Positron Annihilation Spectroscopy for vacancy defects studies in irradiated tungsten: Combination of modelling and experiments for vacancy size distribution and impurities interaction determination

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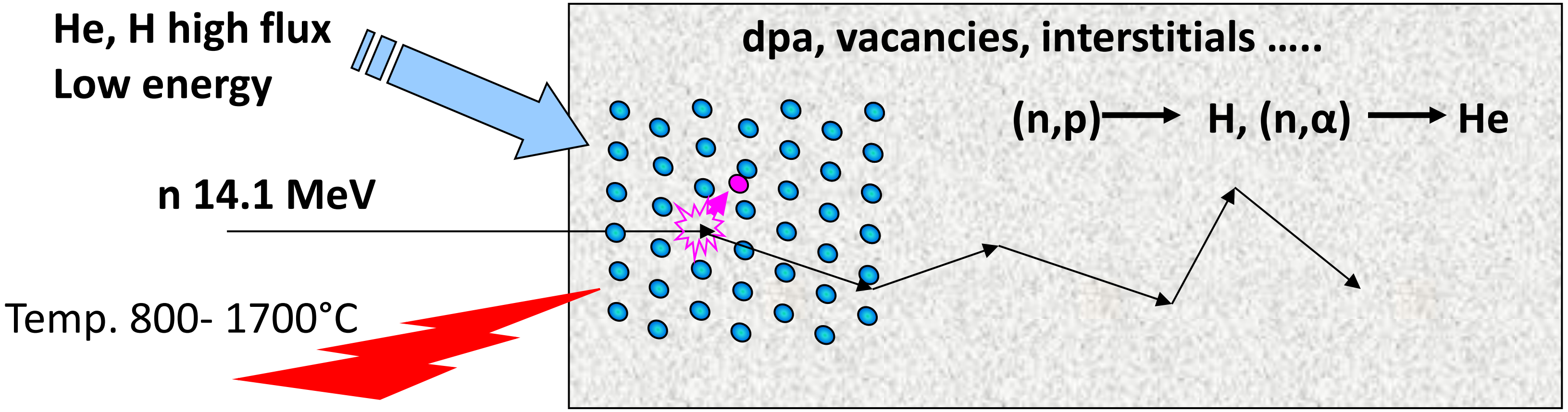
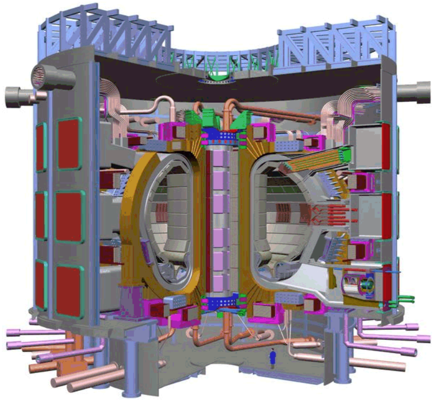
- ITER, DEMO : very hard conditions for materials

- Fusion reaction $^{2}H + ^{3}H \rightarrow ^{4}He(3,5\ MeV) + n\ (14.1\ MeV)$

Plasma and neutrons irradiations





ITER Tokamak

Elastic collision

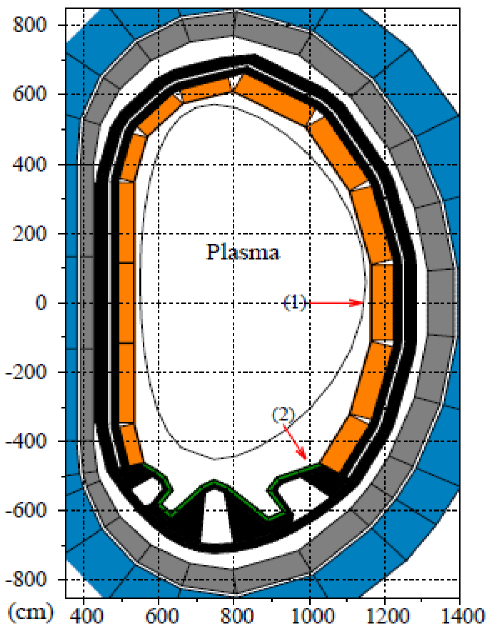
Pka : Primary Knocked on atom, recoil atom

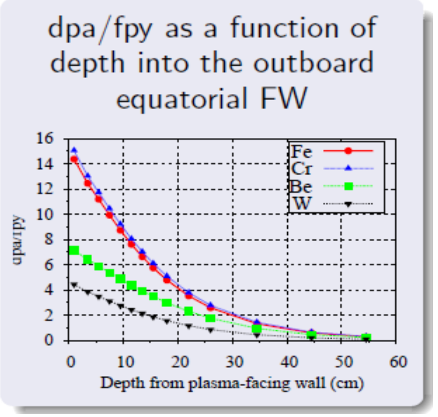
dpa : displacements per atom

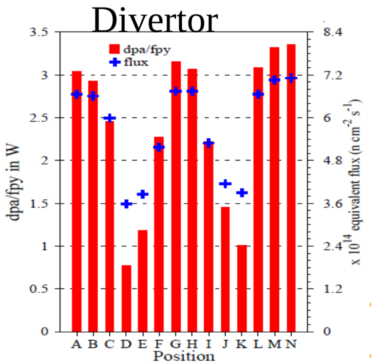
Big challenges : for thermal, electrical and mechanical properties

Tungsten divertor and first wall (ITER) , first wall? (DEMO)

Calculations in DEMO

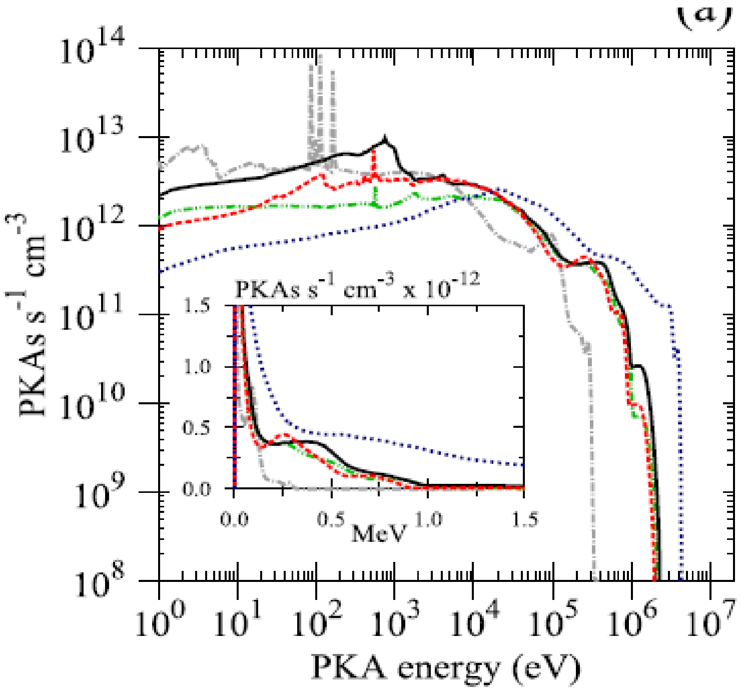






W for FW or divertor

Damage dose max in 3 years = 12dpa



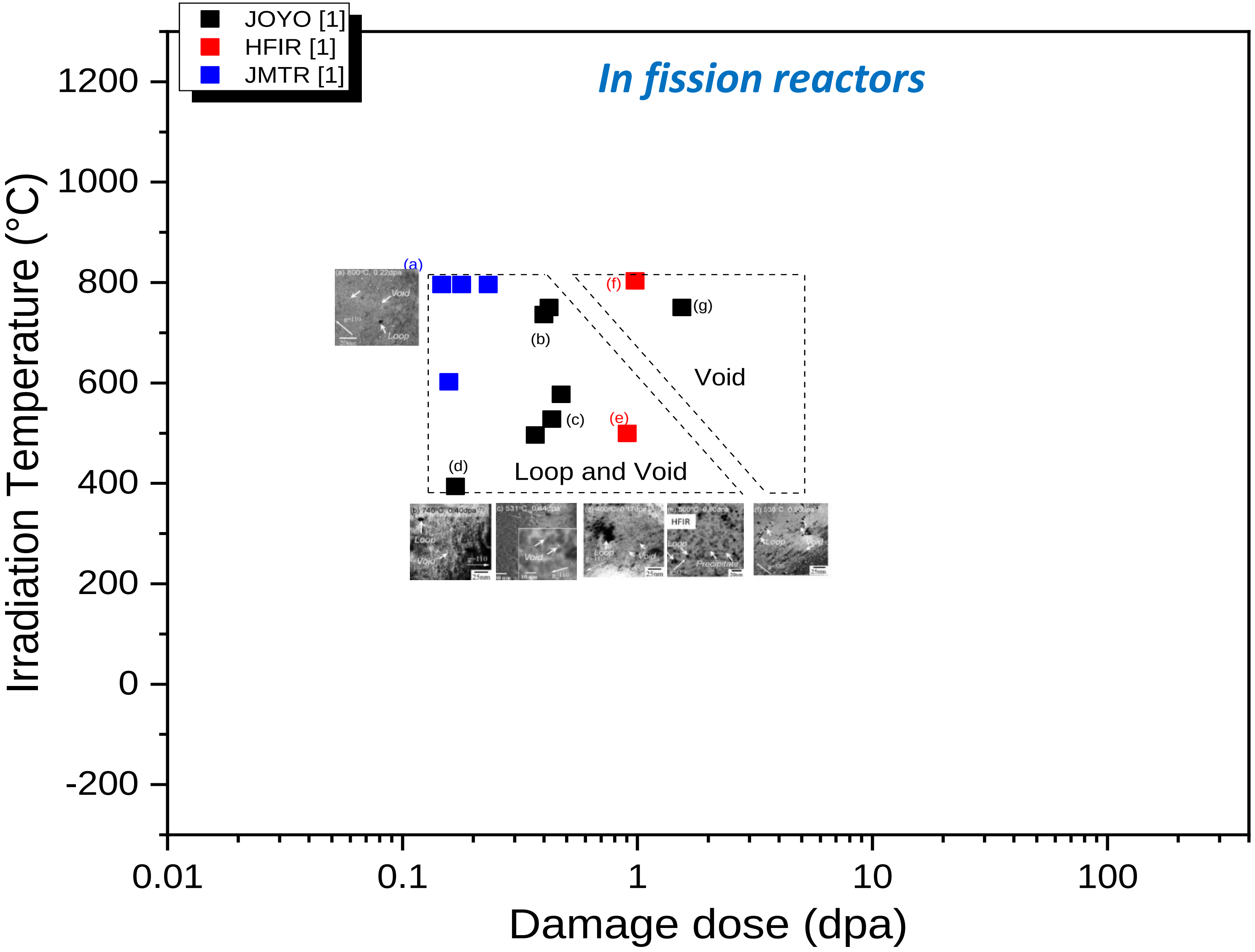
W = predominant recoil

- **Large energy distribution (up to 2 MeV) mean value at 150 keV**

CCFE MCNP

[1] M.R. Gilbert et al. / JNM 442 (2013) S755–S760, M.R. Gilbert et al. / JNM 467 (2015) 121

Damage induced by neutron irradiation in W



[1] A. Hasegawa et al. / Fusion Engineering and Design 89 (2014) 1568–157, [2] A. Barabash et al. / Journal of Nuclear Materials 283–287, (2000) 138-146. [3] M. R. Gilbert et al / (2013).Journal of Nuclear Materials 442, (2013) S755-S760

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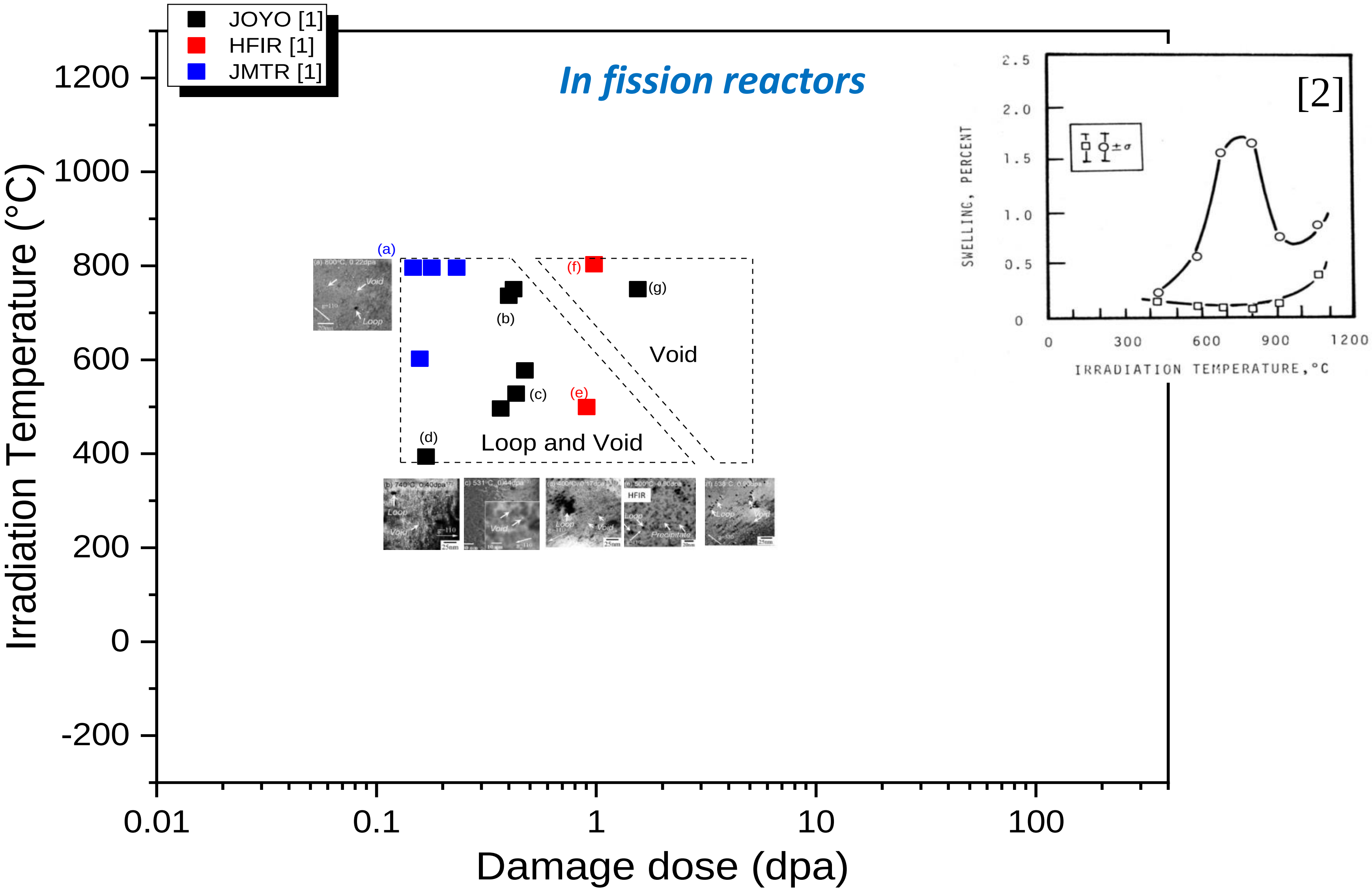

Swelling
→Vacancy defects ?

[1] A. Hasegawa et al. / Fusion Engineering and Design 89 (2014) 1568–157, [2] A. Barabash et al. / Journal of Nuclear Materials 283–287, (2000) 138-146. [3] M. R. Gilbert et al / (2013).Journal of Nuclear Materials 442, (2013) S755-S760

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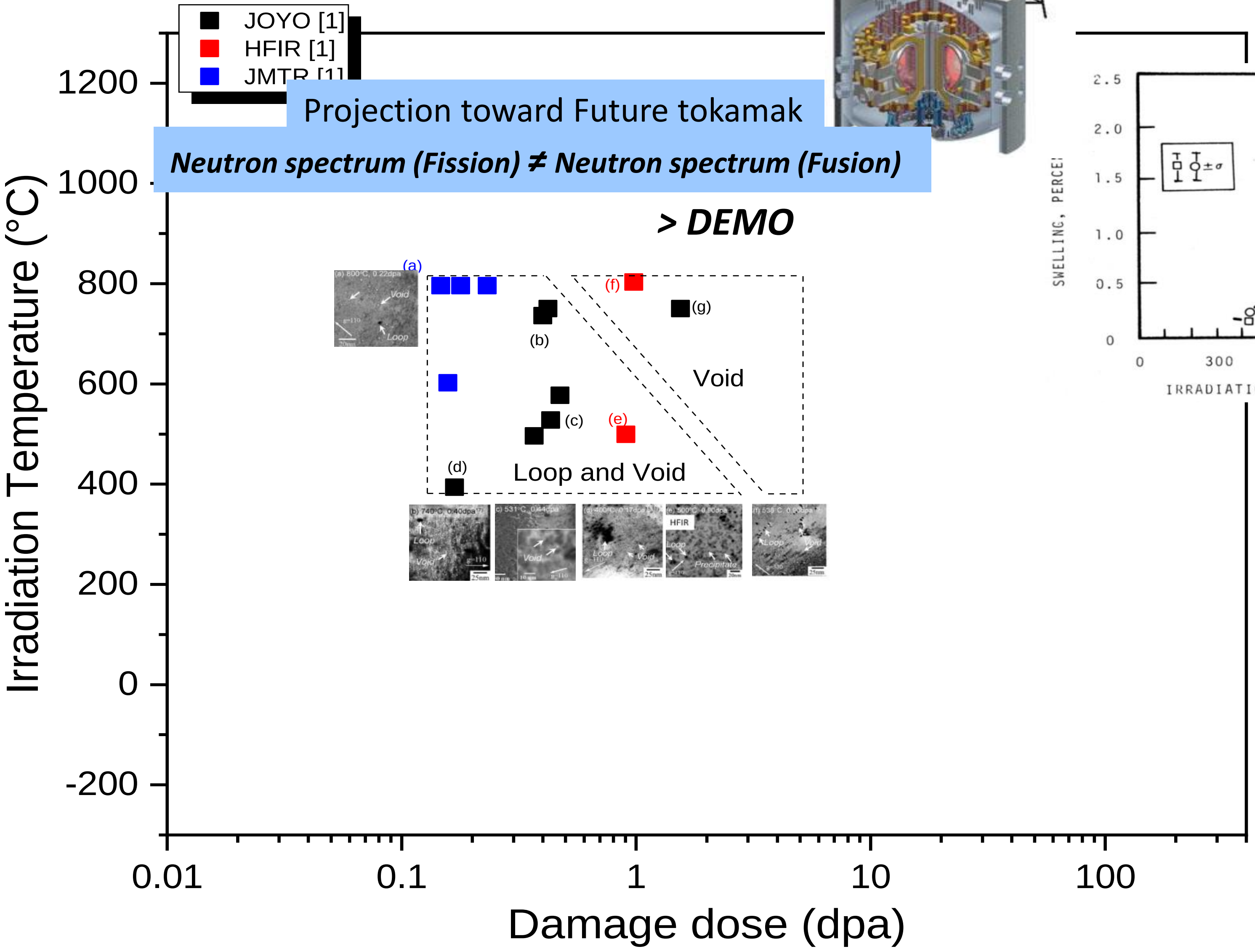
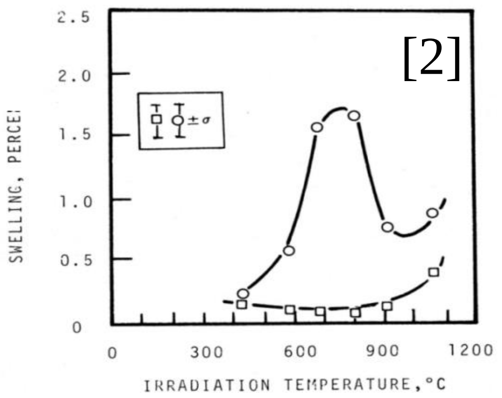


Projection toward Future tokamak

Neutron spectrum (Fission) ≠ Neutron spectrum (Fusion)

