



# Diffusion of helium in the perfect and non perfect uranium dioxide crystals and their local structures



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## ABSTRACT

Local nano structures and their changes relevant with the diffusion of helium was determined by applying the density functional theory (DFT). With its help we calculated deformation of the crystal lattice while wandering helium atoms between octahedral sites. The optimal mutual coordinates of the atoms were determined by minimizing the Hellman–Feynman forces, allowing at the same time precisely specify dynamic height and the shape of the potential barrier. For a crystal containing single oxygen or uranium vacancies, has been described both the deformation associated with the presence of vacancy, as well as additional deformation related to the migration of the helium atom in the lattice. It was found that in the case of vacancies, the migration of helium atoms between the octahedral sites is not along a straight line but along a polyline. In addition, the presence of uranium vacancy causes that helium atoms in the octahedral sites, situated in the I and II coordination shell of uranium vacancy, have different energies. Migration between such positions must be carried out with the participation of the emission–absorption of phonons. Applying two site – model we evaluated the time for an over-barrier jump and diffusion of interstitial He. The obtained values for diffusion coefficient are compared with the experimentally obtained values and with the theoretical values of other authors.

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## 1. Introduction

It is a well known accumulation ability of huge amount helium by  $\text{UO}_2$  crystals during several billions of years in their minerals. Similar phenomena of helium accumulation occurs in the nuclear fuel under irradiation where helium is produced as a result of the alpha decay of certain actinides. Initially it was considered, although helium is the noble gas, that a weak chemical bonding can be induced in the environment of heavy atoms.

The first attempt of explanation the helium incorporation in  $\text{UO}_2$  crystal was undertaken in the early 1990s [1]. They estimated the bond energy of helium atoms in the uranium dioxide crystal equal to  $-0.1$  eV. As the result was negative so the helium atom could be permanently chemically bond in the uranium dioxide crystal.

The later study using the density functional theory (DFT) generalized gradient approximations (DFT-GGA) [2,3] frame-work did not confirmed this result. The obtained results of bond energies lying in the range from  $+0.77$  to  $+1.83$  eV exclude ability of chemical bond.

In Ref. [4] another approach of the issue was presented. Instead of chemical bond – the helium atom immobilization in a deep

potential well inside the crystallographic lattice was proposed. The methods estimate the energy barrier between interstitial sites in perfect lattice  $\text{UO}_2 + \text{He}$  on about 8 eV. We have shown there, that in these circumstances the helium atom creates local bond state and performs oscillation of small amplitude, so the probability of over barrier jump to neighbor interstitial site, and hence the diffusion coefficient are close to zero.

In our later work [5], in contrast to [4] in the calculations we took into account changes in local deformation during He wandering between free octahedral interstitial positions and its impact on the barrier height, what appeared to be significant. Over barrier jump of helium from one interstitial site to the next neighboring one is connected with overcoming the potential barrier equal to about 4 eV. According to our calculations the diffusion coefficient value for the potential barrier equal to 4.15 eV at 300 K should be in the case of a perfect crystal without defects about  $10^{-48}$   $\text{cm}^2 \text{s}^{-1}$ . So small values of diffusion coefficient effectively prevent the helium atoms from any movement even at very high temperatures.

The height of the potential barrier between interstitial sites in perfect lattice was evaluated in [1], which appeared to be equal to  $+3.8$  eV. All these estimates were obtained using methods of molecular thermodynamics. Authors in Ref. [6] give two potential values 2.56 eV and 2.3 eV making reference to [7]. Later in this work the discrepancy will be discussed over.

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Diffusion significantly favor the crystal lattice defects. In the case of  $\text{UO}_2$ , as shown by experimental results, the effect is large. Authors of Ref. [8] using  $^3\text{He}(d,\alpha)^1\text{H}$  Nuclear Reaction Analysis Technique obtained for the crystalline  $\text{UO}_2$  in the temperature  $1000^\circ\text{C}$  the diffusion coefficient equal to  $D = 3.7 \pm 0.74 \times 10^{-14} \text{ cm}^2\text{s}^{-1}$ , while authors of Ref. [9], applying the same method, obtained for the  $\text{UO}_2$  matrix and the same temperature the diffusion coefficient equal once to  $D = 2.9 \times 10^{-13} \text{ cm}^2\text{s}^{-1}$  and once to  $D = 3.7 \times 10^{-14} \text{ cm}^2\text{s}^{-1}$  depending on the flux value.

Annealing, reducing the amount of defects, reduces the diffusion coefficient  $D$ , in other words the defects enhance the diffusion mechanism. So, for example the authors [10] obtained the value of diffusion coefficient equal to  $D = 6 \times 10^{-13} \text{ cm}^2\text{s}^{-1}$ , and in [11], after annealing at  $1100^\circ\text{C}$  during 25 min its value decreased below  $2 \times 10^{-14} \text{ cm}^2\text{s}^{-1}$ .

Defects in the obvious way reduce the values of the potential barrier. In the work [1] the height of the potential barrier between interstitial positions and oxygen and uranium vacancies were estimated theoretically. The potential barriers appeared to be equal to 0.38 and 0.24 eV respectively. In the work [6] these values are estimated on 0.54 and 0.43 eV respectively, and in [7] on 0.5 and 0.2 eV. In all cases these values were obtained applying (using) the half classic method of the molecular dynamics.

In this work, in order to verify the barrier parameters, the “ab initio” calculations were applied taking into account both the local deformation of crystal lattice caused by the presence of vacancy, as well as the additional deformation associated with the presence of helium atoms and their migration through the net.

