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Alain Chartier, Paul Fossati, Laurent van Brutzel. Molecular dynamics simulations of microstructural evolution of irradiated (U,Pu)O<sub>2</sub> studied via simulated XRD patterns. *Journal of Nuclear Materials*, 2022, 567, pp.153834. 10.1016/j.jnucmat.2022.153834 . cea-03714011

**HAL Id: cea-03714011**

**<https://cea.hal.science/cea-03714011v1>**

Submitted on 22 Jul 2024

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# Molecular dynamics simulations of microstructural evolution of irradiated (U,Pu)O<sub>2</sub> studied via simulated XRD patterns

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## Abstract

Molecular dynamics simulations of microstructural evolution under irradiation of (U,Pu)O<sub>2</sub> solid solutions have been carried out with the Frenkel pair accumulation method with two empirical potentials. Simulated X-Ray diffraction patterns have been systematically generated along the irradiation pathway from the computed atomistic configurations. Description of the X-Ray diffraction patterns for each of these well characterized damage microstructure snapshots is discussed. Attempt to correlate the features of the X-Ray diffraction peaks with the microstructural evolution with irradiation dose is also provided. Special attention is dedicated to the swelling effect.

*Keywords:* Molecular dynamics, MOX fuel, irradiation, XRD pattern

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## 1. Introduction

2 Mixed oxide nuclear fuel (MOx), composed primarily of uranium and  
3 plutonium oxide, provides a significant percentage of the nuclear fuel used

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4 in new Pressurized Water Reactors or in envisaged future Generation IV  
5 nuclear plants. During its lifetime in these reactors, it undergoes chemical,  
6 structural, and physical changes due mainly to high thermal gradient and  
7 irradiation. One of the most important property which influences safety and  
8 fuel design is the swelling effect. This increase in volume of the fuel occurs  
9 under irradiation and is usually attributed to the creation of defects such  
10 nanocavities or accumulation of fission products. To study this behaviour,  
11 direct analysis of the sample density or X-Ray diffraction (XRD) are usually  
12 carried out. Several XRD studies in  $\text{UO}_2$  confirmed that lattice parameter  
13 and microstrain increase with the increasing dose [1–5]. However, XRD pat-  
14 tern interpretation can be sometimes controversial due to the complexity of  
15 the burnup fuel system. Moreover, heavy ions external irradiation techniques  
16 on pristine fuel leads usually to a thin irradiated surface and an undefected  
17 material underneath. For this type of sample, XRD analysis is difficult to  
18 deconvolve.

19 Recently, combination of experimental XRD results and Molecular Dy-  
20 namic Simulations (MD) [6, 7] helps to sort out the different defect contri-  
21 butions of the XRD patterns in SiC and ZrC. In this article the authors  
22 endeavour to deconvolve the elastic strain obtained from XRD with the dif-  
23 ferent defect contributions calculated from molecular dynamics simulations.  
24 These atomistic simulations provide the microstructure evolution as a func-  
25 tion of the increasing dose via Frenkel pair accumulation method [11, 12].  
26 This method, consists on the accumulation of Frenkel pairs at regular time  
27 intervals, which can recombine or reorganize into more complex extended  
28 defects such as dislocation or nanocavity within a very short time. It thus

29 probes the microstructure evolution created during the spontaneous defect  
30 reorganization regime.

31 In  $\text{UO}_2$  Chartier *et al.* [8] and Jin *et al.* [5, 9] also attempt, using the same  
32 method, to deconvolve the global lattice parameter evolution as a function of  
33 irradiation dose with the different defect contributions. However, in these last  
34 studies the defects from the oxygen sub-lattice were not taken into account  
35 and relaxation volume for the uranium vacancy has to be hypothesis positive  
36 in order to fit the experimental results, which is in contradiction with ab-  
37 initio calculations [10].

38 Following these studies, the same methodology is invoked herein to in-  
39 vestigate simulated XRD patterns from several well-characterized damaged  
40  $(\text{U,Pu})\text{O}_2$  solid solutions. The damaged configuration snapshots are cre-  
41 ated with the Frenkel pair accumulation method. Each configuration is  
42 rigorously analysed and XRD patterns are systematically calculated using  
43 the Debye scattering equation with the corresponding atomic coordinates.  
44 This database of XRD patterns with corresponding well-defined damaged mi-  
45 crostructures can help the deconvolution and interpretation of experimental  
46 XRD patterns from real physical systems. Furthermore, correlation between  
47 the microstructure evolution in both cation and anion sub-lattices and the  
48 simulated XRD patterns is also discussed.

49 The paper is organized as follow: section 2 describes briefly the method-  
50 ology employed to irradiate the  $(\text{U,Pu})\text{O}_2$  solid solution and simulated the  
51 associated XRD patterns, section 3 describes the simulated XRD patterns  
52 and subsequently discusses the correlation between the microstructural evo-  
53 lution and the XRD pattern changes as a function of the increasing dose.

## 54 **2. Computational method**

### 55 *2.1. Potential interactions*

56 For this study we used Molecular Dynamics simulations to simulate the  
57 evolution of the microstructure of (U,Pu)O<sub>2</sub> solid solution under increasing  
58 radiation damage. All simulations have been performed via the LAMMPS  
59 code [13]. The study herein concerns three (U,Pu)O<sub>2</sub> compositions: pure  
60 uranium dioxide (UO<sub>2</sub>), a mix with 50% uranium atoms (U<sub>0.5</sub>Pu<sub>0.5</sub>O<sub>2</sub>), and  
61 pure plutonium dioxide (PuO<sub>2</sub>). It is known experimentally that the ternary  
62 system U<sub>1-x</sub>Pu<sub>x</sub>O<sub>2</sub> forms an ideal solid solution for the full range of Pu  
63 content and from room temperature to nearly melting point [14]. Therefore,  
64 for the mix, the initial positions of the cations are randomly distributed into  
65 the regular sites of the face-centered structure. All the initial structures  
66 are the fluorite structure of space group  $Fm\bar{3}m$ . The system box size is  
67  $22 \times 22 \times 22$  nm<sup>3</sup>, involving 768 000 atoms.