> DEMO



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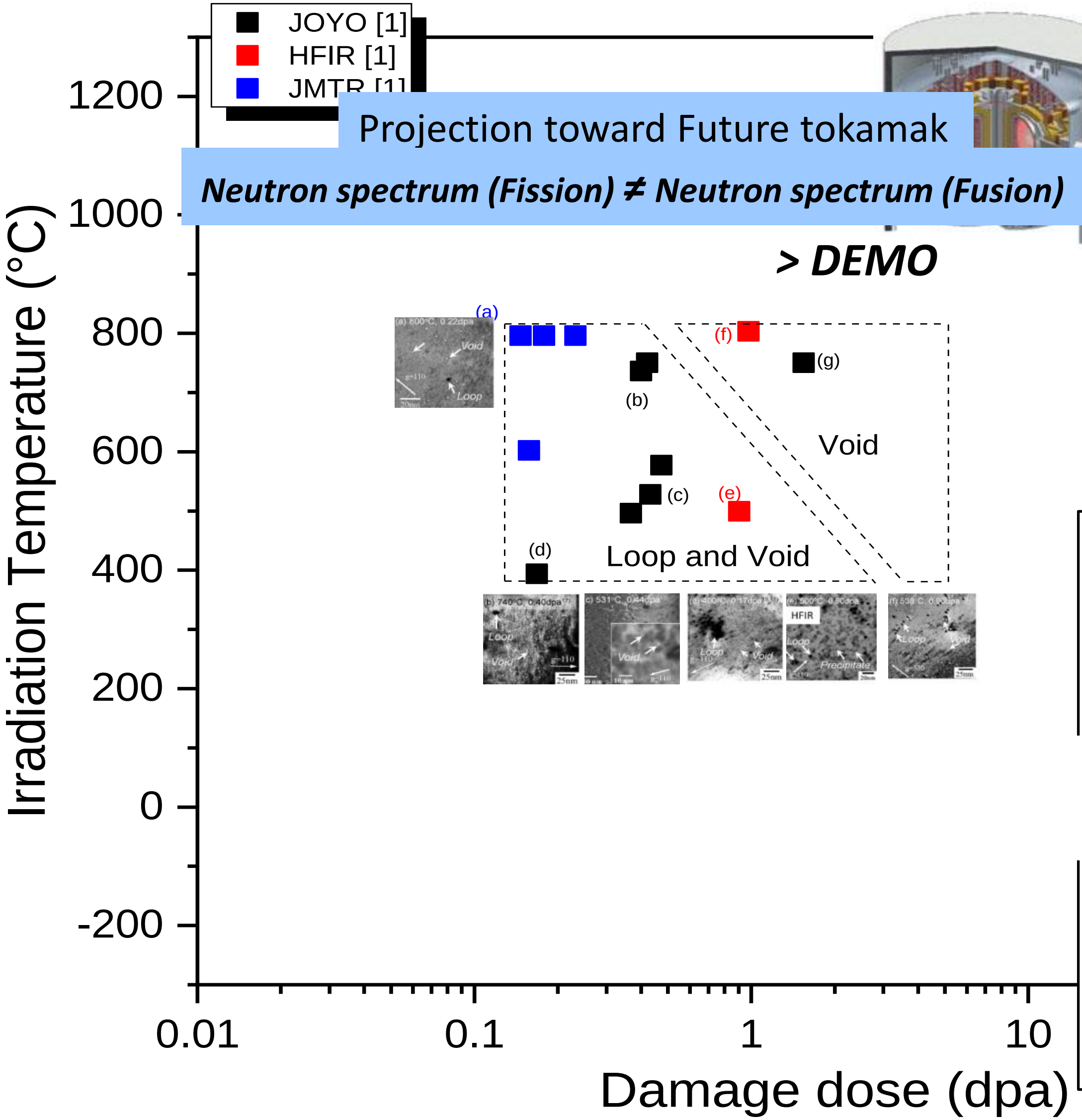

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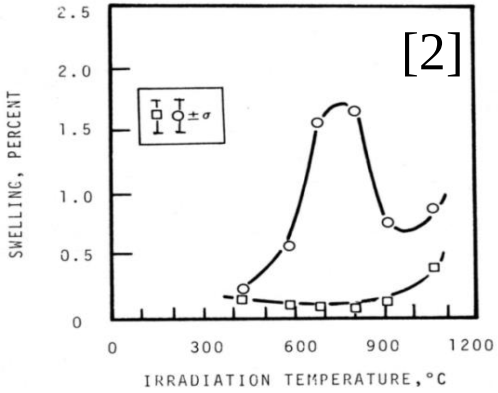

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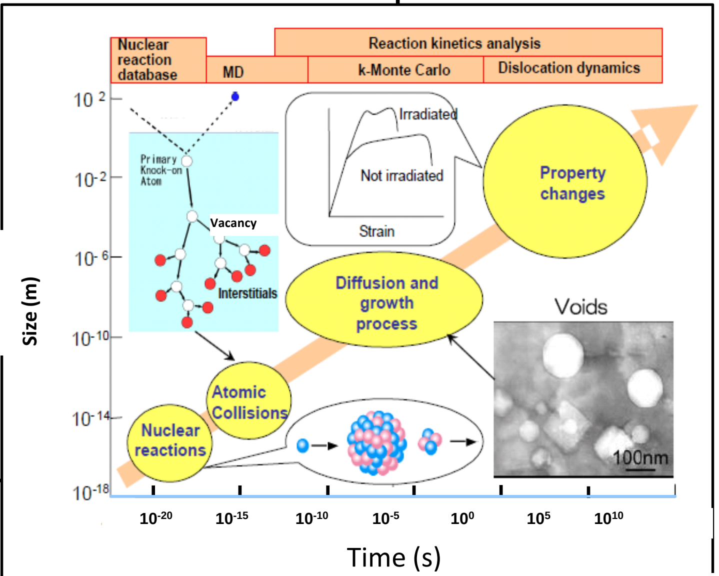

From **atomic** to **macroscopic** scale

Multiscale Modelling / experiments

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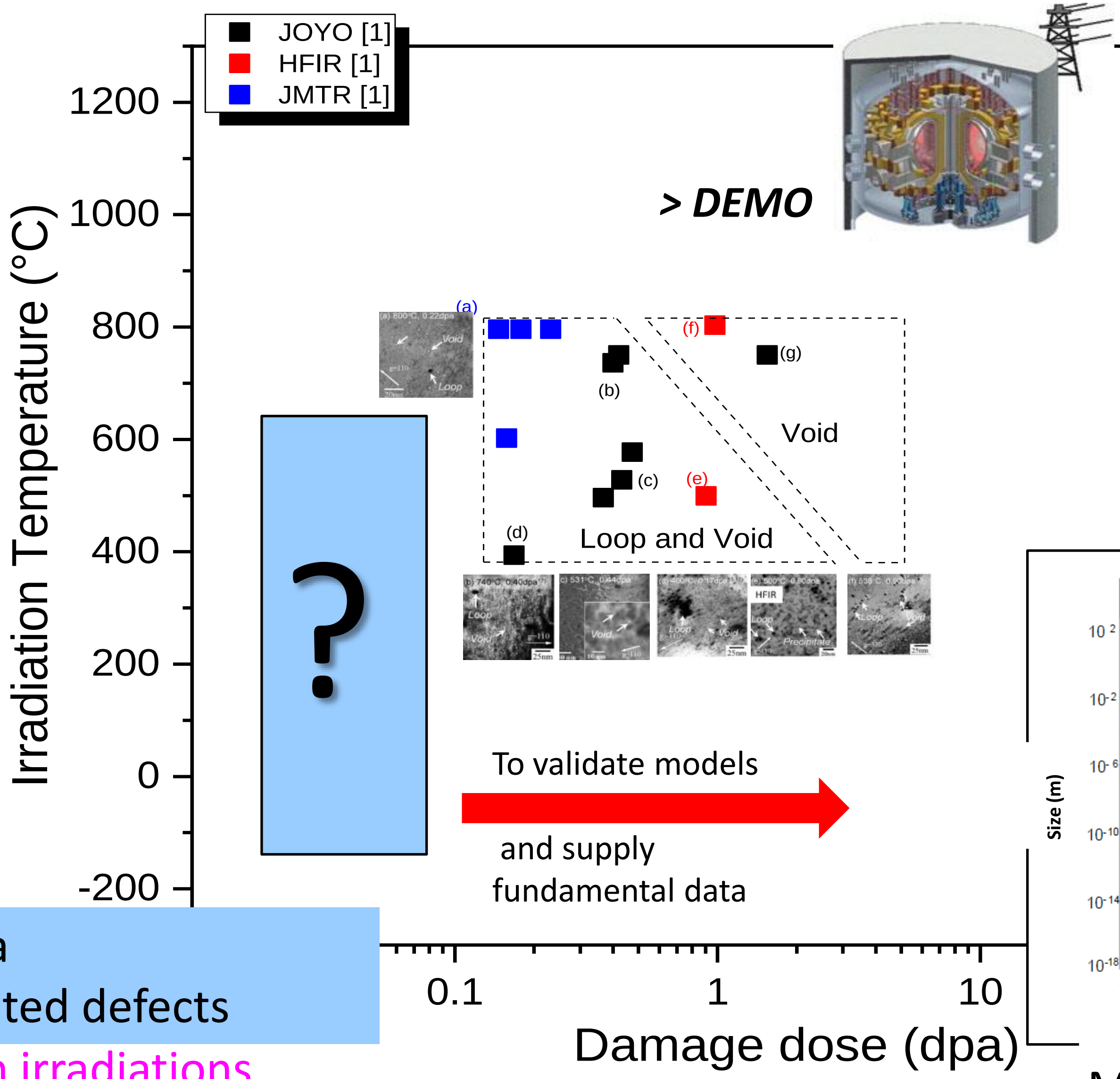
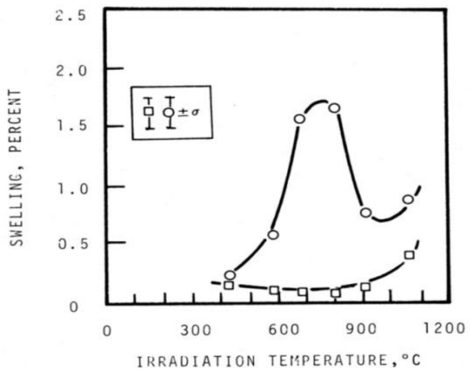


> DEMO

To validate models and supply fundamental data



Swelling
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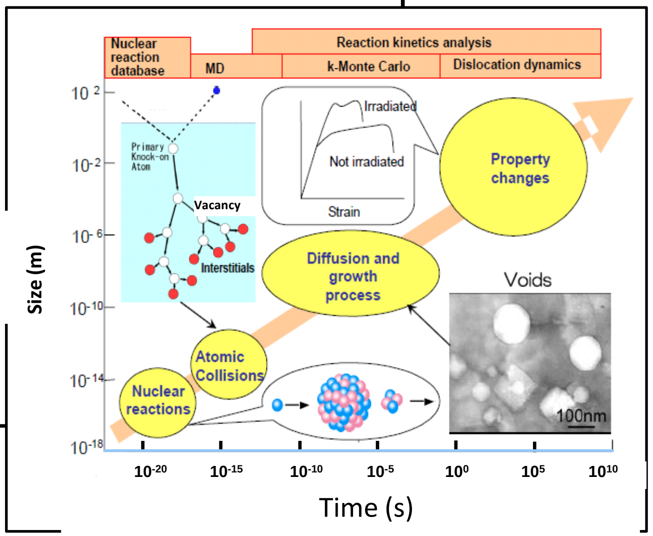

From **atomic** to **macroscopic** scale

Quantitative data
On all the generated defects

Using ion irradiations

Multiscale Modelling / experiments

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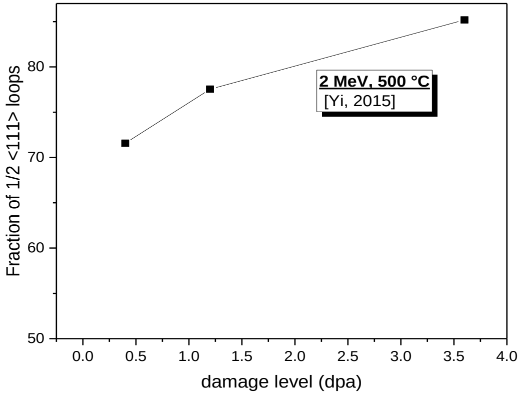
Self irradiations : W (150-2 MeV) ions

Dislocation loops: ½<111> , <100>



2 MeV W, 0.4 dpa, 500°C [1] :

Loops ½<111> : 3.3 x10^{22} m^{-3}

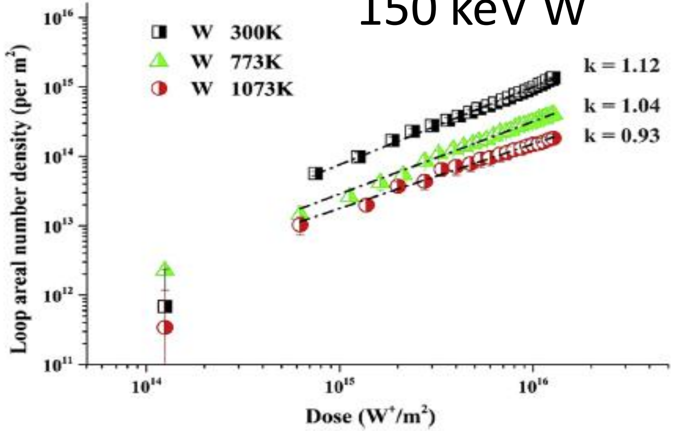
mean size 3-4 nm [1]

✓ For irradiation at 500°C, preferential formation of <100> loops at low dpa

[1] X Yi et al Acta Materialia 92 (2015) 163–177

✓ Density and size depend on temperature

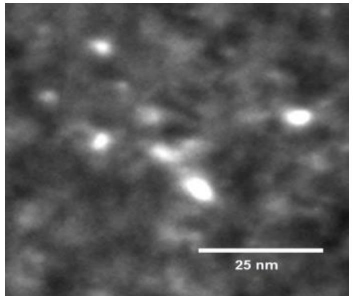
150 keV W



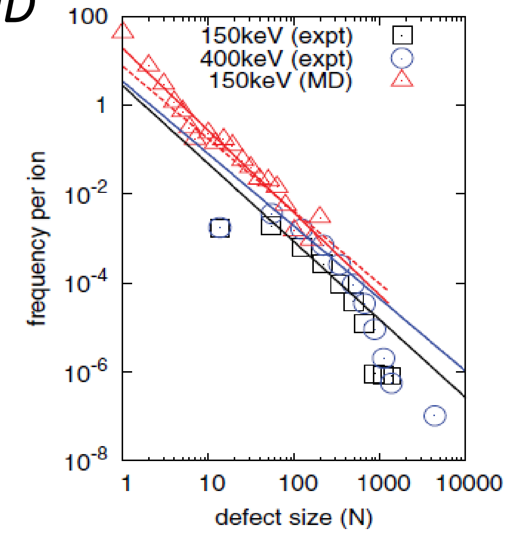
X. Yi et al. / Acta Materialia 112 (2016) 105-120

✓ Size distribution is a power law

as calculated in MD



150 keV W, LN2



Yi, X., *et al.*, EPL **110** (2015) 36001

Source of impurities

- H, He from Plasma and transmutations[2]
  - bubbles, fuzz…
- Transmutation elements (Re, Os, Ta..) [3]
  - precipitates…
- Reactor's environment light elements **impurities (C, N, O…**
  - **in material** [3]

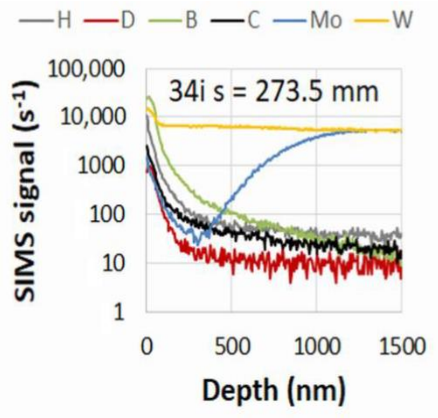
SIMS

	Concentration (at. ppm) (100-700 nm)		
	3N 99.95%		6N 99.9999%
H	910 [a]		Ud[b]
C	460 [a]	~ 90 [c]	~ < 65[c]
N	130 [a]		Ud[b]
O	345 [a]	1200 [105 : 3000][c]	~ 100[c]

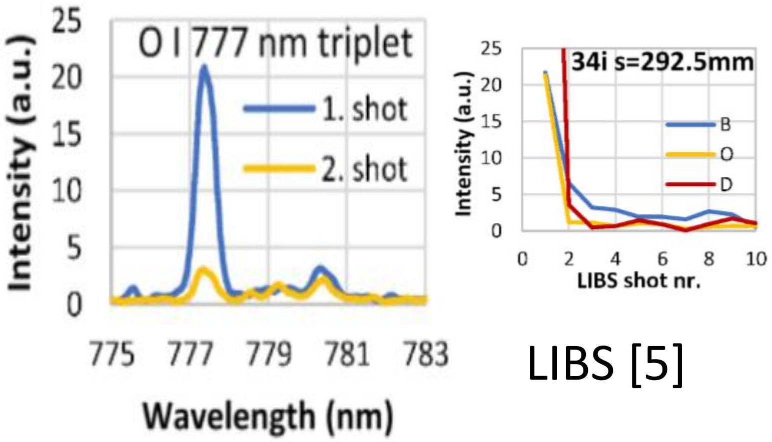
a/ provided concentration by supplier *b/* undetectable by LA-ICP-MS *c/* SIMS

  - **plasma (C, N, O… in WEST [5])**

WEST Campaign C3 [5]



SIMS [5]



LIBS [5]

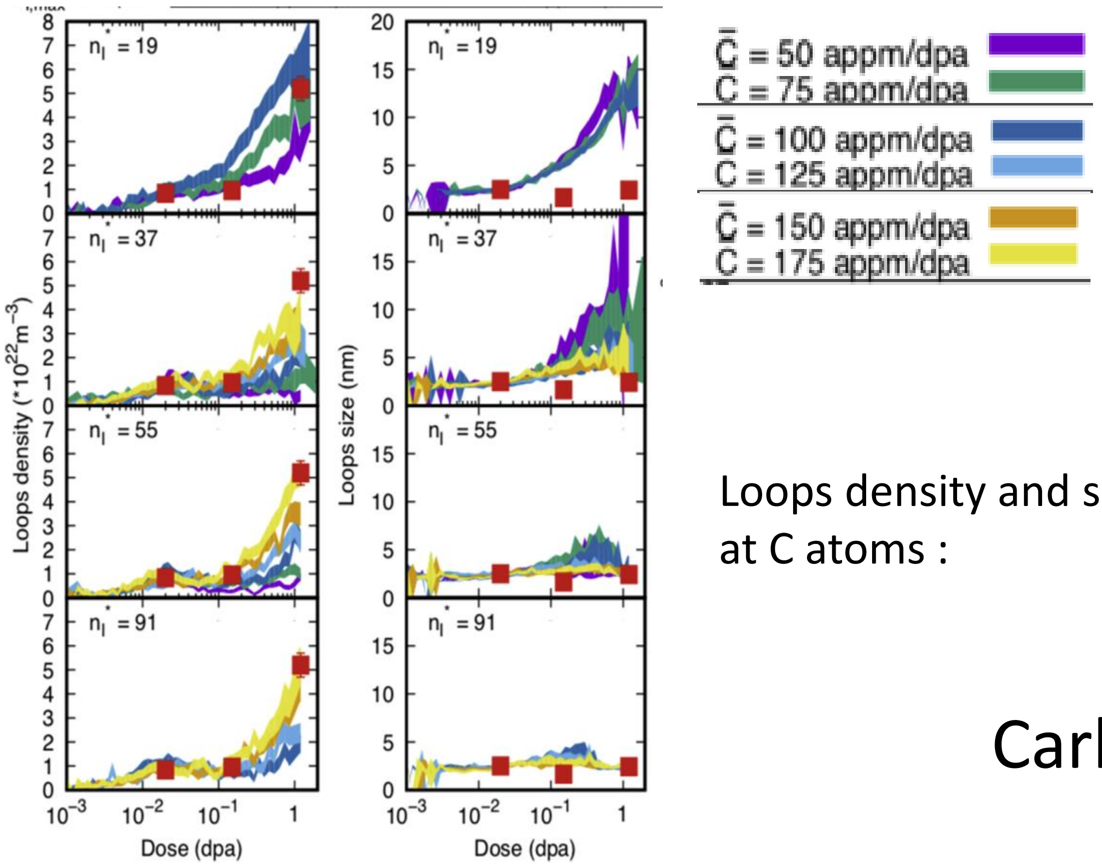
- Impurity in plasma
- Impurity-defects complexes and role on microstructure

2 Greenwood.al 212–215, 635–639 (1994). 3 *Computational Materials Science* **184**, 109932 (2020). 3 Liu. Computational Materials Science 50, 3213–3217 (2011). 4 Hu z. et al.., Journal of Nuclear Materials 556 (2021) 15317 . 5 Jogi I. et al J. Nucl. Eng. 2023,.

