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# 1 Revealing the role of oxygen on the defect evolution of electron- 2 irradiated tungsten: A combined experimental and simulation study

3 *Zhiwei Hu<sup>a</sup>, Qigui Yang<sup>b, e, f</sup>, François Jomard<sup>c</sup>, Pierre Desgardin<sup>a</sup>, Cécile Genevois<sup>a</sup>, Jérôme*  
4 *Joseph<sup>a</sup>, Pär Olsson<sup>b</sup>, Thomas Jourdan<sup>d, \*</sup>, Marie-France Barthe<sup>a, \*</sup>*

5 <sup>a</sup> CEMHTI, CNRS, UPR3079, University of Orléans, F-45071 Orléans, France

6 <sup>b</sup> KTH Royal Institute of Technology, Nuclear Engineering, Roslagstullsbacken 21, 114 21  
7 Stockholm, Sweden

8 <sup>c</sup> Groupe d'Etude de la Matière Condensée, CNRS, UVSQ, 45 avenue des Etats-Unis, 78035  
9 Versailles cedex, France

10 <sup>d</sup> Université Paris-Saclay, CEA, Service de recherche en Corrosion et Comportement des Matériaux,  
11 SRMP, F-91191 Gif-sur-Yvette, France

12 <sup>e</sup> Institute of High Energy Physics, CAS, 100049 Beijing, China

13 <sup>f</sup> China Spallation Neutron Source, Institute of High Energy Physics, CAS, Dongguan 523803, China

## 14 **Keywords**

15 Tungsten, Electron irradiation, First-principles calculations, Cluster dynamics, Frenkel pairs  
16 recombination, O-vacancy complexes, Positron annihilation spectroscopy

## 17 **Abstract**

18 The evolution of Frenkel pairs has been studied experimentally and theoretically in  
19 tungsten, a Body-Centered Cubic metal. We used positron annihilation spectroscopy to  
20 characterize vacancy defects induced by electron irradiation in two sets of polycrystalline  
21 tungsten samples at room temperature. Doppler Broadening spectrometry showed that some  
22 positrons were trapped at pure single vacancies with a lower concentration than expected. At  
23 the same time, positron annihilation lifetime spectroscopy revealed that positrons are  
24 annihilated in unexpected states with a lifetime 1.44-1.64 times shorter than that of single  
25 vacancy (200 ps), namely unidentified (X) defects. Secondary ions mass spectrometry detected  
26 a significant concentration of oxygen in these samples, of the same order of magnitude as  
27 electron-induced single vacancy. In addition, Cluster dynamics simulated defect behaviors  
28 under experimental conditions, and Two-component density functional theory was used to  
29 calculate defect annihilation characteristics that are difficult to obtain in experiments. Finally,

30 by combining the theoretical data, we simulated the positron signals and compared them with  
31 the experimental data. This enabled us to elucidate the interactions between oxygen and Frenkel  
32 Pairs. The X defects were identified as oxygen-vacancy complexes formed during irradiation,  
33 as oxygen is mobile in tungsten at room temperature, and can be trapped in a vacancy, while its  
34 binding to self-ion atoms leads to their immobilization thus reducing defect recombination.  
35 Therefore, we anticipate oxygen to play an important role in the evolution of tungsten  
36 microstructure under irradiation.

## 37 **1. Introduction**

38 Refractory metals are essential in future nuclear industrial infrastructure, thanks to their  
39 high melting point, high thermal conductivity, and low sputtering rate. For instance, tungsten  
40 and its alloys [1–5] are the most mentioned candidates as plasma-facing components and  
41 divertor in fusion applications [3,4,6]. In future fusion power plants, they will be exposed to  
42 high fluxes of Hydrogen (H) and Helium atoms and will have to withstand intense neutron  
43 irradiation. Such extreme conditions modify the crystal structure, displacing atoms from their  
44 initial lattice sites, and creating Frenkel pairs (FPs) i.e. a displaced self-interstitial atom (SIA),  
45 leaving a vacant site (single vacancy,  $V_1$ ). The diffusion and interaction of FPs induce other  
46 defects (voids, dislocation loops, vacancy complexes, etc.), at the origin of microstructure  
47 evolution [7], which is harmful to materials [8–11], degrades their properties [8,12], and then  
48 limits reactor performance [13–15]. Hence, understanding microstructural evolution is a  
49 preliminary step towards improving, adapting materials, and extending the active service life  
50 of future fusion power plants.

51 Electron irradiation is an efficient method to induce isolated FPs in metallic materials and  
52 can be used to study defect properties in detail. Was and Allen claimed that the FP production  
53 rate is near 100 % in nickel (Ni) with 1 MeV electron [16]. Numerous resistivity recovery (RR)  
54 experiments on electron-irradiated metals were realized in the 70s-80s [17–19], revealing the

55 different defect evolution stages, in which Stage I was attributed to the migration of SIAs. In  
56 iron, Body-Centered Cubic (BCC) metal, Takaki et al. [20] isolated two sub-stages of Stage I,  
57 i.e.  $I_{D2}$ , and  $I_E$ , corresponding to the recombination of correlated and uncorrelated FPs. Twenty  
58 years later, Fu et al.[21] have obtained similar results by performing simulations based on  
59 kinetic Monte Carlo. For Face-Centered Cubic (FCC) metals, RR experiments in electron-  
60 irradiated platinum showed a recombination fraction of 63 % for non-correlated FPs [22]. In  
61 tungsten, due to the high mobility of SIAs, a non-negligible population of electron-induced FPs  
62 should be recombined. However, the recombination rate ( $R_c$ ) in this material is still an unsolved  
63 issue.

64 Furthermore, light-element impurities (LEs) may play an important role on the defect  
65 evolution. Lu et al. [23,24] summarized numerous theoretical works and showed that vacancy-  
66 oxygen (O) and carbon (C) complexes can bind with hydrogen (H) atoms and act as H-trapping  
67 sites. These complexes can be germs for clustering of H which is considered as the origin of  
68 the blisters observed in tungsten [25,26].

69 Experimentally, we also demonstrated that LEs act on the evolution of vacancy-type  
70 defects in self-ion irradiated tungsten [27]. While the effect of C [28,29] has been addressed in  
71 numerous works, the effect of O on the behavior of defects in tungsten has yet to be studied,  
72 particularly with experimental methods. In vanadium, Zhang et al.[30] argued that the  
73 hardening induced by dislocation accumulation is not sufficient to explain their experimental  
74 data suggesting that the missing strain hardening component is due to oxygen-vacancy  
75 complexes and conclude that detection of such defects is very challenging.

76 Positron annihilation spectroscopy (PAS) was demonstrated to be a well-adapted technique  
77 to characterize vacancy-type defects [31,32]. The complementarity of Doppler Broadening and  
78 lifetime spectroscopies makes it possible to quantify the vacancy defects and access their nature  
79 using simulation [33–35]. Accordingly, in the present work, we have combined theoretical and

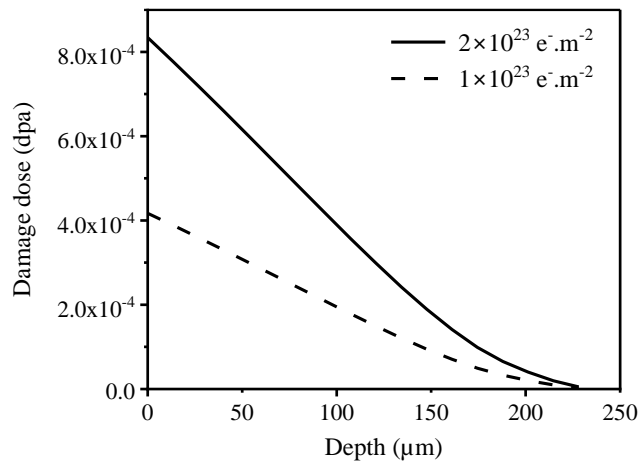
80 experimental studies to better understand the properties of defects and the impact of O on the  
81 PAS signals and defect recombination. We investigated the behavior of FPs in a typical BCC  
82 metal, i.e. tungsten, using 2.5 MeV electron irradiation at room temperature (RT) to introduce  
83 a quantifiable fraction of FPs. We employed PAS and, as a complement, transmission electron  
84 microscopy (TEM) to characterize damaged samples. In addition, secondary ion mass  
85 spectrometry (SIMS) was used to quantify the LEs in our samples. In terms of theory, we chose  
86 Cluster dynamics (CD) which has proven to be an appropriate and accurate method for  
87 simulating the evolution of simple homogeneously dispersed defects in metals [36] such as  
88 those induced by electron irradiation. Furthermore, referring to the promising findings that have  
89 been discovered for vacancies in tungsten[37], we have used Two Component Density  
90 Functional Theory (TCDFT), to calculate the positron annihilation characteristics -lifetime and  
91 Doppler broadening spectrum- for various vacancy-oxygen complexes. Finally, we applied the  
92 positron trapping model [31,38] to calculate positron annihilation signals in irradiated samples  
93 using CD and TCDFT data. The comparison of calculations with experimental results  
94 highlighted the effect of O on the evolution of defects during irradiation.

## 95 **2. Methods**

### 96 **2.1 Material and irradiation conditions**

97 High purity (HP, 99.95 wt.%) tungsten samples ( $7 \times 7 \times 0.3 \text{ mm}^3$  plates, and  $\text{Ø}3 \text{ mm}$  discs)  
98 were purchased from Neyco (**Nc**) and Goodfellow (**GF**) companies. The Nc samples were  
99 mechanically polished and annealed at  $1600 \text{ °C}$  for 1 hour under high vacuum ( $\sim 10^{-7} \text{ mbar}$ ) to  
100 eliminate the native and polishing-induced defects. However, this temperature was insufficient  
101 to eliminate all the defects for the sample recently purchased from Goodfellow (GF series). The  
102 annealing temperature was subsequently raised to  $1700 \text{ °C}$ , and the duration was extended to 3  
103 h. After the annealing, a few discs were electropolished to create thin areas in the center, using  
104 Tenupol-5 with a double jet of NaOH solution ( $0.05 \text{ mol. L}^{-1}$ ,  $20 \text{ °C}$ , and a voltage of 15 V) for

105 10 min. The configuration of the samples i.e. plates and thinned discs was adapted to the  
 106 characterization techniques i.e. PAS and TEM, respectively.



107

108 Fig.1: Calculated damage profile of 2.5 MeV electrons in tungsten using POLY ET SMOTT program for two fluences LF: 1  
 109  $\times 10^{23} \text{ m}^{-2}$  and HF:  $2 \times 10^{23} \text{ m}^{-2}$

110 2.5 MeV electron irradiations were performed using the SIRIUS accelerator [39] at  
 111 Laboratoire des Solides Irradiés (LSI). The tungsten samples (plate: **Nc**, disc: **GF**) were  
 112 damaged with an electron flux of  $\sim 5.5 \times 10^{17} \text{ m}^{-2} \cdot \text{s}^{-1}$  at about 50 °C for 2.5 and 5 days, to obtain  
 113 two fluences, namely a low fluence (LF:  $1 \times 10^{23} \text{ m}^{-2}$ ) and a fluence twice as high, the high  
 114 fluence (HF:  $2 \times 10^{23} \text{ m}^{-2}$ ), respectively. The damage dose was calculated using the POLY et  
 115 SMOTT program [38–40] with a threshold displacement energy of 55.3 eV [43]. The estimated  
 116 damage profiles, i.e. displacement per atom (dpa) as a function of depth are plotted in Fig.1.  
 117 For both fluences, the damage dose decreases linearly until 150 μm and becomes negligible  
 118 beyond 220 μm. Within the maximum slow positron penetrated region ( $\sim 700 \text{ nm}$  in tungsten  
 119 [44]), the damage dose can be considered approximately constant, corresponding to an average  
 120 value of about  $8.33 \times 10^{-4} \text{ dpa}$  for HF, and  $4.16 \times 10^{-4} \text{ dpa}$  for LF with the same standard  
 121 deviation of about  $1 \times 10^{-6} \text{ dpa}$ .

