectra in SiC with and without vacancies

\( \gamma \) Energy (keV)

\[
\begin{align*}
504 & \\
506 & \\
508 & \\
510 & \\
512 & \\
514 & \\
516 & \\
518 & \\
\end{align*}
\]

Count number

Epitaxial layer 6H-SiC, 
\((n = 10^{17} \text{ cm}^{-3}, 4 \mu m)\)

Core electrons

Valence electrons

\( S_L, W_L \)

Annihilation characteristics in Lattice (without defects)

Vacancies \( \rightarrow W, S \)

\( S = \text{annihilation fraction of e- e+ with low momentum,} \quad S = \frac{A_S}{A_T} \)

\( W = \text{annihilation fraction of e- e+ with high momentum,} \quad W = W_L + W_R = \frac{A_{WL} + A_{WR}}{A_T} \)
**Doppler broadening**

**Experimental Spectra in SiC**  
**with** and **without** vacancies

- **Core electrons**
- **Valence electrons**

- **Energy (keV)**
  - 504, 506, 508, 510, 512, 514, 516, 518

- **Count number**
  - 100, 1000, 10000

- **Epitaxial layer 6H-SiC**,  
  - (n = 10^{17} cm^{-3}, 4 µm)

- **H^+** ion implantation, 4.10^{18} H^+ cm^{-2} and 900°C annealed

- **H^+** as-received

- **Vacancies**
  - **W**, **S**

- **S**, **W**
  - Annihilation characteristics in **Lattice** (without defects)

- **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

- **V_N**: N \rightarrow S, R \rightarrow W
Positron Annihilation Lifetime Spectroscopy

Positron lifetime
\[ \tau = \left( \pi r_0^2 c n_{e-}^* \right)^{-1} \]

- \( r_0 \): electron radius
- \( c \): light velocity
- \( n_{e-}^* \): Local electronic density

Lifetime spectrum
\[ S(t) = BG + R(t) \cdot P(t) \]

- \( P(t) \): prob. for positron to annihilate at time \( t \)
  \[ P(t) = \sum I_i \exp(-t/\tau_i), \quad \text{with} \quad \sum I_i = 1 \]
  \( \tau_i = 1/\lambda_i \): lifetime component \( i \) and its intensity \( I_i \)

2 lifetime components
- at least 2 annihilation states
- \( \tau_2 \) long component = \( \tau_{\text{vacancy defect}} \)

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Positron lifetime in W

Theory (DFT) [1]

Specific lifetime for each type of defects

\[ \tau_{\text{Lattice}} = 108 \text{ ps} \]

\[ \tau_{VN} = 440 \text{ ps} \]

\[ \tau_V = 200 \text{ ps} \]

Lacunes \( V_N \): \( N \rightarrow \Rightarrow \tau \)

[1] T. Troev, E. Popov, P. Staikov, N. Nankov, T. Yoshiie, NIMB 267, 3, 335
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

**Temp.** 800-1700°C

He, H high flux
Low energy

\( n \ 14.1 \text{ MeV} \)

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

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Damage dose calculations in DEMO

Damage dose max in 3 years = 12dpa
[He]max in 3 years = 20-30 appm
He/damage = 1.6-2.5 appm/dpa

W for FW or divertor

- W = predominant recoil
  - Large energy distribution (up to 300 keV) mean value at 3.3 keV

Macroscopic properties: Irradiations with neutrons

- Swelling in W irradiated with neutrons (E>0.1MeV), 5.5x10²⁶n.m² (9.5dpa) [1]

Experimental approach

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

Implantation to induce defects

³He 800 keV
Fluence de 10¹³ à 5.10¹⁶ cm⁻²

Study of defects in the
Track region with PAS

<table>
<thead>
<tr>
<th>Fluence</th>
<th>Estimated Damage (dpa)[SRIM] 0 to 700 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>10¹⁴</td>
<td>2.5×10⁻⁴</td>
</tr>
<tr>
<td>10¹⁵</td>
<td>2.5×10⁻³</td>
</tr>
<tr>
<td>10¹⁶</td>
<td>0.025</td>
</tr>
<tr>
<td>5×10¹⁶</td>
<td>0.13</td>
</tr>
</tbody>
</table>