OKMC (Object Kinetic Monte Carlo) simulations [6]

→ Impurity-defects complexes

Carbon in tungsten

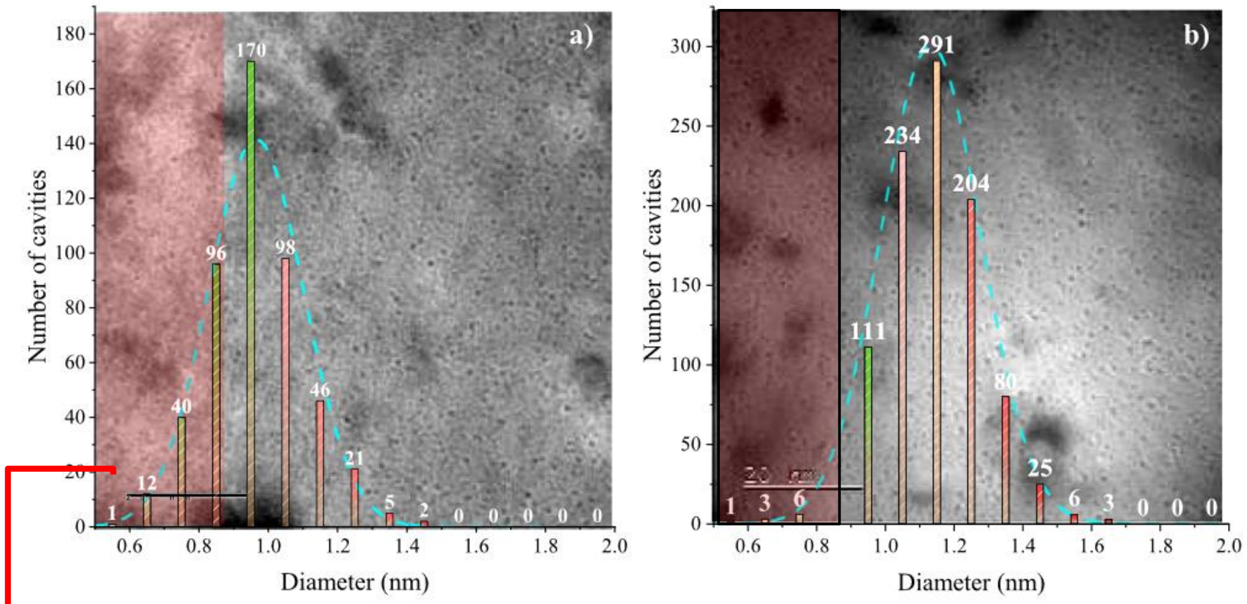


Loops density and size depends on C content due to trapping of loops at C atoms :

Carbon can trap dislocation loops

[6] N. Castin, et al J. Nucl. Mater. 527 (2019);

Self irradiations : vacancy defects



TEM Over focused (+300 nm) images

1.2 MeV W, 0.02 dpa, 500°C in 3N and 6N W [1] :

Damage level (dpa)	0.02	
Observation conditions	JEOL ARM200, 200 kV, 500 kX,	
Irradiation Temperature (°C)	500	
Purity	3N-HP	6N-XHP
Thickness (nm)	55 ± 20 (EFTEM)	90 ± 30 (EFTEM)
Mean diameter (nm)	0.97 ± 0.19	1.13 ± 0.21
Density (10^{24} m^{-3})	1.73 ± 0.71	1.56 ± 0.52
Swelling%	0.09 ± 0.02	0.12 ± 0.04

Small vacancy defects (<1nm) ? By TEM difficult to observe and to count them

Less data on vacancy defects and cavities

➔ Self irradiations and characterization of the microstructure using TEM and PAS

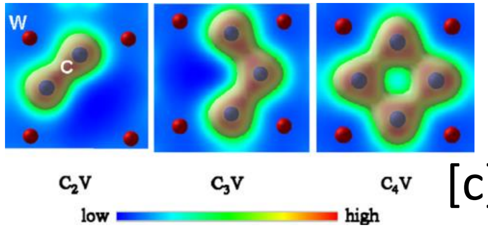
1. Z. Hu, P. Desgardin, C. Genevois et al. Journal of Nuclear Materials 556 (2021) 153175

Role of impurities on the irradiation induced damage microstructure

Impurity-Vacancy interactions

DFT calculations

X	E_m^X (eV)	$E_b^{V-X_1}$ (eV)	$E_{diss}^{V-X_1}$ (eV)
H	0.21 (TIS-TIS) [24]	1.24 [a]	1.45
C	1.46 (TIS-OIS) [20]	1.93 [b]	3.39
N	0.73 (TIS-OIS) [26]	2.48 [c]	3.21
O	0.17 (TIS-TIS) [22]	3.05 [d]	3.22



[c]

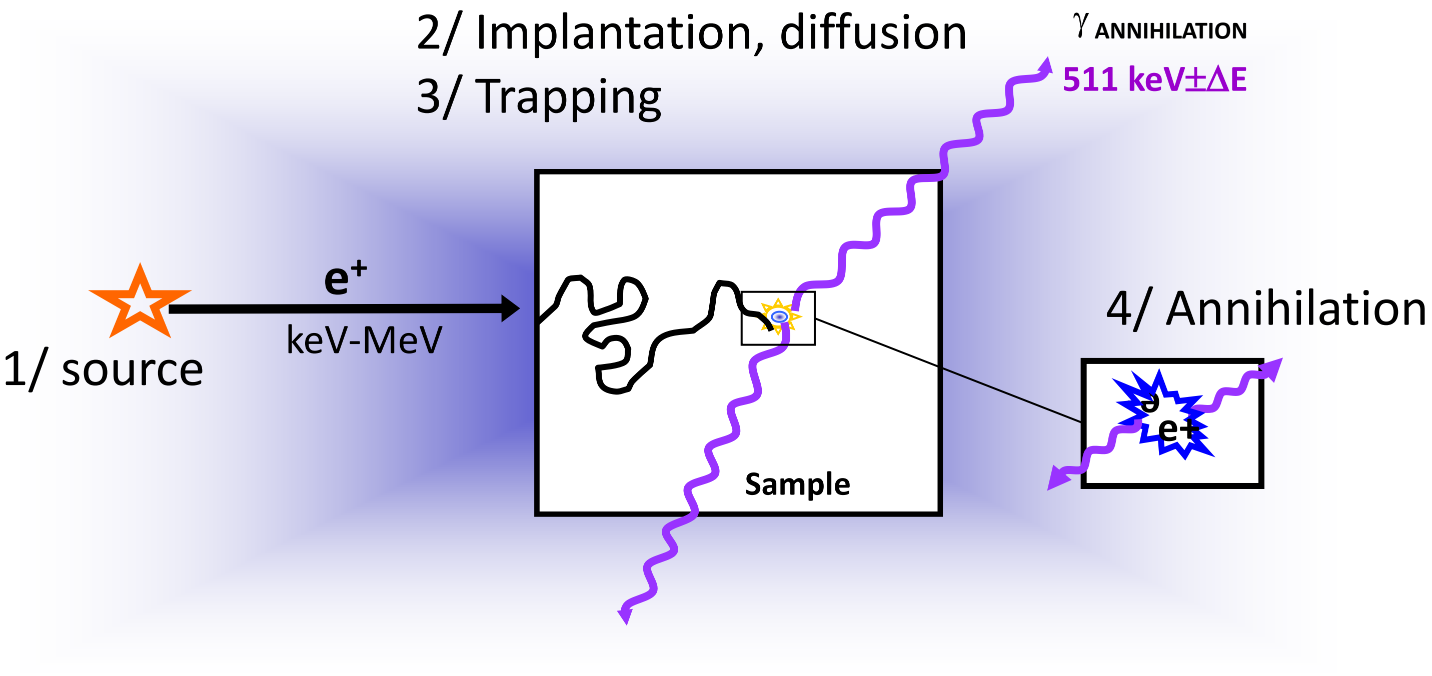
Strong interaction between **Vacancy** interactions with **LEs** (H,C,N,O..)

[a] Yang, L. et al. Comp. Mat. Science 184, 109932 (2020) [b] Liu, Y.-L et al. Comp. Mat. Science 50, 3213 (2011) [c] Y.-L. Liu, et al, Comp. Mat. Science. 83 (2014) 1. [d] A. Alkhamees, Y.-et al JNM437 (2013) 6

Principle of positron Annihilation Spectroscopy

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

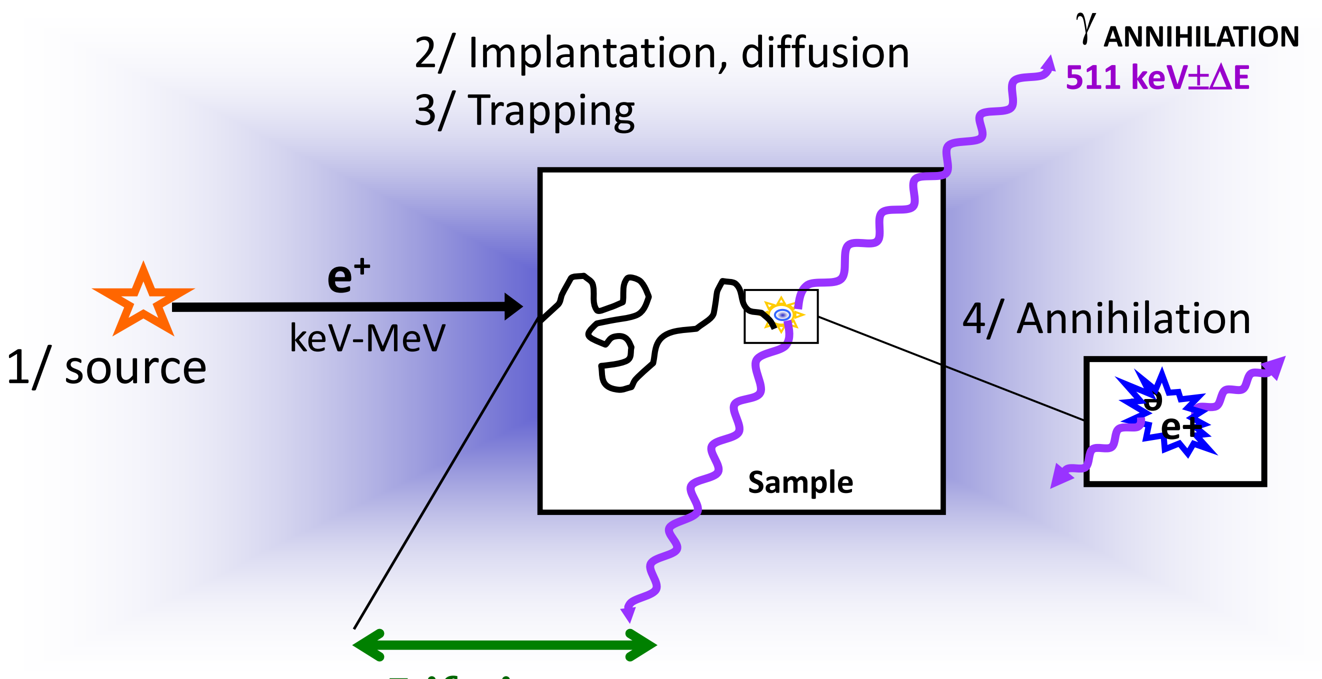
- ✓As antipârticle of electron, positron annihilates with it, leading to emission of **2** γ rays : E= 511 keV ± ΔE
- ✓**Trappping** in vacancy defects



⟹ Electronic Structure of solids

Probe for **vacancy defects** and **free volumes**

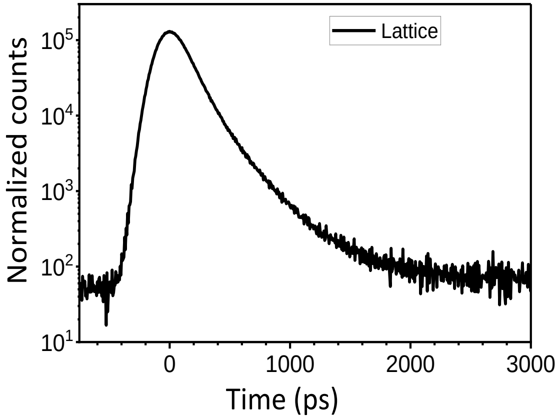
Principle of positron Annihilation Spectroscopy



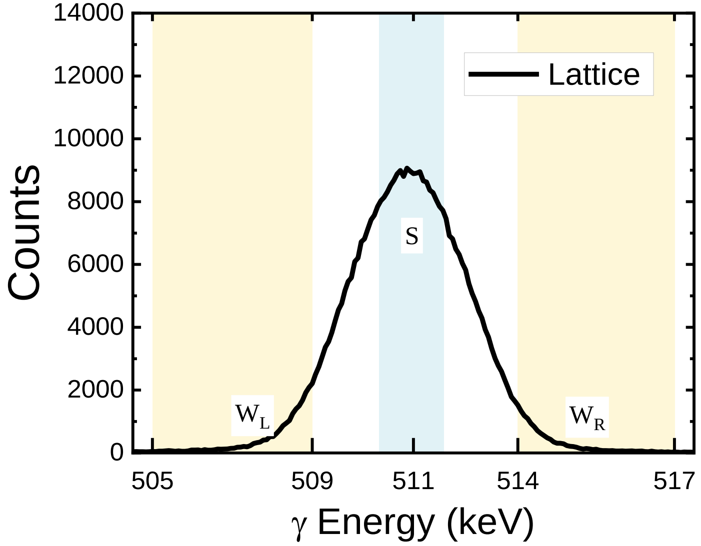
$$\tau = (\pi r_0^2 c n_{e-}^*)^{-1}$$

r_0: electron radius
c : light velocity
n_{e-} : local electronic density*

PALS



Doppler broadening Spectroscopy

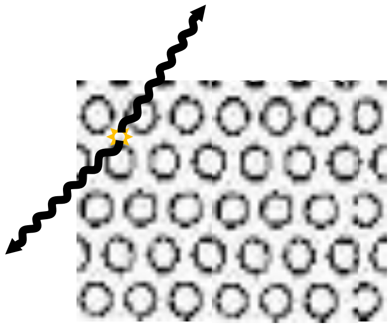


Annihilation fractions of e- e+

S = with low momentum

W = with high momentum

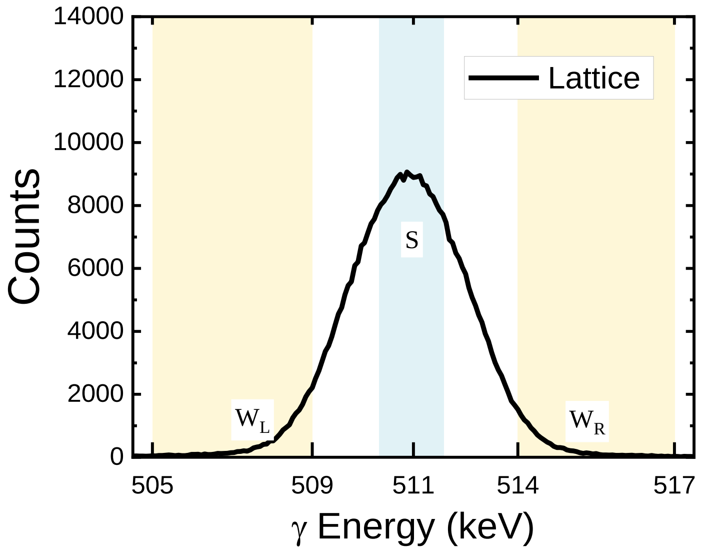
Principle of positron Annihilation Spectroscopy



τ_L, S_L, W_L

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

Doppler broadening Spectroscopy



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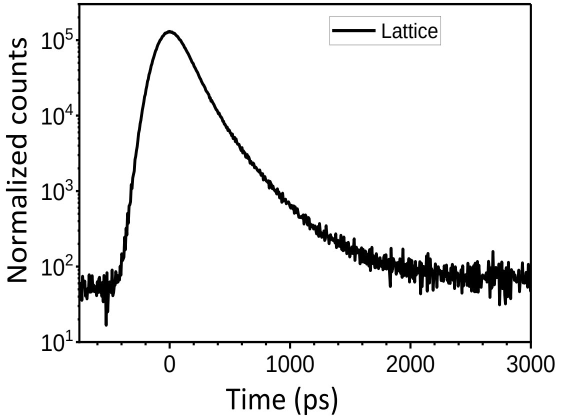

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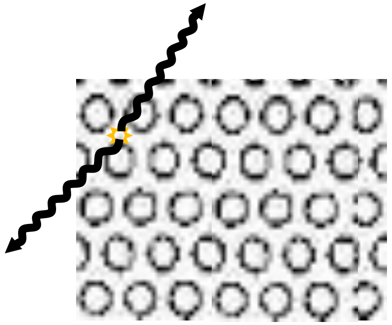

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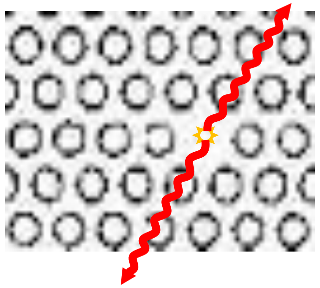
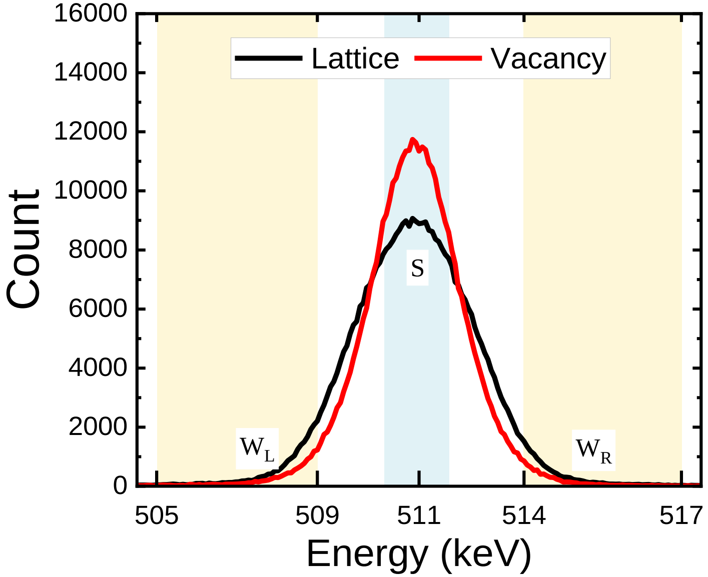


τ_V, S_V, W_V

Annihilation characteristics of Vacancy

Doppler broadening Spectroscopy

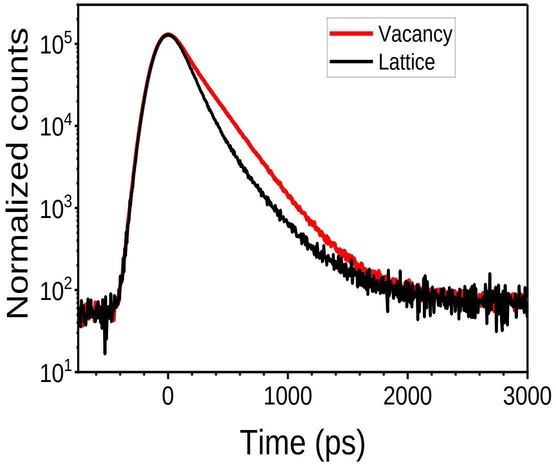


Lifetime t

PALS

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

r_0: electron radius
c : light velocity
n_{e-} : local electronic density*

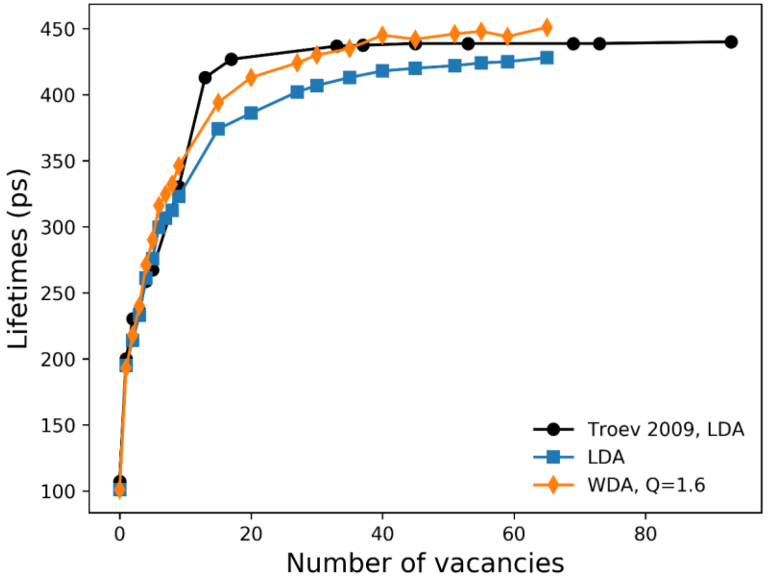


Vacancy defects

τ , *S* increases

W decreases

Lifetime τ



Exp: τ_L = **105 ± 3 ps**

τ_V = **200 ± 5 ps**

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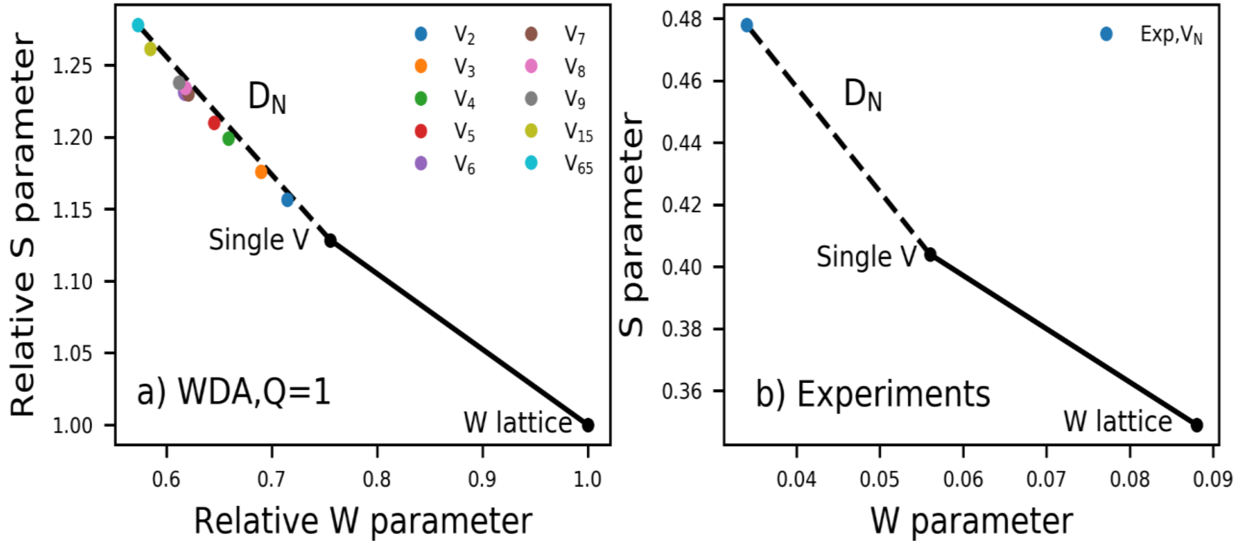
Qigui Yang[a,1], Zhiwei Hu[b,1], Ilja Makkonen[c], Pierre Desgardin[b], Werner Egger[d], Marie-France Barthe[b,*], Pär Olsson[a,*]

