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# Krypton Diffusion in $UO_2$ Assuming a Strong Bonding Krypton-Oxygen. A Molecular Dynamics Simulation[1]

**Abstract:** a molecular dynamic simulation of Kr bulk diffusion in UO2 isolated nanocrystals is conducted in the assumption of a strong krypton-oxygen bonding. Thecrystals consisted of 5460 ions.The modeling carried out by parallelizing the computations on the graphics processing units of the CUDA architectures GK110 and GP102 using the NVIDIA GeForce GTX 780Ti and 1080Ti video cards. The frequencies of the diffusion jumps and the values of the diffusion coefficient are calculated at temperatures from 2325 K to 2800 K. The interstices surrounded by the eight closest oxygen neighbors are shown to be the equilibrium positions of the krypton atom. The main observed migration mechanism is movement of the atom between the interstitial positions via the anionic vacancies. The values of the diffusion coefficient are from $5 \cdot 10^{-7}$ to $2 \cdot 10^{-5}$, and the diffusion activation energy is $E_D = (4.8 \pm 0.3)$ eV.

**Keywords:** the oxide nuclear fuel, the potentials of interaction, the diffusion coefficient, krypton diffusion.

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**Introduction.** Radiogenic krypton is formed in reactor fuel as one of the products of nuclear decay. The accumulation of radiogenic gases, particularly xenon and krypton, can lead to swelling of the fuel and a decrease in its thermal conductivity. The release of the gases from the fuel pellet creates excess pressure under the fuel cladding. The amount of krypton produced in a reactor is 7.5 times less than that of xenon [1]. The fraction of krypton atoms in the bubbles that the gas forms together with xenon in the fuel bulk is also about 1:7 (the PWR reactors, [2]). These values, although small, are not negligible. Therefore, it is important to study the radiogenic krypton behavior in order to predict the changes in the nuclear fuel properties during operation and storage.

Similar to xenon, the main mechanism for krypton release to the surfaces of oxide fuel crystals is the diffusion of single atoms through the bulk. The existing experimental data on this process in UO2 [1, 3] diverge significantly both in the magnitude of the diffusion coefficient and in the activation energy. Krypton transport mechanisms remain unclear. A comparatively small number of works have been devoted to the computational simulation of the solution and migration of krypton in uranium dioxide [4-6]. The studies were mainly focused on static first-principle methods. In a recent paper [5], the mechanisms and values of the krypton diffusion coefficient were estimated using the DFT+U approximation and the nudged elastic band method (NEB). Still, a quantitative correspondence between the simulation results and experimental data has not yet been reliably established.

In works [4] and [6], the empirical pair interaction potentials of the Kr atom with uranium and oxygen ions in $UO_2$ crystal were proposed, based on first-principles calculations. These potentials are applicable for molecular dynamics simulation. Using the potentials [6], the diffusion of krypton in isolated uranium dioxide nanocrystals was studied by the molecular dynamics method [7]. It is important to note that the known empirical sets of potentials [4] and [6] do not imply strong binding of the krypton atom to the environment. These potentials take into account the repulsion of the overlapping electron shells, along with the dispersion attraction. Meanwhile, there are some experimental and calculated data [8, 9] indicating the possibility of the formation of a chemical

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bond of krypton atom with oxygen ions. In [9], the Dmol method [10] had been applied to obtain an interaction potential of the Kr–O$^{2-}$ pair, that was characterized by the depth of the potential well equal to 1.1 eV. In the present work, this potential [9] is used to simulate krypton diffusion in $UO_2$ by the molecular dynamics.