## 122 2.2 Experimental characterizations

### 123 2.2.1 Positron annihilation spectroscopies

124 When a positron penetrates the solid, under interaction with the host atoms, it is thermalized  
125 and diffuses into the lattice. During the diffusion phase, the positron encounters an electron,  
126 and the electron-positron ( $e^-e^+$ ) pair is then annihilated by emitting gamma rays. In a perfect  
127 lattice, a positron annihilates in a delocalized state called “lattice state”. If a positron finds open  
128 volumes along its diffusion path, it has a high probability of being trapped [31,32] in such  
129 vacancy-type defects, where it experiences relatively weak coulomb repulsion from the nucleus.  
130 Once the positron is trapped, it annihilates in this localized state, the vacancy defect-related  
131 state. The electronic density is different in each annihilation state (lattice or different types of  
132 vacancy defects). Therefore, the annihilation characteristics vary from one defect to another.  
133 This makes PAS a sensitive and widely used technique for probing vacancy-type defects in  
134 materials [31,32]. For this reason, Slow Positron Beam Doppler Broadening Spectroscopy  
135 (SPB-DBS) and Positron Annihilation Lifetime Spectroscopy (PALS) measurements were  
136 employed to characterize the electron-induced defects in tungsten.

137 A Doppler Broadening spectrometer is coupled to a slow positron accelerator at the  
138 CEMHTI laboratory [45]. This instrument provides a variable monoenergetic positron beam,  
139 with energies ranging from 0.5 to 25 keV. The positron beam has a diameter of 1 mm and moves  
140 over a 3 mm spot as its energy increases from 0.5 to 25 keV. The penetration depth of slow  
141 positrons can be estimated by the Makhovian model [46]. For the highest energy (25 keV), the  
142 positron reaches a maximum of  $\sim 700$  nm in tungsten [44]. In the SPB-DBS measurement,  
143 Doppler Broadening - or emitted gamma rays - spectra, corresponding to the momentum  
144 distribution of annihilated  $e^-e^+$  pairs, are recorded using a high-purity germanium detector as a  
145 function of positron energy  $E$ . The dead time of the spectrometer is about 10 % and the energy  
146 resolution of  $\sim 1.25$  keV (full width at half maximum, FWHM), equivalent to a momentum  
147 resolution of  $4.89 \times 10^{-3} m_0c$  ( $m_0$ : electron mass,  $c$ : light speed). Gamma-ray detection  
148 efficiency is higher than 25 % at 1.33 MeV. From each DB spectrum, the low momentum  $S$

149 and high momentum  $W$  annihilation fractions or parameters can be extracted. They are the ratio  
150 of the count number in defined momentum ranges over the total count in the spectrum. The  
151 momentum ranges are between  $0 - |2.64| \times 10^{-3} \text{ m}_0c$  for  $S$ , and  $(|9.80| - |24.88|) \times 10^{-3} \text{ m}_0c$  for  
152  $W$ , respectively. To further investigate the defect distribution in the sample, the VEPFIT  
153 program [47,48] is used to model the sample as several homogenous layers and convert  $S$  and  
154  $W$  measured as a function of positron energy i.e.  $S(E)$  and  $W(E)$  into a depth profile i.e.  $S(z)$   
155 and  $W(z)$ . Each layer has specific annihilation characteristics i.e.  $S$ ,  $W$ , and an effective  
156 diffusion length  $L_{eff}^+$ , which is physically linked to the defect concentration, and the intrinsic  
157 diffusion coefficient of positrons.

158 Compared to DB measurement, PALS is more quantitative, in particular for determining the  
159 nature of the defects. For this study, a fast positron-emitting source was fabricated by depositing  
160  $^{22}\text{NaCl}$  on 6  $\mu\text{m}$ -thick aluminum foil. The encapsulated source is a square of about  $4 \times 4 \text{ mm}^2$ .  
161 and the  $^{22}\text{Na}$  enriched NaCl salt deposit has a maximum diameter of 3 mm at the center. The  
162 source was sandwiched between two equivalent samples ( $7 \times 7 \text{ mm}^2$ ). By detecting the gamma  
163 photons emitted simultaneously to the birth (1.274 MeV), and the annihilation ( $\sim 511 \text{ keV}$ ) of  
164 the positron, using two fast detectors in coincidence. The spectrometer resolution is a Gaussian  
165 function with a Full Width at Half Maximum (FWHM) of about 212 ps. The lifetime spectrum  
166 is a convolution of the spectrometer resolution with a sum of decreasing exponential functions,  
167 reflecting the different annihilation states experienced by positrons. The contribution of  
168 positrons annihilated in the  $^{22}\text{Na}$  source is taken into account in the data processing. Each  
169 experimental spectrum contains more than  $5 \times 10^6$  counts, which ensures a correct  
170 decomposition of the spectra. It is important to note that a fraction of the positrons annihilate  
171 in the source. ANAPC program was employed to deconvolve the lifetime spectra. As is  
172 generally done, three main contributions from the source are subtracted from the experimental  
173 lifetime spectrum [49,50]. These contributions depend on the quality of the source and the



174 nature of the samples. In this study, the source contributions were determined from the  
175 experimental spectra of a pair of extra-high purity W samples (Plansee 99.9999 wt.%) annealed  
176 at 1700 °C for 3h. The first source contribution ( $C_1$ ) has been identified as coming from the  
177 source wrapping foil and has a lifetime of 230 ps and an intensity of 23.59%. Its intensity is  
178 calculated using the Bertolaccini formula given in [51]. The second component ( $C_2$ )  
179 corresponds to the annihilations in the NaCl salt itself and or at the surface of the wrapping foil.  
180 The corresponding lifetime is 450 ps. The third one ( $C_3$ ), generally weak, is due to annihilations  
181 of positronium probably formed on the surface of the samples or in the air between them [49,50].  
182 The corresponding lifetime is 1500 ps. The intensities of the two longest correction sources are  
183 estimated at  $(1.3 \pm 0.3) \%$  and  $(0.35 \pm 0.05) \%$ , respectively. Apart from these source  
184 contributions, a single compound of the Lattice was revealed of about 103 ps.

185 The measured annihilation parameters (lifetime and  $S$ ,  $W$ ) depend on the specific  
186 annihilation characteristics of the lattice,  $X_L$ , and traps  $i$  detected by the positron  $X_i$  (where  $X$  is  
187 given for  $S$ ,  $W$  or lifetime), and on the trapping rate  $k_i$  being the product of their respective  
188 concentrations  $C_i$  by their specific trapping coefficient  $\mu_i$ . The relationship between measured  
189 annihilation parameters (lifetime and  $S$ ,  $W$ ) and  $k_i$  can be formulated using trapping models  
190 [38].

### 191 2.2.2 SIMS

192 In our previous works, we demonstrated that the LEs probably interplay with vacancy-type  
193 defects, leading to variation on the SPB-DBS signals [15,80]. DFT predicted very low  
194 migration energy for O (0.17 eV) and high interactions with vacancy-type defects in tungsten  
195 [24,52–54]. Hence, we employed SIMS to quantify O in some samples using a CAMECA IMS  
196 7f available at Groupe d'Etude de la Matière Condensée (GEMaC). The cations and anions were  
197 collected in ultra-high vacuum ( $\sim 10^{-9}$  mbar) by  $\text{Cs}^+$  (15 kV, 40 nA,  $23^\circ$  respect to surface normal)  
198 and  $\text{O}_2^+$  ions (5 kV, 100 nA,  $45^\circ$  respect to surface normal), respectively. The beams scanned

199 the sample surface over a square area of about  $150 \times 150 \mu\text{m}^2$ , and secondary ion collection  
200 was carried out in a smaller circular area ( $\varnothing 33 \mu\text{m}$ ) to avoid edge effects. The mass resolution  
201  $M/\Delta M$  was 400. The  $^{16}\text{O}$  signal is measured together with W ones as a function of time. To  
202 evaluate the oxygen concentration, we applied the relative sensitivity factors (RSF) method [55]  
203 determined in oxygen-implanted W samples. A profilometer (DEKTAK 8) was used to measure  
204 the depth of the craters, allowing us to determine the sputtering rate, and to convert time profile  
205 into depth. In addition, the error bar on the oxygen concentration determination is estimated to  
206 be about 28 %.

### 207 **2.2.3 TEM**

208 The irradiated thin foil was observed using a JEOL ARM200F cold field emission gun  
209 electron microscope operating at 200 kV and equipped with double spherical aberration  
210 correctors. The observations were carried out in the zone axis [001] at different magnifications  
211 from 50 to 600 kx, in various regions of the thin part of the sample. The dislocation structure  
212 was characterized by weak-beam imaging mode using various diffraction beams, i.e.  $g(200)$ ,  
213  $(020)$ , and  $(110)$ , which were used to distinguish the two types of dislocation loops expected in  
214 tungsten, those with  $\frac{1}{2}a\langle 111 \rangle$  and  $\langle 100 \rangle$  Burgers vectors ( $b$ ) due to the extinction rule  $g \cdot b = 0$   
215 [56].

## 216 **2.3 Simulation methods**

### 217 **2.3.1 Density Functional Theory**

218 In parallel to the experiments, density functional theory (DFT) calculations were performed  
219 with the Vienna *Ab initio* Simulation Package (VASP) [57] with the projector augmented wave  
220 (PAW) [58] method. We utilized the generalized gradient approximation (GGA) with the  
221 Perdew-Burke-Ernzerhof exchange-correlation functional [59] for the electron exchange and  
222 correlation potential. The  $4 \times 4 \times 4$  supercells with  $4 \times 4 \times 4$   $\Gamma$ -centered  $k$ -point mesh was used  
223 to investigate tungsten. The plane-wave cutoff energy was set to 520 eV for all calculations.

224 The structures of oxygen-vacancy complexes,  $O_pV_1$  ( $p = 1-6$ ) were built by referring You et al.  
225 [53]. The  $5p^65d^46s^2$  and  $2s^22p^4$  electrons were treated as valence states for tungsten and O,  
226 respectively. The criterion of convergence for the electronic loop was  $10^{-5}$  eV. For ionic  
227 relaxation, the force tolerance was  $0.01$  eV/Å.

228 After calculating the electron densities with the standard DFT, the positron densities were  
229 calculated using TCDFT in the relaxed structures. The TCDFT implementation used in this  
230 work was developed by Makkonen et al. [60] based on VASP and the details can be found in  
231 [60,61]. The Boroński-Nieminen local density approximation (LDA) [62] was used for  
232 electron-positron correlation and enhancement factor. The positron was approximated to not  
233 affect the average electron density, and the zero-positron-density limit was used [62]. This is  
234 the so-called conventional scheme. It has been shown that this scheme provides results that  
235 agree well with more self-consistent modeling due to certain compensation and feedback effects  
236 [63]. The vacancy-type defects were fully relaxed by taking into account the repulsive forces  
237 on ions induced by positron [60]. The momentum distribution of annihilated electron-positron  
238 pairs was calculated with the state-dependent scheme [64] and PAW method [58,60]. The  
239 computed Doppler spectra were convoluted with a Gaussian function with a FWHM  
240 corresponding to the experimental resolution ( $4.89 \times 10^{-3}$   $m_0c$ ) and theoretical  $S$  and  $W$  values  
241 were extracted using the same momentum windows as in experiments.

### 242 **2.3.2 Cluster dynamics**

243 To simulate the kinetic evolution of small vacancy-O and SIA-O clusters, we used a mean  
244 field cluster dynamics approach as implemented in the CRESCENDO code [65]. Equations of  
245 cluster concentrations are solved as a function of time. Physical phenomena taken into account  
246 are: the production of defects (SIAs and vacancies) by electron irradiation, absorption of  
247 migrating clusters by other clusters and by grain boundaries, and thermal dissociation of clusters.  
248 Migration is assumed to be exclusively thermally activated, except for vacancies for which

249 electron-induced diffusion is also considered [66,67]. The effect of grain boundaries is taken  
250 into account through sink strengths, which also take into account the transition from 1D to 3D  
251 mobility [66]. Parameters of the model are shown in [Tab. 1](#).

252 The parametrization of pure vacancy and SIA clusters closely follows the OKMC  
253 parametrization proposed by Becquart *et al.* [68]. In particular, we consider 3D mobility for  
254 vacancies and vacancy clusters, 1D mobility for SIA clusters, and mixed 1D-3D mobility for  
255 SIAs. Reaction rates for this latter case can be found in references [69,70].