[a] KTH Royal Institute of Technology, Nuclear Engineering, Roslagstullsbacken 21, 114 21 Stockholm, Sweden
[b] CEMHTI, CNRS, UPR3079, University of Orléans, F-45071 Orléans, France
[c] Department of Physics, University of Helsinki, P.O. Box 43, FI-00014 Helsinki, Finland
[d] Institut für Angewandte Physik und Messtechnik, Universität der Bundeswehr München, D-85579 Neubiberg, Germany

Doppler broadening Spectroscopy (*S* &*W*)



*In vacancy clusters : WDA (Q=1)

N in V_N increases

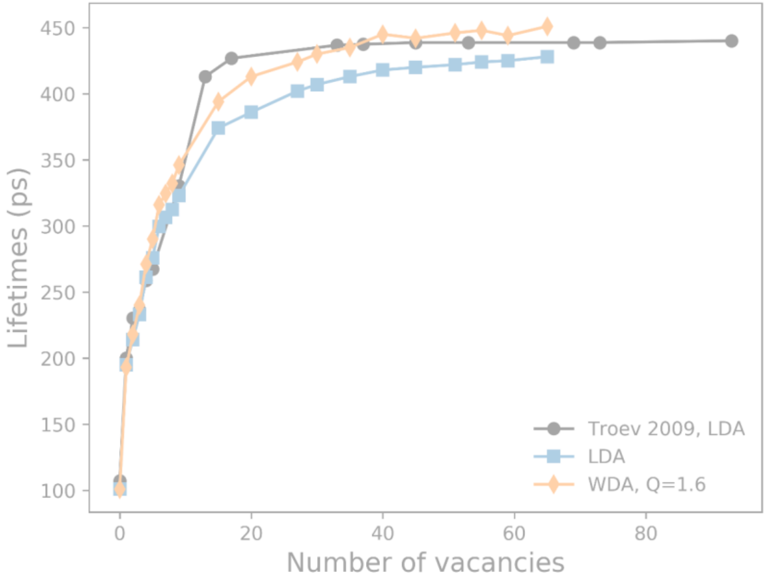
τ_{VN} , S_{VN} increases

W_{VN} decreases

Until saturation for N~30

TC- DFT calculations of annihilation characteristics in tungsten

Lifetime τ



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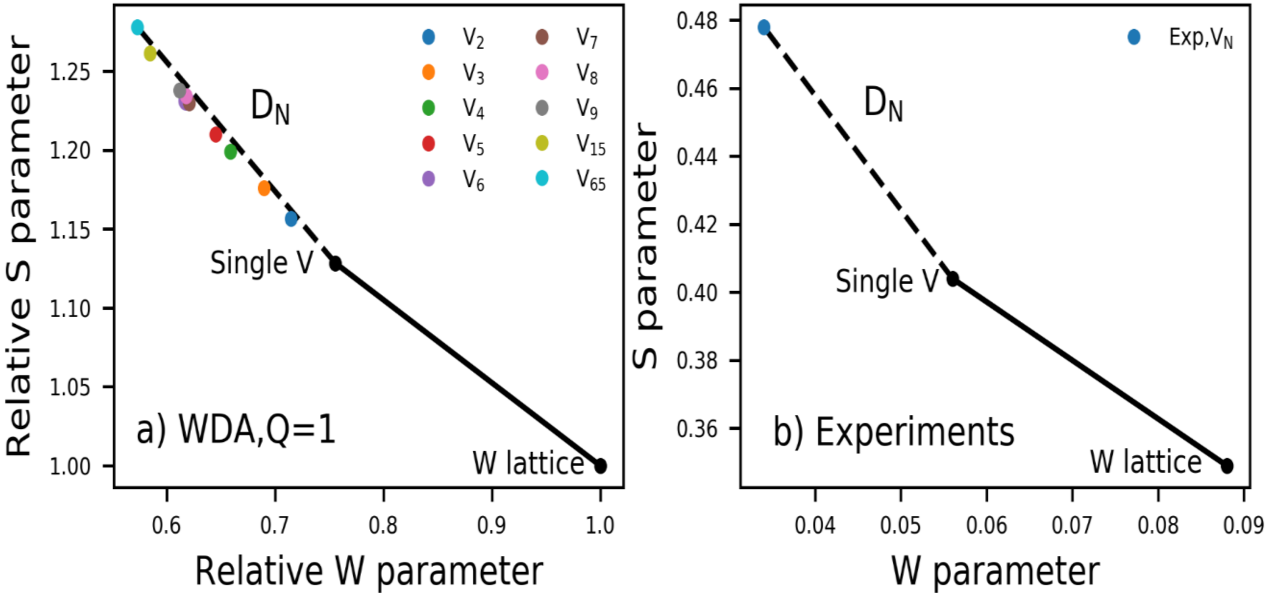
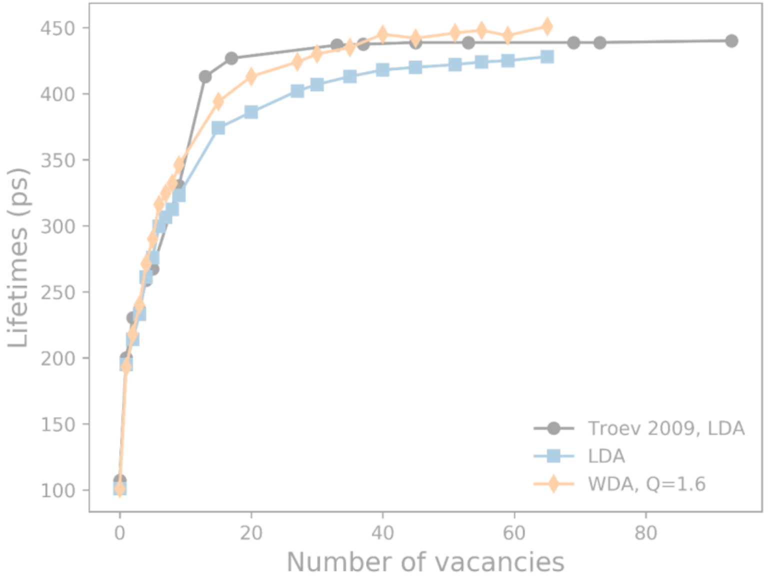


*In vacancy clusters : WDA (Q=1)

SW points aligned on a straight line D_N
Same trend for both experiment and theory

Lifetime τ



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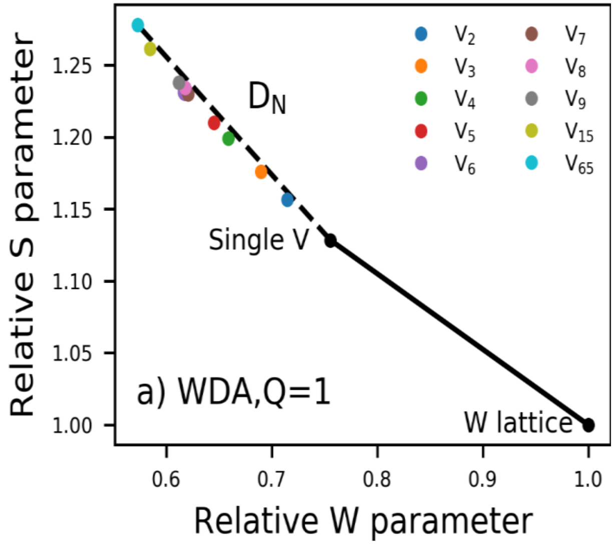
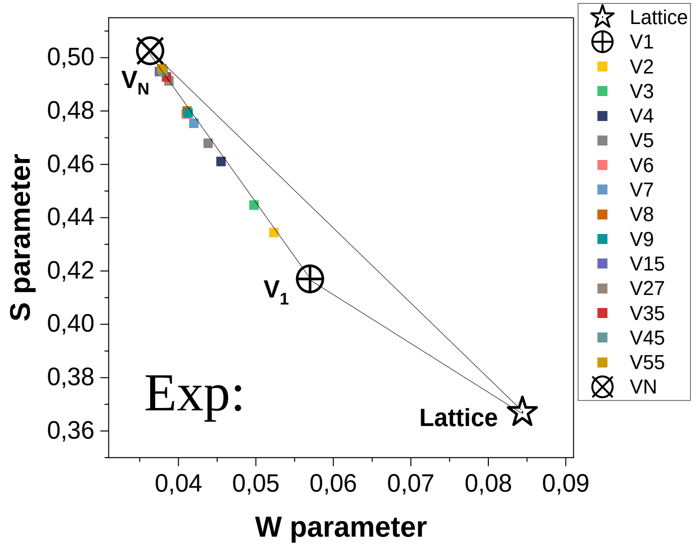
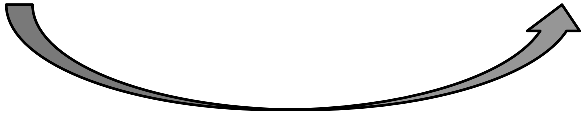




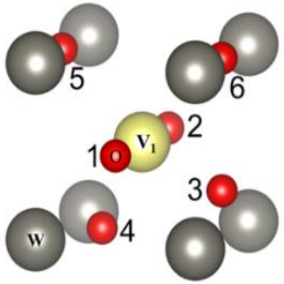


Relative S & W annihilation characteristics

[1] *Q Yang, Z. Hu, I. Makkonen, P. Desgardin, W. Egger, M-F. Barthe, P. Olsson,* Journal of Nuclear Materials 571 (2022) 154019

O_pV_1 properties calculated by TC-DFT

- One V_1 can trap until 6 O atoms, forming $O_{1\text{-}6}V_1$ complexes **[1]**



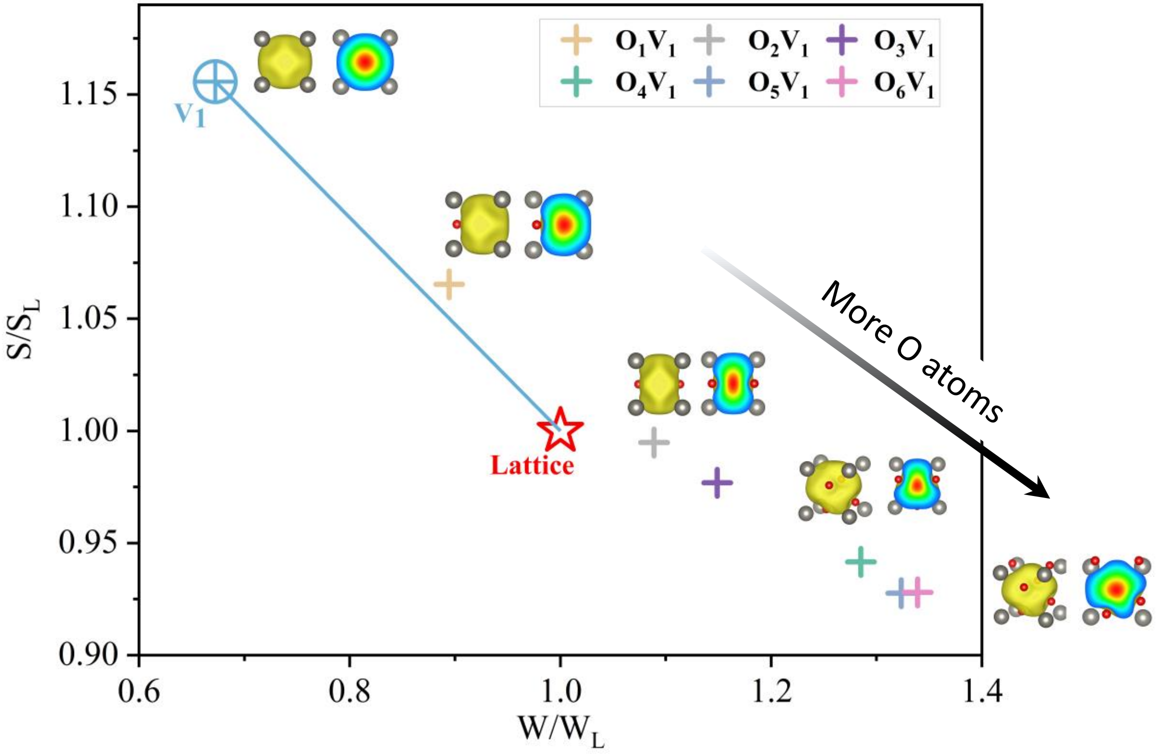
PALS [3]

O_pV_1, p	$E_{binding}^{O_pV_1}$ (eV)	τ (ps)
1	3.0	170
2	5.9	142
3	6.9	143
4	8.56	130
5	10.06	124
6	11.92	132

More O atoms

Pure V_1, τ_{V_1}=195 ps (Theo.) **[2]**

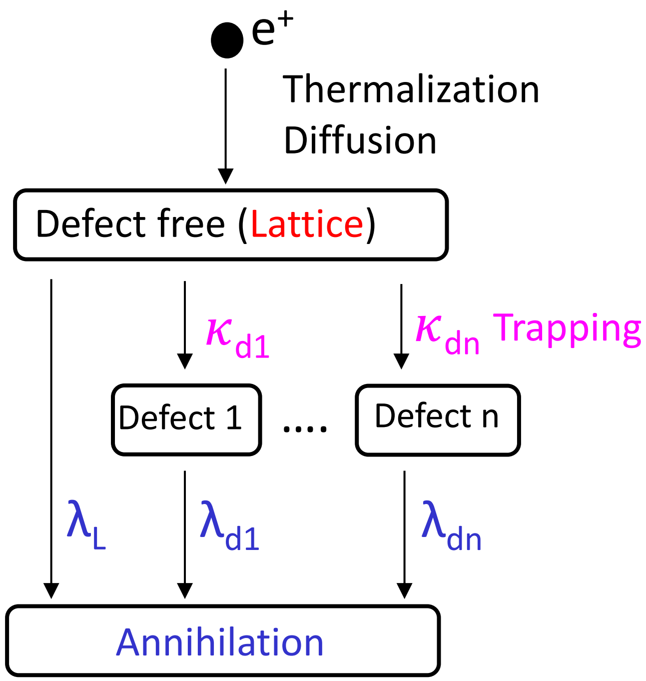
DB-PAS [3]



[1] You et al. RSC Adv. 5 (2015) 23261–23270. **[2]** Q. Yang et al. Journal of Nuclear Materials. 571 (2022) 154019..
[3] Z. Hu et al., Journal of Nuclear Materials 602 (2024) 155353.

Positron Trapping model

Assuming **n independent defects** and **no de-trapping** from defects **[1]**



1. $\boldsymbol{PALS(t)} = R(t) * \sum\left(\frac{I_{di}}{\tau_{di}} e^{-\frac{t}{\tau_i}}\right) + \frac{I_1}{\tau_1} e^{-\frac{t}{\tau_1}} + BG$ $R(t),\ BG$: experimental values

2. $\begin{cases} \boldsymbol{S} = S_L \cdot f_L + \sum S_{di} \cdot f_{di} \\ \boldsymbol{W} = W_L \cdot f_L + \sum W_{di} \cdot f_{di} \end{cases}$

τ_{di}, S_{di} and W_{di} calculated using TCDFT

$\begin{cases} I_{di} = \frac{k_{di}}{\lambda_L - \lambda_i + \sum k_{di}} \text{, and } I_1 + \sum_{di} I_{di} = 1 \\ f_{di} = \frac{k_{di}}{\lambda_L + \sum k_{di}} \text{, and } f_L + \sum_{d_1} f_{di} = 1 \end{cases}$

I_i : Intensity of lifetime component i

f_i: Fraction of annihilation state i

Where trapping rate, $\kappa_{di} = \boldsymbol{c_{di}} \cdot \mu_{di}$

C_{di}: vacancy (V_i) concentration

μ_{di}: specific trapping coefficient

[1] K. Saarinen, P. Hautojärvi, C. Corbel, Chapter 5 Positron Annihilation Spectroscopy of Defects in Semiconductors, in: Semiconductors and Semimetals, Elsevier, 1998: pp. 209–285.

Trapping model +TC- DFT

Assuming n independent defects and no de-trapping from defects [1]

Theoretical S, W, and PALS(t)

e^+

Thermalization
Diffusion

Defect free (Lattice)

κ_{d1} κ_{dn} Trapping

Annihilation

1. $\boldsymbol{PALS(t)} = R(t) * \sum\left(\frac{I_i}{\tau_i} e^{-\frac{t}{\tau_i}} + \frac{I_1}{\tau_1} e^{-\frac{t}{\tau_1}}\right) + BG$

$R(t)$, BG: experimental values

2. $\begin{cases} \boldsymbol{S} = S_L \cdot f_L + \sum S_i \cdot f_i \\ \boldsymbol{W} = W_L \cdot f_L + \sum W_i \cdot f_i \end{cases}$

τ_i, S_i and W_i calculated using TCDFT

- **Vacancy distribution (C_i) can be extracted from Experimental data : PALS spectrum, S_{exp}, W_{exp}**

Or

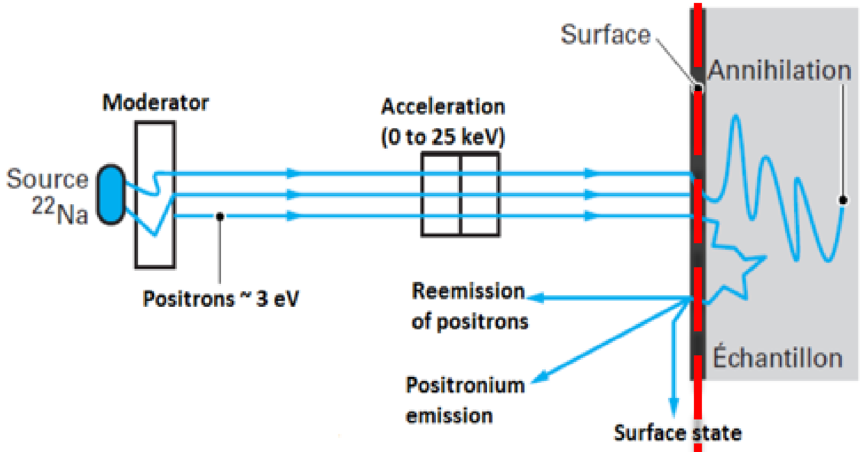
- **PALS spectrum, *S*, *W* can be calculated and compared to Experimental data**

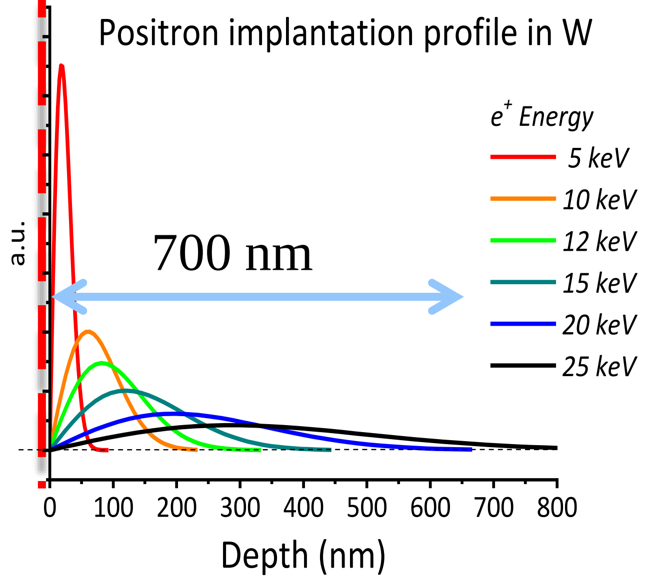
Where trapping rate, $\kappa_i = \boldsymbol{c_i} \cdot \mu_i$

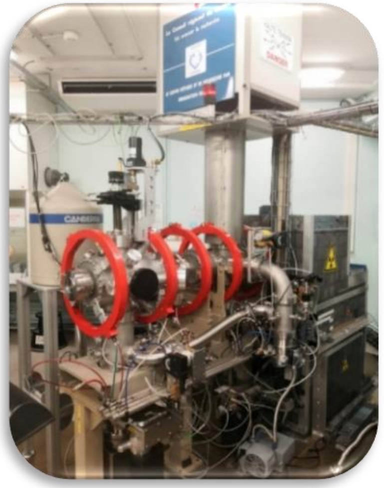
C_i: *vacancy (V_i) concentration*
μ_i: *specific trapping coefficient*

[1] K. Saarinen, P. Hautojärvi, C. Corbel, Chapter 5 Positron Annihilation Spectroscopy of Defects in Semiconductors, in: Semiconductors and Semimetals, Elsevier, 1998: pp. 209–285.

