

Morse Parameters of α -Uranium by Ab-initio Calculation

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1. Introduction

Uranium oxide fuels are mainly used in conventional nuclear power reactors. Nowadays, uranium alloys are actively being developed for fast reactors and research reactors [1-4]. For fuel design, the effects of radiation damage on the fuel performance should be considered. However, there are limitation to the experiments of radioactive materials. Computer simulation can help to overcome these limitations.

Molecule dynamics (MD) is widely used to predict material properties and structures, understand the atomic motion and identify a mechanism in chemical reactions. There are two types of MD; *ab-initio* MD and classical MD. *Ab-initio* MD provides accurate and reliable results. However, it is affected by the system size and timescale. Only hundreds of atoms and several picoseconds are generally calculated. On the other hand, classical MD is suitable for large scale calculations such as plastic deformation and radiation damage. However, the accuracy of classical MD is dependent on interatomic potentials.

There are many types of interatomic potentials. Many body potentials such as embedded atom method (EAM) [5,6] and modified embedded atom method (MEAM) [7] are usually used for alloys. However, the many body potentials exist only in popular materials and to development of new many body potentials is complicated. When proper many body potentials do not exist, Morse potentials can be used instead of many-body potentials. There are applications of the Morse potential function to cubic structure metals. However, there is no application to orthogonal structure such as α -uranium. In this study, we obtained Morse potential function of α -uranium using the result of *ab-initio* and analyze the reliability by comparing it to the existing potentials of uranium [8,9].

2. Methods and Results

The details of *ab-initio* and results of *ab-initio* are described in Section 2.1. In 2.2 section, the theory of Morse potential is described and Morse parameters are described. The results of MD simulation with Morse potential and previous potentials of uranium are described and compared in Section 2.3.

2.1 *Ab-initio* calculation

Ab-initio calculation is based on density functional theory(DFT) which is implemented in the Vienna *ab*

initio Simulation Package (VASP) [10,11]. The plane-wave basis set with an energy cutoff of 550eV within the framework of the projector augmented wave (PAW) method [12,13] is used to describe the valence electrons. The exchange-correlation functional parameterized in the generalized gradient approximation (GGA) [14] by Perdew, Burke, and Ernzerhof (PBE) [15] is used. We treat $6s^2 6p^6 7s^2 5f^3 6d^1$ as valence electrons for α -U. A Monkhorst-Pack k-points grid [16] is used for sampling of the Brillouin zone, with an $18 \times 9 \times 11$ mesh. The partial occupancies are set using the Methfessel-Paxton method [17] of order one with a smearing width of 0.2 eV. The electronic and ionic optimizations are performed using a Davidson-block algorithm [18] and a Conjugate-gradient algorithm [19], respectively. The stopping criteria for self-consistent loops are 0.1 meV/cell and 1 meV/cell tolerance of total energy for the electronic and ionic relaxation, respectively. Bulk modulus is calculated by elastic constants. Elastic constants are calculated as the displacement of all atoms by 0.015 Å with x, y, and z direction. The rotationally invariant DFT + U method introduced by Dudarev et al. [20], Eq. (2.5) is used for $5f^3$ electrons in α -U with $U_{\text{eff}} = 1.24$ eV [21] and $U_{\text{eff}} = 1$ eV.

The results of *ab-initio* calculation are listed in Table I. We choose $U_{\text{eff}} = 1$ eV for later calculation because it is more similar with experimental data than $U_{\text{eff}} = 1.24$ eV.

Table I: Ground-state properties of α -U. Volume and lattice constants are in units of Å, the bulk modulus in GPa, and the cohesion energy in eV/atom. Experimental lattice constants are measured at about 4 K [22], the bulk modulus is measured at room temperature [23], cohesion energy is obtained at 0 K [24].

	$U_{\text{eff}} = 1.24\text{eV}$	$U_{\text{eff}} = 1\text{eV}$	Ref [25]	Exp.
V/N	20.86	20.71	20.67	20.58
a	2.862	2.851	2.845	2.844
b	5.868	5.863	5.818	5.869
c	4.97	4.956	4.996	4.932
u	0.1004	0.1	0.1025	0.1023
B	135.4	136.5	133	135.5
E_c	-5.27	-5.46	-	-5.55

2.2 Morse potential parameters

The potential energy $\varphi(r_{ij})$ of two atoms i and j separated by a distance r_{ij} is given in terms of the Morse function by

$$\varphi(r_{ij}) = D_e \left\{ e^{-2\alpha(r_{ij}-r_0)} - 2e^{-\alpha(r_{ij}-r_0)} \right\}, \quad (1)$$

where α is a constant with dimensions of reciprocal distance, r_0 is the equilibrium distance of the two atoms, and D_e is dissociation energy.