68 MD simulations rely on the quality of the interatomic potential for ac-  
69 curate results; hence, we have investigated systematically two interatomic  
70 potentials, in order to compare and contrast the results and estimate the  
71 errors due to the interatomic models. The first set of potentials have been  
72 developed by Potashnikov and al. [15] and will be referenced herein as MOX-  
73 07. Previous studies assessed thermodynamics and transport properties as  
74 well as point defect formation energies for these potentials [16, 17]. The re-  
75 sults are in good agreement with experimental data however, they slightly  
76 underestimate the bulk and shear moduli and show isotropic behaviour for  
77 the elastic stiffness with a Zener's ratio close to 1. This is due to the fact  
78 that these potentials have been fitted with experimental data coming from

79 polycrystal samples. The second set of potentials used herein have been  
80 developed by Cooper *et al.* [18, 19] and will be coined CRG. These poten-  
81 tials provide also really good thermodynamic and transport properties as  
82 well as mechanical properties with anisotropic behaviour for the elastic stiff-  
83 ness. This potential reproduces also accurately the thermal conductivity and  
84 heat capacity, which are related to anharmonic effects [20]. However, they  
85 yields to metastable configurations under irradiation in the oxygen sublattice,  
86 which imposes longer simulations before stability is reached [17]. This  
87 made them less handy to use for irradiation studies.

88 The long-range Coulombic interactions is calculated via the particle-  
89 particle/particle-mesh (PPPM) method provided in the LAMMPS code [21].

## 90 *2.2. Modelling irradiation dose*

91 At the atomistic length scale, irradiation events lead mainly to electronic  
92 excitation but also to the creation of point defects such as vacancies or in-  
93 terstitials. As the irradiation dose increases, these point defects accumulate  
94 and aggregate to change the microstructure. It is these changes that we are  
95 trying to describe with MD simulations. Usually in MD simulations, irradiation  
96 damage is performed by modelling displacement cascades. This type of  
97 simulation is computationally expensive but gives a fairly good description  
98 of the full process of an irradiation event including the thermal spike and  
99 the structural recovery. However, it describes only the primary damage of  
100 one single event, which mainly consists in the case of MOx fuel of few point  
101 defects as shown in previous studies [17]. Therefore, in order to study the  
102 dose effect (accumulation of damage), we use an alternative method: the  
103 Frenkel Pair Accumulation Method (FPA) [11, 12]. This method consists

104 on introducing periodically and consistently Frenkel pair defects, while the  
105 structure is continuously allowed to relax under constant pressure and tem-  
106 perature. Here, the introduced Frenkel pairs mimic the remaining damage  
107 after displacement cascades. In that respect, this method corresponds to  
108 the accumulation of the final stage of displacement cascades within the same  
109 volume.

110 Previously Chartier *et al.* [8] showed that the oxygen sublattice seems  
111 to follow the cation disorder. Consequently, only cation Frenkel pairs (C-  
112 FP) are introduced in order to reduce the computational time. The time  
113 interval between two subsequent C-FP introductions is set to 2 ps. This  
114 time is large enough to allow spontaneous C-FP recombination, which has  
115 no dependence with the temperature and for which the distance between  
116 the vacancy and the interstitial is up to 1.5 nm corresponding to the 5<sup>th</sup>  
117 cation nearest-neighbour [16, 22]. We have checked that within the time-lapse  
118 between two FP introductions the temperature and pressure of the system  
119 reach the desired values and that just expected thermal fluctuation occurs.  
120 The system is then considered stabilized enough to permit the introduction  
121 of the next set of defects. All the simulations have been carried out at room  
122 temperature (300 K) and 0 GPa. Due to the high increase in energy arising  
123 from each FP introduction, the NPT relaxation for this FPA procedure is  
124 done with the Berendsen algorithm provided by the LAMMPS code [23].

125 Each C-FP introduction sequence involves the creation of 700 FPs for the  
126 MOX-07 potential and 300 for the CRG potential within the simulation box.  
127 Because the defect recombination time is higher for CRG potential, less FPs  
128 can be introduced within the same time interval. It is also worth noticing

129 that this number corresponds approximatively to the remaining number of  
130 Frenkel pairs remaining after a displacement cascade simulation initiated  
131 with a primary knock-on atom energy of 80 keV [17].

132 A common way to measure irradiation dose on materials is the use of  
133 displacements per atom (dpa). This is also a very simple metric from the  
134 atomistic simulations point of view. It is defined simply by the number of  
135 displacements (on average) of one atom, which exactly corresponds to what is  
136 simulated with the FPA method. Since in our study only C-FPs are created,  
137 we express the dose in displacements per cation (MD-dpc) rather than the  
138 classic dpa. Therefore, for each C-FP introduction, the dose is increased by  
139  $1.17 \times 10^{-3}$  MD-dpc and  $2.73 \times 10^{-3}$  MD-dpc for CRG and MOX-07 potentials  
140 respectively. It is worth noting that this unit of dose does not correspond  
141 directly to the experimental dpa unit of dose, which is usually calculated  
142 via SRIM calculations. Straight quantitative comparison between both units  
143 should not be considered. Nonetheless, increasing MD-dpc indicates that  
144 the number of displaced atoms increases and hence that the irradiation dose  
145 increases as well.

146 The analysis of the structural evolution is carried out using OVITO soft-  
147 ware [24]. We determined the dislocation density with the DXA algorithm  
148 provided in OVITO and examined the point defects with a fine structural  
149 detection via a homemade software, ACME [25]. This last method was cho-  
150 sen over the Wigner-Seitz or the Voronoi cell analysis because numerous  
151 disoriented fluorite subdomains appear during the simulation.



152 *2.3. Simulated XRD pattern*

153 Beside the analysis of the point defects and the dislocations, we are gen-  
154 erating simulated X-Ray powder diffraction (XRD) patterns via the Debyer  
155 software [26] from irradiated configurations. During the FPA procedure,  
156 sampling of irradiated configurations are saved. These configurations are  
157 systematically relaxed for 20 ps under constant temperature (300 K) and  
158 constant pressure (0 GPa) with the Parrinello and Rahman algorithm [27]  
159 in order to further anneal the system and eliminate any residual unstable  
160 defects. Subsequently, the simulated XRD patterns are calculated with the  
161 atomic coordinates averaged over the last 5 ps of the relaxation. The defect  
162 analysis is also carried out at this stage. XRD patterns are calculated simply  
163 using the Debye scattering equation:

$$I(Q) = \sum_i \sum_j f_i f_j \frac{\sin(Qr_{ij})}{Qr_{ij}} \quad (1)$$

164 where  $Q$  is the scattering vector defined as:  $Q = |\mathbf{Q}| = 4\pi \sin \theta / \lambda$ , where  
165  $\theta$  is the diffraction half-angle and  $\lambda$  is the wavelength, ( $\lambda = 1.5406 \text{ \AA}$ ).  
166  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$  is the distance between atoms  $i$  and  $j$ , and  $f_i$  is the atomic  
167 scattering factor of the  $i^{\text{th}}$  atom.