Slow positron beam for thin layer characterization







Slow e^+ beam
at CEMHTI

Variable slow positron beam + Doppler Broadening

Monoenergetic e^+ beam (Ø 2-3mm, 10^5 $e^+.cm^{-2}.s^{-1}$) from 0.5 to 25 keV **[1]**

→ ***S(E)*** and ***W(E)***
Vacancy-type defects in thin layers

[1] Desgardin et al. « Slow Positron Beam Facility in Orléans ». *Materials Science Forum* 363-365 (avril 2001): 523-25

✓ 2 illustrations

- Oxygen vacancy interactions
- Vacancy clusters distribution in self-irradiated tungsten

✓ 2 illustrations

- ➢ Oxygen vacancy interactions
- ➢ Vacancy clusters distribution in self-irradiated tungsten

Journal of Nuclear Materials 602 (2024) 155353

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Revealing the role of oxygen on the defect evolution of electron-irradiated tungsten: A combined experimental and simulation study

Zhiwei Hu [a], Qigui Yang [b,e,f], François Jomard [c], Pierre Desgardin [a], Cécile Genevois [a], Jérôme Joseph [a], Pär Olsson [b], Thomas Jourdan [d], Marie-France Barthe [a,*]

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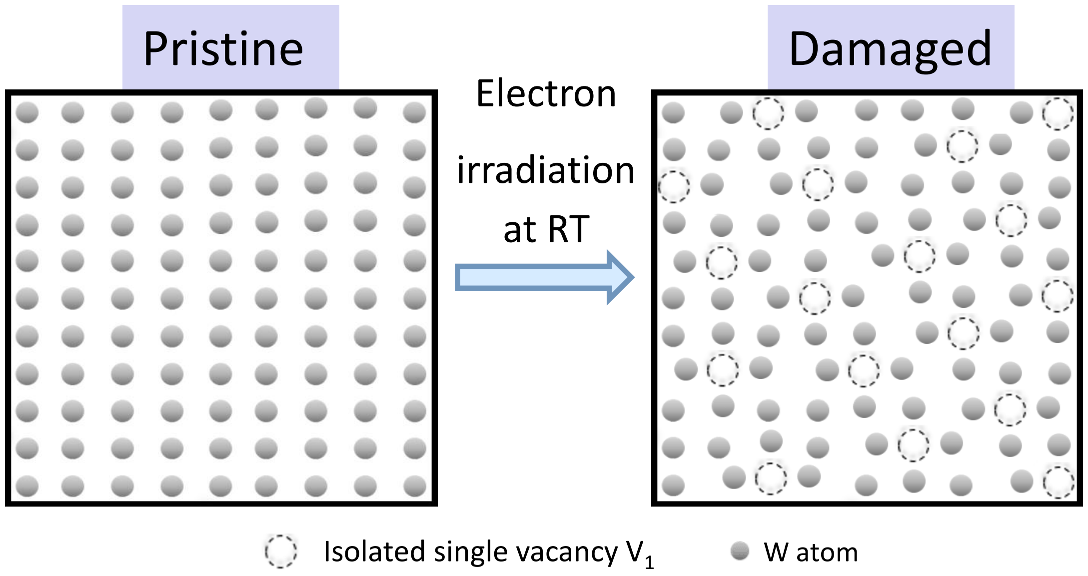
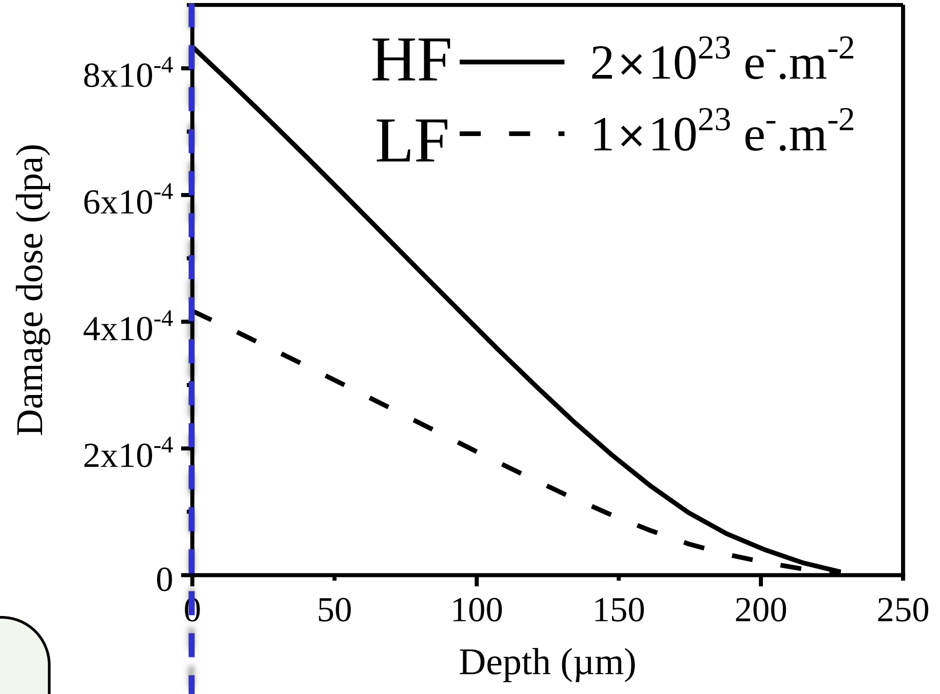
[b] KTH Royal Institute of Technology, Nuclear Engineering, Roslagstullsbacken 21, 114 21 Stockholm, Sweden
[c] Groupe d'Etude de la Matière Condensée, CNRS, UVSQ, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France
[d] Université Paris-Saclay, CEA, Service de recherche en Corrosion et Comportement des Matériaux, SRMP, F-91191 Gif-sur-Yvette, France
[e] Institute of High Energy Physics, CAS, 100049 Beijing, China
[f] China Spallation Neutron Source, Institute of High Energy Physics, CAS, Dongguan 523803, China

2.5 MeV electron irradiation at Room temperature (RT)

99,95% (3N) polycrystalline tungsten



Damage profiles using POLY et SMOTT code [1-3]



Max damage

HF: ~8×10^{-4} dpa

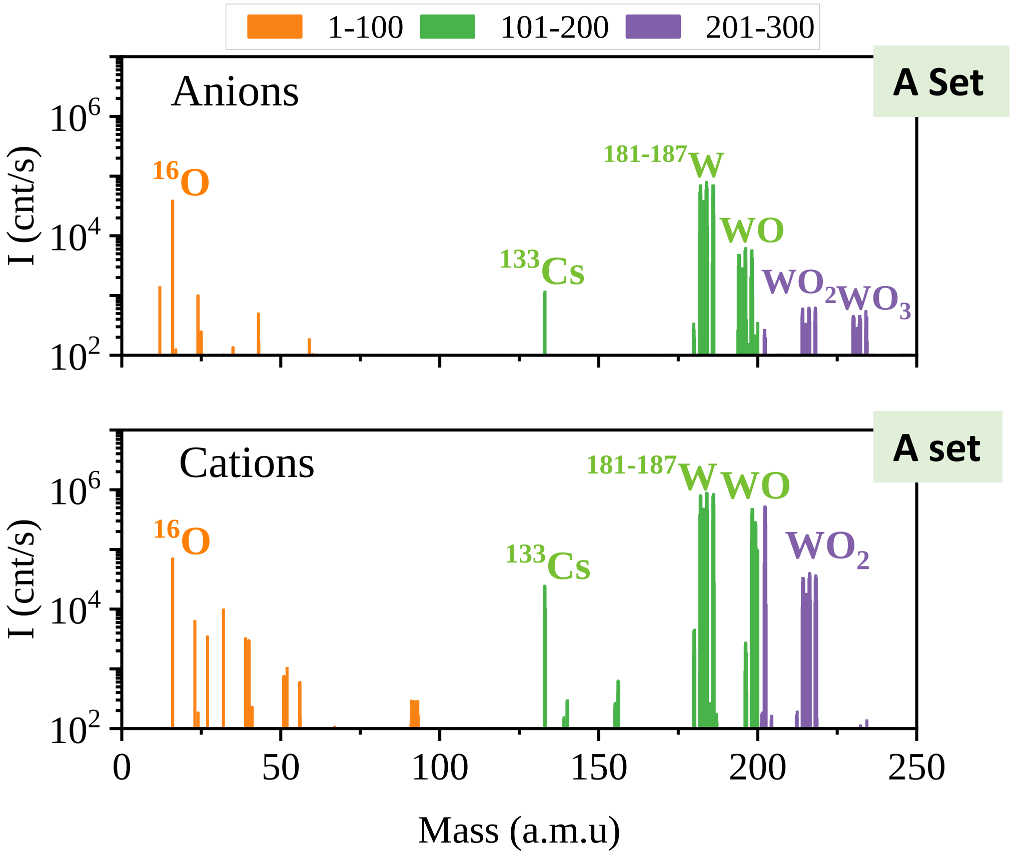
LF: ~4×10^{-4} dpa

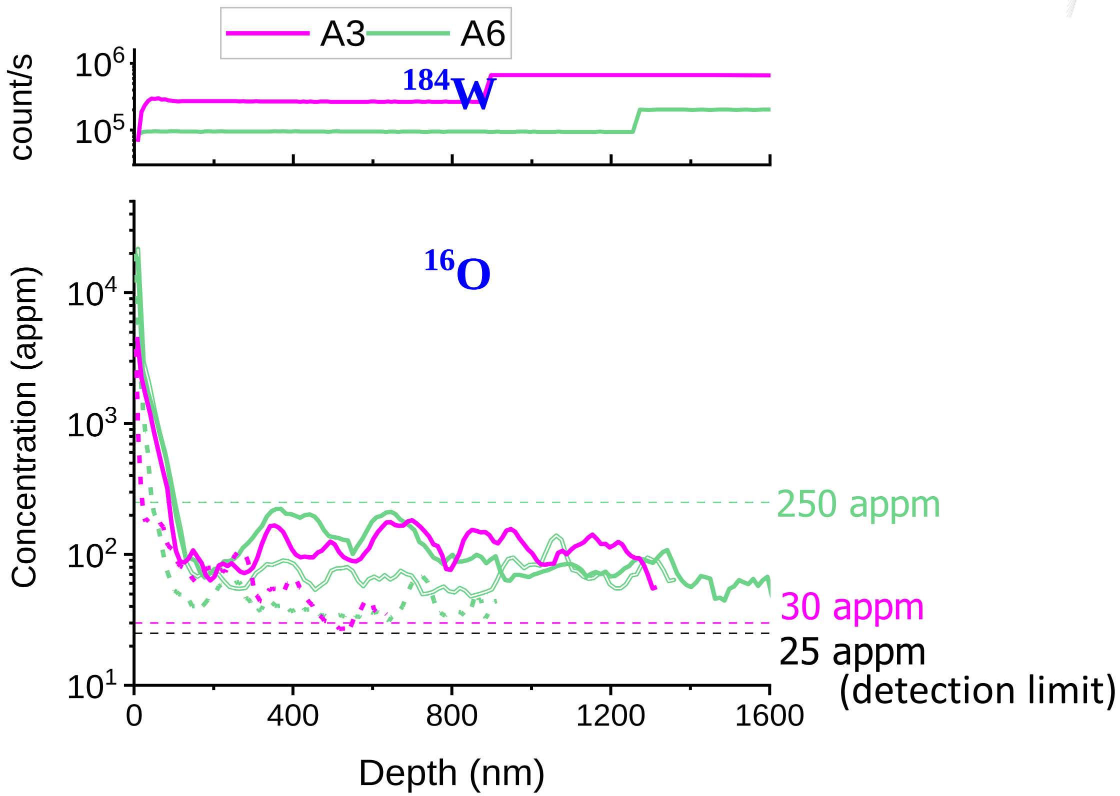
Characterizations

- Positron annihilation spectroscopy (*PAS*) : Vacancy-type defects
- *SIMS* : LE atom Impurities

[1] McKinley et Feshbach, Phys. Rev. 74 (1948) 1759–1763
[2] Lesueur, PMA 44 (1981) 905–929
[3] Dunlop et al. NIMPRSB 42 (1989) 182–192

O Quantification in irradiated samples **A3**, and in the pristine sample **A6**

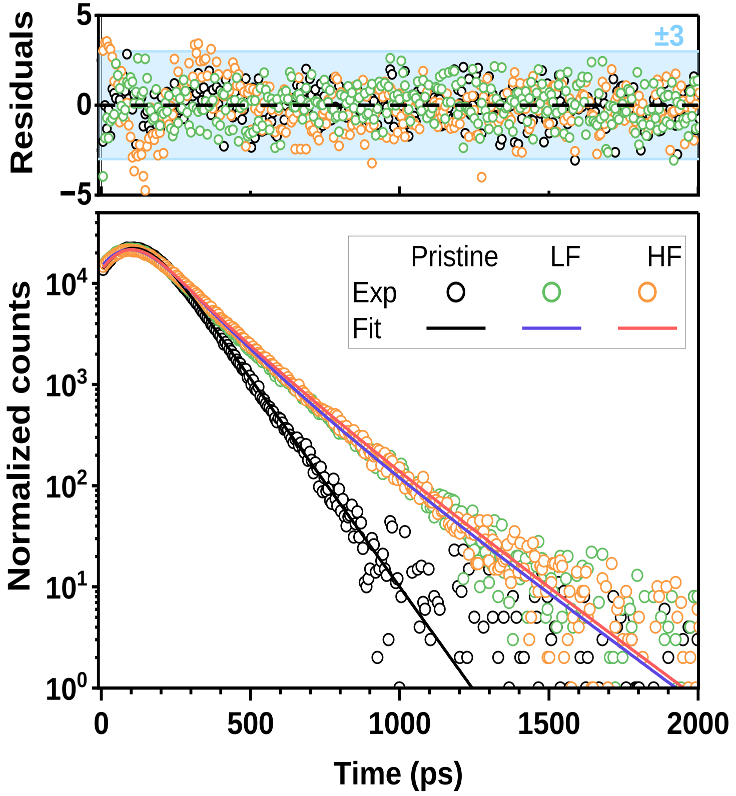




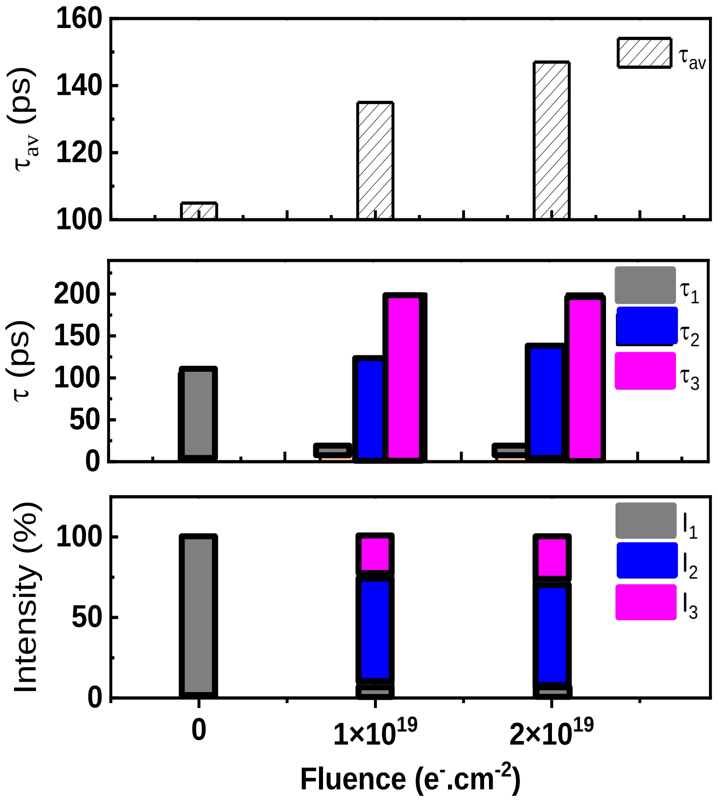
- Signifiant signal of Oyxgen (O) and oxygen-tungsten molecules (WO_{1-3})

- **A set:** heterogeneous distribution, [O]: 30-250 appm.

PALS in irradiated samples (A set)



Vacancy defects are detected



3 components are extracted

3 annihilation states

- Single vacancies 200 ps [1]
- Reduced-lattice ~10 ps
- ***Unidentified (X) defects (120-140 ps) ??***

Defects with free volumes smaller than V_1

→ Oxygen –vacancy complexes, O_pV_1 ?

p	τ (ps)
1	170
2	142
3	143
4	130
5	124
6	132

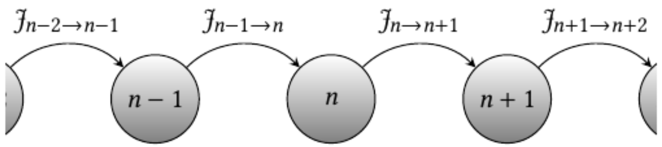
?

[1] Lhuillier et al.*Physica Status Solidi (c)* 6, nº 11 (novembre 2009): 2329-32.