It is necessary to sum Eq. (1) to obtain the potential energy of the whole crystal. The total potential energy is given by

$$\Phi = \frac{1}{2} N D_e \sum_j \left(e^{-2\alpha(r_j-r_0)} - 2e^{-\alpha(r_j-r_0)} \right), \quad (2)$$

where N is the total number of atoms in crystal and r_j is the distance from the origin to the j th atom.

It is convenient to define the following quantities

$$\beta = e^{\alpha r_0}, \quad r_j = M_j a, \quad (3)$$

where M_j is the position coordinates of j th atom in the lattice with a lattice constant, a . The structure of α -uranium is orthogonal. So, internal parameters such as b/a ratio, c/a ratio, and u are needed to express position coordinate as the ratio of a .

Then, the total potential energy can be rewritten as

$$\Phi(a) = \frac{1}{2} N D_e [\beta^2 \sum_j e^{-2\alpha a M_j} - 2\beta \sum_j e^{-\alpha a M_j}]. \quad (4)$$

At $T = 0\text{K}$, a_0 is the equilibrium lattice constant. Then, $\Phi(a_0)$ is the energy of cohesion, the first derivative of Φ at a_0 is equal to 0, and the second derivative of Φ at a_0 is related to the bulk modulus. That is,

$$\Phi(a_0) = N * E_c, \quad (5)$$

where E_c is the cohesion energy per atom at zero pressure and temperature,

$$\left(\frac{d\Phi}{da} \right)_{a_0} = 0, \quad (6)$$

and the bulk modulus is given by

$$B = V_0 \left(\frac{d^2\Phi}{dV^2} \right)_{a_0} = \frac{1}{9cNa_0} \left(\frac{d^2\Phi}{da^2} \right)_{a=a_0}, \quad (7)$$

with

$$V/N = ca^3$$

where V_0 is the equilibrium volume at zero temperature, B is the bulk modulus at zero temperature and pressure, and c varies with the crystal structure.

Solving Eq. (6), we obtain

$$\beta = \frac{\sum_j M_j e^{-\alpha a M_j}}{\sum_j M_j e^{-2\alpha a M_j}}. \quad (8)$$

From Eqs. (4), (5), (6), and (7), we derive the relation

$$\frac{\beta \sum_j e^{-2\alpha a M_j} - 2 \sum_j e^{-\alpha a M_j}}{4\alpha^2 \beta \sum_j M_j^2 e^{-2\alpha a M_j} - 2\alpha^2 \sum_j M_j^2 e^{-\alpha a M_j}} = \frac{E_c}{9ca_0 B}. \quad (9)$$

We obtain α and β by solving Eqs. (8) and (9). We solve Eqs. (8) and (9) with the iteration method. Substituting the α and β into above Eqs, we obtain r_0 and D_e . In other words, the Morse potential parameters α , r_0 , and D_e are determined by the lattice parameters, bulk modulus, and cohesion energy per atom.

The Morse potential parameters are listed in Table II. These values are calculated by *ab-initio* calculation in section 2.1.

Table II: Morse potential parameters of α -U. Units of α , r_0 , and D_e are \AA^{-1} , \AA , and eV, respectively.

Structure	α	r_0	D_e
α -U, A20, ort.	1.2144	3.3751	0.5933

2.3 MD simulation

For the computation of the reference potentials and the obtained potential in this study, we need to create a structure of α -U. The structure contains about 4000 atoms in a simulation box with the periodic boundary conditions in all three dimensions. For each of the simulations we perform a 5 ps MD-run for equilibrium at 0K temperature. Classical MD calculations are performed using the LAMMPS code [26].

The results of MD simulations are listed in Table III. Orthogonal structure is slightly distorted. It seems that orthogonal structure is difficult expressed with Morse potential function. This is because Morse potential function is not considered about directionality and orthogonal structure is anisotropic.

Table III: Ground-state properties of α -U at 0K using MD simulation with Morse potential, MEAM, and EAM. Volume and lattice constants are in units of \AA , the bulk modulus in GPa, and the cohesion energy in eV/atom.

Property	This Work	MEAM[8]	EAM[9]	Exp.
V/N	20.55	21.09	20.10	20.58
a	3.074	2.721	2.824	2.844
b	5.325	6.381	5.762	5.869
c	5.021	4.858	4.941	4.932
u	0.167	0.093	0.1015	0.1023
E_c	-5.67	-5.55	-4.28	-5.55

3. Conclusions

Morse potential functions for the α -uranium by using results of the *ab-initio* calculations. And the lattice constants and cohesive energy are calculated by MD simulations with Morse potential and other reference many body potentials. The orthogonal structure is distorted during relaxation because orthogonal structure is anisotropic. Therefore, even though Morse potential is used as a substitute for many body potentials with BCC and FCC materials, Morse potentials must be used carefully in anisotropic materials such as α -uranium.

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