256 We then assume that O is the only impurity acting on the clustering process, due to its  
257 rather high mobility and its strong binding with vacancies [54]. The exact concentration of O  
258 dissolved in the matrix is not precisely known experimentally. O may form oxides and migrate  
259 to grain boundaries, leading to a much lower concentration in the matrix than the one measured  
260 by SIMS. Taking into account the formation of oxides and the interaction of O with grain  
261 boundaries is beyond the scope of the present study. Instead, we perform a parametric study of  
262 the role of O, by varying its concentration as dissolved in the matrix from 0 to 220 appm.  
263 Accordingly, grain boundaries are considered only when the O concentration is zero.

264 In our model, Vacancy-O clusters are 3D objects that can contain up to 6 O atoms. This  
265 assumption is probably more valid for small vacancy clusters. We will see in the next section  
266 that Vacancy-O clusters indeed remain small in the present experimental conditions. These  
267 clusters are also assumed to be immobile. The binding energies of vacancies and O atoms to  
268 these clusters are deduced from formation energies calculated by DFT for  $O_pV_1$  clusters [54].  
269 For other cluster sizes, we determine the vacancy binding energy as the maximum of the value  
270 given by a capillary law (assuming that vacancies will essentially bind together) and the binding  
271 of a vacancy with an O atom (assuming that a vacancy will preferentially bind with an O atom).  
272 No formation of pure O clusters is permitted, as their diffusion behavior is unknown.

273 SIA-O clusters may also form in our model, under the form of dislocation loops trapped on  
 274 O impurities. Such clusters are thus assumed to be immobile, unlike pure SIA clusters which  
 275 migrate very quickly along their glide cylinder. Binding energies of O are given by an analytical  
 276 model fitted to DFT results [29], whereas no effect of O on the binding energies of SIAs and  
 277 vacancies to loops is considered. It is assumed that an interstitial loop cannot host more than  
 278 one O atom every  $2b$  along the dislocation line, where  $b$  is the norm of the Burgers vector of  
 279 the loop.

280 *Tab. 1: Parameters for the cluster dynamics simulations.*

Parameter	Value	Reference
Temperature	323 K	EXP
Electron energy	2.5 MeV	EXP
Electron flux/damage rate	$5.5 \times 10^{17} \text{ m}^{-2} \text{ s}^{-1} / 2.3 \times 10^{-9} \text{ dpa s}^{-1}$	EXP
Grain size	10 $\mu\text{m}$	EXP
Lattice parameter $a_0$	0.316 nm	-
Norm of the Burgers vector of interstitial loops	0.274 nm	-
Diffusion prefactor of $v_n$ ( $n = 1, \dots, 3$ )	$4 \times 10^{-6} / (10^3)^{n-1} \text{ m}^2 \text{ s}^{-1}$	[68,71]
Migration energy of $v_n$ ( $n = 1, \dots, 3$ )	1.66 eV	[54]
Diffusion prefactor of O	$3.75 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$	[72]
Migration energy of O	0.17 eV	[54]
Diffusion prefactor of $I_n$ ( $n = 1, \dots, 10$ )	$1.5 \times 10^{-3} / n^{1/2} \text{ m}^2 \text{ s}^{-1}$	[68]
Migration energy of $I_n$ ( $n = 1, \dots, 10$ )	0.013 eV	[68]
Rotation frequency of a crowdion ( $i_1$ )	$6.59 \times 10^{12} \text{ Hz}$	[72]
Rotation energy of a crowdion	0.38 eV	[72]
Formation energy of vacancies and vacancy clusters $V_n$	DFT values for $n \leq 8$ Capillary model for larger sizes	[65,68]
Binding energies of $O_p V_n$ clusters ( $1 \leq p \leq 6$ )	DFT values for $O_p V_1$ ( $p \leq 6$ ) See text for other cluster sizes	[53]
Formation energy of SIAs and SIA clusters $I_n$	DFT values for $n \leq 12$ , discrete-continuum model for larger sizes	[73]
Binding energies of $O_p I_n$ clusters	DFT values and analytical model for the binding of O No influence of O for the binding of SIAs and vacancies	[69]
Recombination distance of SIAs and vacancies	$2 a_0 = 0.632 \text{ nm}$	
Absorption efficiency of SIAs by loops $Z_i$	1.1	

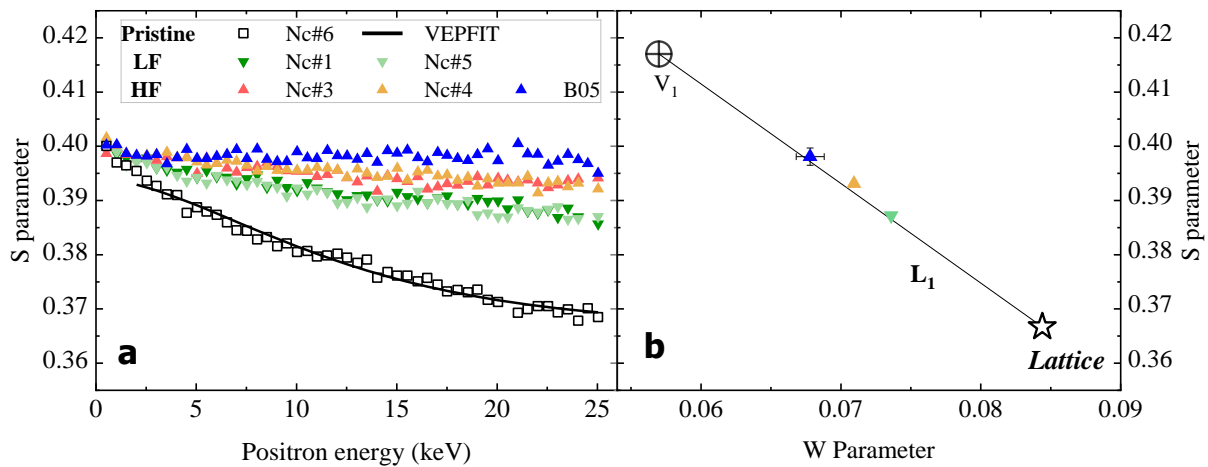
## 281 3. Results

### 282 3.1 SPB-DBS

283 Fig.2a shows the  $S$  parameter as a function of the positron energy  $E$  of pristine and electron-  
284 irradiated samples. **For the pristine sample (Nc#6)**, within the energy range from 0.5 to 25  
285 keV,  $S$  decreases progressively with increasing positron energy  $E$ .  $S$ - $W$  plot in Fig.2b shows  
286 that annihilation characteristics of the bulk tend toward the ones of the tungsten *Lattice* ( $S_L =$   
287 0.367,  $W_L = 0.0844$ ) which have been identified for **GF** samples in [74]. By operating the  
288 VEPFIT program, the  $S(E)$  and  $W(E)$  curves of the pristine sample were fitted by a single-layer  
289 model. The  $S$  (0.366 (3)), and  $W$  (0.0855(3)) of the fitted layer are close to the tungsten *Lattice*  
290 values, and an effective diffusion length of about 121 (4) nm indicates a low defect  
291 concentration, which can be roughly estimated below the detection limit of the SPB-DBS  
292 measurement ( $\sim 10^{23} \text{ m}^{-3}$  [74]).

293 **For electron-irradiated samples with two fluences** (LF: **Nc#1 & 3** ( $1 \times 10^{23} \text{ m}^{-2}$ ) and HF:  
294 **Nc# 4, & 5** ( $2 \times 10^{23} \text{ m}^{-2}$ )),  $S(E)$  curves were plotted with downward and upward triangle,  
295 respectively, in Fig.2 a.  $S$  increases with the fluence at all energies higher than 2 keV. Above 2  
296 keV, the annihilation fraction at the surface decreases quickly, due to more annihilation at the  
297 defects,  $S$  differs from the pristine sample value, and this deviation increases with positron  
298 energy. Comparable evolution is observed for the samples irradiated together at the same  
299 fluence (LF: **Nc#1 & 5** and HF: **Nc#3 & 4**). It confirms a homogenous fluence on the surface  
300 of the samples. However, the  $S(E)$  value dispersion reveals a heterogeneous distribution of  
301 defects in the **Nc** samples.  $S$  decreases until 25 keV for samples irradiated at low fluence (LF:  
302 **Nc#1 & 5**), while it only decreases up to 18 keV and then plateaus for samples irradiated at  
303 high fluence (HF: **Nc#3 & 4**). Because of this heterogeneous distribution, the homogeneous  
304 multi-layer model used in the VEPFIT program is inappropriate to fit the defect distribution in  
305 irradiated samples. Moreover, Fig.2 a shows the  $S(E)$  curve measured in **B05**, a **GF** disc

306 irradiated at HF at the same time with **Nc#3 & 4** plates. The  $S$  values are less dispersed in **B05**  
 307 compared to other samples. When the positron energy increases from 0 to 5 keV, the  $S$   
 308 parameter decreases. Within the energy range from 5 to 25 keV, the  $S$  values fluctuate in B05  
 309 with a mean value of 0.3981 (16), in contrast to the declining trend in other samples. The  $S$   
 310 plateau value is higher than those measured in the same energy range for the irradiated **Nc**  
 311 samples. Furthermore, Fig.2 b shows the  $S$ - $W$  plot, for both fluences.  $S$ - $W$  points are located  
 312 close to the line  $L_1$ , which was identified as the characteristic line of annihilation at  $V_1$  with the  
 313 saturated point ( $S_{V_1}, W_{V_1}$ ) [75]. These results suggest that the positrons annihilated mainly at  $V_1$   
 314 with a more or less heterogeneous distribution in **Nc** samples. Their concentration is greater in  
 315 samples after longer irradiation. The highest concentration was found in the GF B05 sample  
 316 but still did not reach the saturation signal of the single vacancy ( $V_1$  point in Fig.2) in tungsten  
 317 [75].



318  
 319 Fig.2: Annihilation characteristics of pristine sample (Neyco, square) in comparison with 2.5 MeV electron-irradiated ones at  
 320 two fluences, LF  $1 \times 10^{23}$  (downward triangle) and HF  $2 \times 10^{23}$   $m^{-2}$  (upward triangle) at RT, **a**: low momentum parameter  $S$  as  
 321 a function of the positron energy  $E$ , and **b**:  $S$  versus  $W$ , fitted value (using VEPFIT) for pristine (Nc#6), mean values in the 5-  
 322 25keV range for B05, and value at 25 keV for damaged Nc samples, with the standard deviation as the error bars.

### 323 3.2 PALS

324 According to the damage profile in Fig.1, 2.5 MeV electrons induce damage until about  
 325 220  $\mu m$ . To complement the SPB-DBS measurements in the surface region ( $\sim 700$  nm), PALS  
 326 was used to obtain more information on the induced defects in the in-depth bulk (the first 50

327  $\mu\text{m}$ ). Fig.2a shows processed PALS spectra (after source corrections, and deduction of  
 328 background noise) of the pristine and irradiated samples: the LF pair (Nc#1 & 5) and the HF  
 329 pair (Nc#3 & 4). Obviously, after irradiation, the spectra contain longer-lifetime components.

330 Tab. 2: Lifetime components deconvoluted from experimental spectra using the ANAPC program for pristine and electron-  
 331 irradiated sample pairs at 2.5 MeV, taking into account 3 components, the third being fixed at 200 ps.