Cluster dynamics (CRESCENDO code) : to simulate irradiation process

- Mean field description of microstructure evolution, evolution of cluster concentrations C_n:

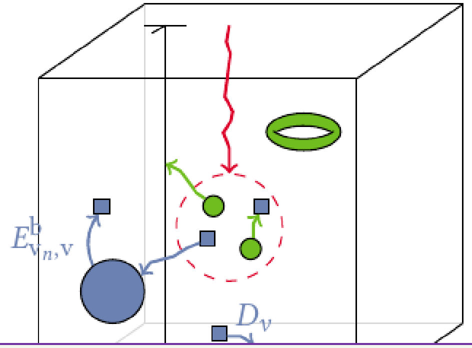
$$\frac{\mathrm{d}C_n}{\mathrm{d}t} = \underbrace{G_n}_{\text{irradiation}} + \underbrace{\sum_{m\in M} J_{n-m\to n} - \sum_{m\in M} J_{n\to n+m} - \sum_{m\in \Omega} J_{m\to m+n}}_{\text{association/dissociation}} \underbrace{- k_{d,n}^2 D_n (C_n - C_n^{\mathrm{e}})}_{\text{sinks (ex.: dislocations)}}$$



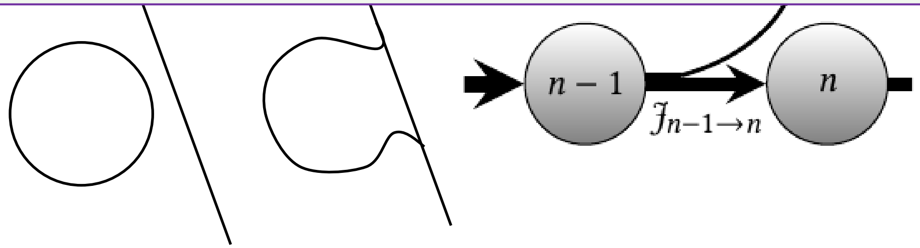
with

$$J_{n\to n+m} = \underbrace{\beta_{n,m}\, C_n C_m}_{\text{association}} - \underbrace{\alpha_{n+m,m} C_{n+m}}_{\text{dissociation}}$$

Sink strengths: $k_{n,m}^2 = \beta_{n,m} C_n / D_m$

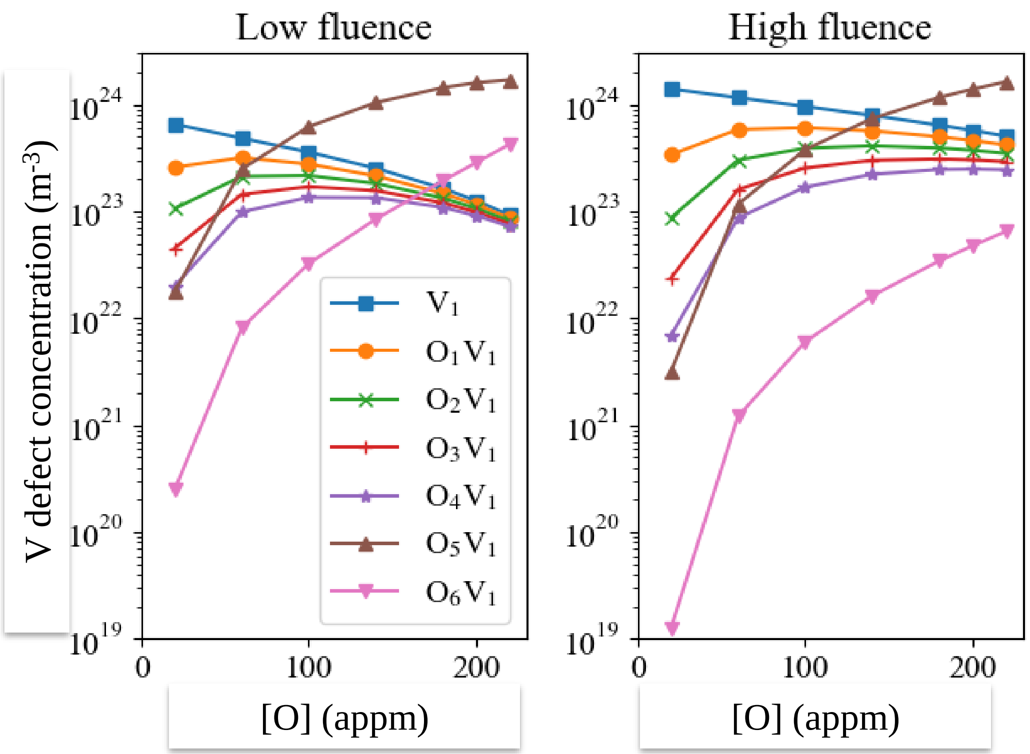


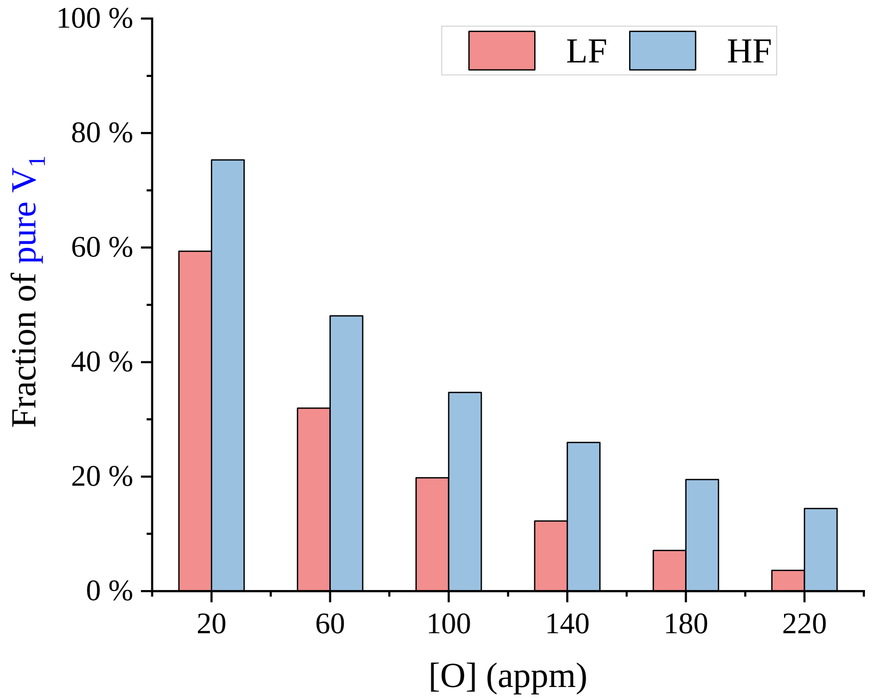
Defects (Vn, SIAn) evolution in matrix with O and without O



[1] T. Jourdan, J. Nucl. Mater. 467 (2015) 286

Cluster dynamics (CD) : Vacancies





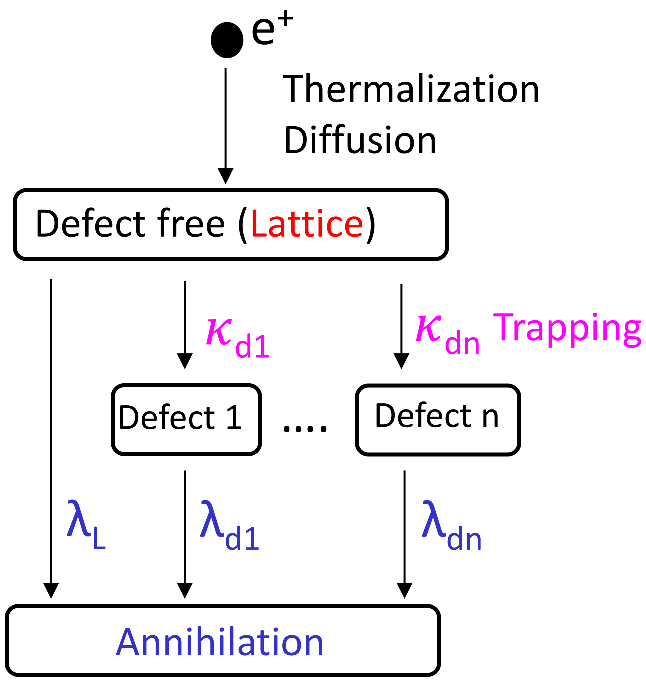
Concentration of pure V_1 decreases with increasing of O, depends on fluence

→ pure V_1 and Oxygen-vacancy complexes ($O_{1\text{-}6}V_1$) coexist

Z. Hu et al., Journal of Nuclear Materials 602 (2024) 155353

Assuming n independent defects and no de-trapping from defects [1]

Theoretical PALS(t)



$$\textbf{1. } \boldsymbol{PALS(t)} = R(t) * \sum \left(\frac{I_{di}}{\tau_{di}} e^{-\frac{t}{\tau_{di}}}\right) + \frac{I_1}{\tau_1} e^{-\frac{t}{\tau_1}} + BG$$

$R(t),\ BG$: experimental values

$\boldsymbol{\tau_{di}}$ **($1/\lambda_{di}$) calculated using TCDFT**

$$I_{di} = \frac{k_{di}}{\lambda_L - \lambda_i + \sum k_{di}}$$, and $$I_1 + \sum_{di} I_{di} = 1$$

I_{di} : Intensity of lifetime component d_i

Where trapping rate, $\kappa_{di} = \boldsymbol{c_{di}^{\text{Cluster Dynamics}}} \cdot \mu_{di}$

C_i: vacancy (V_i) concentration

μ_i: *specific trapping coefficient*

[1] K. Saarinen, P. Hautojärvi, C. Corbel, Chapter 5 Positron Annihilation Spectroscopy of Defects in Semiconductors, in: Semiconductors and Semimetals, Elsevier, 1998: pp. 209–285.

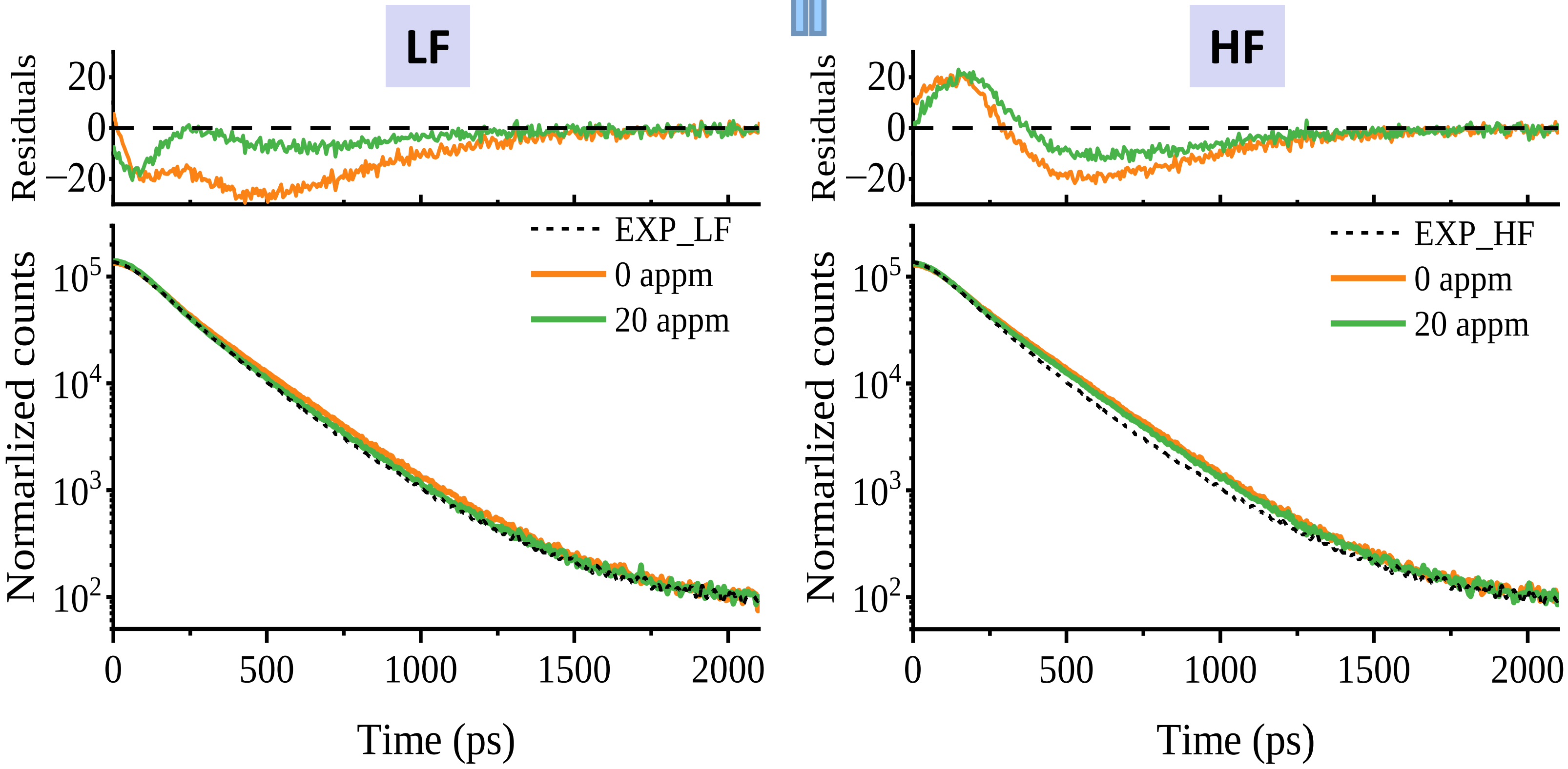
Theoretical and experimental PALS spectra

$$\boldsymbol{PALS(t)} = R(t) * \sum \left(\frac{I_{di}}{\tau_{di}} e^{-\frac{t}{\tau_{di}}}\right) + \frac{I_1}{\tau_1} e^{-\frac{t}{\tau_1}} + BG$$

\+

CD: Concentration
DFT: Lifetime

=



Trapping-model *without O* :

- $\text{PALS}(t)_{th} \neq \text{PALS}(t)_{Exp}$

→ Other defects

Trapping-model *with O* :
better agreement

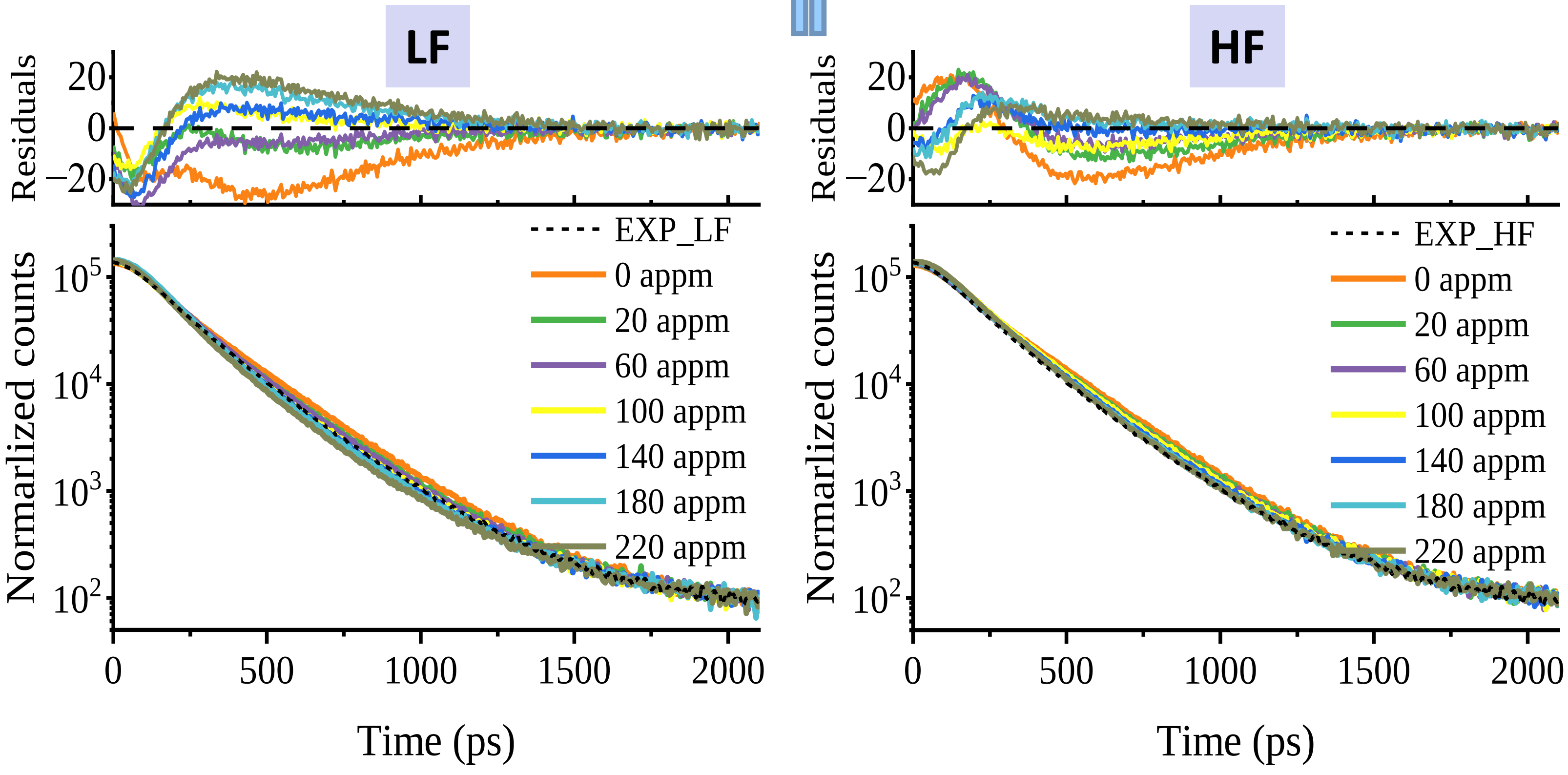
Theoretical and experimental PALS spectra

$$\boldsymbol{PALS(t)} = R(t) * \sum \left(\frac{I_{di}}{\tau_{di}} e^{-\frac{t}{\tau_{di}}}\right) + \frac{I_1}{\tau_1} e^{-\frac{t}{\tau_1}} + BG$$

+

CD: Concentration
DFT: Lifetime

=



Trapping-model *without O* :

- $\mathrm{PALS}(t)_{th} \neq \mathrm{PALS}(t)_{Exp}$

→ Other defects

Trapping-model *with O* :

- $\mathrm{PALS}(t)_{th} \approx \mathrm{PALS}(t)_{Exp}$

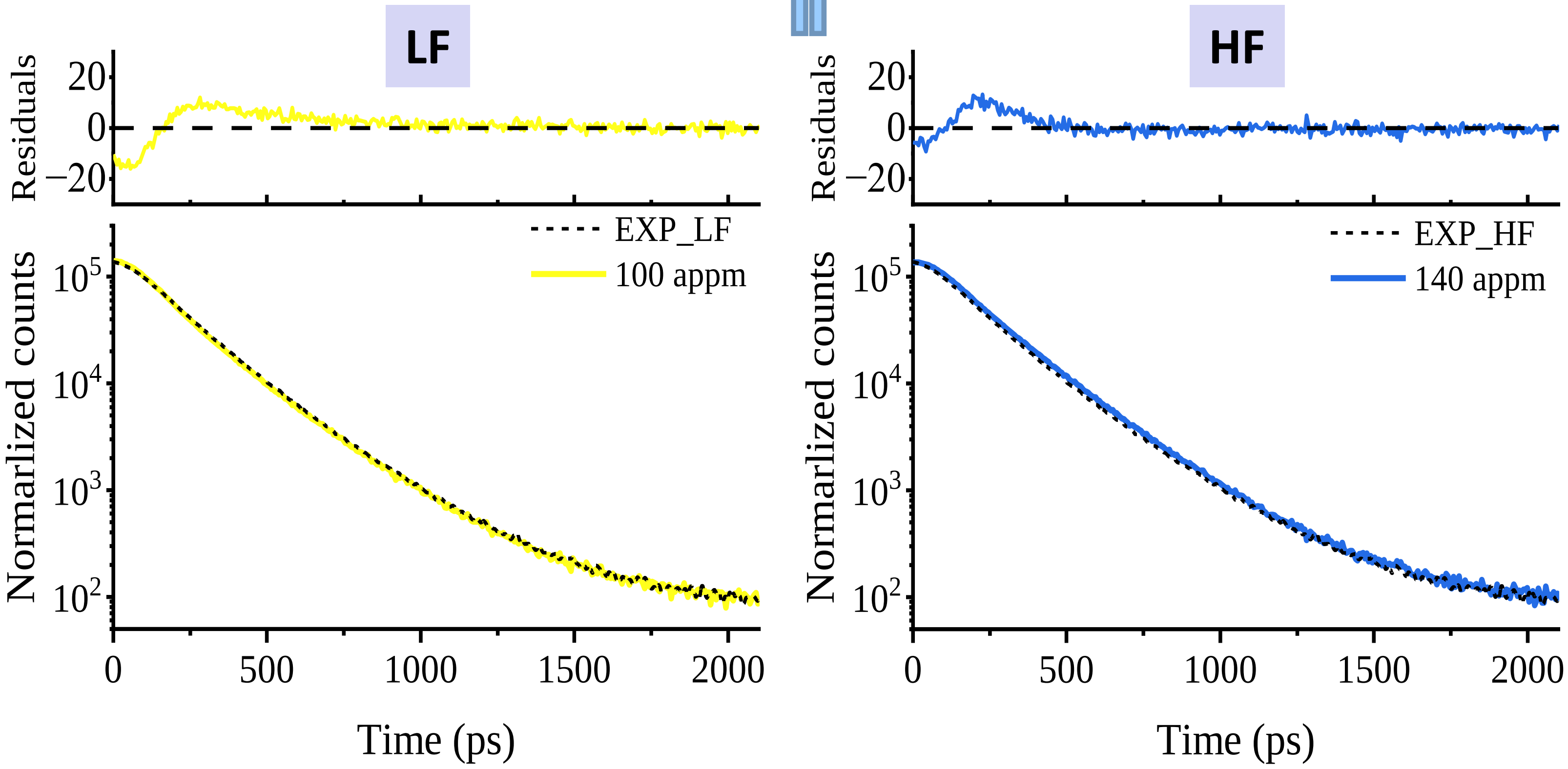
Theoretical and experimental PALS spectra

$$\boldsymbol{PALS(t)} = R(t) * \sum\left(\frac{I_{di}}{\tau_{di}} e^{-\frac{t}{\tau_{di}}}\right) + \frac{I_1}{\tau_1} e^{-\frac{t}{\tau_1}} + BG$$