168 Because our simulation uses periodic boundary conditions ("infinite" bulk  
169 material) a cut-off radius is applied to limit the number of atomic pairs  
170 accounted in the Debye formula. Only pairs with distances inferior to this  
171 radius are considered. However, a correction term is added to avoid large  
172 sinusoid. Therefore, the normalized intensity of the scattered wave becomes:

$$I(Q)/N = f^2 \left\{ \frac{1}{N} \left[ \sum_i \sum_{j, r_{ij} < R_c} \frac{\sin(Qr_{ij})}{Qr_{ij}} \right] + \frac{4\pi\rho}{Q^3} \left[ QR_c \cos(QR_c) - \sin(QR_c) \right] \right\} \quad (2)$$

173 where  $R_c$  is the cut-off radius equals in our simulation to half the box size,  
 174 *i.e.* 11 nm.

175 The resulting simulated XRD patterns are further analysed with Fityk  
 176 software [28] in order to identify the feature of the different peaks. It appears  
 177 that the best fit for the peaks in our simulated XRD pattern is Gaussian  
 178 function.

### 179 **3. Results and discussion**

#### 180 *3.1. Microstructure evolution with irradiation dose*

181 Before presenting the simulated XRD patterns as a function of the irra-  
 182 diation dose, it is important to describe the evolution of the microstructure  
 183 and the nature of the associated damage with the irradiation dose. Figure 1  
 184 depicts the point defect evolution (vacancies and interstitials) and the dis-  
 185 location density as a function of dose expressed in MD-dpc for the three  
 186 Pu contents studied (0%, 50%, and 100%) at 300 K for the MOX-07 poten-  
 187 tials. Likewise, Figure 2 depicts the same results for the CRG potential. To  
 188 illustrate the type of damage created, snapshots of the simulation in  $\text{UO}_2$   
 189 analysed with the DXA tool from OVITO are also displayed. As previously  
 190 detailed for  $\text{UO}_2$  [8] and for the  $\text{U}_{1-x}\text{Pu}_x\text{O}_2$  solid solution [17] carried out at

191 1600 K, we show that the evolution of the microstructure in these materials  
192 mainly follows a five-stage process:

- 193 1. For doses lower than 0.2 MD-dpc, isolated point defects are first cre-  
194 ated. This is demonstrated by a rapid increase of the number of va-  
195 cancies and interstitials (highlighted by the pink area in Figure 1 and  
196 Figure 2). It is noteworthy that within this stage the number of vacan-  
197 cies is equal the number of interstitials because only isolated Frenkel  
198 pairs are created.
- 199 2. Subsequently and up to 0.5 MD-dpc, for the MOX-07 potential the  
200 number of interstitials decreases rapidly while the number of vacancy  
201 continues to increase steadily. This indicates that most of the intersti-  
202 tials aggregate into clusters while the vacancies remain isolated. For  
203 CRG potential,  $\text{UO}_2$  compounds follows the same behaviour. In the  
204 mix and pure  $\text{PuO}_2$  the decrease of the interstitials is less pronounced  
205 yet still occurs while the number of vacancies seems to stabilize.
- 206 3. For the MOX-07 potential, the interstitial clusters nucleate mostly into  
207 Frank loops as demonstrated by the peak density of Frank loops high-  
208 lighted in blue in Figure 2. For the CRG potential this stage seems to  
209 be skipped as almost no Frank loops are created.
- 210 4. Around 0.5 MD-dpc, for the MOX-07 potential the Frank loops trans-  
211 form into perfect dislocations whereas for the CRG potential the inter-  
212 stitial clusters form perfect dislocations directly.
- 213 5. Subsequently, for both potentials, the density of perfect dislocations  
214 decreases even if for the mix with CRG is less abrupt indicating in  
215 that case a growth of the small loops. After about 2 MD-dpc a steady

216 state is reached and dislocations reorganize into forest of dislocations  
 217 creating few disoriented nanodomains.

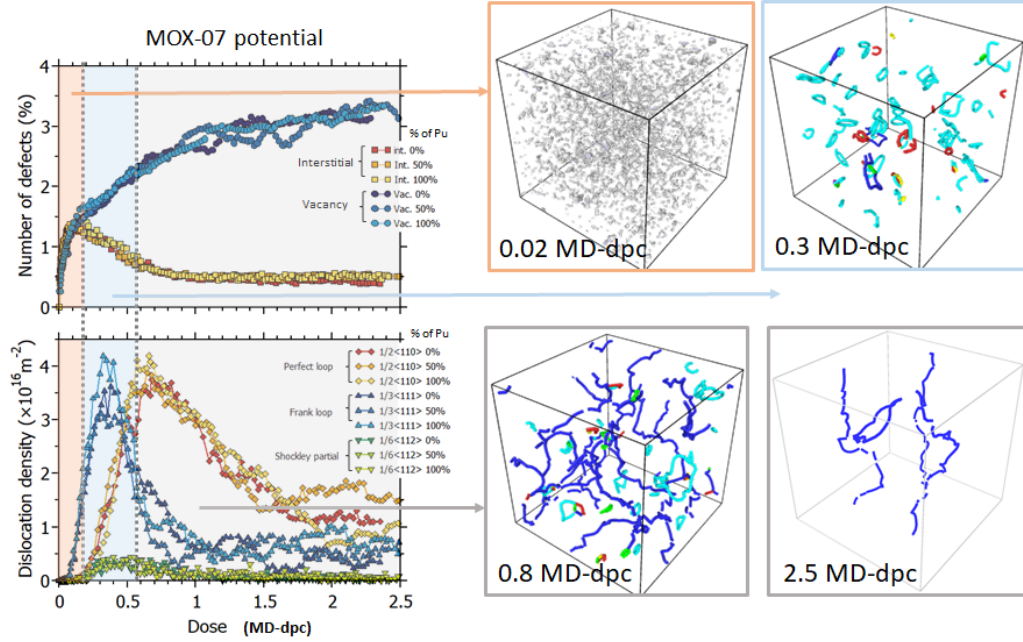


Figure 1: Evolution of the number of point defects and dislocation density as a function of dose for the MOX-07 potential at 300 K. Three snapshots of the simulation box of  $\text{UO}_2$  analysed with the DXA tool from OVITO are also displayed to illustrate the damage. In these figures the grey dots at 0.02 MD-dpc represent the track of the point defects. For clarity only the dislocation lines are represented in the figure at 0.3, 0.8, and 2.5 MD-dpc (dark blue: perfect loop, cyan: Frank loops, green: Shockley partials, and red: Stair-Rod).

