

Multi-scale model for point defects behaviour in uranium mononitride

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Abstract. A multiscale approach was used to study the properties of point defects in uranium mononitride (UN). In this work we used combination of several methods: *ab initio* calculations; molecular dynamics simulations with a new interatomic potential; thermodynamic model. Density functional theory (DFT) calculations are used for fitting of the parameters of the angular-dependent interatomic potential, as well as for evaluation of the defects formation and migration energies. Molecular dynamics (MD) simulations are applied to analyze what migration/formation mechanisms are activated at finite temperatures and to calculate diffusion coefficients of point defects. The thermodynamic model for description of concentrations and diffusivities for point defects in non-stoichiometric UN_{1+x} is proposed.

1. Introduction

Uranium mononitride (UN) has been studied extensively due to the huge interest in application of this material as a basis of nuclear fuel. Due to the high thermal conductivity, high melting temperature and high density UN is promising fuel for fourth-generation reactors, such as lead-cooled fast reactor. In spite of the importance of this type of fuel, many physical features of UN have not been studied well.

The present work is devoted to determination of concentrations and diffusivities of point defects in the UN, which is useful for microscopic description of nuclear fuel behavior during burn-out. For instance, the data on concentrations and diffusion coefficients of the defects are important for analysis of the dissociation and sintering of the nitride fuel [1, 2] or for investigation of fission products evolution [3-5].

2. Multi-scale model

In this work we used a multiscale approach for study of point defects behaviour. This research combines three models describing various scales: (1) density functional theory calculations; (2) molecular dynamics; (3) thermodynamic model. To connect DFT and MD we create the novel interatomic potential, which accurately describes the structure and thermodynamic properties of uranium mononitride. In this combination of computational approaches one method discovers important features, which must be taken into account when the other one is applied. Stochastic nature of MD (detailed discussion can be found in Ref.[6]) provides convenient way for analysis of the diffusion processes activated at finite temperatures. The developed interatomic potential becomes a bridge between DFT and MD approaches. In this manner, this study describes two basic levels (quantum and atomistic modeling) of the multiscale approach. In addition, we use the thermodynamic model for description of point defects concentrations in non-stoichiometric UN.



2.1. Density functional theory

Main details of DFT calculation were described in our work [7]. All quantum calculations were performed using the DFT code VASP 5.2 [8]. Characteristics of the point defects have been studied by DFT computations and classical MD simulations. It is noteworthy that the DFT calculations are used in two different ways. On the one hand, results of the DFT calculations provide a database necessary for the development of an interatomic potential for the atomistic simulation. On the other hand, DFT is used for direct calculations of properties of the defects. At the same time, the simulation based on application of created interatomic potential helps to find important atomic configurations for the DFT computations. Atomic configurations obtained from the energy minimization performed with the MD usually do not correspond exactly to the energy minima according to DFT and should be subjected to additional relaxation within the appropriate procedure in DFT. However, preliminary calculation/minimization with MD significantly simplifies search of the stable defects states. In such a manner, these two methods (DFT and atomistic simulations with the potential) supplement each other.

2.2. Novel interatomic potential

In this work we develop an interatomic potential for UN in the form of the Angular-Dependent Potential (ADP). Details of development and verification were described in our work [7]. The force-matching method [9] is used for the development of the potential, as implemented in the Potfit code [10]. This method provides a way to construct physically justified interatomic potentials from the fitting database that does not contain experimental data. The idea is to adjust the interatomic potential functions to optimally reproduce per-atom forces (together with total energies and stresses) computed at the *ab initio* level for a fine-tuned set of reference structures.

The verification shows that the potential reproduces defect energies in agreement with the DFT estimations [7]. In addition, ADP correctly describes the thermodynamic properties.

2.3. Atomistic simulation

Characteristics of point defects have been studied by DFT computations and classical MD simulations. Most of the details were described in [7]. We used created Angular-Dependent Potential to describe atomic system in the molecular dynamics.

It is shown that the uranium antisite defects (U_N) play an important role in defects behavior. Uranium atom from the interstitial site (I_U) passes to the place of nitrogen atom in a regular lattice position. In this case, formation of U_N occurs with displacing nitrogen atom to the interstitial defect (I_N). Antisite defects are common for compounds formed from the components of similar chemical nature, such as SiC or metallic alloys. In case of uranium mononitride, U_N is quite favorable defect due to relatively small displacements produced in the uranium sublattice. Table 1 shows the basic formation energies of point defects and energy barrier for formation of U_N and I_N from I_U .

Table 1. The formation energies of composition-conserving defects and the energy barrier for formation of the pair of defects $U_N + I_N$ (obtained from DFT and MD). The energies are given in eV.

	MD	DFT
Uranium Frenkel pair, E_{FP}^U	6.2	7.1
Nitrogen Frenkel pair, E_{FP}^N	4.0	4.9
Schottky defect, E_{SD}	4.6	4.7
$I_U \rightarrow U_N + I_N$, E_{As}	0.7	0.6

It should be noted that the energies from DFT calculations are more accurate than the values that were calculated in MD. However, the difference between the energies calculated by various methods is small, and MD agrees well with quantum calculations.