The calculation of the diffusion coefficient we made applying two site model which was for the first time used for the system  $\text{UO}_2 + \text{He}$  in [4] and we evaluated the time for an over barrier jump. The same method used in [5], made it possible to determine the temperature dependence of the diffusion coefficient.

## 2. Method of calculations

Ab initio calculations of the electronic structure were performed using the Wien2k program package [12] based on the density functional theory (DFT), developed by Hohenberg and Kohn [13] and Kohn and Sham [14]. The Kohn–Sham equations are solved self-consistently in an interactive process using the linearized augmented plane wave (LAPW) method.

The accuracy of the basis set is determined by the k-space integration by a mesh of 2000 k-points in the full Brillouin zone.

Taking into consideration the above, in all DFT calculations we use several exchange–correlation energy functional  $E_{xc}[n(\vec{r})]$  within the generalized gradient (GGA) approximations. All the calculation were performed using the Hubbard model (DFT +  $U$ ), corrective exchange–correlation energy functional  $E_{xc}[n(\vec{r})]$ , namely: PBE-GGA +  $U$ . In accordance with earlier studies DFT the  $U$  and  $J$  values were set to  $U = 4.6 \text{ eV}$  and  $J = 0.5 \text{ eV}$  [3].

The electron spin-polarization was taken into account.

While computing we look for the optimal atom location that ensure a minimum value of internal energy. The lattice parameters and local lattice coordinates were computed in three stages:

- Stage 1 – minimization of the total energy through the change of lattice parameters (volume).
- Stage 2 – at the obtained equilibrium lattice constants-zeroing of forces acting on the separate atoms in the lattice (Hellman-Feynman forces) through the change of atom coordinates within the unit cell.
- Stage 3 – iterative minimization of the total energy through the change of lattice parameters.

The energy and change convergence criteria used in the computation are 0.01 mRy and 0.0001 e.

## 3. Deformation of the perfect crystal lattice while wandering helium atoms between octahedral sites

Compounds  $\text{UO}_2$  are isomorphic, with a face-centered cubic lattice (fcc) of the calcium fluorite type structure, with similar lattice

parameters:  $a = 5.396 \text{ \AA}$  [15] respectively and space group Fm-3m (#225). The ideal structure of perfect uranium dioxide is presented in Fig. 1. In order to visually separate the interstitial sites we have placed in them helium atoms. Helium atom, located in the octahedral site causes local increase in lattice parameters. This change, because of the small ionic radius of He is small. Thus, in the case of  $\text{UO}_2 + \text{He}$ , according to [3], depending on the model assumed, it is only from 0.04 to 0.02 Å. According to our calculations [5], it is formed at the level of 0.017 Å, which is only about 0.3% of the lattice parameter. Above mentioned calculations concern the situation, when the atom of helium is in the equilibrium position, e.g. in octahedral site  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ . The deformation of the lattice grows up significantly, when the atom of helium moves in the direction of the top of the barrier of the potential, in this case of the position e.g.  $\frac{1}{4}\frac{1}{2}\frac{1}{4}$ . The lattice constant parameter grows up by 0.105 Å [5]. Additionally, when the atom of helium “squeezes” through between the atoms of oxygen, it causes enlarged, the local deformation of the lattice, separating mainly the closest oxygen atoms by approximately 0.648 Å. Bearing in mind the fact, that they were located initially at a distance about 2.698 Å, this makes up the growth of the distance about approximately 24% [5]. Such an increase in the local deformation has a huge impact on the height of potential barrier. In [5] we have shown that in the ideal lattice of  $\text{UO}_2$  taken into account the deformation of the lattice reduced the potential barrier from 8.122 eV to 4.15 eV. Having in mind of the above we carried out the calculations of the parameters of the potential barrier taking into account the change of the lattice parameter, as well as the local deformation, caused by the presence of vacancy.

## 4. Nano deformation of lattice containing single oxygen or uranium vacancies

The considered case is more complicated from this one considered above in Section 3. Here, instead of a perfect crystal, already at the beginning we have local deformation, caused by the presence of vacancy. The above deformation this time are considerably larger, especially in the case of uranium vacancies, and spread on greater distances.

In order to clarify the model we will assume that the oxygen vacancy is in the position  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ , while the uranium vacancy is in

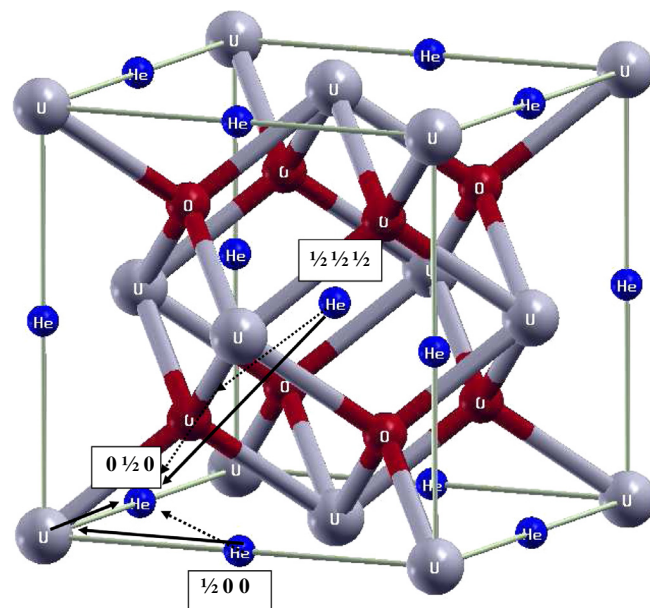


Fig. 1. Crystal lattice of perfect  $\text{UO}_2$ . Helium atoms mark octahedral positions.

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