The atomistic simulation of pressure-induced phase transition in uranium mononitride

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\textbf{Abstract.} Phase transition in uranium mononitride (UN) at high pressure has been studied using molecular dynamics. At low pressure, UN has the cubic structure like NaCl (with the space group \(Fm\overline{3}m\)). The research based on Gibbs energy calculation shows that cubic UN turns into rhombohedral face-centered structure (with the space group \(R\overline{3}m\)) at pressure about 32 GPa. It is shown that parameters of \(R\overline{3}m\)-structure change at increasing of the pressure. At various pressures, the parameters of structures with isotropic stress tensor are different.

1. Introduction
Currently, actinides and their compounds have been studied because of the huge interest in using these substances as nuclear fuel. Due to the high thermal conductivity, high melting temperature and high density, uranium mononitride (UN) is promising fuel for fourth-generation reactors. Consequently, the proper phase diagram is important for further understanding of the nitride behaviour under irradiation.

Pressure-induced phase transition in UN has been the object of plenty of experimental and theoretical researches \cite{1–4}. UN has the cubic structure like NaCl (with the space group \(Fm\overline{3}m\)) at low pressure. According to experimental researches \cite{1,4} the cubic structure of UN turns into rhombohedral structure (with the space group \(R\overline{3}m\)) at pressure about 30 GPa.

In this work, pressure-induced phase transition in UN is studied by atomistic simulation. According to the performed simulation, the cubic structure of UN turns into rhombohedral structure at pressure about 32 GPa. It is shown that parameters of \(R\overline{3}m\)-structure change at increasing of the pressure.

2. Methodology
Basic knowledge about rhombohedral structure are important for further research. We can represent rhombohedral \(R\overline{3}m\)-structure as deformed \(Fm\overline{3}m\)-structure. Also we can represent cubic \(Fm\overline{3}m\)-structure as the combination of two simple face-centered cubic (fcc) lattices: fcc lattice for uranium and fcc lattice for nitrogen. These sublattices are shifted to each other by half a period. Therefore we can analogously represent rhombohedral structure as the combination of two rhombohedral face-centered lattices \cite{2}.
The rhombohedral face-centered structure is defined by two parameters $a_{\text{rhom}}$ and $\alpha_{\text{rhom}}$. It should be noted that rhombohedral structure with parameter $\alpha_{\text{rhom}} = 90^\circ$ is identical to fcc structure (see figure 1a).

Triple-hexagonal structure is used because it is more convenient to perform calculations using triple-hexagonal representation than rhombohedral. It is considered by crystallography that any rhombohedral structure can be represented as triple-hexagonal lattice (figure 1b). Parameters of the hexagonal lattice are related to parameters of rhombohedral structure by the formulas:

$$a_{\text{hex}} = a_{\text{rhom}} \sin \frac{\alpha_{\text{rhom}}}{2},$$

$$c_{\text{hex}} / a_{\text{hex}} = 3 \sqrt{\frac{1}{\sin \frac{\alpha_{\text{rhom}}}{2}} - \frac{4}{3}}.$$

It should be noted that $Fm\overline{3}m$ structure (like NaCl) is identical to triple hexagonal structure with ratio of the parameters $c_{\text{hex}} / a_{\text{hex}} = 2.45$.

The analysis of structure is based on the simple thermodynamic law: Gibbs free energy $G$ of thermodynamic system reaches minimum if system is stable at constant temperature and constant pressure. The equation $G = U + PV - TS \approx U + PV = H$ is correct at low temperature. Therefore, the most stable structure at low temperature has a minimum of enthalpy. In addition, the structure having anisotropy of stress tensor is unstable. To sum up, we need to find out such parameters of the structure that meets two conditions at given pressure. The first condition is isotropy of stress tensor and the second one is that the system has the minimum of enthalpy.

We created the calculated cell of rhombohedral structure ($R\overline{3}m$) to carry out the simulation. The orthogonal bases were made and coordinates of U and N were found at those bases. The calculations were performed by using package LAMMPS [5]. The calculated system contains 1500 atoms and has periodic boundaries. A time step of 0.1 fs was used at simulations with non-zero temperatures.

The interatomic angular dependent potential [6] was used for description of uranium mononitride [7]. The potential was created using force-matching technique, previously the same method was used in [8]. The used potential describes energetic properties of point defects and thermodynamic properties in consistency with density functional theory calculations.