In this work we calculate the diffusivity for various point defects (i.e. diffusion coefficients of atoms *via* defect diffusion). The calculation was realized for the simulation box containing approximately 2000 atoms and a one point defect. The figure 1 shows results of molecular dynamics simulation in the Arrhenius form. Details of such calculation method were described in [7, 11]. The diffusivity of atoms (U or N) at the presence of given defect is determined by the displacements of all atoms in a system with time:

$$D_{def}^Y = \frac{\sum_{i=1}^M \delta r_i^2}{6t}, \quad (1)$$

where δr is displacement of the i -th atom, t is the computation time, index Y may be U or N, index def may be I (interstitial) or V (vacancy), M is the number of atoms of the same type (uranium or nitrogen). Such calculated coefficient is related to the diffusion coefficient of point defect: $D_{def}^Y = \alpha \cdot D_{def}$, where D_{def} is diffusion coefficient of point defect and α is a constant about 1 (see [12] for details). Unlike the uranium dioxide [12], the diffusivities of atoms in both sublattices of UN are quite close to each other. The existence of two regions in the dependence $D_I^U(T)$ was discussed in [7].

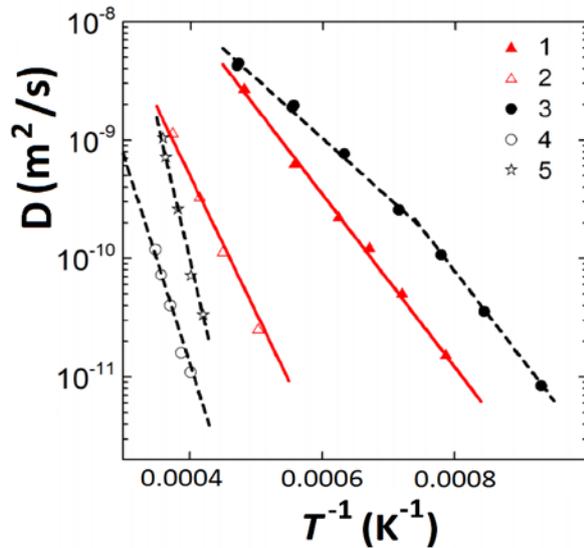


Figure 1. Temperature dependence of diffusion coefficients of nitrogen *via* defects: 1 – interstitial D_I^N ; 2 – vacancy D_V^N . Diffusion coefficients of uranium *via* defects: 3 – interstitial D_I^U ; 4 – vacancy D_V^U ; 5 – uranium in the antisite state D_{As}^U .

2.4. Thermodynamic model

The thermodynamic model contains several equations for point defects concentrations that are described by thermodynamics equilibrium:

$$[I_U][V_U] = \exp(S_{FP}^U / k) \cdot \exp(-E_{FP}^U / kT), \quad (2)$$

$$[I_N][V_N] = \exp(S_{FP}^N / k) \cdot \exp(-E_{FP}^N / kT), \quad (3)$$

$$[V_N][V_U] = \exp(S_{SD} / k) \cdot \exp(-E_{SD} / kT), \quad (4)$$

$$\frac{[U_N][I_N]}{[I_U]} = \exp(S_{As} / k) \cdot \exp(-E_{As} / kT), \quad (5)$$

$$x = [I_N] - [I_U] + [V_U] - [V_N] - 2 \cdot [U_N], \quad (6)$$

where $[def]$ is defects concentration, k is Boltzmann constant, S_{def} is vibration formation entropy of the defect and x is deviation from stoichiometry in UN_{1+x} . Symbols I and V denote interstitial defect and vacancy. Such system of equations may be resolved in direct way for the given x . The values of S_{def} may be estimated as $6k$ [13]. The figure 2 illustrates the solution of equations (2)-(6) at various temperatures T .