+

CD: Concentration
DFT: Lifetime

=



Trapping-model *without O* :

- $\mathrm{PALS}(t)_{th} \neq \mathrm{PALS}(t)_{Exp}$

→ Other defects

Trapping-model *with O* :

- $\mathrm{PALS}(t)_{th} \approx \mathrm{PALS}(t)_{Exp}$

✓ LF: 100 appm O

✓ HF: 100-180 appm O

→Agree ***with SIMS:***

[O] =30-250 *appm*

→X defects = mix of O_PV_1

✓ 2 illustrations

- ➢ Oxygen vacancy interactions
- ➢ Vacancy clusters distribution in self-irradiated tungsten

New methodology

New insight into quantifying vacancy distribution in self-ion irradiated tungsten: a combined experimental and computational study

Zhiwei Hu [a,‡], Jintong Wu [b,‡], Qigui Yang [c,d], François Jomard [e], Fredric Granberg [b], Marie-France Barthe [a,]*

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[b] Department of Physics, Post-office box 43, FIN-00014 University of Helsinki, Finland
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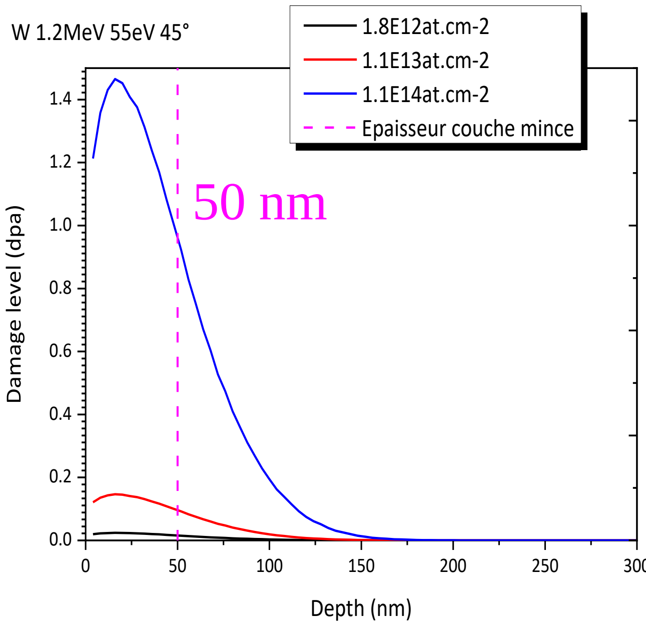
[e] Groupe d'Etude de la Matière Condensée, CNRS, UVSQ, 45 avenue des Etats-Unis, 78035 Versailles cedex, France

Accepted in NANO LETTERS

Before irradiation : Annealing at 1600°C/1H/Vacuum

Irradiation with **W ions, SRIM calculations (KP)**

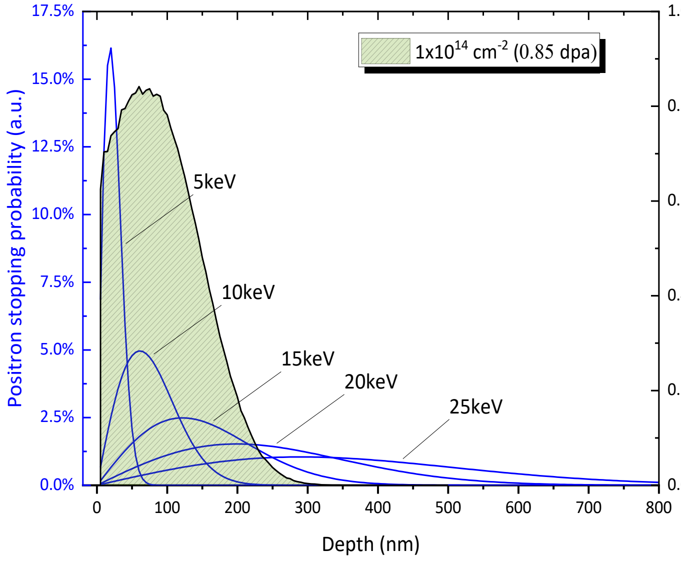
- **1.2 MeV** in thin and thick samples:



Dpa* : mean dpa value in the thin foil

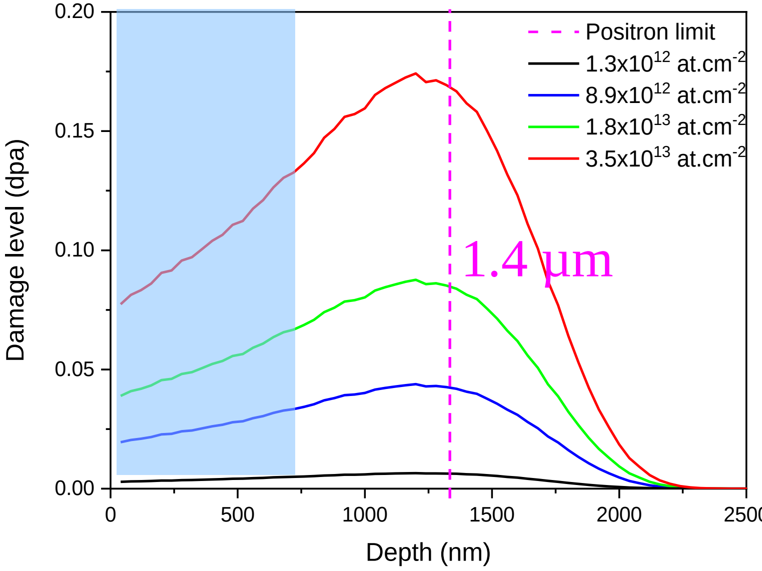
- **2 or 20 MeV** in thick samples:

W 2 MeV



Dpa* : at the mximum of the peak

W 20 MeV



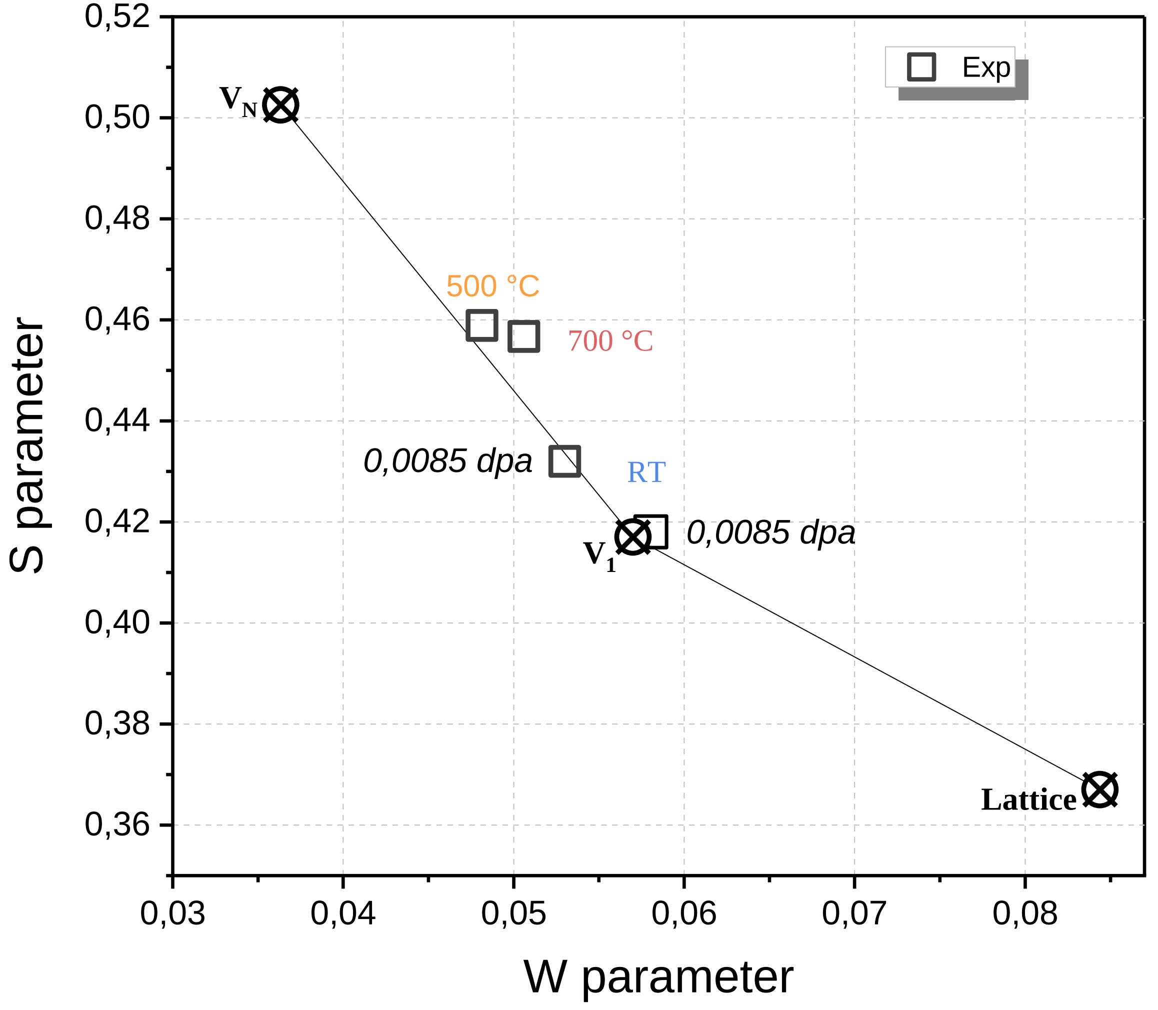
Dpa* : mean dpa value in **700nm** surface region,

post- mortem characterizations : PAS (with slow positron beam, S(E) & W(E)) and TEM

S and *W* annihilation characteristics in self-irradiated tungsten

	Ion energy (MeV)	dpa	Temp (°C)	W	S
[1]	2	0.0085 (peak)	RT	0.058(1)	0.418(1)
		0.085 (peak)		0.053(1)	0.432(1)
[2]	20	0.02 (mean 0- 700 nm)	500	0.0481(1)	0.459(2)
			700	0.051(1)	0.457(4)

[1] Mean value of 5 fits



What is the distribution of Vacancy defects ?

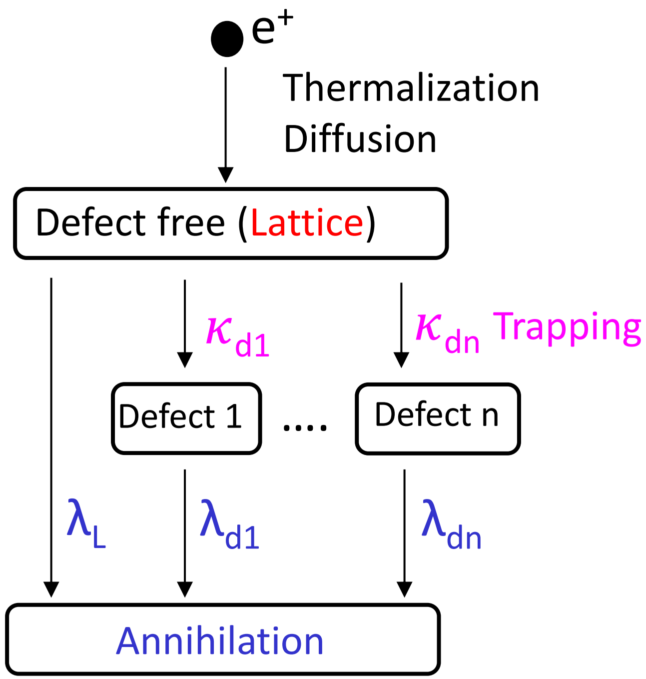
[1] A. Hollingsworth, M.-F. Barthe, M.Y. Lavrentiev et al., JNM 558 (2022) 153373. [2] Z. Hu, MF Barthe et al , Journal of Nuclear Materials 556 (2021) 153175

Positron Trapping model

$$\begin{cases} \boldsymbol{S} = S_L \cdot f_L + \sum S_{di} \cdot f_{di} \\ \boldsymbol{W} = W_L \cdot f_L + \sum W_{di} \cdot f_{di} \end{cases}$$

***S_i* and *W_i* calculated using TCDFT**

f_{di}: Fraction of annihilation state d_i



Assuming n independent defects and no de-trapping from defects [1]

Total trapping, $f_L = 0$ and $\kappa_{di} >> \lambda_L - \lambda_{dn}$

$$\Rightarrow f_1 = \frac{\kappa_{d1}}{\kappa_{d1} + \cdots + \kappa_{dn}} \ \ldots \ f_{dn} = \frac{\kappa_{dn}}{\kappa_{d1} + \cdots + \kappa_{dn}}$$

$$\text{and } f_L + \sum_{d_1} f_{di} = 1$$

Where trapping rate, $\kappa_{di} = C_{di} \cdot \mu_{di}$

If d_i is a vacancy cluster V_i

C_{di}: vacancy (V_i) concentration

μ_{di}: specific trapping coefficient

[1] K. Saarinen, P. Hautojärvi, C. Corbel, Chapter 5 Positron Annihilation Spectroscopy of Defects in Semiconductors, in: Semiconductors and Semimetals, Elsevier, 1998: pp. 209–285.

Experimental **PAS results** S_{exp} & W_{exp}

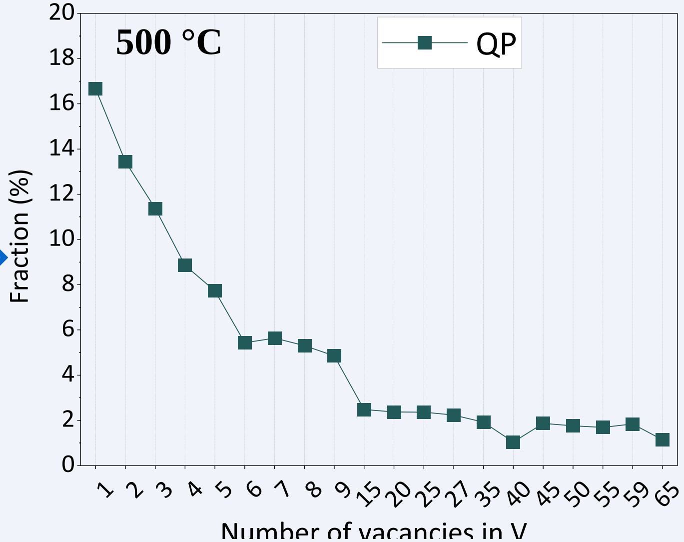
Theoretical (TCDFT) e^+ annihilation characteristics of defect d_i, S_{di}^{th} & W_{di}^{th}

Quadratic Programming (QP)

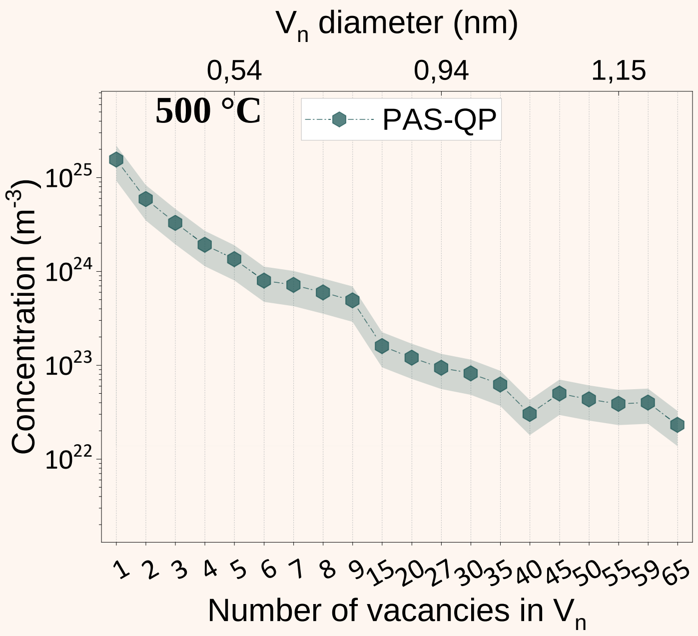
$$min_f \left\| \begin{pmatrix} W_{exp} \\ S_{exp} \end{pmatrix} - \begin{pmatrix} W \\ S \end{pmatrix} f \right\|^2$$

Positron (e^+) trapping model

$$\begin{pmatrix} \mathbf{W} \\ \mathbf{S} \end{pmatrix} \mathbf{f} = \begin{pmatrix} W_{exp} \\ S_{exp} \end{pmatrix}, \; f_{di} \geq 0 \; and \; \sum_i f_{di} = 1$$