<i>Fluence</i> ( $\times 10^{19} \text{ cm}^{-2}$ )	$\tau_{av}$ (ps)	Component 1		Component 2		Component 3		$\tau_M$ (ps)
		$\tau_1$ (ps)	$I_1$ (%)	$\tau_2$ (ps)	$I_2$ (%)	$\tau_3$ (ps)	$I_3$ (%)	
0	105	$105 \pm 0.3$	100	-	-	-	-	-
1	135	$11 \pm 0.1$	$11 \pm 3$	$122 \pm 2$	$56 \pm 2$	200	$33 \pm 1$	62
2	147	$12 \pm 0.2$	$7 \pm 2$	$135 \pm 2$	$63 \pm 1$	200	$30 \pm 1$	84

332  
 333 Using ANAPC to fit the spectra, a 105 ps lifetime component was extracted for the pristine  
 334 samples. This value lies within the lifetime range of the tungsten *Lattice*, from 100-110 ps [76–  
 335 79]. For irradiated samples, we have first tested a 2-component fit. The results showed a long  
 336 lifetime of  $187 \pm 2$  and  $197 \pm 4$  ps for High and Low electron fluence respectively and an  
 337 intensity of 53 and 40% respectively. These lifetimes are close to those expected for a single  
 338 vacancy. Meanwhile, a short lifetime with a value (102 ps and 127 ps respectively) close to that  
 339 of the perfect Lattice in tungsten was also found for both fluences. It's noteworthy that when  
 340 positrons annihilate in more than one state, for example in a deep trap (defect with no detrapping)  
 341 and the lattice (delocalized state), the short lifetime indicating the time that positrons spend in  
 342 the lattice before being trapped or annihilated, this lifetime should be shorter than the lifetime  
 343 of the perfect Lattice. Furthermore, the  $\tau_M$  estimated with eq.1 was 135 and 148 ps respectively,  
 344 i.e. larger than that of the Lattice. This indicates at least a second trap (X defect) exists apart  
 345 from the single vacancy. Hence, a 3-component fit was attempted, but the number of free  
 346 parameters and the close values of the lifetime components prevented the fit. It should be noted  
 347 that in these analyses, vacancy clusters larger than the single vacancy were not considered, as  
 348 they are not expected to form in electron irradiation at RT: (1) due to the low energy of PKA,  
 349 the local density of displacements is low and no cascade is expected; and (2) because single

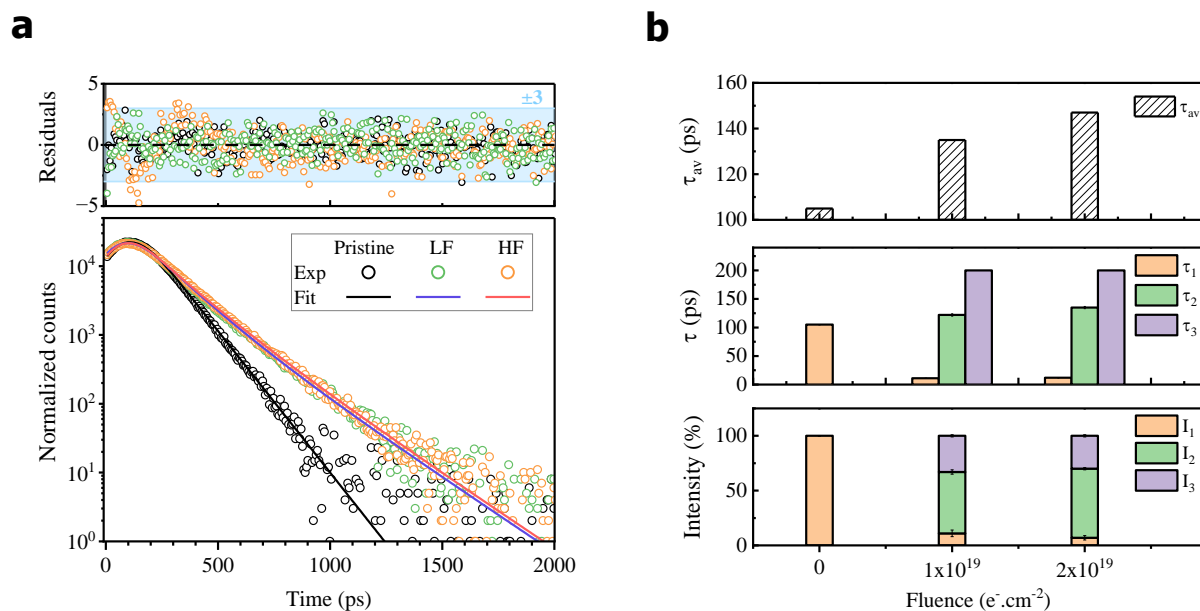


350 vacancies are not mobile at RT, their migration energy is high i.e.  $E_{V_1}^m = 1.66$  eV [80]. To fit the  
 351 data with three components, the lifetime component  $\tau_3$  was fixed to 200 ps a value previously  
 352 identified for the single vacancy, i.e. 193-199 ps reported by theoretical works [82–84], and  
 353 195-200 ps obtained experimentally [75,84]. The fitted results are reported in

354 **Tab. 2.** The intensity of the third component  $\tau_3$  (fixed at 200 ps) was of approximately 30 %  
 355 was for both fluences. Meanwhile, a component with a very short lifetime  $\tau_1$  of about 10 ps with  
 356 a quite low intensity of about 10%, was also extracted. This component corresponds to the  
 357 ‘reduced lattice’ lifetime, i.e. the time that positrons spend in the lattice before being trapped or  
 358 annihilated. Its value is very short compared to the lifetime of the perfect Lattice because most  
 359 positrons are trapped before annihilation. This indicates a minor fraction of positrons  
 360 annihilated in the **Lattice**. Such a short lifetime probably means that the limit of the  
 361 deconvolution was reached. This short component was taken into account because the  
 362 decomposition with three components shows the best variance compared to the two-component  
 363 decomposition. In addition, a component with an intermediate lifetime  $\tau_2$  of about 122, and 135  
 364 ps was deconvoluted from the spectra of samples damaged with both fluences, i.e. LF and HF,  
 365 respectively. Its intensity is about 56 % for LF and increases to 63 % for the HF. As a result,  
 366 the average lifetime has increased from 135 to 144 ps (**Fig.3 b**), when the electron fluence has  
 367 doubled, from  $1 \times 10^{23}$  to  $2 \times 10^{23}$  m<sup>-2</sup>. This result suggests that, in addition to the **Lattice** and  
 368  $V_1$ , one or more new positron traps (X defect) were created in electron irradiation at RT.  
 369 Furthermore, according to the trapping model [31], if 100 % of the positrons annihilated in the  
 370 identified states  $i$  in the experiments, the sum  $1/\tau_M$  of the ratio between the intensity  $I_i$  and the  
 371 lifetime  $\tau_i$  of each component should be equal to the reciprocal of the **Lattice** lifetime, i.e.  $\tau_{Lattice}$ .  
 372 (eq.1)

$$373 \quad \frac{1}{\tau_M} = \sum_1^i \frac{I_i}{\tau_i} \quad \text{eq. 1}$$

374 However, the  $\tau_M$  value obtained for both fluences is shorter than the tungsten *Lattice*  
 375 lifetime (  
 376 [Tab. 2](#)), suggesting that the positrons annihilate at more than three states.



377  
 378 Fig.3: a) Processed experimental lifetime spectra without source correction nor background noise of the pristine and 2.5 MeV  
 379 electron irradiated samples **Nc#1 & 5** for low fluence and **Nc#3 & 4** for high fluence, and b) the deconvoluted lifetime  
 380 components (lifetime and corresponding intensity) and average lifetime extracted from the lifetime spectra using the ANAPC  
 381 program versus irradiation fluence. The quality of the fit was checked by calculating the residual standard deviation between  
 382 the experimental and fitted spectra which is  $\pm 3$  over the entire time scale.

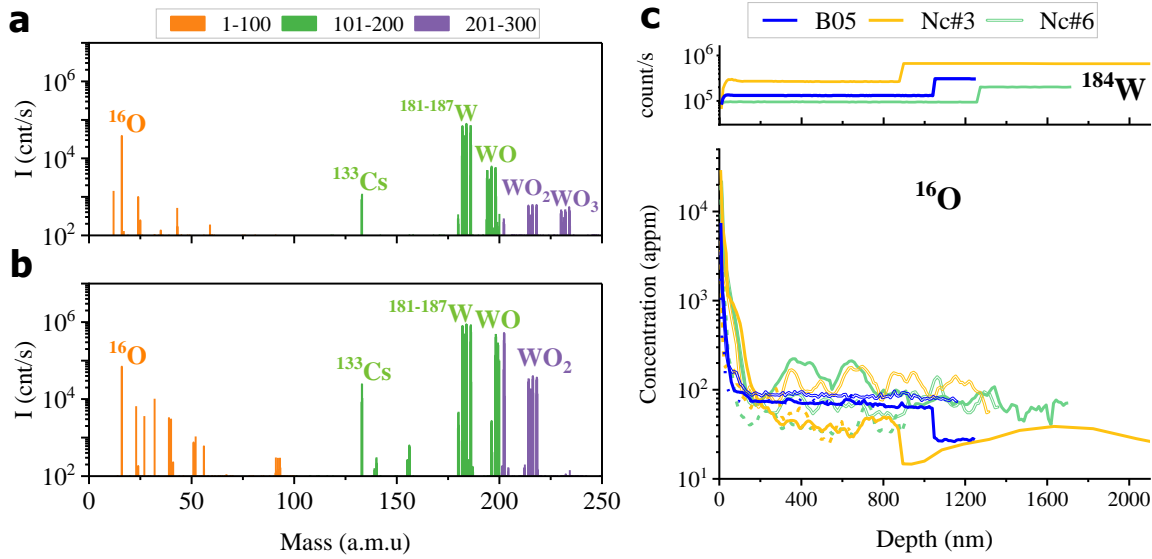
### 383 384 3.3 SIMS

385 [Fig.4 a](#) and [b](#) show the secondary anions and cations collected in **Nc#3** within a mass range  
 386 from 0 to 250 a.m.u with  $\text{Cs}^+$  and  $\text{O}_2^+$  as the primary ions, respectively. Not surprisingly, the  
 387 tungsten isotopes appear with the highest intensity. Moreover, O appears as a major impurity  
 388 in spectra acquired with  $\text{Cs}^+$  sputtering. In addition, it should be noticed that significant  
 389 intensities are detected at around 200, 216, and 232 a.m.u. respectively, which probably  
 390 correspond to O tungsten molecules ( $\text{WO}_x$ ) for several tungsten isotopes. It should be noted  
 391 that O cations collected with primary  $\text{O}_2^+$  ions cannot be used as an argument for the presence  
 392 of O in the samples, as is possible for anions collected after sputtering with  $\text{Cs}^+$ .

393 Then, the analysis was focused on the quantification of O, in the pristine (**Nc#6**) and  
394 irradiated samples (**Nc#3**, **B05**). Fig.4 c shows the O profiles collected by SIMS at three random  
395 positions with primary Cs<sup>+</sup> ions. The O profiles are both comparable for **Nc#3** and **Nc#6**,  
396 suggesting that there was no significant introduction of O during irradiation. O concentration is  
397 high at the surface and decreases rapidly, probably merely due to a native oxidized layer [85].  
398 Beyond 200 nm, the profiles fluctuate down to 1.5 μm depth, and the concentration varies from  
399 30 to 250 appm, depending on the craters for a sputtered area of 150 × 150 μm<sup>2</sup>. After reducing  
400 the sputtered area to 100 × 100 μm<sup>2</sup>, no obvious change in the O profile is observed in **Nc#6** (at  
401 ~1250 nm), while there is a decrease for one crater in **Nc#3** (at ~900 nm). We emphasized that  
402 the O concentration returns to the value of a larger sputtered area between 900 and 2000 nm.  
403 These results indicate that oxygen concentration is nonhomogeneous in the **Nc** samples. It  
404 changes not only with depth but also with the characterized area

405 In contrast, O profiles obtained from the HF-damaged **B05** sample are rather 'clean':  
406 concentrations from three craters are comparable. A plateau is obtained from 200 to 1500 nm.  
407 A clear decrease in O concentration was revealed after reducing the sputtering area, leading to  
408 a new plateau with a lower concentration of about 25 appm. These results suggest that the SIMS  
409 detection limit (<25 appm) of O was reached in **B05**, and its distribution is homogeneous.

410 To summarize, a heterogeneous distribution of O concentration was revealed in **Nc#3** and  
411 **Nc#6** (30 to 250 appm). The highest values are probably due to the presence of a significant  
412 fraction of oxide nanoparticles. The lowest values revealed that O atoms could be dissolved in  
413 the matrix with a concentration between 30 to 80 appm, as already observed in [86], in contrast,  
414 the oxygen concentration is homogeneous and less than or equal to 25 appm in the **B05**.