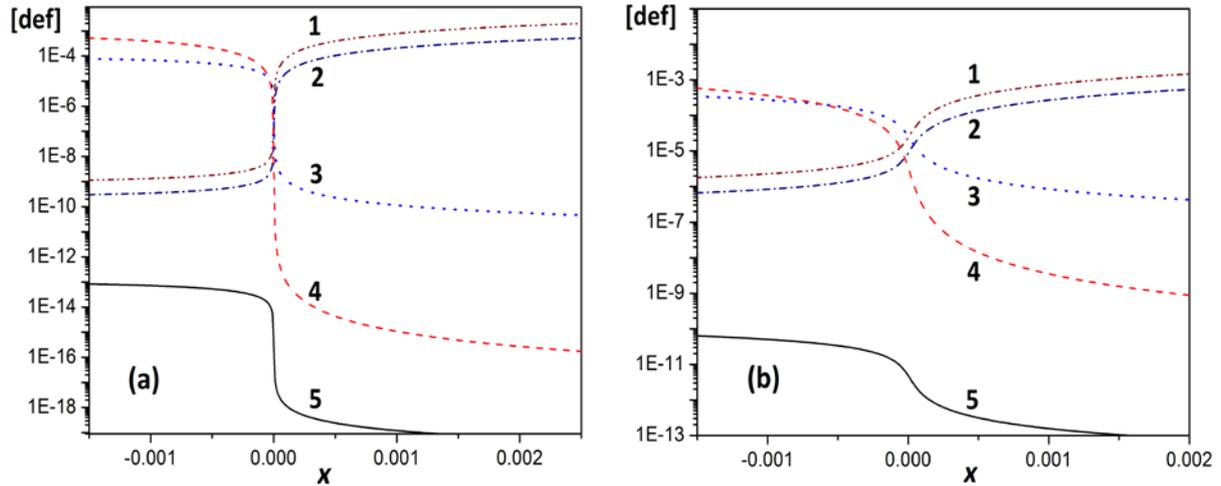


Figure 2. The dependencies of defects concentrations on x : 1 – V_U ; 2 – I_N ; 3 – V_N ; 4 – U_N ; 5 – I_U . The results are given for two different temperatures: (a) $T = 1500K$; (b) $T = 2000K$.

There is a boundary of physically justified solution for the equations (2)-(6). The uranium antisite defects may be considered as nanosized nuclei of pure uranium. At negative value of x , the concentration $[U_N]$ may be about 0.001 that can be interpreted as the formation of uranium. On the other hand, at positive value of x , large concentrations $[V_U]$ and $[I_N]$ correspond to formation of U_2N_3 . It can be assumed that in case when any defect concentration $[def]$ achieves value about 10^{-3} , the formation of pure uranium (at negative x) or U_2N_3 (at positive x) takes place. The existence of the narrow area of UN homogeneity agrees well with the experimental data. However, more accurate model must take into account thermodynamic properties of all phases. The question about accurate description of phase transitions and phase decomposition requires further investigation and will be considered in future works.

For verification of our model we calculated coefficient of uranium self-diffusion (D_S^U) and nitrogen self-diffusion (D_S^N) at various temperatures and at $x = 0$. The calculated defects concentrations and diffusivities of atoms *via* defects were used together to get estimation of self-diffusion coefficients:

$$D_S^U = [I_U] \cdot D_I^U + [V_U] \cdot D_V^U + [U_N] \cdot D_{As}^U \quad (7)$$

$$D_S^N = [I_N] \cdot D_I^N + [V_N] \cdot D_V^N + [U_N] \cdot D_{As}^N \quad (8)$$

The results of simulation are given in figure 3. We compared our results with self-diffusion coefficients of nitrogen from the experiment [14] and with self-diffusion coefficients of plutonium in uranium-plutonium mononitride from the experiment [15]. The difference between calculated and measured values of D_S^N may be caused by difference in conditions. We use $x = 0$, but more correct condition must be connected with the nitrogen pressure P_{N_2} (for instance, nitrogen pressure is equal to 1 atm.) The nitrogen pressure may be estimated using equation $P_{N_2} = A \cdot [I_N]^2$, where A is a constant.

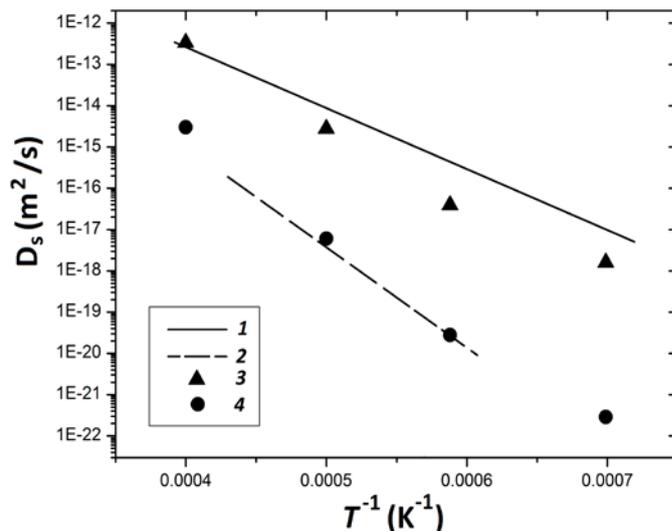


Figure 3. Temperature dependence of self-diffusion coefficients of nitrogen and actinide: 1 – D_s^N from experiment [14]; 2 – D_s^{Pu} from experiment [15]; 3 – D_s^N (calculated in this work); 4 – D_s^U (calculated in this work)

3. Conclusion

It is shown that the U-antisite defects play an important role at negative deviation from stoichiometry in UN_{1+x} (in U-rich area). During migration, the interstitial uranium is able to knock-out nitrogen atom, and this act leads to formation of U in antisite and N interstitial. This effect results in dependence of the diffusivity of U-interstitials on the concentration of defects in the N sublattice. Another peculiarity of UN is the large athermal concentration of U-vacancies in the N-rich UN_{1+x} . This is due to close formation energies of nitrogen Frenkel pairs and Schottky defects.

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