218 Even if there is a quasi-absence of Frank loops generation with the CRG  
 219 potential the damage process evolution is roughly similar with both poten-  
 220 tials. However, it is worth noticing that with CRG potential the Pu content  
 221 has some influence. Namely, as the Pu content increases the total density of  
 222 dislocation loops decreases and the peak in the dislocation density appears

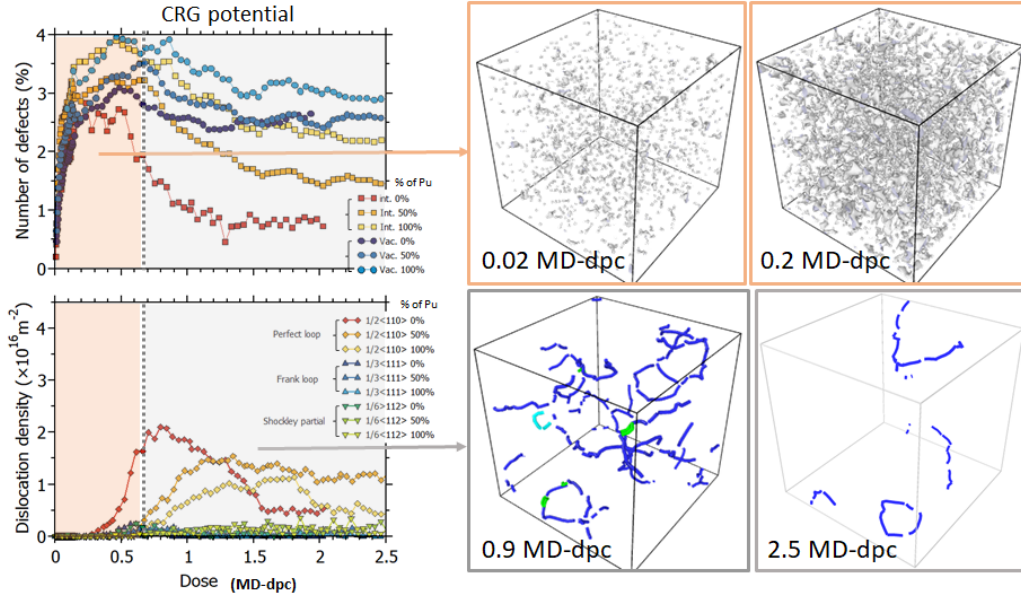


Figure 2: Evolution of the number of point defects and dislocation density as a function of dose for the CRG potential at 300 K. Three snapshots of the simulation box of  $\text{IO}_2$  analysed with the DXA tool from OVITO are also displayed to illustrate the damage. In these figures the atoms in fluorite crystallographic position are removed for clarity. The grey dots at 0.02 and 0.2 MD-dpc represent the track of the point defects. In the last two snapshots at 0.9 and 2.5 MD-dpc only the dislocation lines are represented for clarity (dark blue: perfect loop, cyan: Frank loops, green: Shockley partials).

223 for higher dose. This could indicate either that the formation of dislocation  
 224 loops is easier with low Pu content or that with this potential the charac-  
 225 teristic time for the formation of dislocation loops assisted by spontaneous  
 226 reorganization of defects is slower.

227 In the following this five-stage process will be reduced into three main  
 228 domains of microstructures. The first one from 0 to 0.2 MD-dpc highlighted  
 229 in pink in figures denotes the isolated point defects microstructure, the sec-

230 ond one appearing only with the MOX-07 potential from 0.2 to 0.5 MD-dpc  
231 highlighted in blue represents the microstructure dominated by Frank loops,  
232 and the third one from 0.5 to 2.5 MD-dpc highlighted in light grey desig-  
233 nated microstructures containing mainly perfect dislocations. It is important  
234 noticing that in this last microstructure numerous point defects, principally  
235 vacancies, are remaining. After analysing the spatial distribution of these  
236 vacancies, we found that 50% of the vacancies are isolated (mono-vacancy)  
237 however about 25% form bi- or tri-vacancy clusters. The remaining 25% is  
238 distributed among larger clusters that could include more than 30 vacancies  
239 for both potentials forming nanocavities.

240 The damaged microstructures is here generated by the reorganization of  
241 close defects over a very short time-scale. This microstructural evolution,  
242 considered as spontaneous, involves sometime complex pathways that could  
243 be thermally activated. However, diffusion kinetics over long distances of  
244 extended defect, such as dislocations or nanocavities is out of reach with the  
245 time frame of the MD simulations. Nevertheless, simple order-of-magnitude  
246 calculation based on the characteristic distance between displaced atoms es-  
247 timated from typical dose rate compared to characteristic self-diffusion dis-  
248 tance shows that defects anneal mainly by close defect interactions. As a  
249 matter of fact, characteristic distance between two displaced atoms can be  
250 determined by  $d = (V_{at}/K)^{1/3}$ , where  $V_{at}$  is the atomic volume (13.6 Å<sup>3</sup> in  
251 MOx) and  $K$  is the dose rate (typically around  $10^{-3}$  dpa.s<sup>-1</sup>). This distance  
252 within one second is equal to approximately 3 nm. On the other hand, cation  
253 irradiation-induced solid-state diffusion is generally taken from Matzke rec-  
254 ommendation [29] and is expressed as:  $D = 1.2 \times 10^{-39} \cdot \dot{F} \text{ m}^2 \cdot \text{s}^{-1}$ , where  $\dot{F}$  is

255 the fission rate. Fission rate calculated by T. Sekine et al. [30] using Monte-  
256 Carlo simulations in MOx fuel ranges from  $10^{11}$  to  $10^{14}$  fission.m<sup>-3</sup>.s<sup>-1</sup>. This  
257 yields to diffusion coefficient close to  $D = 1.2 \times 10^{-25}$  m<sup>2</sup>.s<sup>-1</sup>, for the highest.  
258 The cation characteristic distance travelled by diffusion within one second is  
259 then approximatively equal to 0.003 nm, which is a thousand times smaller  
260 than the characteristic distance between defects. Therefore, recombination  
261 regime handled by our MD simulations plays a significant role on the forma-  
262 tion of the damaged microstructure. Consequently, the damaged structural  
263 configurations studied herein should be representative of some first stage  
264 damages of the real system.