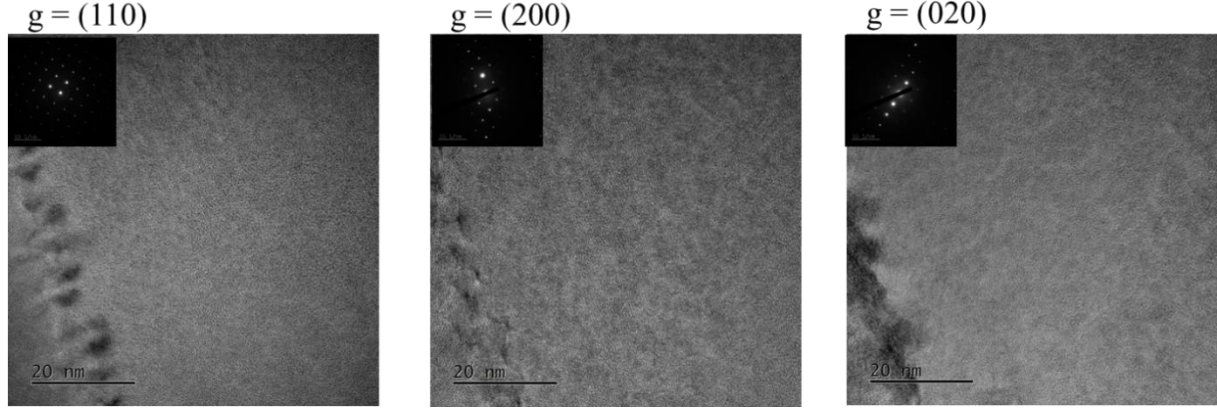


415

416 Fig.4: Mass spectra ranging from 0 to 250 a.m.u. of the secondary particles sputtered from the sample Nc#3 ( $2 \times 10^{23} \text{ m}^{-2}$ ), a  
 417 collected anions with  $\text{Cs}^+$  primary ions, and b) collected cations by using  $\text{O}_2^+$  primary ions. c) O profiles of pristine (Nc#6,  
 418 yellow), and electron-damaged -HF- (Nc#3, green), and B05 (blue) for three random positions (Crater 1 to 3) plotted using  
 419 different line types.

### 420 3.4 TEM

421 During irradiation experiments, one tungsten-thinned disc (GF, 99.95 wt.%) was also  
 422 damaged at the HF (i.e.  $2 \times 10^{23} \text{ m}^{-2}$ ) simultaneously with thick samples. No dislocation loops  
 423 nor any black dots were observed (Fig.5) in the images indicating that no defects with a size  
 424 greater or equal to 1 nm were created during irradiation. This size is the minimum size for which  
 425 the diffuse contrast can be distinguished in TEM [87]. The thickness of the observed region  
 426 was estimated using EFTEM (Energy Filtered Transmission Electron Microscopy)  
 427 measurements and measures about 30 nm. Several zones over the thin region were observed for  
 428 a total surface of  $3 \times 10^{-27} \text{ m}^2$ . It follows that if some defects larger than 1 nm exist, their  
 429 maximum concentration should be about  $1 \times 10^{19} \text{ m}^{-3}$ .



430

431 Fig. 5: bright field TEM images acquired using different  $g$ -vectors ( $g=(110)$ ,  $g=(200)$  and  $g=(020)$ ) in a tungsten foil  
 432 irradiated with 2.5 MeV electrons at RT with a fluence of  $2.10^{19} \text{ cm}^{-2}$ .

### 433 3.5 TCDFT

434 Since SIMS analysis shows an O concentration of the same order of magnitude as that of  
 435 induced  $V_1$ , we focused our TCDFT calculations on the interaction between O atoms and  $V_1$ .  
 436 [Tab. 3](#) contains the total binding energy of oxygen-vacancy complexes and positron lifetimes  
 437 calculated for  $O_pV_1$  complexes. Our binding energy values are in good agreement with the  
 438 values in [53]. The calculated positron lifetimes for annihilation in the tungsten *Lattice* and as  
 439 trapped in  $V_1$  are 101 ps and 195 ps respectively as already reported in [37]. These values  
 440 calculated based on TCDFT are comparable with the experimental ones found in the present  
 441 work.

442 Tab. 3: Binding energy  $E_{binding}^{O_pV_1}$ , and position lifetime  $\tau$  calculated using TCDFT-LDA for  $O_pV_1$  ( $p=1-6$ ) complexes, and  
 443 estimated specific trapping coefficient  $\mu_{O_pV_1}$  of the complexes. These trapping coefficients were estimated using the value of  
 444  $V_1$  in Ta [31] for  $V_1$  and reduced by the ratio of the Voronoi volume of  $O_pV_1$  complexes to that of pure  $V_1$  ( $0.0159 \text{ nm}^{-3}$ ) for  
 445 the complexes. <sup>a</sup>Reference [53], <sup>b</sup>Reference [88]. The error on the values of  $\mu_{O_pV_1}$  is calculated from that of  $\mu_{V_1} = (6 \pm 3) \times 10^{-}$   
 446  $^{15} \text{ m}^{-3} \cdot \text{s}^{-1}$  [31]

447

448

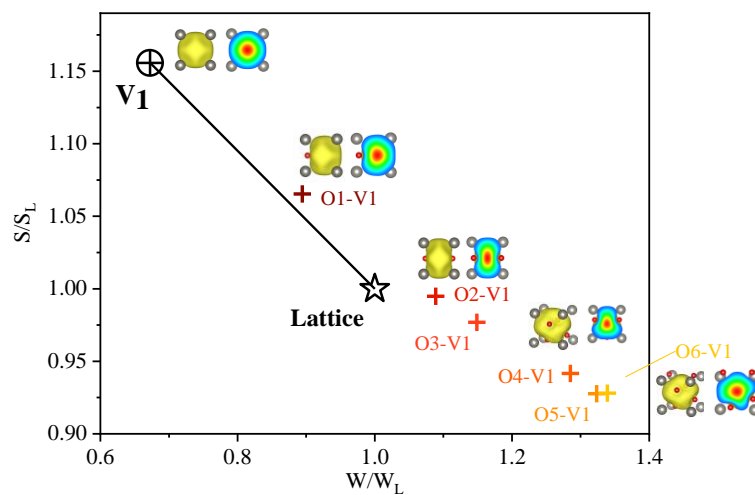
449

450

451

Number of associated O atoms, $p$	$E_{binding}^{O_pV_1}$ (eV)	$\tau$ (ps)	$\mu_{O_pV_1}$ ( $10^{-9} \text{ cm}^3 \cdot \text{s}^{-1}$ )
1	3.0, (3.04 <sup>a</sup> )	170 (170.6 <sup>b</sup> )	$4.89 \pm 3.46$
2	5.9, (5.96 <sup>a</sup> )	142 (136.8 <sup>b</sup> )	$3.91 \pm 2.77$
3	6.9, (7.29 <sup>a</sup> )	143 (129.4 <sup>b</sup> )	$3.67 \pm 2.60$
4	8.56, (8.80 <sup>a</sup> )	130 (123.6 <sup>b</sup> )	$2.75 \pm 1.94$
5	10.06, (10.37 <sup>a</sup> )	124 (121.6 <sup>b</sup> )	$2.42 \pm 1.71$
6	11.92, (11.21 <sup>a</sup> )	132 (128.3 <sup>b</sup> )	$2.50 \pm 1.76$

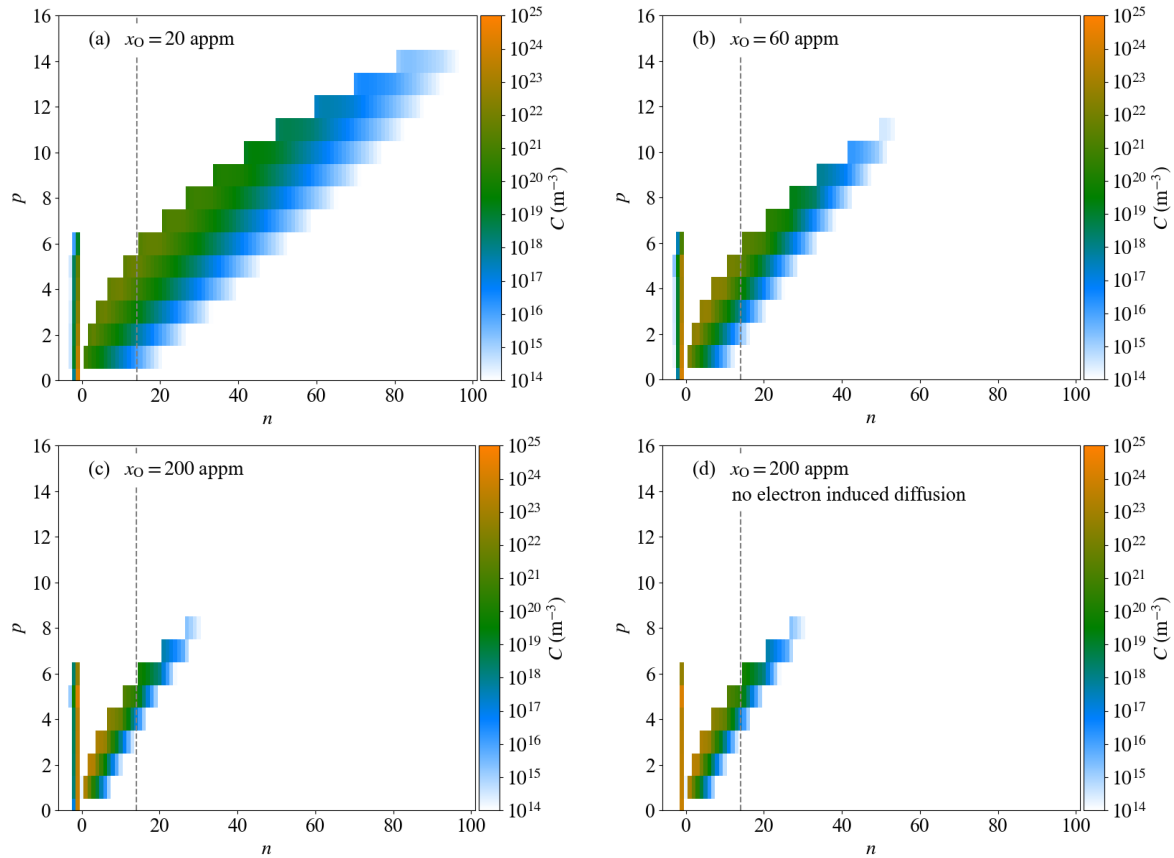
452 **Tab. 3** shows that the positron lifetime of  $O_pV_1$  complexes decreases with the number  $p$  of  
 453 associated O atoms when  $p$  remains inferior or equal to 5. The lifetime of  $O_1V_1$  is 170 ps, then  
 454 drops drastically to near 140 ps for  $O_2V_1$  and  $O_3V_1$ , and decreases to 130 ps and 124 ps for  $O_4V_1$   
 455 and  $O_5V_1$ , respectively. Interestingly, the positron lifetime rebounds to 132 ps for  $O_6V_1$ , a result  
 456 also reported in [88] with different positions of O atoms in the vacancy. These changes are due  
 457 to the change in electronic density in  $V_1$ . Moreover, the positron remains localized in the center  
 458 of the complex for all  $p$  values (see local positron density in **Fig.6**) indicating that trapping can be  
 459 expected in all the  $O_pV_1$  complexes. **Fig.6** shows the computed **S-W** plot for  $O_pV_1$  complexes.  
 460 The **S-W** annihilation fractions are very sensitive to the presence of O atoms in the vacancy. A  
 461 clear trend emerges: The **S-W** points move down to the bottom-right with the increasing number  
 462 of O atoms. The calculated **S-W** points of  $O_{2-6}V_1$  deviate from the line segment connecting the  
 463 **Lattice** and  **$V_1$** , called  $L_1$  in our experiments, as  $p$  increases, while that of the  $O_1V_1$  complex is  
 464 close to the middle of  $L_1$ .