**The Simulation Technique.** The systems studied in this work were model $UO_2$ nanocrystals of octahedral shape, isolated in avacuum. Similar to [7], the crystals consisted of 5460 ions. At the beginning of a computational experiment, a single krypton atom was placed in one of the central interstitial positions. The krypton diffusion coefficient D was determined from the Einstein relation $<a^2(t)> = 6D \cdot t$, averaging the mean squared displacement $<a^2(t)>$ over 20 computational experiments at the temperatures from 2325 K to 2800 K. The displacements were limited by the crystal size. Hence, the Einstein relation was used only at times much shorter than the characteristic time required for the atom to reach the surface. In contrast to work [7], no release of the atoms from the crystal through the surface was observed, due to the strong binding of krypton to oxygen. Still, the surface could act as a source of vacancies assisting the migration of the Kr atom. Interaction of the particles was modeled using the empirical pair potentials that included the Coulomb term, the valence interaction of the electron shells in the Born-Mayer and Morse forms, and the dispersion attraction (1):

$$U_{ij}(R) = K_E \frac{q_i q_j}{R} + A_{ij} e^{-B_{ij} R} + \varepsilon_{ij} \cdot (e^{-2\beta_{ij}(R-R_{ij})} - 2e^{-\beta_{ij}(R-R_{ij})}) - \frac{C_{ij}}{R^6} \qquad (1)$$

For the pairs U-U, U-O and O-O, the parameters (1) belonged to the MOX-07 potential set [11] obtained from the $UO_2$ and $PuO_2$ lattice constant dependence on temperature. The interaction Kr-U was described by the *ab-initio* pair potential [6] based on the density functional theory. Non-zero parameters of this interaction were $A_{KrU} = 8258.00$ eV, $B_{KrU} = 3.53104$ Å$^{-1}$, $C_{KrU} = 18.0624$ eV$\cdot$ Å$^6$ [6]. The pair potential Kr-O was taken from a Dmol calculation [9]. It described the strong bonding of krypton and oxygen using the parameters $\varepsilon_{KrO} = 1.10$ eV, $\beta_{KrO} = 1.30$ Å$^{-1}$, $R_{m,KrO} = 2.42$ Å(the parameters not listed were taken to be zero).

All the particles moved according to the Newton's equations of motion that were integrated by the Leapfrog method using the time step $\Delta t = 3 \cdot 10^{-15}$ s. The computational power required to calculate the pair forces at each step was provided by parallelizing the computations on the graphics processing units of the CUDA architectures GK110 and GP102 using the NVIDIA GeForce GTX 780Ti and 1080Ti video cards, respectively.

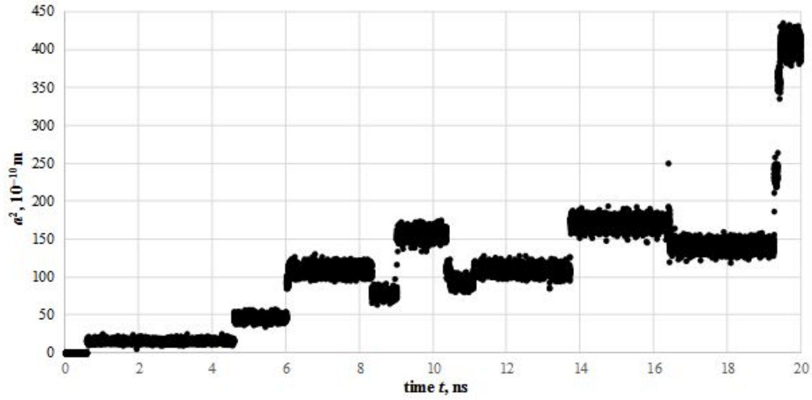

FIGURE 1 – A time dependence of the squared displacement $a^2(t)$ of a single krypton atom in the model $UO_2$ crystal. T = 2450 K

**Results and discussion.** The mechanism of migration of the krypton atom in this work was analyzed at a relatively low-temperature T = 2450 K, in order to avoid high thermal disordering of the crystal lattice. A time dependence of the squared displacement a$^2$(t) of a single atom at this temperature is shown in Figure 1. The steps on the graph correspond to individual diffusion jumps. The equilibrium krypton positions were the interstices, in which the first coordination sphere of the atom consisted of eight oxygen anions. Figure 2 shows the time dependences of the x, y and z Cartesian coordinates of the krypton atom when moving from an interstitial position with coordinates (0.75, 0.25, 0.25) to a position with coordinates (0.75, -0.25, 0.75), the coordinates are expressed in the units of the lattice constant. Despite the equality of x values at the beginning and at the end of the trajectory, the atom changes x-coordinate during the jump as it passes near the point with coordinates (1.0, 0.0, 0.5) that correspond to an anionic vacancy. The same travel mechanism was observed for most other diffusion jumps.