### 265 3.2. Simulated XRD patterns

266 As mentioned above, for each configuration saved and relaxed as the irra-  
267 diation dose increases a simulated XRD pattern is generated with the Debyer  
268 software. About a hundred configurations are investigated for each com-  
269 pound and for both interatomic potentials. The XRD patterns are generated  
270 for diffraction angles from  $2\theta = 20^\circ$  to  $2\theta = 90^\circ$ . As an illustration of these  
271 results, figures 3(a) and 3(b) display 3D plots of the simulated XRD patterns  
272 in UO<sub>2</sub> as a function of dose in MD-dpc from configurations calculated with  
273 the MOX-07 and the CRG potential respectively.

274 Overall, the main behaviour of the XRD patterns is the same for both  
275 interatomic potentials. All the XRD patterns are rather well defined without  
276 any background noise, which eases the analysing of the peaks. No change of  
277 phase is found as the irradiation dose increases. However, changes appear in  
278 the intensity, the full width at half maximum (FWHM), and in the position  
279 of the peaks, *i.e.* the diffraction angle for the peak maxima.

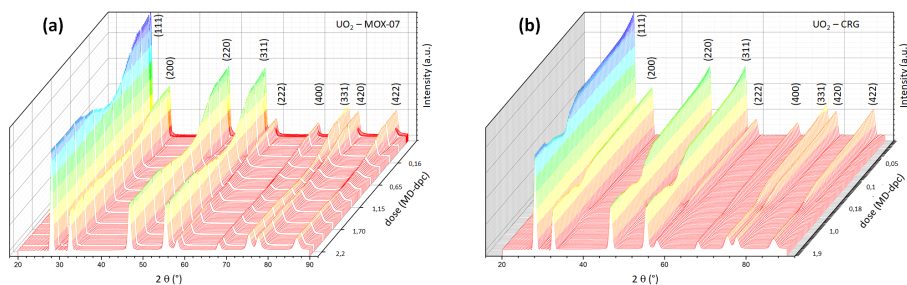


Figure 3: 3D representations of the simulated XRD patterns of  $\text{UO}_2$  as a function of irradiation dose from configurations calculated with (a) MOX-07 potential and (b) CRG potential. It is worth noticing that the scale for the doses is not linear.

280 To illustrate more precisely these changes, the relative intensity defined  
 281 as the intensity at a certain dose divided by the intensity of the pristine ma-  
 282 terial (*i.e.*  $I(\text{MD-dpc})/I(0)$ ) for the most intense peak at the Miller indices  
 283 (1 1 1) is reported in figure 4(a) for all the compounds and for both em-  
 284 pirical potentials. For all the compounds calculated with MOX-07 and for  
 285  $\text{UO}_2$  calculated with CRG, the diffraction peaks intensity decreases as the  
 286 irradiation dose increases until approximatively 0.5 to 0.7 MD-dpc before in-  
 287 creasing back and reaching a plateau. For  $\text{U}_{0.5}\text{Pu}_{0.5}\text{O}_2$  and  $\text{PuO}_2$  calculated  
 288 with CRG, the intensities decrease and reach a plateau around 1.2 MD-dpc  
 289 like the others compounds.

290 An other interesting feature of the peaks is the evolution of the FWHM,  
 291 which is reported in figure 4(b). Peak broadening in the case of one phase  
 292 single crystal usually indicates microstrains, which are related to the forma-  
 293 tion of defects in the crystal structure such as dislocation or stacking faults.  
 294 For this feature, we observe an increase and a drop with a maximum around  
 295 0.6-0.7 MD-dpc followed by a plateau at around 1.5 MD-dpc for all the com-



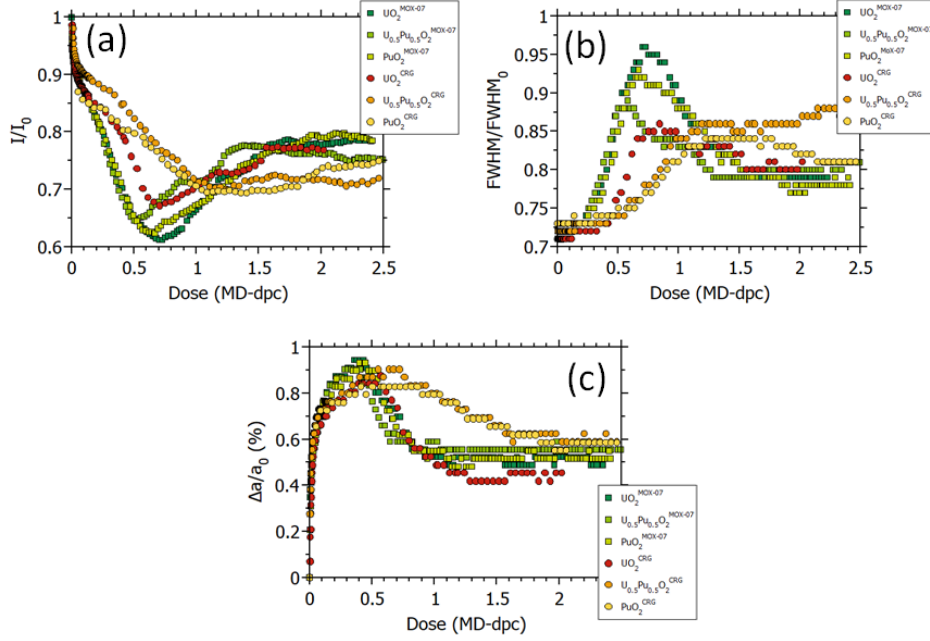


Figure 4: Evolution as a function of irradiation dose of (a) the relative intensity ( $I(\text{MD-dpc})/I(0)$ ), (b) the relative full width at half maximum ( $\text{FWHM}(\text{MD-dpc})/\text{FWHM}(0)$ ), and (c) the relative lattice parameter ( $(a(\text{MD-dpc})-a(0))/a(0)$ ) calculated of the peak of Miller indices (1 1 1) for  $\text{UO}_2$ , MOx ( $\text{U}_{0.5}\text{Pu}_{0.5}\text{O}_2$ ), and  $\text{PuO}_2$  calculated with both empirical potentials.

296 pounds calculated with MOX-07 and  $\text{UO}_2$  calculated with CRG. Conversely,  
 297 for  $\text{U}_{0.5}\text{Pu}_{0.5}\text{O}_2$  and  $\text{PuO}_2$  calculated with CRG, the FWHM increases till  
 298 about 1.2 MD-dpc where it plateaus.