466  
 467 **Fig.6:** a-1) Theoretical **S-W** plot for  $V_1$  associated with O atoms in tungsten. The computational results are convoluted with a  
 468 Gaussian function with a FWHM of  $4.89 \times 10^{-3} m_0c$ , which corresponds to the experimental resolution. (-left) 3D structure –O  
 469 atoms (red sphere) location in the vicinity of  $V_1$  (gold sphere)- and (right) local positron density are illustrated for  $V_1$ ,  $O_1V_1$ ,  
 470  $O_2V_1$ ,  $O_4V_1$ , and  $O_6V_1$ .

### 471 3.6 Cluster dynamics

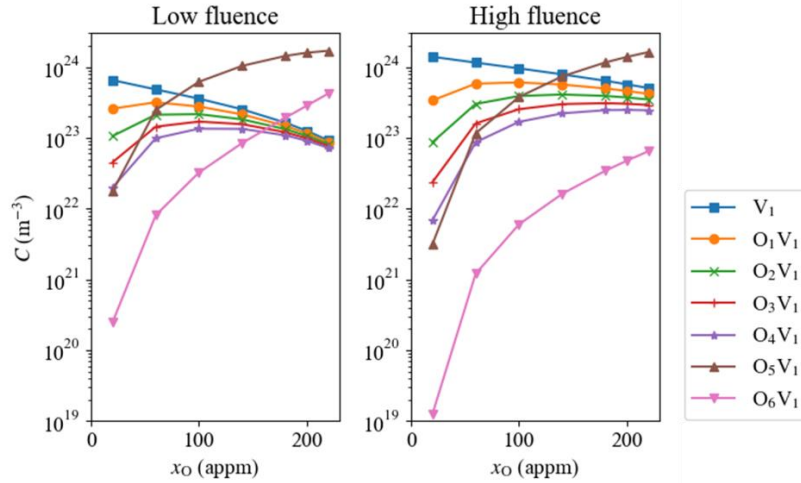
472 Cluster distributions at HF ( $2 \times 10^{23} \text{ e}^- \text{ m}^{-2}$ ), for three different O concentrations in the  
473 matrix, are shown in Fig.7 (a-c). We also represent cluster distributions for  $x_o = 200$  appm,  
474 when electron-induced diffusion is turned off (Fig.7 d). By comparing Fig.7 c to Fig.7 d, it can  
475 be seen that electron-induced diffusion plays a marginal role in these experimental conditions.  
476 It slightly promotes vacancy mobility, which results in a small number of clusters containing  
477 two vacancies ( $n = -2$ ) and some O atoms. Most vacancy defects (more than 99, 99 %) contain  
478 only one vacancy ( $n = -1$ ) and up to six O atoms ( $p = 1 - 6$ ), due to the high mobility of O  
479 atoms. As expected, the increasing O concentrations lead to more decorated vacancy clusters,  
480 i.e. the number of clusters with large  $p$  values increases. In addition, the number of SIA clusters  
481 ( $n \geq 2$ ) increases. They all contain at least one oxygen atom. Given the larger diffusion  
482 coefficient of SIAs with respect to oxygen atoms, the formation of such SIA clusters can be  
483 seen as a heterogeneous nucleation on O impurities. As the loop density increases with O  
484 concentration, the loop size decreases. The maximum number of SIAs in a cluster declines from  
485 around 95 to 30 as O concentration increases from 20 to 200 appm (Fig. 6 a-c). These smaller  
486 dislocation loops are more difficult to detect with TEM. The number of SIAs corresponding to  
487 a loop size of 1 nm, which can be considered as a detection limit in TEM, is shown by a vertical  
488 gray line on the cluster distributions. The density of SIA clusters larger than 1 nm decreases  
489 from  $6 \times 10^{22} \text{ m}^{-3}$  to  $3 \times 10^{20} \text{ m}^{-3}$  as oxygen concentration increases from 20 to 200 appm,  
490 and more than 99.95 % of them are smaller than 2 nm. Apart from the case  $x_o = 20$  appm,  
491 loops of size larger than 1 nm are too scarce to be detectable in TEM.



492 Fig.7: cluster size distributions at high fluence obtained by cluster dynamics. (a,b,c): Cluster distributions with a concentration  
 493 of O in the matrix equal to 20, 60, and 200 appm respectively. (d): same as (c) but without taking into account electron-induced  
 494 vacancy mobility. In these graphs, positive values of  $n$  refer to the number of SIAs in a cluster, whereas negative values are  
 495 used for the number of vacancies ( $-n$ ) in vacancy clusters. The number of O atoms in a cluster is noted in  $p$ . The vertical grey  
 496 line corresponds to a loop of size 1 nm.

497 We also show the concentration of small vacancy-O complexes for low and high fluence  
 498 conditions, as a function of the O concentration in the matrix (Fig.8). As expected, populations  
 499 of complexes containing more O atoms increase with the concentration of O in the matrix.  
 500 However, these populations decrease with the fluence. Indeed, owing to the low mobility of  
 501 vacancies, these complexes tend to absorb more SIAs than vacancies. Assuming that the  
 502 vacancy-O complexes are immobile at RT like the pure single vacancies, SIA that are highly  
 503 mobile at RT can be absorbed by non-mobile oxygen-vacancies complexes. As a consequence,  
 504 O atoms are released in the matrix and can freely migrate to dislocation loops or other vacancy  
 505 clusters. On the contrary, the vacancy concentration steadily increases with the damage dose  
 506 due to the continuous production of vacancies by irradiation and the low mobility of vacancies.





507

508 Fig.8: Concentration of vacancy-O clusters as a function of the atomic fraction of O in the matrix, for the low and high  
 509 fluence cases. Clusters with more than one vacancy are not represented, as their concentration is negligible.

#### 510 4. Discussion

511 Generally, low-energy electron irradiation generates mainly FPs. In our SPB-DBS  
 512 experiments, in the near-surface region (0~700 nm), the presence of  $V_1$  was detected by  
 513 positrons at both fluences, and their concentration increased with the fluence. PALS results  
 514 confirmed the annihilation of positrons as trapped at  $V_1$  and, more interestingly, revealed new  
 515 positron traps (*X defects*) with high annihilation probability. These traps have an average  
 516 lifetime of about 122, and 135 ps for LF- and HF-damaged samples, respectively. Their nature  
 517 is discussed below.

518 The *X defects* have a lifetime shorter by a factor of 1.44-1.64 than  $V_1$  (195-200 ps), and it  
 519 therefore could be related to defects with smaller open volumes than  $V_1$ . Two types of defects  
 520 can be envisaged: (i) dislocation loops or (ii) impurity-vacancy complexes.

521 From TEM observations, no defects were detected in the **GF** disk irradiated at HF,  
 522 indicating that the dislocation loop size and concentration were rather low i.e. lower than 1 nm  
 523 and  $\sim 1 \times 10^{19} \text{ m}^{-3}$ , respectively. CD calculations predict a negligible concentration of interstitial  
 524 clusters (around  $1 \times 10^{13} \text{ m}^{-3}$ ) all smaller than 1 nm in pure tungsten irradiated under  
 525 experimental conditions, which is well below the experimental detection limits. Arakawa et  
 526 *al.*[89] and Tamino et *al.*[90] observed an average density of dislocation loops of about  $4 \times 10^{22}$

527  $\text{m}^{-3}$  at 105 K in high-purity polycrystalline tungsten (99.9999 wt.%, JX Nippon Mining &  
528 Metals Co) irradiated with 2 MeV electrons at low temperatures ( $\leq 290$  K) [89,90]. The average  
529 size of the dislocation loops is mentioned to be approximately 3–4 nm [89]. In these  
530 experiments, the fluence ( $\sim 4 \times 10^{25} \text{ m}^{-2}$ ) and the flux ( $1 \times 10^{24}$  [89] and  $3.0 \times 10^{22} \text{ m}^{-2} \cdot \text{s}^{-1}$  [90]  
531 respectively) are remarkably higher than those used in current work, by a factor of 200, and 3  
532 to 6 orders of magnitude respectively. In such high flux irradiation conditions, the estimated  
533 damage rate is  $1.3 \times 10^{-4} \text{ dpa} \cdot \text{s}^{-1}$  (for  $3.0 \times 10^{22} \text{ m}^{-2} \cdot \text{s}^{-1}$ ) in [89,90], which is five orders of  
534 magnitude higher than in the present study ( $2.3 \times 10^{-9} \text{ dpa} \cdot \text{s}^{-1}$ ). These differences give rise to a  
535 much higher local density of SIA in Arakawa's experiments, leading to a high probability of  
536 cluster formation. SIA interaction is much less likely to be under our irradiation conditions, and  
537 cluster formation remains limited in pure tungsten. Furthermore, CD results predict that an  
538 increase in O concentration promotes small SIA clusters ( $<1$  nm) production for less pure  
539 tungsten, whereas it limits the formation of larger SIA clusters. It is expected that a cluster  
540 including more than 7 SIAs will reach a stable configuration and become an interstitial  $\frac{1}{2}\langle 111 \rangle$   
541 loop [91] with a diameter of approximately 0.7 nm. The concentration of these clusters is  
542 predicted by CD to be at most  $1.55 \times 10^{23} \text{ m}^{-3}$  for the O concentration of 60 appm. Could these  
543 TEM-invisible SIA clusters be detected by PAS? Their concentration is close to the PAS  
544 detection limit for  $V_1$  ( $\sim 10^{23} \text{ m}^{-3}$ ), but such a low concentration of defects could be detected  
545 only if their positron trapping coefficient,  $\mu_{intL}$  was higher than that of  $V_1$ . Despite the  $\mu_{intL}$ , is  
546 unknown to date, nevertheless, the positron binding energy  $E_B^p$  at an edge dislocation line has  
547 been calculated about -0.28 eV in iron by E. Kuramoto et al. [92]. Like the edge dislocation  
548 line, the interstitial loops have reduced free volume concerning the lattice on the line or at the  
549 loop periphery respectively, so a low  $E_B^p$  should also be expected for interstitial loops. This

550 suggests that the probability of a positron being trapped in such interstitial loops should be less  
 551 probable, at least at RT. Thus, the *X defects* are unlikely to be dislocation loops.

552 According to TCDFT results, one V<sub>1</sub> can be associated with 1 to 6 O atoms, forming O-  
 553 vacancy complexes with a lifetime close to the *X defects*. CD simulation with 20 to 220 appm  
 554 oxygen, predicts that all these O-vacancy complexes coexist. Next, we use the trapping model  
 555 to calculate theoretical lifetime spectra *PALS(t)* for the damage dose of  $4.1 \times 10^{-4}$  and  $8.3 \times 10^{-4}$   
 556 dpa. In these models, we assume that the positron can annihilate in several states: O<sub>1-6</sub>V<sub>1</sub>  
 557 complexes, pure V<sub>1</sub>, and *Lattice*. The trapping rate  $k_i$  for each defect (V<sub>1</sub>, O<sub>1-6</sub>V<sub>1</sub>) can be  
 558 estimated by multiplying their concentration by their specific trapping coefficient,  $\mu_i$ . The  
 559 concentration of defects is given by CD simulations. The specific trapping coefficient for pure  
 560 V<sub>1</sub> is  $\mu_{V1} = (6 \pm 3) \times 10^{-15} \text{ m}^{-3} \cdot \text{s}^{-1}$  [31], and  $\mu_{O_p V_1}$  for the O<sub>p</sub>V<sub>1</sub> (with  $p = 1-6$ ) complexes were  
 561 estimated by reducing  $\mu_{V1}$  by a ratio of the Voronoi volume of each O complex to that of pure  
 562 V<sub>1</sub> (Tab. 3). Once the trapping rates  $k_i$  of each trap ( $t_1 = \text{pure V}_1$  and  $t_{2-7} = \text{O}_{1-6}\text{V}_1$  complexes)  
 563 are determined, the intensity of the lifetime components  $I_i$ , and the theoretical lifetime spectra  
 564 *PALS(t)* can be calculated, using a trapping model including several annihilation states: *Lattice*,  
 565 pure V<sub>1</sub> and O<sub>1-6</sub>V<sub>1</sub> complexes ( eq. 2)