PAS; Positron Annihilation Spectroscopy

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Virgin sample annealed 1600°C/1h/vacuum

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

One single type of defect V

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 in W

Virgin sample: annealed 1500°C/1h/ArH₂
³He 800 keV irradiation
Fluence from $10^{14}$ to $5 \times 10^{16}$ 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] $\tau_{\text{Calc}} = 200\, \text{ps}$ [2]

Single vacancy (V)

\[ \text{Lattice} \]

\[ S_V, W_V \]

\[ \text{Initial State} \]

\[ \text{Virgin sample} \]

Implantation fluence

- $10^{13}$ cm⁻²
- $10^{14}$ cm⁻²
- $10^{15}$ cm⁻²
- $5 \times 10^{16}$ cm⁻²

Virgin sample: annealed 1500°C/1h/ArH₂
³He 800 keV irradiation
Fluence from 10^{14} to 5 \times 10^{16} 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 \cdot \mu_V
\mu_V = 4 \pm 2 \times 10^{14} \text{ s}^{-1}[1]

[1] PE Lhuillier Thesis CEMHTI 2010,
800 keV $^3$He irradiated W

Trapping in one trap = 2 annihilation states

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

[Diagram with positrons and traps]

Trapping rate, $K_V = C_V \cdot \mu_V$

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

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

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

800 keV $^3\text{He}$ irradiated W

LAKIMOCA (C. Domain EdF) [3]

800 keV $^3$He irradiated W

LAKIMOCA (C. Domain EdF) [3]

800 keV $^3$He irradiated W

LAKIMOCA (C. Domain EdF) [3]

Species | $E_m$ (eV)
---|---
mono-SIA (1I) | 0.013
mono-$\nu$ (1$\nu$) | 1.66

Virgin sample: annealed 1500°C/1h/ArH₂
³He 800 keV irradiation
Fluence from $10^{14}$ to $5 \times 10^{16}$ cm⁻²

⇒ One single type of defect
Single vacancy (V)

Annealing

Virgin sample: annealed 1500°C/1h/ArH₂
³He 800 keV irradiation
Fluence from $10^{14}$ to $5\times10^{16}$ cm⁻²

One single type of defect
Single vacancy (V)

Annealing
³He 800 keV (25 keV)
$5\times10^{16}$ cm⁻²

V-clusters $V_N$ with $N>30$ [2]

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

$S_V$, $W_V$

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

Mean lifetime
1st component
2nd component

<table>
<thead>
<tr>
<th>$\tau_m$ (ps)</th>
<th>$\tau_1$ (ps)</th>
<th>$I_1$ (%)</th>
<th>$\tau_2$ (ps)</th>
<th>$I_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>331</td>
<td>176</td>
<td>54</td>
<td>458</td>
<td>45</td>
</tr>
</tbody>
</table>

Vacancy defects in self ions irradiated W:

Positron annihilation spectroscopy
Transmission electron microscopy
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
Ex situ TEM observation: post-mortem

**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

Diam. = 0.6 ± 0.1 nm for visible V clusters

C > 4.2 ± 1.2 x 10^{23} V-clusters.m^{-3}

Smaller V-clusters can not be excluded
20 MeV W irradiation: effect of dpa

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
∀dpa clustering occurs in the same temperature range as for single vacancies mainly due to V migration and agglomeration on small clusters

V migration, ~ 573K

$E_m(V) = 1.66$ eV [4]
Vacancy defects in $\text{UO}_2$:
Experiments: Indirect detection of defects in UO$_2$

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

RBS/C in Xe and He implanted UO$_2$ [4]

Thermal properties in (U,Pu)O$_2$ samples, [5]

Experiments: Indirect detection of defects in UO$_2$

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


Indirect information about primary defects
No direct observation of vacancy defects

Thermal properties in (U,Pu)O$_2$ samples, [5]
Vacancy defects in irradiated UO$_2$