299 The evolution of the relative lattice parameter calculated from the first  
 300 most intense peak at the Miller indices (1 1 1) is reported in figure 4(c).  
 301 The relative lattice parameter is defined as  $[a(\text{MD-dpc})-a(0)]/a(0)$ , where  
 302  $a(\text{MD-dpc})$  is the lattice parameter at a given irradiation dose. The lat-  
 303 tice parameter for a given irradiation dose is calculated with the following

304 equation:

$$a(hkl) = \frac{\lambda\sqrt{h^2 + k^2 + l^2}}{2\sin(\theta/2)} \quad (3)$$

305 where  $\lambda$  is the wavelength and hkl the Miller indices of the peak, here  
306  $\sqrt{h^2 + k^2 + l^2} = \sqrt{3}$ . This quantity can be directly related to the swelling of  
307 the material. Conversely to the relative intensity, all the lattice parameter  
308 first increases to reach a maximum then drops to a plateau at higher doses.  
309 This means that the material initially swells before shrinking and then sta-  
310 bilizes but yet to a lattice parameter higher than its original parameter. The  
311 maximum of swelling is found for the compounds calculated with MOX-07  
312 around 0.4 MD-dpc. For those calculated with CRG, the maximum is ob-  
313 served around 0.6 to 0.7 MD-dpc. For  $U_{0.5}Pu_{0.5}O_2$  and  $PuO_2$  the relative  
314 lattice parameters decrease like for the other system However, it decreases  
315 at a slower rate reaching its plateau around 1 MD-dpc.

316 Overall, the main behaviour of the simulated XRD pattern is similar for  
317 both potentials, even if with the CRG potential the Pu content is much more  
318 pronounced.

### 319 *3.3. Correlation with microstructure evolution*

320 All these features are interesting because they show that the evolution  
321 with the increasing dose is rather complex with probably different microstruc-  
322 ture influence. In the following, we will try to correlate these behaviours with  
323 the microstructural evolution involved in our simulated irradiated systems.

324 After some investigations, it appears clearly that the FWHM features  
325 are directly correlated with the evolution of the perfect dislocation loops  
326 (Burger's vector:  $b=a/2\langle 110 \rangle$ ). To illustrate this hypothesis, we plot on the

327 same graph in figure 5 the FWHM and the density of dislocation loops as a  
328 function of irradiation dose. For clarity, the results calculated from both em-  
329 pirical potentials are displayed in two different figures: 5(a) for MOX-07 and  
330 5(b) for CRG. In these figures the curves of the perfect dislocation density  
331 follow the exact shape of the FWHM curves for both potentials. Differences  
332 only appear on the relative amplitude for the  $U_{0.5}Pu_{0.5}O_2$  compounds for  
333 both potentials and for  $PuO_2$  with the CRG potential. It also appears that  
334 there is no correlation with the Frank loop density for the compound calcu-  
335 lated with MOX-07. For compounds calculated with CRG, the Frank loop  
336 density is very small; hence comparison is difficult. However, this behaviour  
337 indicates that the broadening of the simulated XRD peaks are mainly due  
338 to the presence of microstrains generated by perfect dislocations surround-  
339 ing the disorientated nanodomains. As the irradiation dose increases, the  
340 number of perfect dislocation segments decrease resulting in the diminution  
341 of the number of nanodomains but an increase of their size. Indeed, at the  
342 highest irradiation dose only a few nanodomains remain, separated by few  
343 long lines of perfect dislocations (see figure 1 and figure 2 at 2.5 MD-dpc).  
344 This microstructure evolution toward fewer defects of nanometre size yields  
345 to the release of the local strain and subsequently to sharpener peaks into  
346 the simulated XRD patterns.

347 For intermediate irradiation doses (*i.e.* 0.4-0.5 MD-dpc), new small peaks  
348 appear in the simulated XRD patterns calculated with the MOX-07 poten-  
349 tials. An example of this pattern is displayed in figure 6(a) where the extra  
350 small peaks are underlined with arrows. They are all located to the right of  
351 the classical peaks of the fluorite structure. After investigation, these peaks

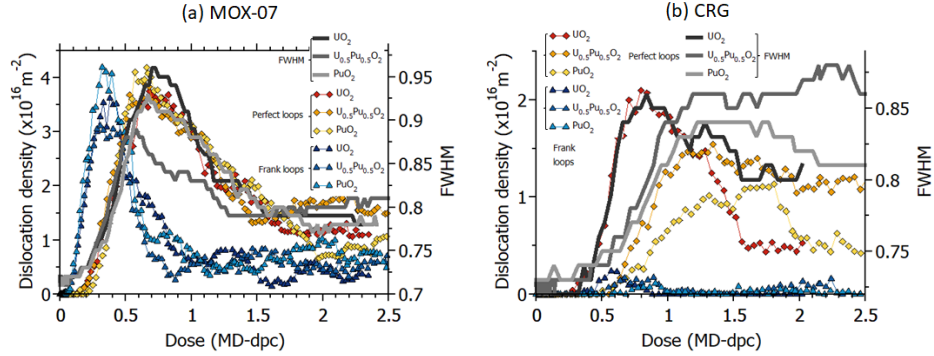


Figure 5: Evolution as a function of irradiation dose of the density of dislocation loops and fwhm calculated from the (111) peaks of the simulated XRD patterns for (a) compounds calculated with MOX-07 and (b) compounds calculated with CRG.

352 do not appear as artefacts of the simulation but seem rather directly cor-  
 353 related with the density of Frank loops. In figure 6(b), we reported on the  
 354 same graph the maximum intensity of the new peak at around  $2\theta = 29^\circ$   
 355 corresponding to the first arrow in the figure 6(a) and the evolution of the  
 356 dislocation densities for both Frank loops and perfect loops. The intensity of  
 357 this new peaks follows almost perfectly the shape of the Frank loop densities  
 358 for all the compounds. It is also important to notice that no new peak is  
 359 detected on the simulated XRD patterns calculated with the CRG potential  
 360 for which very few Frank loops are found. Since these new peaks follow the  
 361 regular fluorite peaks, they could be interpreted as a fluorite-like structure  
 362 with a smaller lattice parameter (*e.g.* for the configuration in figure 6(a), the  
 363 lattice parameter of the small peaks is approximatively equal to  $a = 5.3 \text{ \AA}$   
 364 instead of  $a = 5.5 \text{ \AA}$  for the regular peaks.). These fluorite-like structures  
 365 could then correspond to the structure inside a Frank loop, which is more

366 constrained than in the bulk leading to smaller lattice parameter.