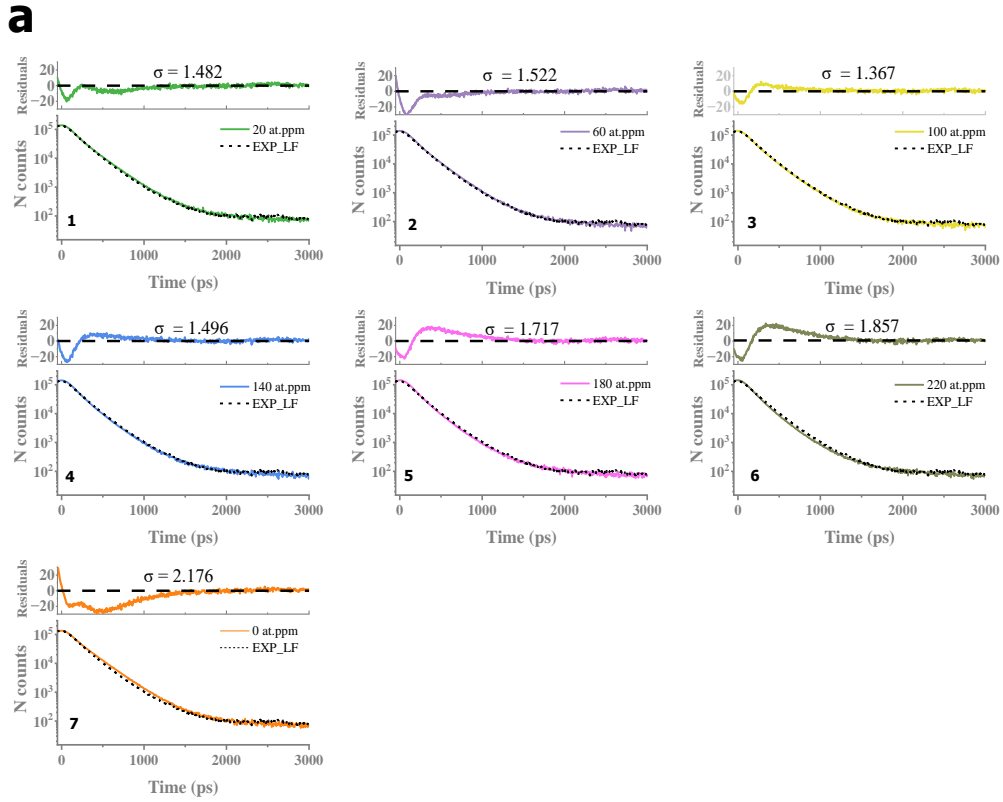
$$566 \left\{ \begin{array}{l} I_i = \frac{k_i}{\lambda_L - \lambda_i + \sum k_i}, \text{ and } I_0 + \sum_i I_i = 1 \\ \mathbf{PALS}(t) = R(t) * \left[ \sum_i \left( \frac{I_i}{\tau_i} e^{-\frac{t}{\tau_i}} \right) + \sum_j \left( \frac{I_{Cj}}{\tau_{Cj}} e^{-\frac{t}{\tau_{Cj}}} \right) + \frac{I_0}{\tau_0} e^{-\frac{t}{\tau_0}} \right] + BG \end{array} \right. \quad \text{eq. 2}$$

567 where defects  $i$  could be pure V<sub>1</sub>, or O<sub>1-6</sub>V<sub>1</sub> complexes,  $\lambda_L$ , and  $\lambda_i$  are the annihilation rate at the  
 568 lattice and in each trap  $i$  respectively i.e. the reciprocal of their lifetime  $\tau_L = 105$  ps for the lattice,  
 569 and  $\tau_i$  ( $\tau_1 = 200$  ps for pure V<sub>1</sub>, and the values of complexes reported in Tab. 3), and  $I_0$  is the  
 570 intensity of the reduced lifetime  $\tau_0$ .  $\tau_{Cj}$  and  $I_{Cj}$  are respectively the lifetimes and intensities for  
 571 the source corrections. As a result, theoretical lifetime spectra were calculated by applying a  
 572 trapping model with the parameters obtained from eq. 2 for various concentrations of O,

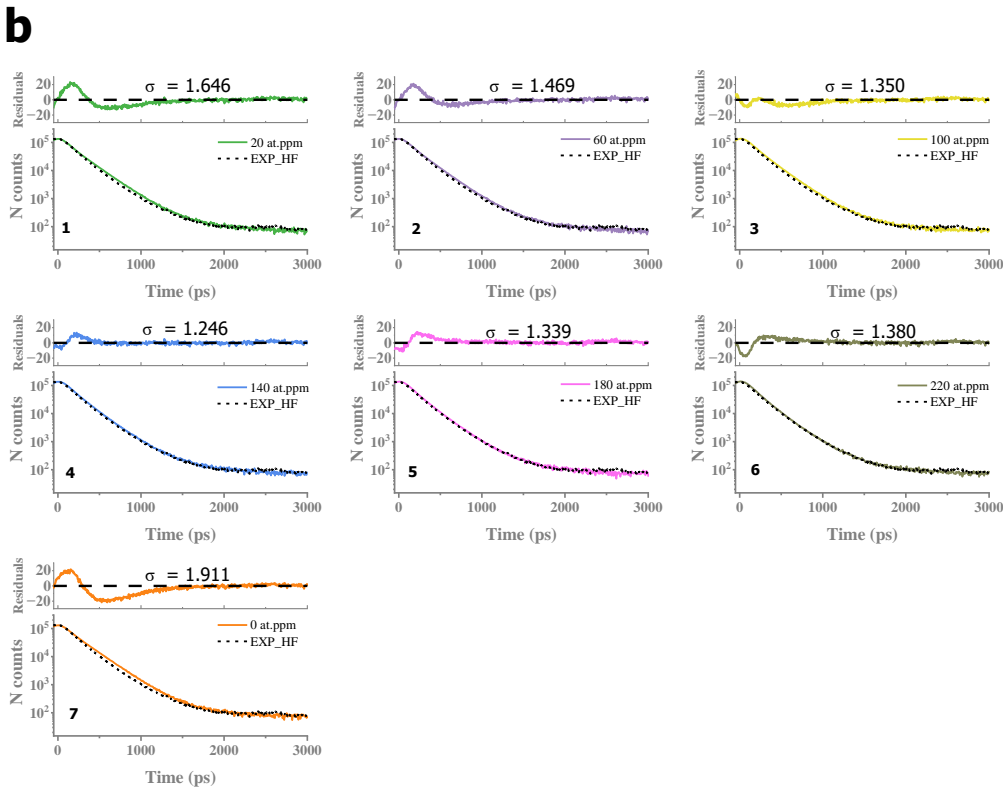
573 and taking into account the spectrometer resolution (FWHM= 212 ps) and an experimental the  
574 background noise of about 60 counts. Fig.9 a (LF) and b (HF) show the theoretical spectra for  
575 a matrix containing 0 to 220 O appm in comparison with their respective experimental spectrum.

576 Firstly, in the absence of O, positrons annihilate only in pure  $V_1$  and in the *Lattice*. The  
577 corresponding theoretical lifetime spectrum differs greatly from the experimental one: in the  
578 region between 360 and 1400 ps, the number of counts is higher in the theoretical spectra than  
579 in the experimental ones for both fluences, i.e. LF (Fig.9a.7) and HF (Fig.9b.7) as highlighted  
580 in the residual standard deviation plotted above the lifetime spectra. It confirms that a  
581 component with a lifetime between that of  $V_1$  and that of the *Lattice* is hidden in the  
582 experimental spectra, as extracted in the deconvolution fits of experimental spectra. This  
583 component corresponds to new positron **traps X**.

584 Theoretical spectra with O concentration ranging from 20 to 220 appm agree much better  
585 with experimental spectra than those without O. The best agreement corresponds to an O  
586 concentration in the matrix of 140 appm, for HF (Fig.9a.1-4), and 100 appm, LF (Fig.9b.2-6)  
587 shows a relatively lower residual between experimental and theoretical spectra. This  
588 concentration range is comparable to the SIMS results measured with an error bar of 28 %  
589 (Fig.4 c). Residual values can be explained by either experimental error bars or approximations  
590 made in simulations, including CD and TCDFT, and also in estimating the specific trapping  
591 coefficients. Despite all these approximations, these comparisons indicate that the trapping of  
592 positrons in oxygen-vacancy complexes agrees with the experimental results and confirms that  
593 **traps X** are oxygen-vacancy complexes.



594



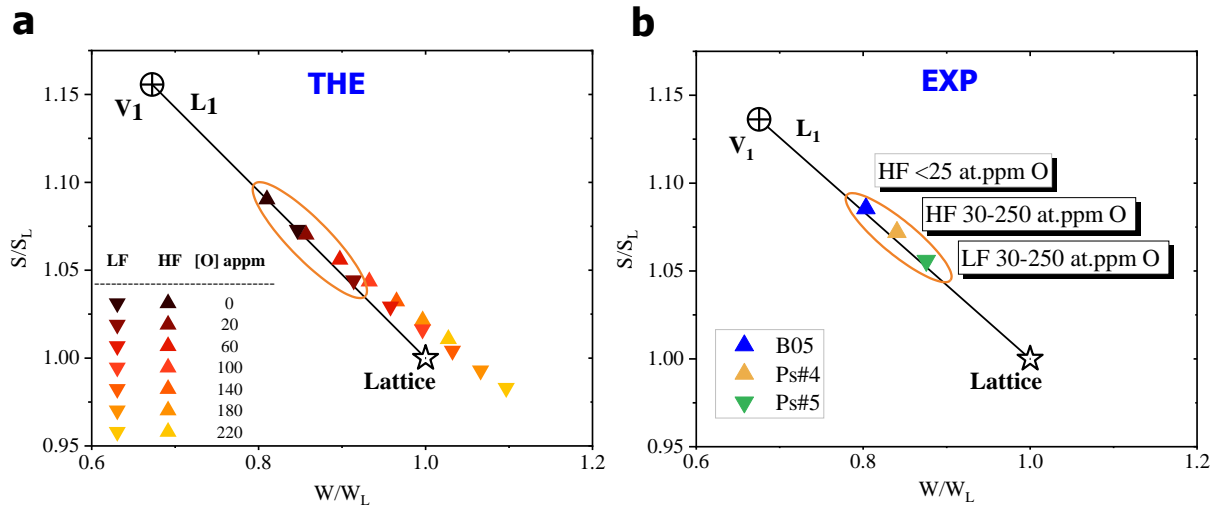
595

596 Fig.9: Comparison of theoretical and experimental lifetime spectra measured in  $N_c$  samples a: low fluence (LF). and b: high  
 597 fluence (HF). The theoretical spectra were calculated by employing trapping models, with parameters calculated from *eq.*  
 598 *2*. The residual standard deviation (Residual) and its average absolute value ( $\sigma$ ) highlight the difference between the two spectra  
 599 on a time scale.

600 After comparing the lifetime spectra, we calculated the theoretical  $S$ - $W$  values still based  
 601 on the same two- or three-state trapping model (eq.3) depending on O concentration ranging  
 602 from 0 to 220 appm using eq. 3.

$$603 \quad \begin{cases} \mathbf{S} = S_L \cdot f_L + \sum S_i \cdot f_i \\ \mathbf{W} = W_L \cdot f_L + \sum W_i \cdot f_i \\ f_i = \frac{k_i}{\lambda_L + \sum k_i}, \text{ and } f_L + \sum_{t_1}^{t_7} f_i = 1 \end{cases} \quad \text{eq. 3}$$

604 where  $f_L$  and  $f_i$  are the fractions of annihilation in the delocalized state and the localized  
 605 state of traps  $i$  respectively, determined using (eq. 3). The relative  $S/S_L$ - $W/W_L$  points calculated  
 606 for both fluences LF and HF are shown in Fig.10. a.



607  
 608 Fig.10 a: Theoretical relative ratio to lattice  $S$ - $W$  using trapping model in the case of 0 to 220 appm O vs b: Experimental  $S$ - $W$   
 609 points, an average of 5-25keV for B05, and at 25 keV for damaged Nc samples (HF: yellow triangle, LF: green triangle with  
 610 30-250 appm O, and HF: blue triangle with <25 appm O), the error of SIMS measurement is estimated to 28 %.