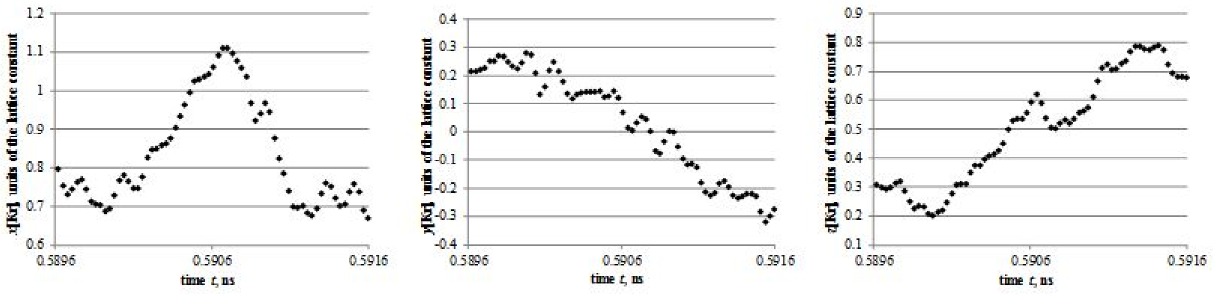

Figure 2 – The coordinates of the krypton atom during a jump between two interstitial positions. T = 2450 K

The mechanism of krypton diffusion by the interstices via the anionic vacancies was also obtained in the case of non-chemical krypton-oxygen bonding [7]. In this work, krypton atom occupied the vacancies for a very short time, compared with the time spent in the interstitial positions. Contrary, in [7] the residence times of the krypton atom in anion vacancies and in interstitial positions were of the same order of magnitude. In [7], the oxygen ion was displaced by the krypton atom from its site to an interstitial position. Here, the configurations of the vicinity of the atom in the anionic vacancy were not determined, since the atom occupied these positions for too short a time. So, the thermal mechanism of formation of the anionic vacancies assisting diffusion was not excluded. At temperatures below 2550 K, averaging of the mean squared displacements for calculating the diffusion coefficient was hindered due to the low frequency of the diffusion jumps. To control the correctness of the calculation of the diffusion coefficient, we also monitored the frequency f of the Kr diffusion jumps in the range from 2325 K to 2800 K and plotted its temperature dependence in the Arrhenius coordinates ln$f$(1/T). The obtained graph is shown in Figure 3. It can be seen that the values ln$f$(1/T) fell on a straight line with the activation energy E$_f$ = 4.8 ± 0.5 eV. The energy obtained is overestimated in comparison with the experimental data [1, 3]. On the other hand, it is lower than an ab initio calculation of the activation energy of the Kr interstitial diffusion in [5] (E$_A$ = 8.57 eV).

The krypton diffusion coefficient D in this work was calculated using the Einstein relation at temperatures from 2325 K to 2800 K (Figure 4). Its values are in the range from $5 \cdot 10^{-7}$ to $2 \cdot 10^{-5}$ cm$^2$/s. These numbers are very high in comparison with both the extrapolation of the experimental data to the model temperatures and the estimate of the interstitial diffusion coefficient from [5]. The divergence from the experiment may be due to the trapping of krypton in real crystals by cationic vacancies and vacancy clusters, or to a change in the main transport mechanism with increasing temperature. Compared to the dynamic model with no significant bonding of krypton to oxygen [7], the diffusion coefficient decreased by an order of magnitude.