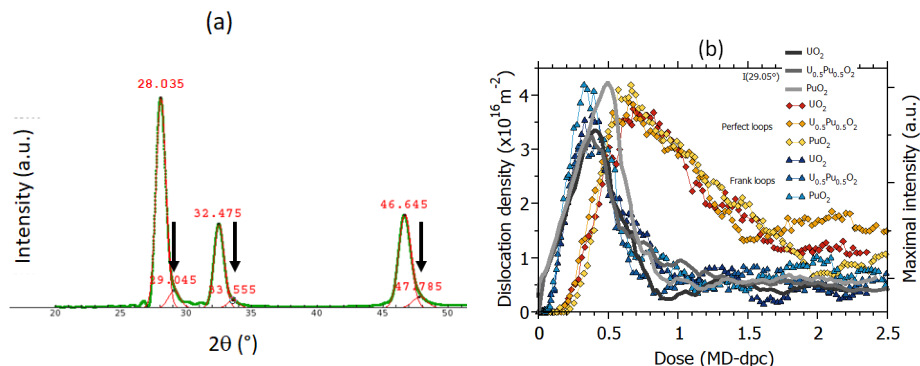


Figure 6: (a) Close up of the simulated XRD pattern of  $\text{UO}_2$  calculated with MOX-07 potential at 0.4 MD-dpc. The arrows indicate the position of the new peaks found for this configuration. (b) Evolution as a function of irradiation dose of the density of dislocation loops and the maximum intensity of the new peak at around  $2\theta = 29^\circ$  corresponding to the first arrow in the figure 6(a).

367 Another interesting feature that can be analysed from XRD pattern is the  
 368 evolution of the lattice parameter, which gives an indication of the swelling  
 369 of the material under irradiation. We already computed the evolution of  
 370 the lattice parameter as a function of the increasing irradiation dose in fig-  
 371 ure 4(c). We now compare these graphs for  $\text{UO}_2$  with the theoretical ex-  
 372 pansion derived from each defect relaxation volume contributions as the  
 373 following equation:

$$\frac{\Delta a}{a_0} = \frac{1}{3} \left[ C_{\text{int.}}(\text{U}) \frac{V_{\text{int.}}^{\text{rel}}(\text{U})}{\Omega} + C_{\text{vac.}}(\text{U}) \frac{V_{\text{vac.}}^{\text{rel}}(\text{U})}{\Omega} \right. \\ \left. + C_{\text{int.}}(\text{O}) \frac{V_{\text{int.}}^{\text{rel}}(\text{O})}{\Omega} + C_{\text{vac.}}(\text{O}) \frac{V_{\text{vac.}}^{\text{rel}}(\text{O})}{\Omega} \right] \\ + \frac{\pi b^2}{4} \rho_{\text{perfect}} + \frac{b \bar{R}_{\text{Frank}}}{2} \rho_{\text{Frank}} \quad (4)$$

374 where  $C_{\text{int.}}$  and  $C_{\text{vac.}}$  are the interstitial and the vacancy concentrations  
375 (respectively),  $V^{\text{rel}}$  is the relaxation volume of each defect expressed in atomic  
376 volume unit  $\Omega$ ,  $b$  is the Burger's vector associated to the type of loop (*i.e.*  
377  $b = a/\sqrt{2}$  for perfect loops and  $b = a/\sqrt{3}$  for Frank loops),  $\bar{R}_{\text{Frank}}$  is the  
378 average radius size of the Frank loops found in our simulation (2 nm), and  
379  $\rho$  is the dislocation density expressed in  $\text{m}^{-2}$ . The defect concentrations  
380 and dislocation densities are directly calculated from the MD simulations,  
381 relaxation volumes of each defect are taken from the DFT calculations carried  
382 out by Bruneval *et al.* [10]. The values of all the relaxation volumes are  
383 reported in the table 1.

$V_{\text{int.}}^{\text{rel}}(\text{U})/\Omega$	$V_{\text{vac.}}^{\text{rel}}(\text{U})/\Omega$	$V_{\text{int.}}^{\text{rel}}(\text{O})/\Omega$	$V_{\text{vac.}}^{\text{rel}}(\text{O})/\Omega$
1.02	-0.23	0.02	0.175

Table 1: Relaxation volume of point defects calculated with DFT by Bruneval *et al.* [10] in  $\text{UO}_2$ .

384 Figure 7(a) and (b) report the comparison of the lattice parameter expansion  
385 as a function of irradiation dose between those found with the simulated  
386 XRD in  $\text{UO}_2$  and the theoretical values calculated with the equation 4. Only

387  $\text{UO}_2$  compounds have been investigated because to our knowledge the re-  
 388 laxation volume of defects in  $\text{MOx}$  or  $\text{PuO}_2$  have not been yet calculated.  
 389 However, we hypothesis that their behaviour would follow the one of  $\text{UO}_2$ .

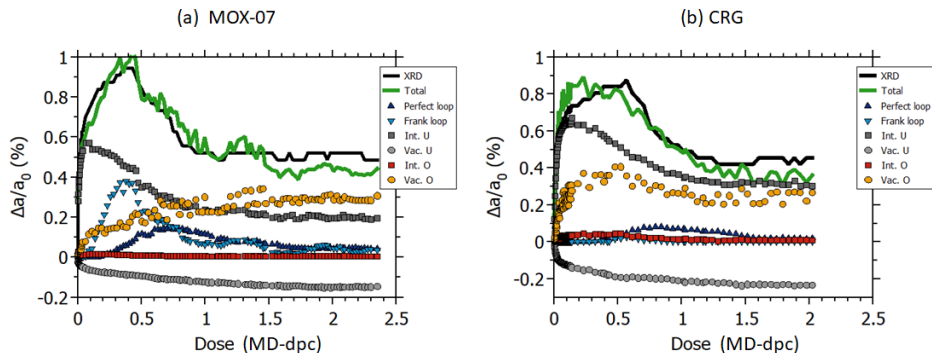


Figure 7: Theoretical contribution of the different defects to the relative lattice parameter  $[a(\text{MD-dpc})-a(0)]/a(0)$  corresponding to the swelling as a function of irradiation dose calculated with (a) MOX-07 and (b) CRG potentials. These contribution are compared with the relative lattice parameter calculated from the simulated XRD.

