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Calculations of thermodynamic properties of PuO_2 by the first-principles and lattice vibration

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ABSTRACT

Plutonium dioxide (PuO_2) is a key compound of mixed oxide fuel (MOX fuel). To predict the thermal properties of PuO_2 at high temperature, it is important to understand the properties of MOX fuel. In this study, thermodynamic properties of PuO_2 were evaluated by coupling of first-principles and lattice dynamics calculation. Cohesive energy was estimated from first-principles calculations, and the contribution of lattice vibration to total energy was evaluated by phonon calculations. Thermodynamic properties such as volume thermal expansion, bulk modulus and specific heat of PuO_2 were investigated up to 1500 K.

1. Introduction

Plutonium, which is generated in an operating nuclear reactor due to transmutation of uranium, is one of the important element as nuclear fuel. It is necessary to evaluate the thermodynamical properties at high temperature for development of nuclear fuel. Sobolev proposed a semi-empirical model to calculate the thermodynamical properties based on simple models of phonon and electron spectra [1]. In this paper, we propose a theoretical model based on first-principles results. The first-principles calculations are limited to a few 100 atoms and do not provide the concept of temperature. Generally, first-principles calculations are performed for the ground state, i.e., at zero temperature. Recently, a coupling of first-principles calculation and lattice dynamics has been shown to provide computational thermodynamic data [2–4].

In this paper, we apply the coupling method to evaluate thermodynamic properties based on first-principles results. First-principles molecular dynamics simulation has been carried out using the Vienna Ab Initio Simulation Package (VASP) [5], which is a density functional theory-based code for systems with periodic boundary conditions. The electron cohesive energy and the electronic structure have been calculated by the projector augmented-wave (PAW) method within the generalized gradient approximation (GGA) for exchange-correlation density and potential, using the Perdew–Wang parameterization. The calculations were performed with the HITACHI/SR-8000 at Tohoku University. The phonon code by Parlinski [6] was used to calculate the vibrational properties.

2. Computational methodology

2.1. Thermodynamical quantities

Kuwabara calculated phonon vibrations and their density of states in ZrO_2 by first-principles lattice dynamics calculations [3]. To compute thermodynamical quantities such as specific heat, the phonon contribution to the Helmholtz free energies was investigate as follows;

$$F(V,T) = E_c(V,0\,\mathrm{K}) + F_{ph}(V,T) + F_{el}(V,T), \tag{1}$$

where V is the volume, T is the temperature, $E_C(V,0\,\mathrm{K})$ is the volume-dependent cohesive energy from first-principles calculations. F_{ph} is a lattice vibration energy, which is calculated based on the phonon density of states. F_{el} is an electron excitation energy. Here we focused on only the contribution of atom vibrations. Thus the energy of electron excitation is not discussed. The lattice vibration energy F_{ph} is given by,

$$F_{ph}(V,T) = k_B T \sum_{\mathbf{q}} \sum_{j} \ln\left(2\sinh\frac{\hbar\omega(\mathbf{q},V)}{2k_B T}\right), \tag{2}$$

where $\hbar$ and k_B are reduced Plank constant and Boltzmann constant, respectively. $\omega(\mathbf{q},V)$ represents a vibration frequency of jth phonon at wave vector $\mathbf{q}$.

The specific heat for constant volume C_V is obtained directly from,

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$$C_V = \left(\frac{\partial F}{\partial T}\right)_V = rk_B \int_0^\infty g_{vib}(\omega)\left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{\exp\frac{\hbar\omega}{k_BT}}{\left(\exp\frac{\hbar\omega}{k_BT}-1\right)^2} d\omega, \tag{3}$$

where r is the degree of freedom, g_{vib} is the phonon density of states. Then the specific heat at constant pressure C_P is given by,

$$C_P - C_V = \alpha_V^2(T)\beta(T)V(T)T, \tag{4}$$

where the constant volume thermal expansion α_V is defined by,

$$\alpha_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p. \tag{5}$$

In order to relate the energy and thermal properties, the third-order Birch–Murnaghan equation of state (BMEOS) is used. Let x be V_0/V,

$$F(V) = E_0 + \frac{9V_0\beta}{16}\left(\left(x^{\frac{2}{3}}-1\right)^3\beta' + \left(x^{\frac{2}{3}}-1\right)^2\left(6-4x^{\frac{2}{3}}\right)\right), \tag{6}$$

where V_0 is the reference volume at 0 K. The bulk modulus $\beta(T)$ of a fluid or a solid given by Eq. (7) is the inverse of the compressibility,

$$\beta(T) = -V\frac{\partial P}{\partial V}, \tag{7}$$

where P is the pressure. The bulk modulus measures the response in pressure due to a change in relative volume, essentially measuring the substance resistance to uniform compression. $\beta' = \partial\beta/\partial P$ is the pressure derivative of bulk modulus.