611 For zero O concentration, the  $S$ - $W$  points calculated for both fluences LF and HF are located  
 612 on line  $L_1$ . This is still the case when O concentration is low (20 appm). As shown in Fig.8,  
 613 increasing O concentration induces a larger population of  $O_{1-6}V_1$  complexes. Annihilations at  
 614 these complexes shift  $S$ - $W$  points to the right-bottom toward the  $Lattice$  point and progressively  
 615 move away from  $L_1$ . We emphasize that only the relative  $S/S_L$ - $W/W_L$  values can be used for  
 616 comparison between theoretical and experimental data [37]. The  $S/S_L$ - $W/W_L$  points measured

617 in **B05** (HF, <25 O appm) and in the **Nc** (LF & HF, 30-250 O appm) samples are shown in  
618 [Fig.10](#).

619 The experimental points are located on or near  $L_1$ . The purest sample **B05** (HF, <25 O  
620 appm) shows the highest  $S$  and lowest  $W$  values, whereas  $S$  decreases and  $W$  increases for less  
621 pure samples **Nc** (LF & HF, 30-250 O appm). The same trend can be observed for the theoretical  
622 values (see [Fig.10.a](#)) showing a decrease of  $S$  and an increase of  $W$  with increasing oxygen  
623 concentration. The agreement between calculated and experimental  $SW$  points appears to be  
624 better for O concentrations of 20 and 60 appm. These concentration values are lower than those  
625 for which better agreement was observed for lifetimes. This discrepancy might be due to  
626 several factors: (i) the O distribution in **Nc** samples is heterogeneous and PALS probes a thick  
627 region ( $\sim \emptyset 3 \text{ mm} \times 0.05 \text{ mm}$ ) whereas, in the SPB-DBS, positrons stopped close to the surface  
628 ( $\sim \emptyset 3 \text{ mm}$ , and 1<sup>st</sup> 700 nm); (ii) the errors propagate from approximations either in simulations  
629 or experiments, making it difficult to achieve ideal agreement between experimental and  
630 theoretical DB spectrum. Thus, only the trend on the variation of  $S$  and  $W$  can be discussed, as  
631 shown by the comparisons made in [34,35].

632 We now focus on the experimental data for **B05**, containing the lowest O concentration. In  
633 this sample, the relative position of the  $S$ - $W$  point is close to the theoretical one calculated for  
634 the zero O content. As the O concentration is below the SIMS detection limit ( $25 \pm 8$  appm),  
635 we can assume that the  $O_{1-6}V_1$  concentration is too low to have a significant annihilation  
636 fraction, while pure  $V_1$  should be the dominant trap. The pure  $V_1$  concentration can simply be  
637 extracted from the DB measurements by using a one-trap (pure  $V_1$ ) trapping model [31,38],  
638 using the following equation.

639 
$$C_{V_1} = \frac{\lambda_L \cdot (X_L - X)}{\mu_{V_1} (X - X_{V_1})} \quad \text{eq. 4}$$

640 where X is *S* or *W* annihilation fractions and  $\lambda_L$  and  $\mu_{V_1}$  were already defined above.

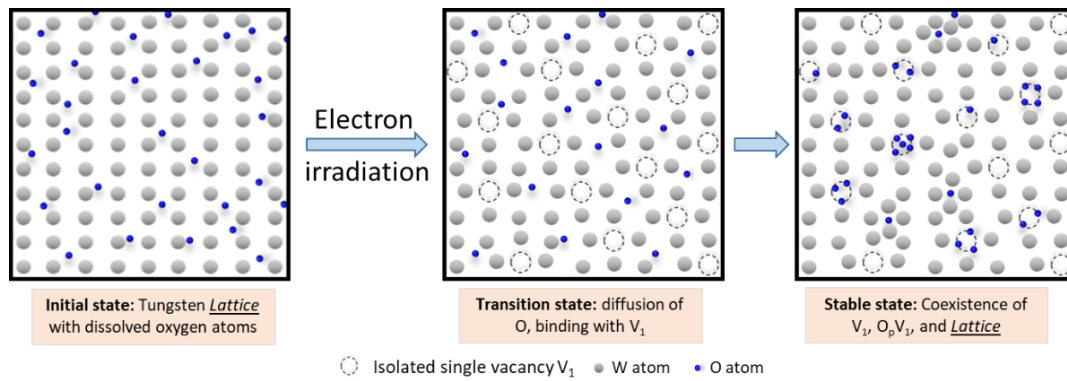
641 The *S* and *W* values give a pure  $V_1$  concentration of about  $(2.63 \pm 1.32) \times 10^{24} \text{ m}^{-3}$ . This  
642 concentration is much lower than that expected from the damage dose calculated in the region  
643 probed by positrons (700 nm in tungsten,  $8.33 \times 10^{-4} \text{ dpa}$ ) which should be  $5.28 \times 10^{25} \text{ m}^{-3}$  if  
644 each displacement effectively leads to a vacancy at the end of irradiation. This reduction of  $V_1$   
645 concentration reveals a high recombination rate  $R_c$  of FPs, which is estimated at around  $\sim 95 \pm$   
646 2 %. This value is in excellent agreement with the theoretical results predicted by CD (96 %).  
647 In electron-irradiated pure iron, Takaki *et al.* [20] found in resistivity recovery experiments that  
648 76 % of recombinations were related to uncorrelated FPs, and 19 % to correlated FPs, for a total  
649 of 95 %. Furthermore, Ortiz *et al.* [93] calculated that up to 90 % of defects have been  
650 annihilated at 400 K in Fe irradiated with electrons at a damage dose of  $10^{-6} \text{ dpa}$ . In tungsten,  
651 De Backer *et al.* [94] showed that  $R_c$  increases from 20 to 96 % for  $^3\text{He}$  800 keV irradiation at  
652 RT with various fluences, ranging from  $10^{17}$  to  $5 \times 10^{20} \text{ m}^{-2}$ , i.e. a range of damage dose from  
653  $1.9 \times 10^{-4}$  to 0.17 dpa (SRIM with  $E_{\text{disp}} = 55.3 \text{ eV}$ , K-P model). In addition, Neely *et al.* [19]  
654 found about 30 % of resistivity recovery in 99.99 % pure irradiated tungsten at 70 K (2.1 MeV  
655  $e^-$ ,  $5 \times 10^{21} \text{ e}^- \cdot \text{m}^{-2}$ ), and the authors claimed that the recovery rate can be impacted by a non-  
656 negligible concentration of impurities.

657 In tungsten, at RT, the SIA has very low migration energy ( $< 0.2 \text{ eV}$  [68,95,96]), whereas the  
658 vacancy is immobile. A high recombination rate can be expected. When oxygen or other  
659 impurities that interact strongly with SIA immobilize SIA, the probability of recombination  
660 decreases. In our CD results, the  $R_c$  ratio decreases from 96 to 87% when the O/FP ratio  
661 increases from 0 to 0.53. These results are consistent with the close relative position for  
662 theoretical and experimental *S-W* point observed for the lowest O content (0 appm HF, in Fig.10  
663 a and B05 in Fig.10 b). Despite all the approximations used in this work, agreement between  
664 simulations and experiments confirms that O affects the evolution of vacancy and interstitial



665 defects in tungsten irradiated at RT as illustrated in Fig.11. When a fraction of O atoms is  
666 dissolved in the matrix, they can diffuse during irradiation. Electron irradiation induces  
667 vacancies and SIAs. O atoms can be bound to  $V_1$  and immobilize the SIA, leading to the  
668 formation of oxygen-vacancy and O-SIA complexes in a proportion that increases with the  
669 O/dpa ratio and the dpa rate. The presence of oxygen can increase the concentration of vacancy  
670 defects by a factor of up to four and of the interstitial clusters by more than two orders of  
671 magnitude depending on the ratio O/dpa, creating a large majority of O-decorated defects.

672 This effect has already been observed for carbon at high temperatures ( $>500^\circ\text{C}$  [28]),  
673 whereas the O effect is demonstrated here for the first time. It should be emphasized that this  
674 effect is demonstrated here at RT. In industrial applications such as in fusion reactors, where  
675 tungsten was chosen for the divertor and is envisaged for the first walls, this material will be  
676 subjected to high temperature  $>500^\circ\text{C}$  irradiation. Under these conditions, the O effect can be  
677 expected to be pronounced. The diffusion coefficient will be higher for O than for C and ac-  
678 cording to the simulations,  $O_pV_1$  complexes have high binding energies of 3 to 12 eV (Tab. 3)  
679 close to those of  $C_pV_1$  complexes, and even slightly higher [53]. Competition between C and O  
680 can therefore be expected at higher temperatures when C atoms become mobile. Both elements  
681 will impact the formation of the vacancy clusters and cavities. These O-decorated defects could  
682 also have an impact on the retention of hydrogen in tungsten [23]. Predicting H retention in the  
683 walls of fusion reactors is of major importance for safety, given the use of tritium, a radioactive  
684 isotope of H, as fuel. Ab initio calculations show a strong interaction between O decorated  
685 vacancies and H. Oxygen is one of the major impurities expected in tokamaks and is also diffi-  
686 cult to avoid in tungsten. At least, for the large amount of material required in the reactor.  
687 Accordingly, this work shows that oxygen has to be taken into account in the prediction of the  
688 microstructure evolution of tungsten.



689

690  
691

Fig.11: Schematic diagram of the evolution of the defects in tungsten samples irradiated with electrons in the presence of oxygen, as in the present work.

## 692 5. Conclusion

693 To summarize, after 2.5 MeV electron irradiation at RT, an unexpected positron  
694 annihilation state (X defect) was revealed by PALS measurement in tungsten. After combining  
695 other characterization techniques (TEM, SIMS) and simulations (TCDFT, CD), we have drawn  
696 the following conclusions regarding the microstructure evolution:

697 (i) According to CD simulations, the nucleation and growth of SIA clusters depend on the  
698 O atoms' presence in the matrix. This is in agreement with TEM results which show no evidence  
699 of dislocation loops.

700 (ii) Theoretical results (TCDFT, CD, and trapping model) with an O concentration of  
701 approx. 100-140 O appm shows a better match of experimental lifetime spectra (Fig.9), which  
702 is in good agreement with SIMS analysis. Consequently, the hypothesis of heterogeneous  $O_{1-6}V_1$   
703 complexes formation is verified.

704 (iii) PAS and CD results highlight the interaction between O atoms and  $V_1$ . In addition, in  
705 the O-free matrix, a very high recombination ratio,  $R_c$  of  $95 \pm 2$  % was determined, in excellent  
706 agreement with the CD result (96 %).

707 (iv) As soon as the O concentration in the matrix is larger than 20 appm, the total population  
708 of  $O_{1-6}V_1$  complexes exceeds that of pure  $V_1$ . The O effect on the evolution of SIAs and  $V_1$  is  
709 therefore demonstrated at RT due to its high mobility and strong binding. This effect should

710 also be pronounced in high-temperature applications, and potentially be more important than  
711 that of the other LEs (H, C, and N).

## 712 **Declaration of Competing Interest**

713 The authors declare that they have no known competing financial interests or personal  
714 relationships that could have appeared to influence the work reported in this paper.

## 715 **Credit authorship contribution statement**

716 *Zhiwei Hu*: Sample preparation, PALS, SPB-DBS experiment, PAS and SIMS data processing  
717 and interpretation, writing – original draft & editing, *Qigui Yang*: TCDFE calculation, data  
718 analysis, writing – original draft & editing *Thomas Jourdan*: CD calculation, data analysis,  
719 writing – original draft & editing *Pierre Desgardin*: Supervision, SPB-DBS experiments  
720 *François Jomard*: Supervision, SIMS experiments *Cécile Genevois*: Supervision, TEM  
721 experiments *Jérôme Joseph*: Sample preparation and technical support *Pär Olsson*:  
722 Conceptualization, supervision, review & editing. *Marie-France Barthe*: Conceptualization,  
723 supervision, data processing and interpretation, writing – review & editing.

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