390 The sum of all the contribution fits quite nicely the expansion calculated  
 391 from the simulated XRD patterns for both empirical potentials. For both  
 392 cases, the main contribution of the expansion arises from the uranium inter-  
 393 stitials followed by the oxygen vacancies, and for MOX-07 the Frank loops  
 394 plays also an important part of the expansion. It is worth noticing that  
 395 this finding is different from what has been previously reported in  $\text{UO}_2$  by  
 396 Chartier *et al.* [8] or by Jin *et al.* [9] who calculated this expansion com-  
 397 parison with another empirical potential and did not take into account the  
 398 oxygen defect contributions. Moreover, in their study, the values of the re-  
 399 laxation volumes were also different especially for the uranium vacancy for

400 which the relaxation volume is positive. Nevertheless, the main contribution  
 401 of the expansion remains the cation interstitials.

402 The swelling of the material under irradiation can also be directly mea-  
 403 sured experimentally by the volume increase of the irradiated sample. Identical  
 404 procedure can be applied to our MD boxes. We measure directly the box  
 405 expansion as a function of increasing dose. Figure 8(a) reports this evolution.  
 406 For comparison the expansion calculated from XRD are also displayed in the  
 407 same graph.

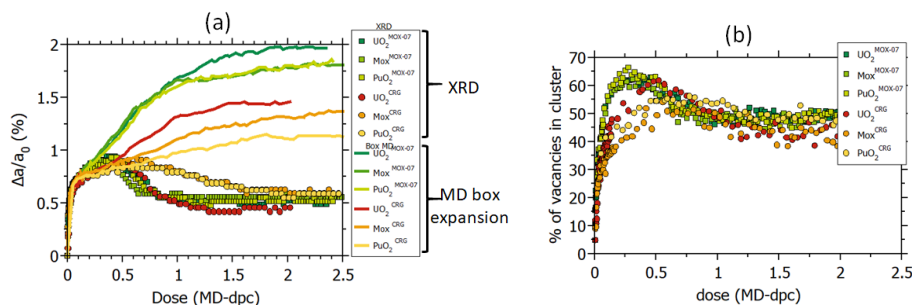


Figure 8: (a) Evolution of the relative lattice parameters  $[a(\text{MD-dpc})-a(0)]/a(0)$  as a function of irradiation dose calculated from the simulated XRD pattern (symbols) and from the direct expansion of the simulation MD boxes (straight lines). (b) Evolution of the percentage of vacancies embedded in vacancy cluster of minimum size 3 as a function of irradiation dose. Both graphs report the results for  $UO_2$ ,  $(U,Pu)O_2$  solid solution noted MOx, and  $PuO_2$  calculated with the MOX-07 and CRG potentials.

408 Differences between both types of measurement appear clearly. For the  
 409 doses corresponding to the point defect regime (*i.e.* area in pink in figures 1  
 410 and 2) the expansion is identical. However, for higher doses corresponding  
 411 to what we have referred as the dislocation regime (*i.e.* area in blue and  
 412 grey in figures 1 and 2) the expansion calculated directly with the MD box



413 continues to increase and reaches a plateau after approximatively 1 MD-dpc.  
414 This behaviour does not correlate with the theoretical expansion calculated  
415 with the equation 4. Nonetheless, it seems to correspond with the evolution  
416 of the vacancy densities reported in figures 1 and 2. Furthermore, vacancy  
417 clustering analysis, namely the number of vacancies that are embedded into  
418 vacancy cluster larger than bi-vacancies, shows that up to 30% of the va-  
419 cancies are not isolated at high doses, see figure 8(b). The maximum size of  
420 these vacancy clusters is found to be between 30 to 50 vacancies correspond-  
421 ing to nanocavities of 1 to 1.5 nm diameter. We believe that this is these  
422 nanocavities that impose the MD box to swell but their influence does not  
423 appear in the expansion of the XRD pattern because it does not affect much  
424 the surrounding matrix lattice parameter.

#### 425 **4. Conclusions**

426 Molecular dynamics simulations have been carried out to investigate the  
427 evolution with irradiation dose of the microstructure of (U,Pu)O<sub>2</sub> solid so-  
428 lutions. Irradiation damage is created using the Frenkel pair accumulation  
429 method and assessed with two empirical potentials. One, MOX-07, gives  
430 good results on the point defects formation energy; while the other, CRG,  
431 provides better results on the mechanical properties. Overall, both potentials  
432 provide the same behaviour even if the CRG potential is influenced more by  
433 the presence of Pu content.

434 Along the irradiation pathway, each microstructure created with sponta-  
435 neous reorganization of defects is analysed directly by determining the point  
436 defects and dislocation densities and by calculating the X-Ray diffraction

437 patterns. Since the atomic configuration is well defined within the molecular  
438 dynamics simulations, correlation between the simulated X-Ray diffraction  
439 patterns and the microstructure evolution could be established. This pro-  
440 vides a database, which can help the interpretation and/or to deconvolve the  
441 experimental XRD patterns of real physical irradiated MOx.

442 Unsurprisingly, we found that the full width at half maximum of the XRD  
443 peaks are directly correlated to the perfect dislocation loop density. The  
444 increase of the FWHM corresponds usually to an increase of the microstrain,  
445 which is related herein to the creation of small disoriented nanodomains.  
446 More unexpected, small peaks appear on the simulated XRD patterns for  
447 intermediate irradiation doses and seem directly correlated to the Frank loop  
448 density. These small peaks represent in our simulation the track of a fluorite-  
449 like structure embedded within the Frank loops. Moreover, this structure-like  
450 has a smaller lattice parameter and corresponding to fluorite structure under  
451 compression stress. This needs to be confirmed, yet it could be a method to  
452 measure the Frank loop density, which is hard to characterize experimentally  
453 due to the small sizes of these loops.

454 Finally, the swelling under irradiation have been investigated. The dilata-  
455 tion found with the XRD pattern mainly originates from the presence of the  
456 cation interstitials and the oxygen vacancies and to a lesser extent from the  
457 frank loop density when it exists. However, the dilation calculated directly  
458 from the dimension of the simulation box is mainly due to the creation of  
459 nanocavities.

460 **Acknowledgements**

461 This research is part of the INSPYRE project, which has received funding  
462 from the Euratom research and training programme 2014-2018 under Grant  
463 Agreement No 754329. This research contributes to the joint programme on  
464 nuclear materials (JPNM) of the European energy research alliance (EERA).  
465 This work was granted access to the HPC resources of [TGCC] under the  
466 allocation 2020-mtt7073 made by GENCI.

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# Simulated XRD pattern of irradiated $\text{UO}_2$

structural damage

● point defects

— dislocation loops