3. Results

In this work we carried out the calculation of enthalpy of $R\overline{3}m$-structures with different values of the parameter $c_{\text{hex}}$ and $a_{\text{hex}}$. The pressure was changed from 0 to 60 GPa. The calculation
Figure 2. The enthalpy of structures with different ratio of the parameters $c_{\text{hex}}/a_{\text{hex}}$ at various pressures: a) 10 GPa, b) 20 GPa, c) 32 GPa, d) 55 GPa. The results of this work and calculation from work [2] are shown.

was performed at zero temperature. The results show that enthalpy reaches the minimum at $c_{\text{hex}}/a_{\text{hex}} = 2.45$ at low pressure (figure 2a). It means that the cubic structure is the most stable at low pressure. As we can see in figure 2b, another local minimum appears at higher pressures (ratio $c_{\text{hex}}/a_{\text{hex}}$ belongs to the interval from 2.9 to 3.0). Also figure 2b shows the difference between the results of quantum calculation from [2] and the results of our simulation. In work [2], the pressure-induced phase transition takes place at pressure about 18 GPa. In this work $R\bar{3}m$-structures become stable at pressure about 32 GPa when local minimum turns into absolute minimum (figure 2c). This fact is confirmed by the further increasing of pressure (figure 2d). This result agrees well with experimental research [1] where pressure-induced phase transition occurs at pressure about 30 GPa.

It should be noted that the used interatomic potential gives the ratio of the elastic constants $C_{12}/C_{44} \approx 1.8$ at zero pressure. This value is closer to experimental data ($\approx 1.3$) in comparison with the calculated ratio in [2] and [3] where $C_{12}/C_{44}$ were equal 4.6 and 2.8, respectively. This circumstance confirms that the used potential more correctly describes the type of interatomic forces (see discussion in [2,3]). This fact takes place despite similarity of the calculations in [2,3]
Figure 3. The dependence of ratio $c_{\text{hex}}/a_{\text{hex}}$ on pressure. The results of this work and calculation from work [3] are shown.

Figure 4. Relative volume of UN as a function of pressure. Black dots are experimental data [1] at room temperature; red dashed line is theoretical data [2] for rhombohedral structure at zero temperature; black line is isotherm for cubic structure at zero temperature (this work); blue triangles correspond to rhombohedral structure at zero temperature (this work).

and the basic calculations at the development of the used potential. The one of possible reasons of such achievement is the choice of the interatomic potential type. The force-matching method allows in some cases to improve the description of matter in comparison with initial quantum calculations. This question will be studied in detail in the future works.

Figure 2 shows that the $c_{\text{hex}}/a_{\text{hex}}$ ratio of the most stable rhombohedral structure depends on pressure. Unfortunately, we cannot calculate this dependence accurately just using only dependence of enthalpy on $c_{\text{hex}}/a_{\text{hex}}$. Using the condition of the isotropy of stress tensor a more precise calculation was performed. This type of calculation is performed at $T = 0$ K. For example, the structure with $c_{\text{hex}}/a_{\text{hex}} = 2.94$ has the isotropy of stress tensor only at the
pressure 36 GPa. The performed calculations show that there are no other structure with different \( c_{\text{hex}}/a_{\text{hex}} \) ratio that belongs to the interval from 2.9 to 3.0 which is isotropic at the same pressure. The dependence of \( c_{\text{hex}}/a_{\text{hex}} \) for isotropy structure on the pressure is shown in figure 3. We can see that isotropy appears at the pressure about 33 GPa which corresponds to the pressure-induced phase transition. Also figure 4 shows the similar dependency from work [3].

To compare our results to other works, it is useful to plot a pressure-volume diagram, which is shown in figure 4. The figure shows that our results agree well with experimental data [1]. It is also interesting that, according to Bihan [1], density changes to 0.8% during the phase transition; according to Olsen [4], it changes to 3.2%; in our work, density changes to 0.7%.

4. Conclusion
The method of atomistic simulation gives a pressure of cubic-rhombohedral phase transition about 32 GPa. This result agrees with other experimental and theoretical data well (32–37 GPa in [1], 26 GPa in [3]). \( c_{\text{hex}}/a_{\text{hex}} \) ratio of stable structure is shown to increase with pressure.

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- http://commons.wikimedia.org/wiki/File:Rhombohedral.svg,
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