e^+ annihilation fraction f_{di} at vacancy defects

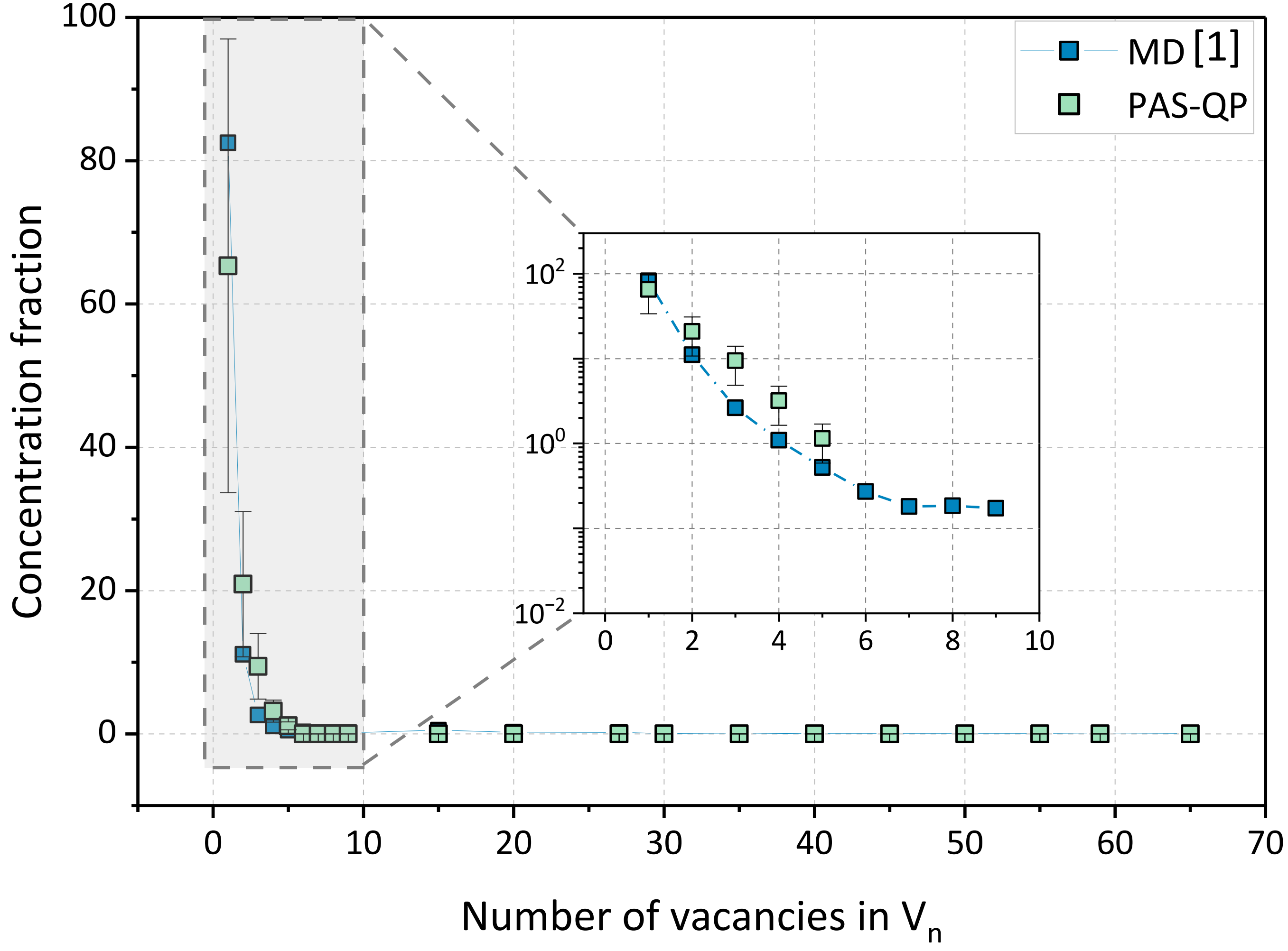


Vacancy defect distribution

Vacancy distribution for irradiation at RT : comparison with MD

*QP preset : **only** Vn with n=1-65*

self-irradiated Tungsten at 0,085 dpa and RT



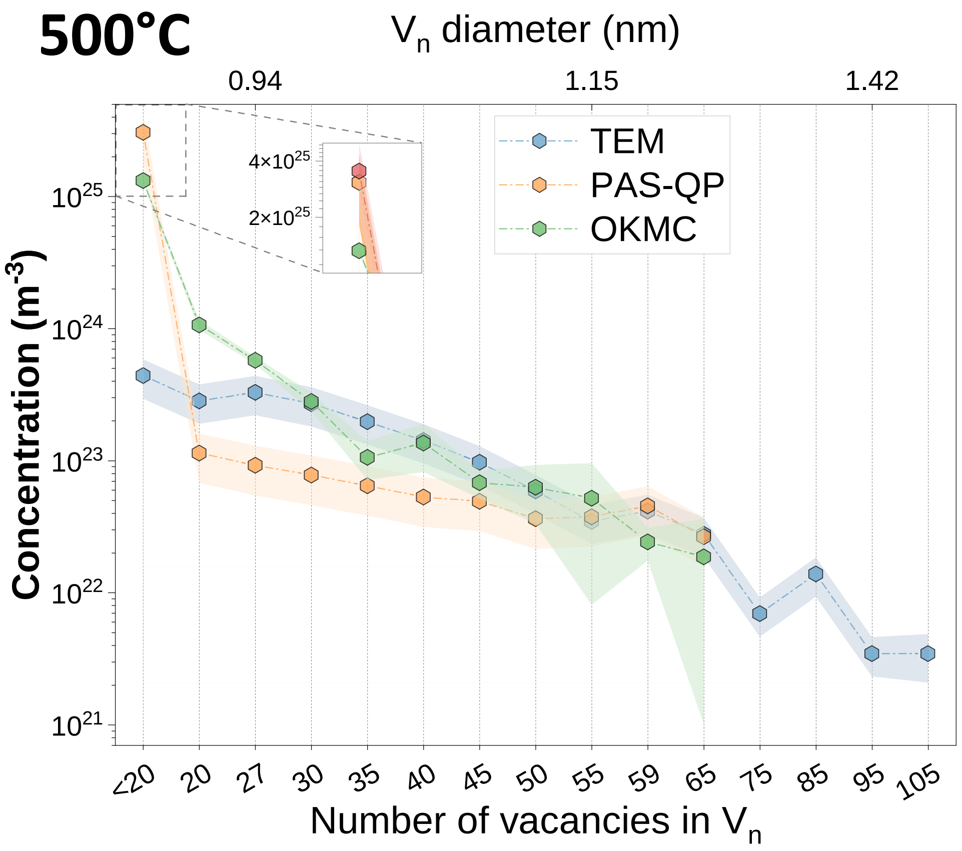
Very close distributions for PAS and MD

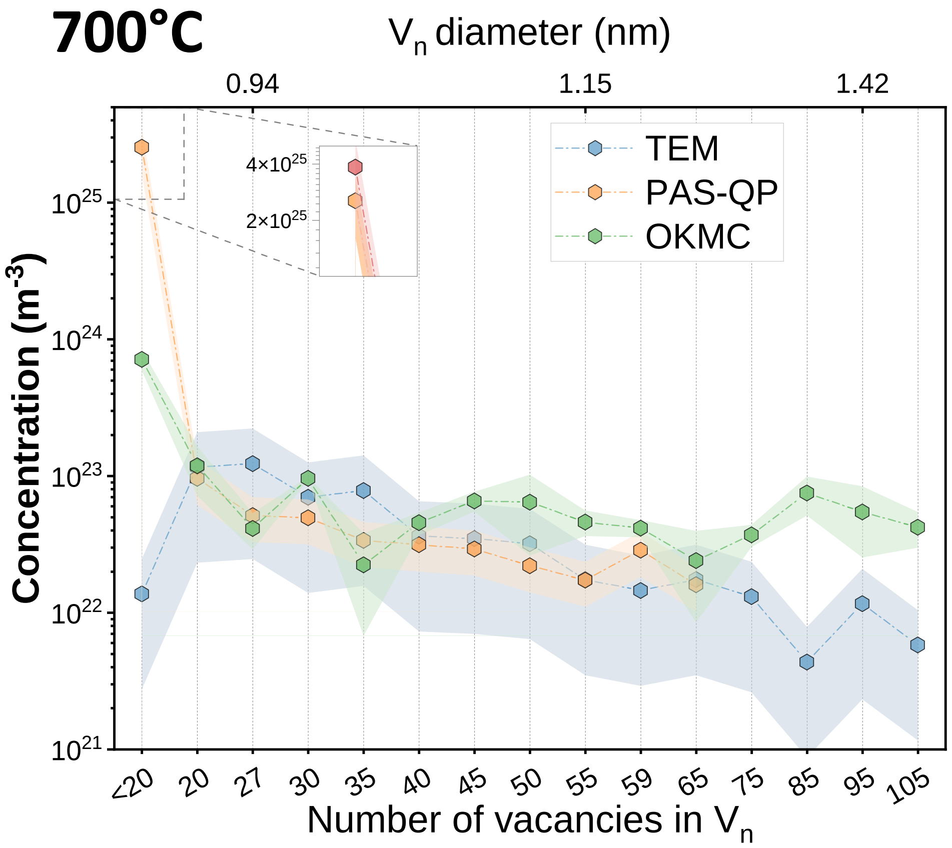
[1] S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics, Journal of Computational Physics 117 (1995) 1–19.

Vacancy distribution for irradiation at HT : comparison with TEM & OKMC

*QP preset : **only** Vn with n=1-65*

self-irradiated Tungsten at 0,0085 dpa and RT





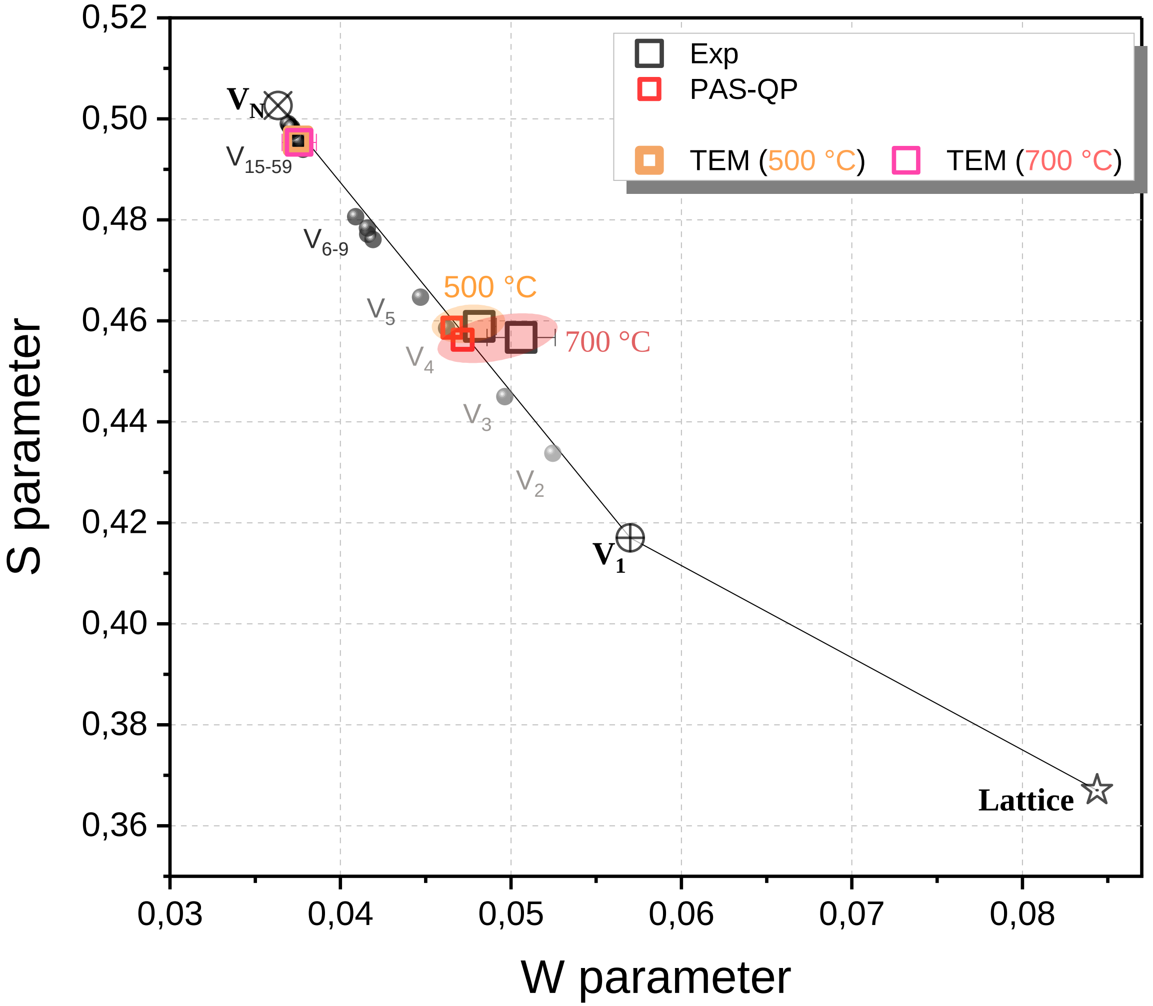
More small vacancy defects (V_n, n<20) in PAS than in TEM (due to detection limit)
OKMC (MMonCa [1]) predicts a large fraction of small vacancy defects (V_n, n<20)

[1] I. Martin-Bragado, et al., Computer Physics Communications 184 (2013)

S&W measured (PAS & TEM) /calculated from extracted V_n distribution

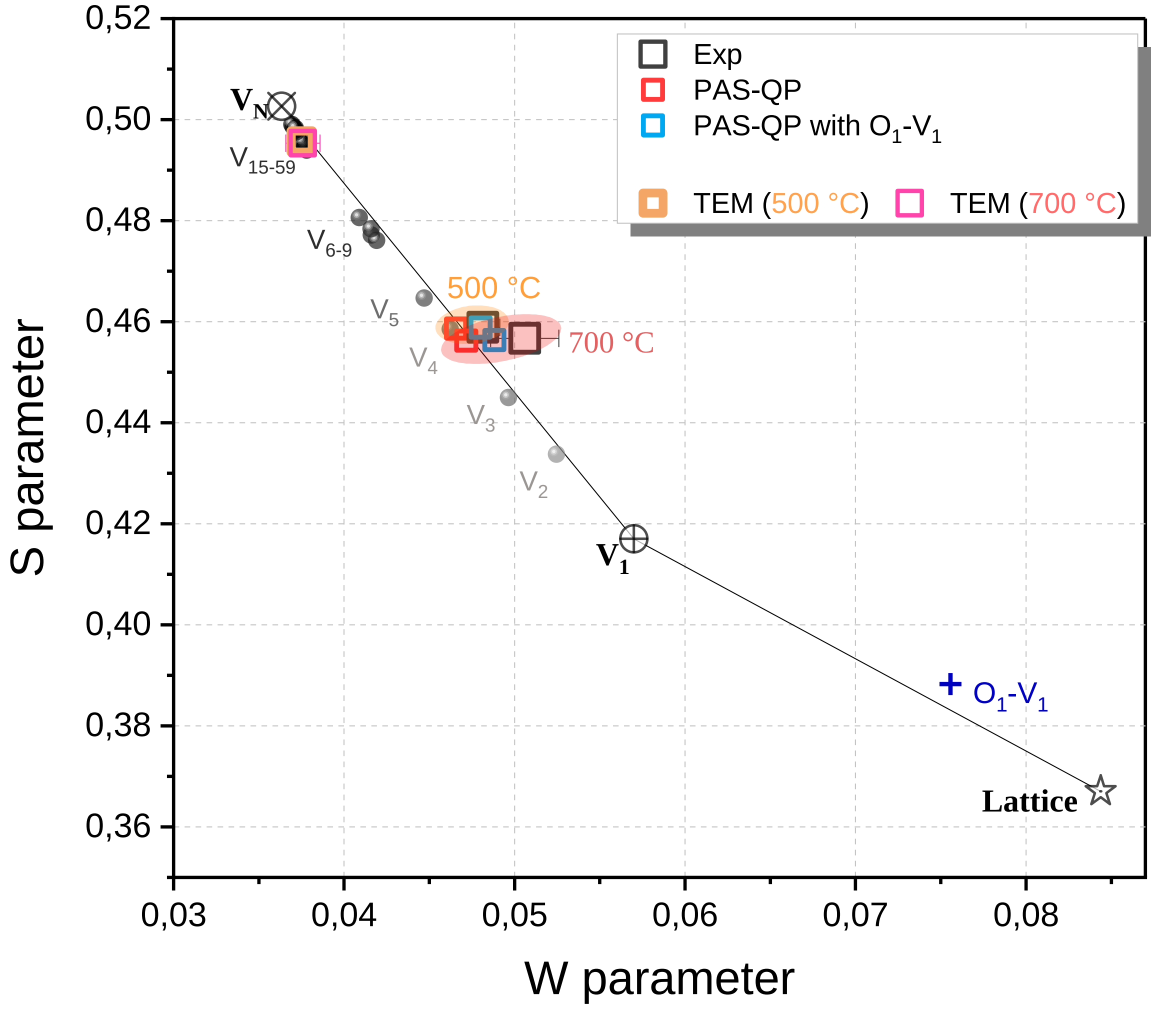
- The large difference between ***S*** & ***W*** calculated from TEM Vn distribution confirms the presence of small vacancy clusters that can not be quantified using TEM.
- The ***S*** & ***W*** points calculated from the Vn distribution extracted using QP (red squares) are on the left of the Experimental data (black squares).
- Positrons annihhlate in a defect different from the Vn (n=1-65) clusters and with a larger ***W*** value.

Oxygen vacancy complexes ?



S&W measured (PAS & TEM) /calculated from extracted V_n distribution

- The large difference between ***S*** & ***W*** calculated from TEM Vn distribution confirms the presence of small vacancy clusters that can not be quantified using TEM.
- The ***S*** & ***W*** points calculated from the Vn distribution extracted using QP (red squares) are on the left of the Experimental data (black squares).
- Positrons annihhlate in a defect different from the Vn (n=1-65) clusters and with a larger ***W*** value.



Oxygen vacancy complexes ?

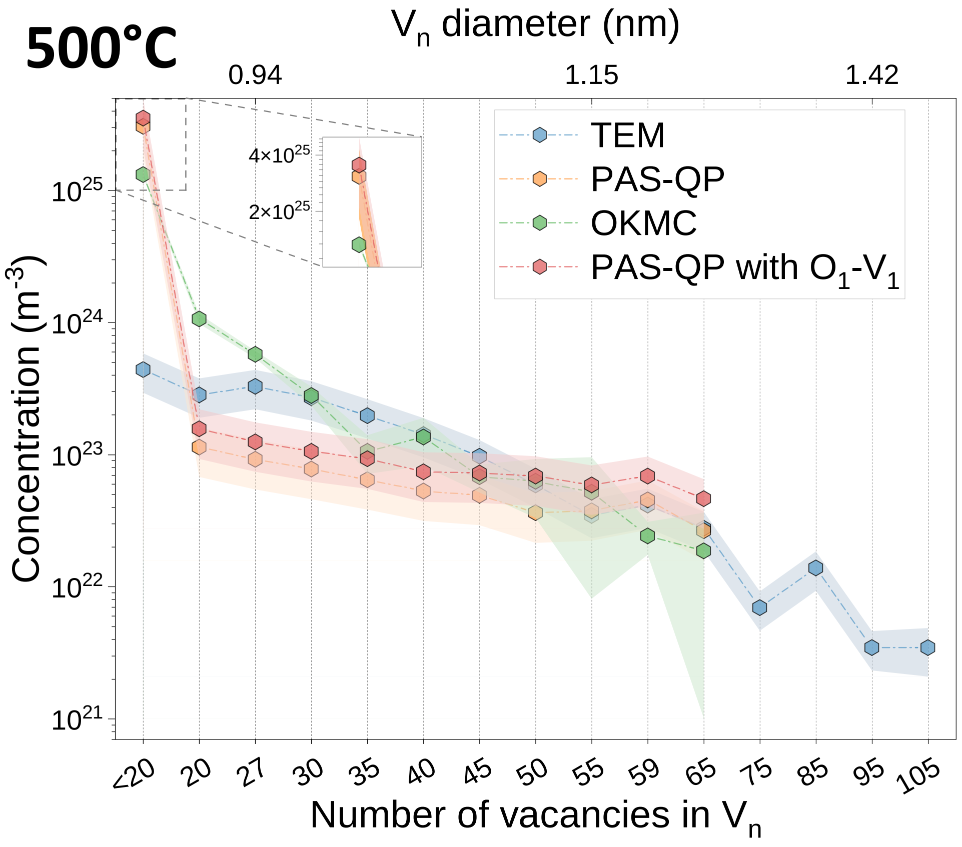
The agreement becomes better when O_1-V_1 complexe is introduced in the QP model

Vacancy distribution for irradiation at HT : comparison with TEM & OKMC

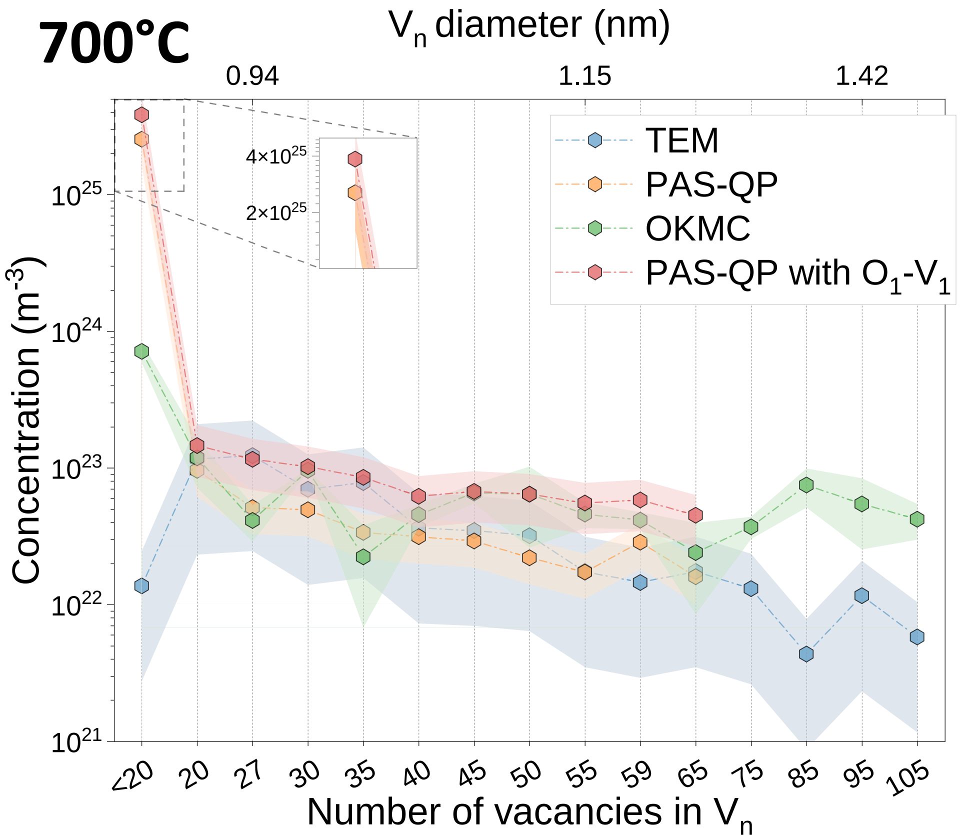
QP preset : Vn with n=1-65 ***+ O_1-V_1***

self-irradiated Tungsten at 0,0085 dpa and RT

500°C



700°C



- With ***O_1-$V_{1,}$*** concentration of vacancy clusters **increases**
- Swelling deduced from PAS is higher than from TEM

	Swelling (%)	
	500°C	700°C
TEM	0.09 (± 0.02) %	0.04 (± 0.02) %
PAS	0.6 (± 0.3) %	0.6 (± 0.5) %

Conclusions

- ❑ Positron Lifetime (PALS) and Doppler Broadening (DB) spectrometry
- ❑ Theoretical annihilation characteristics τ, S, W of defects
- ❑ Trapping model
- ❑ Quadratic Processing

➢ Experimental confirmation of strong interaction between Oxygen and vacancy in tungsten :

➢ Oxygen-vacancy complexes are formed

The Oxygen effect has to be taken into account in modelling

➢ Distribution of vacancy defects in self-irradiated tungsten

➢ Small vacancy clusters are highlighted and can be quantified

➢ **Data to parametrize and validate models**

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MD, OKMC, ??? calculations

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Thank you for your attention