3. The first-principles and lattice vibration calculations

The first-principles and phonons calculations were carried out with 96 atoms for a perfect crystal of $Pu_{32}O_{64}$ that corresponds to a 2 × 2 × 2 unit cell of fluorite structure.

To obtain the thermodynamic data from the first-principles calculation at 0 K, generalized gradient approximation (GGA) was applied and spin polarization was taken into account, and an energy of 500 eV was chosen for the plane-wave cutoff.

A direct method was applied to evaluate the vibrational contribution to the total free energy. We induced single displacements of non-equivalent atoms of the supercell to calculate the force constants from Hellmann–Feynman forces from first-principles calculations. A harmonic approximation for each lattice constant, i.e., quasi-harmonic approximation has been applied. This enabled us to take a thermal expansion into account. A quasi-harmonic approximation that assumes phonon frequencies that only depend on the cell parameters was considered here.

Then a relation between the Helmholtz free energy F and the volume V (F–V curve) was obtained for various temperatures and volumes by Eq. (2).

4. Result and discussion

4.1. Phonon dispersion and the density of states

The phonon band structure and the density of states for a perfect crystal of PuO_2 are shown in Fig. 1. The contribution of the lattice vibrations to the total energy can be obtained from the density of states by Eq. (2).

Plutonium atom is heavier than oxygen atom, thus the vibration frequency of plutonium atom is lower than that of oxygen atom. Therefore, the phonon density of states splits into two parts, one is the lower part up to 5 THz where the vibrations of plutonium atoms are dominant and the other part at higher frequencies where the vibrations of oxygen atoms are dominant. Thus mainly the thermal conductivity depends on the vibrations of plutonium at lower frequencies in Fig. 1.

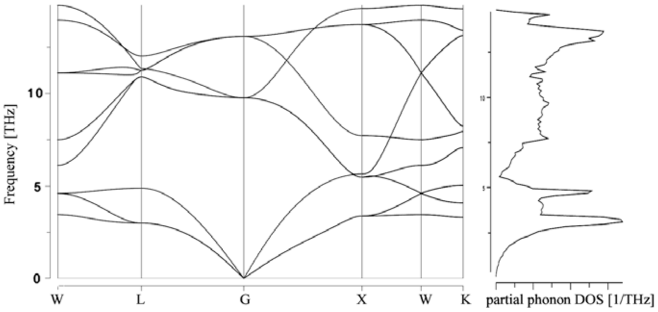

Fig. 1. Phonon dispersion and the density of states of PuO_2.

4.2. Total energy and equilibrium lattice parameter

Fig. 2 shows the Helmholtz free energy at each temperature from 0 K to 1500 K. In order to determine the bulk modulus $\beta(T)$, its derivative $\beta'(T)$ and the equilibrium lattice volume V, we applied the third-order Birch–Murnaghan equation of state (BMEOS) and fitted to the total energy F at each temperature [7].

Minimum points of each (F–V) curve in Fig. 2 mean equilibrium lattice parameters at every temperature. Thus, as temperature increases, the minimum of the free energy curve shifts to larger lattice parameter. The resulting lattice constant at room temperature is 5.399 Å in Fig. 2, while the experimental lattice constant is 5.396 Å.

The bulk modulus for PuO_2 has not been measured experimentally, however, bulk modulus for other similar compounds have been measured. The result of the bulk modulus of PuO_2 from this study is 266 GPa at room temperature, which is realistic compared to other data from Sobolev [1]. For example the bulk modulus of 211 GPa of UO_2 at room temperature, and 198 GPa of ThO_2 were reported [1]. Fig. 3 shows the temperature dependence of the bulk modulus.

4.3. Bulk modulus and lattice parameter

Theoretical and experimental lattice parameters are shown in Fig. 4. A lattice parameter of 5.386 Å at 0 K was used to evaluate

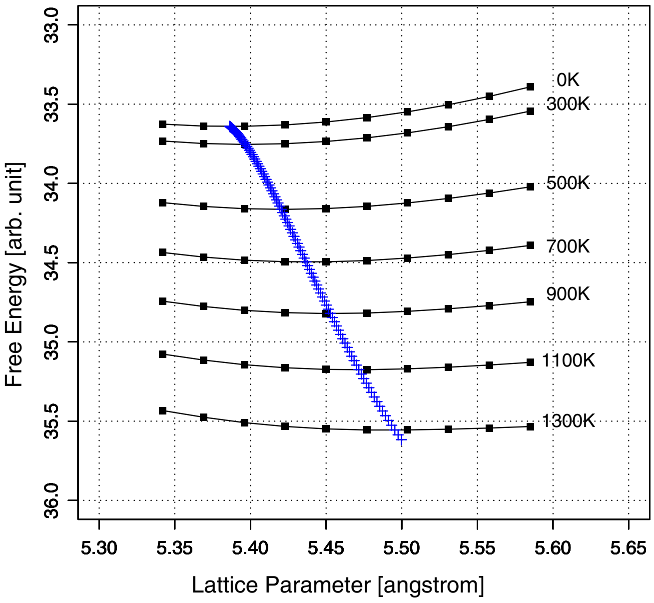

Fig. 2. Helmholtz free energy curve at various temperatures (solid line) and the locus of the minimum of the free energy (symbol "+") for PuO_2.