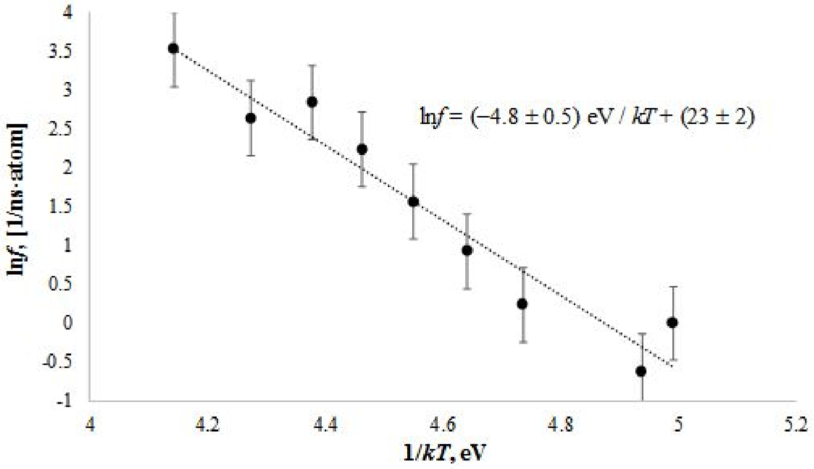

FIGURE 3 – The frequency of the krypton atom diffusion jumps depending on temperature

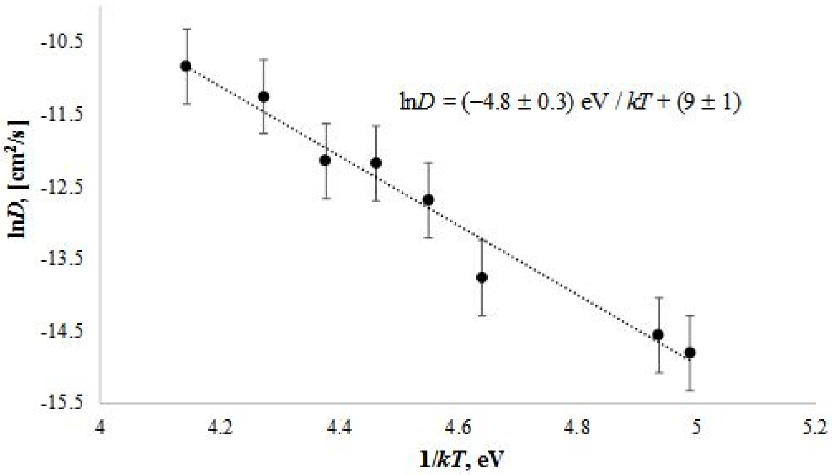

FIGURE 4 – The calculated krypton diffusion coefficient depending on temperature

The interstitial diffusion coefficient and the frequency of jumps f are theoretically linked by the relation

$$D_{interstitial} = \frac{1}{6} \cdot a_0^2 \cdot f = \frac{1}{6} \cdot a_0^2 \cdot f_0 \cdot e^{-E_D/kT} \tag{2}$$

were $a_0$ is the effective length of the jump and $f_0$ is a preexponential factor relatively independent of temperature. In this model, the diffusion activation energy ED coincides with the slopes of the lines describing the dependence of both frequency and diffusion coefficient on temperature in the Arrhenius coordinates ln$f$(1/T), lnD$_{interstitial}$ (1/T).

The calculated effective diffusion activation energy of krypton is $E_D = (4.8 \pm 0.3)$ eV (Figure 4). This value very accurately coincided with the activation energy of the diffusion jumps $E_f = (4.8 \pm 0.5)$ eV corresponding to the plot in Figure 3. The experimental value of the activation energy of krypton diffusion should lie somewhere between 1.4 eV [3] and 3.2 eV [1]. In the absence of strong Kr-O interaction, the calculated activation energy of interstitial diffusion was $(1.00 \pm 0.03)$ eV [7]. Thus, the weakening of the model chemical krypton-oxygen bond could bring the diffusion activation energy into line with experimental data. However, additional studies are needed to compare the model and real mechanisms of krypton diffusion.