- (fast) Positron Lifetime,
- Self-consistent Two Component DFT calculations of positron lifetime
### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (%)</th>
<th>Dopant</th>
<th>Integrated dose before thermal treatment (dpa)</th>
<th>Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(α g⁻¹)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO₂_target</td>
<td>95</td>
<td>–</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>UO₂ G1_1373</td>
<td>95</td>
<td>–</td>
<td>1.5 x 10¹¹</td>
<td>1973, 24</td>
</tr>
<tr>
<td>UO₂ G1_1673</td>
<td>95</td>
<td>–</td>
<td>1.5 x 10¹¹</td>
<td>1373, 5</td>
</tr>
<tr>
<td>UO₂ G1_1773</td>
<td>95</td>
<td>–</td>
<td>1.5 x 10¹¹</td>
<td>1673, 4</td>
</tr>
<tr>
<td>Bi₁d/B₃d</td>
<td>95</td>
<td>²³⁹Pu</td>
<td>0.2 x 10¹⁵</td>
<td>1773, 4</td>
</tr>
<tr>
<td>Bi₁d_1373/B₃d_1373</td>
<td>95</td>
<td>²³⁹Pu</td>
<td>0.2 x 10¹⁵</td>
<td>None</td>
</tr>
<tr>
<td>GIGONDAS</td>
<td>96</td>
<td>²³⁹Pu</td>
<td>27 x 10¹⁸</td>
<td>0.3</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean lifetime (ps)</th>
<th>Lifetime component (µs)</th>
<th>l₁ (%)</th>
<th>τ₂ (µs)</th>
<th>l₂ (%)</th>
<th>τ₃ (µs)</th>
<th>λ₂ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>τ₁ (µs)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO₂_target</td>
<td>179.9 ± 2</td>
<td>179.9 ± 2</td>
<td>100</td>
<td>230</td>
<td>14.7</td>
<td>2195 ± 430</td>
<td>0.3</td>
</tr>
<tr>
<td>UO₂ G1_1373</td>
<td>192.8 ± 2</td>
<td>183 ± 2</td>
<td>85</td>
<td>230</td>
<td>1.5</td>
<td>1798</td>
<td>0.3</td>
</tr>
<tr>
<td>UO₂ G1_1673</td>
<td>178.1 ± 1</td>
<td>177.3 ± 2</td>
<td>98.5</td>
<td>230</td>
<td>1.5</td>
<td>1798</td>
<td>0.3</td>
</tr>
<tr>
<td>UO₂ G1_1773</td>
<td>169.2 ± 0.3</td>
<td>169.2 ± 0.3</td>
<td>100</td>
<td>313 ± 19</td>
<td>30.4</td>
<td>3176 ± 2056</td>
<td>0.1</td>
</tr>
<tr>
<td>Bi₁d/B₃d</td>
<td>240.3 ± 2</td>
<td>204.5 ± 7</td>
<td>69.5</td>
<td>313 ± 19</td>
<td>30.4</td>
<td>3176 ± 2056</td>
<td>0.1</td>
</tr>
<tr>
<td>Bi₁d_1373/B₃d_1373</td>
<td>219.6 ± 1</td>
<td>200 ± 2</td>
<td>93.76</td>
<td>446.5 ± 55</td>
<td>5.8</td>
<td>1798</td>
<td>0.3</td>
</tr>
<tr>
<td>GIGONDAS</td>
<td>352.6 ± 1</td>
<td>222.4 ± 14</td>
<td>41.3</td>
<td>340.6 ± 14</td>
<td>54.9</td>
<td>1916 ± 43</td>
<td>3.9</td>
</tr>
</tbody>
</table>

*²²NaCl source deposited on aluminum foil.

Vacancy defects in UO₂

Irradiations α 45 MeV ($2 \times 10^{-4}$ dpa), 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

Open symbols: average lifetime
Full symbols: Second lifetime component

Vacancy defects in UO₂

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 \( V_U \ 2V_O \)

Fully self-consistent 2 components DFT calculations

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

- LDA SiC
- GGA+U UO$_2$

Self consistent scheme PSN$^2$ with gradient correction GC for the enhancement factor $g$

*Defects were fully relaxed

**Relaxation of defects due to positron localization = iterations**

Positron lifetime calculations in UO$_2$

Calculations in the **ABINIT code** (Two Components DFT) [1]
Self consistent scheme PSN$^2$ with gradient correction GC for the enhancement factor $g$