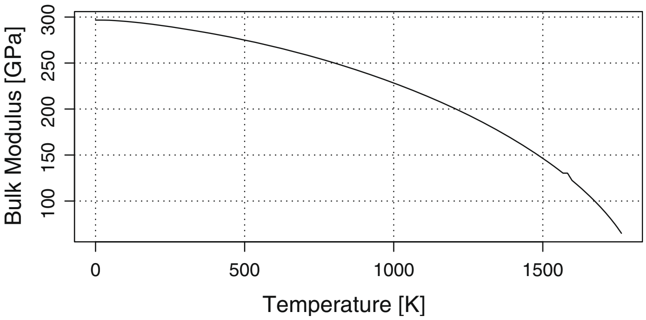

Fig. 3. Temperature dependence of the bulk modulus of PuO_2.

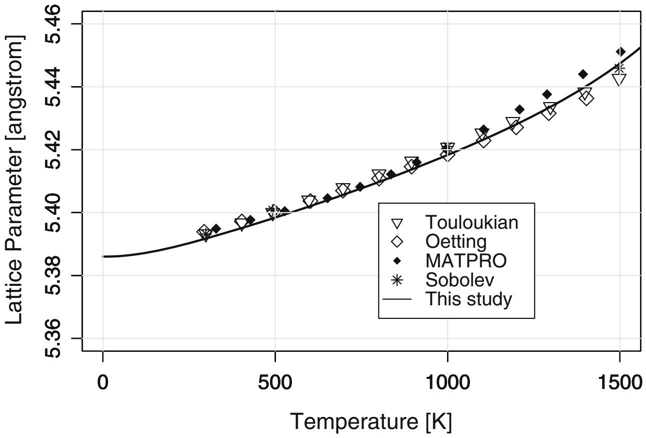

Fig. 4. Calculated and experimental lattice parameters of PuO_2.

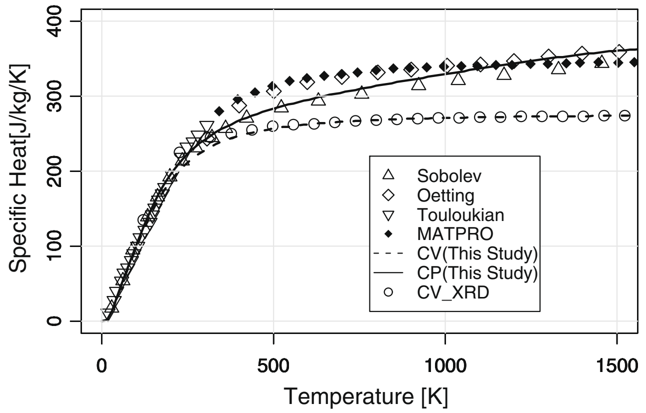

Fig. 5. Calculated and experimental specific heats of PuO_2 (Solid line: calculated specific heat at constant pressure. Dotted line : calculated specific heat at constant volume).

the experimental coefficients of thermal expansion (CTE) [8–11]. The CTE was obtained with equilibrium lattice parameter at various temperatures from a free energy fit to a BMEOS.

4.4. Specific heat

Calculated and experimental C_P [9–11] are shown in Fig. 5. Here we applied the exact expression for α, i.e., fitted to a higher-order polynomial and obtained derivatives analytically from Eq. (5). The disagreement of specific heat at constant pressure at the medium temperature (300–1000 K), also reported by Sobolev [1] can be attributed to the mismatch of the bulk modulus β or mass of atoms [12]. However as Sobolev pointed out that the difference between the calculated and the experimental specific heat in the medium temperature was still a problem. Some models except for lattice vibration have been suggested to improve the disagreement [13,14].

5. Conclusion

The thermodynamic properties of PuO_2 have been investigated at finite temperature with a combination of first-principles and lattice dynamics calculations. In the framework of GGA and quasi-harmonic approximation, the Helmholtz free energy was obtained as a function of volume and temperature. With the derived free energy, equilibrium lattice parameter and bulk modulus were obtained by fitting to the third-order Birch–Murnaghan EOS. The calculated lattice parameter, thermal expansion coefficient, and specific heat reproduced the experimental data well up to 1500 K. It is noteworthy that the thermodynamic properties of PuO_2 were evaluated with no experimental data.

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