**Conclusion.** The results demonstrate that the equilibrium positions of the krypton atom in the model UO $_2$ nanocrystals under the condition of strong krypton-oxygen bonding are interstices surrounded by the eight closest oxygen neighbors. A migrating atom passes from one interstitial position to another through an anionic vacancy. Qualitatively, the mechanisms of solution and transfer of krypton are unchanged compared to the model [7], where the krypton-oxygen attraction was limited to the dispersion force. At that, the diffusion activation energy increased from 1.0 eV to 4.8 eV, and the diffusion coefficient decreased by about an order of magnitude. The time spent by the krypton atom in the anionic vacancies has been substantially reduced. In order to compare the results with the experiment, it is necessary to simulate the trapping of krypton atoms by cationic vacancies and vacancy clusters.

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### Күшті криптон-оттекті байланысындағы UO $_2$ -дегі криптон диффузиясы. Молекулалық динамика модельдеуі

**Аннотация.** UO $_2$ - оқшауланған нанокристалдардағы Kr диффузиясының молекулалық динамикалық модельдеуі күшті криптон-оттегі байланысы туралы ұйғарыммен жүзеге асырылды. Модельденген кристалдар 5460 ионнан тұрды. Модельдеу NVIDIA GeForce GTX 780Ti және 1080Ti видеокарталарын қолдана отырып, CUDA GK110 және GP102 графикалық процессорларында параллельдеп есептеу арқылы жүзеге асырылды. Диффузиялық секірістердің жиіліктері мен диффузия коэффициентінің мәндері 2325 К-ден 2800 К-қа дейінгі температурада қарастырылды. Кристалдық тор аралықтары, сегіз оттегінің ең жақын көршілерімен қоршалған криптон атомының тепе-теңдік күйлері ретінде көрсетілген. Негізгі байқалатын миграция механизмі – атомның аниондық вакансиялар арқылы интерстициалды позициялар арасында қозғалуы. Диффузия коэффициентінің мәндері $5 \cdot 10^{-7}$ ден $2 \cdot 10^{-5}$ см $^2$ /с дейін, ал диффузия активтендіру энергиясы $E_D = (4.8 \pm 0.3)$ эВ құрайды.

**Түйін сөздер:** оксидті ядролық отын, өзара әрекеттесу потенциалы, диффузия коэффициенті, криптондық диффузия.

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### Диффузия криптона в UO $_2$ в предположении сильной связи криптон-кислород. Молекулярно – динамическое моделирование

**Аннотация.** Молекулярно – динамическое моделирование объемной диффузии Kr в изолированных нанокристаллах UO $_2$ проводилось в предположении наличия прочной криптон-кислородной связи. Кристаллы состояли из 5460 ионов. Моделирование проводилось путем распараллеливания вычислений на графических процессорах архитектур CUDA GK110 и GP102 с использованием видеокарт NVIDIA GeForce GTX 780Ti и 1080Ti. Рассчитаны частоты диффузионных скачков и значения коэффициента диффузии при температурах от 2325 K до 2800 K. Показано, что междоузлия, окруженные восемью ближайшими кислородными соседями, являются положениями равновесия атома криптона. Основным наблюдаемым механизмом миграции является перемещение атома между межузельными позициями через анионные вакансии. Значения коэффициента диффузии составляют от $5 \cdot 10^{-7}$ до $2 \cdot 10^{-5}$ см$^2$/с, а энергия активации диффузии $E_D = (4.8 \pm 0.3)$ эВ.

**Ключевые слова:** оксидное ядерное топливо, потенциалы взаимодействия, коэффициент диффузии, диффузия криптона.

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