**DFT**(GGA, PBE)+$U$ formalism$^3$ to treat the 5f electrons
Defects were fully relaxed

<table>
<thead>
<tr>
<th></th>
<th>Charge</th>
<th>Lifetime (ps) PSN+GC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lattice</strong></td>
<td></td>
<td>167</td>
</tr>
<tr>
<td>$V_O$</td>
<td>0</td>
<td>199</td>
</tr>
<tr>
<td>$V_O$</td>
<td>2−</td>
<td>195</td>
</tr>
<tr>
<td>$V_U$</td>
<td>0</td>
<td>304</td>
</tr>
<tr>
<td>$V_U$</td>
<td>4−</td>
<td>293</td>
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<tr>
<td>$V_U+V_O$</td>
<td>0</td>
<td>306</td>
</tr>
<tr>
<td>$V_U+V_O$</td>
<td>2−</td>
<td>301</td>
</tr>
<tr>
<td>$V_U+2V_O(100)$</td>
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<td>304</td>
</tr>
<tr>
<td>$V_U+2V_O(110)$</td>
<td>0</td>
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</tr>
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<td>$2V_U$</td>
<td>0</td>
<td>318</td>
</tr>
<tr>
<td>$2V_U$</td>
<td>8−</td>
<td>289</td>
</tr>
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</tr>
<tr>
<td>$2V_U+2V_O$</td>
<td>4−</td>
<td>319</td>
</tr>
<tr>
<td>$2V_U+4V_O$</td>
<td>0</td>
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</tr>
<tr>
<td>$2V_U+4V_O$</td>
<td>2−</td>
<td>365</td>
</tr>
</tbody>
</table>

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**

Identification of vacancy defects in UO$_2$ irr

<table>
<thead>
<tr>
<th></th>
<th>Charge</th>
<th>Lifetime PSN+GC (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice</td>
<td></td>
<td>167</td>
</tr>
<tr>
<td>$V_O$</td>
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Exp.
Long lifetime $\sim 310 \pm 10$ ps
3 traps model

UO$_2$ (set G, sintered polished and annealed 1700°C/24h/ArH$_2$) irradiated alpha 45 MeV 2x10$^{16}$ cm$^{-2}$ Measurement in ultra vacuum as a function of temperature

Model with 3 Traps: negative ions $\text{IN}$, $\text{V}_1^-$, et $\text{V}_2$

$\tau_{\text{IN}} = 170$ ps and $\tau_{\text{V}_1} = \tau_{\text{V}_2} = 310$ ps

C$\nu$2 (cm$^{-3}$) | $\mu$1
---|---
6,50E+19 | 1,00E+19

$\tau_{\text{V}_1}$ (ps) $\geq 30$ times more neutral vacancies than negatively charged ones

C$\nu$ (cm$^{-3}$) | $\mu_0\tau$ | $\mu_0\text{r}$ | Er(eV) | Vr(s$^{-1}$)
---|---|---|---|---
2.0E+18 | 3,40E+16 | 4,00E+16 | 1,00E-02 | 1,00E+11

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.

Close to stoechiometry, I$_O^{2-}$, V$_O^{2+}$, V$_U^{-4}$ DFT LDA+U [2]

Identification of vacancy defects in UO$_2$

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$V_U$ and $V_U-V_O$ are negatively charged close to the middle of the bandgap in close stoechiometric UO$_2$

We propose
Neutral vacancy defects which are preponderant = Schottky defects
Negatively charged vacancy defects = a mixing of $(V_U-V_O)^{2-}$, $(2V_U-2V_O)^{4-}$

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

$2V_U$ is 8- close to the middle of the bandgap in close stoechiometric UO$_2$
Conclusions

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 precurssors?
• 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
✓ All collaborators
M Sidibe, CEMHTI CNRS
PE Lhuillier, CEMHTI CNRS
H Labrim, CEMHTI CNRS
P Desgardin, CEMHTI CNRS
C. Genevois-Mazellier, CEMHTI CNRS
E. Autissier, CEMHTI CNRS
T Sauvage, CEMHTI CNRS

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P Garcia, CEA/SESC/LLCC
G Jomard, CEA/SESC/LLCC
S Esnouf, LSI
D Roudil, CEA/SECM/LMPA
C Valot, CEA/SESC/LLCC
F Vella, CEA/SECM/LMPA

✓ Accelerators teams Jannus (Orsay and Saclay), LSI, CEMHTI

Thank You for your kind attention