Journal of Nuclear Materials 404 (2010) 6–8

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Ab initio interionic potentials for UN by multiple lattice inversion

P.H. Chen [a,*], X.L. Wang [b], X.C. Lai [a], G. Li [a], B.Y. Ao [a], Y. Long [c]

[a] *State Key Laboratory for Surface Physics and Chemistry, Mianyang 621907, People's Republic of China*
[b] *China Academy of Engineering Physics, Mianyang 621900, People's Republic of China*
[c] *Institute of Applied Physics and Computational Mathematics, P.O. Box 8009, Beijing 100088, People's Republic of China*

ARTICLE INFO

Article history:
Received 10 March 2010
Accepted 9 June 2010

ABSTRACT

Based on the Chen–Möbius lattice inversion and a series of pseudopotential total-energy curves, interionic pair potentials for UN were derived. By means of molecular dynamic (MD), we have examined this interionic potentials. Comparing with the experimental data, the thermal expansion coefficient and the compressibility were well reproduced by this potentials.

1. Introduction

Uranium–plutonium mixed nitride (U, Pu)N is under consideration as a fast breeder reactor fuel because of its many desirable properties, for instance, high melting point, high fuel density and high thermal conductivity [1]. The thermal properties such as thermal expansion coefficient, compressibility and heat capacity of uranium mononitride (UN) have to be known in order to understand the nitride fuel behavior during irradiation. Recent advances in computer power and simulation techniques have allowed us to simulate the materials behavior on the atomic scale. One of the key problems for the atomistic simulations is how to determine the interionic potentials. In most or the previous work [2–4], the interatomic potentials were started from the selection of interatomic potential function forms with adjustable parameters, and then the potential parameters were obtained by fitting to the experimental data or calculation results, such as lattice parameters, lattice energy, phonon frequencies, and elastic properties. These potentials have played a significant role in previous simulation, especially for the ionic materials with lots of experimental data [5,6]. However, for the ionic solids whose properties are hard to obtain, it is hard to determine which set of potentials is the most appropriate. One of the effective solutions for the uncertainty of multiple-parameter fittings may be the lattice inversion method, which was first presented to determine the pair wise potentials from the ab initio calculated or experimentally measured adhesive energy by Carlsson, Gelatt, and Ehrenreich (CGE) [7], and then Chen used the Möbius-inversion formula in number theory to obtain the pair potentials for the pure metals with faster convergence than the CGE method [8,9].

In this paper, a parameter-free method [10] based on the Chen–Möbius lattice inversion was used to derive interionic potentials for UN. First, we constructed the extended phase space including B1 (rocksalt) and three related structures (Fig. 1). The aim was to derive the proper interionic potentials from an extended phase space including equilibrium and nonequilibrium states. This could cover more configurations and interionic spacing of our interest than that only from one equilibrium configuration. Second, the pseudopotential total-energy calculations for four-type UN crystals were performed from lattice constant $\alpha = 4–22$ Å. Finally, the pair potential curves were directly evaluated from a series of the total-energy difference based on Chen–Möbius lattice inversion techniques [8,9]. Then the suitable function forms were selected to fit the pair potential curves. Furthermore, these inverted pair potentials were used to describe the thermal expansibility and compressibility of UN.

2. Computational models

2.1. Total energy calculation for B1-, B3-, T1- and T2-type UN

According to lattice inversion [8,9], in order to extract three kinds of pair potential, ϕ_{+-}, ϕ_{++} and ϕ_{--}, we calculated the pseudopotential total-energy of UN in the B1, B3, T1 and T2 structures with lattice constant α from 4.0 to 22 Å. These calculations were performed using the Vienna ab initio simulation package (VASP) [11–13]. Exchange and correlation are treated in the GGA with the function of Perdew and Wang (PW91) [14]. The K-mesh points over the Brillouin Zone are generated with parameters $4 \times 4 \times 4$ for the largest reciprocal space and $1 \times 1 \times 1$ for the smallest reciprocal space by the Monkhorst–Pack scheme [15]. The energy tolerance for self-consistent-field (SCF) convergence is 10^{-5} eV/atom with the plane wave energy cut-off of 550 eV. The total energies as a function of lattice constant α are shown in Fig. 2.

---

* Corresponding author. Tel.: +86 816 3626738; fax: +86 816 3626739.
E-mail address: chenph@live.cn (P.H. Chen).

0022-3115/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2010.06.017

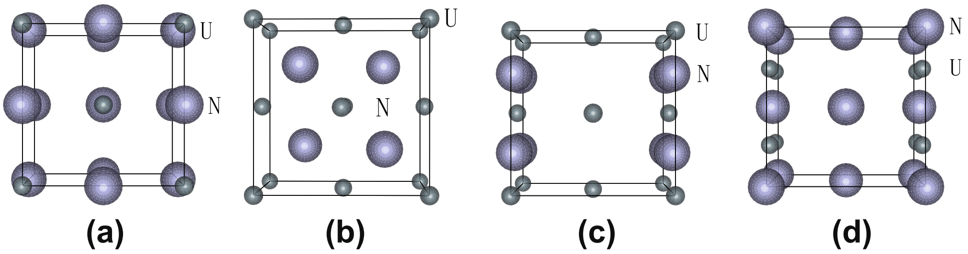

Fig. 1. Virtual structures used for ab initio pseudopotential total-energy calculations. (a) B1 (rocksalt) structure; (b) B3 (zinc blende) structure (virtual structure for cation–anion interaction); (c) T1 structure (virtual structure for anion–anion interaction); (d) T2 structure (virtual structure for cation–cation interaction).

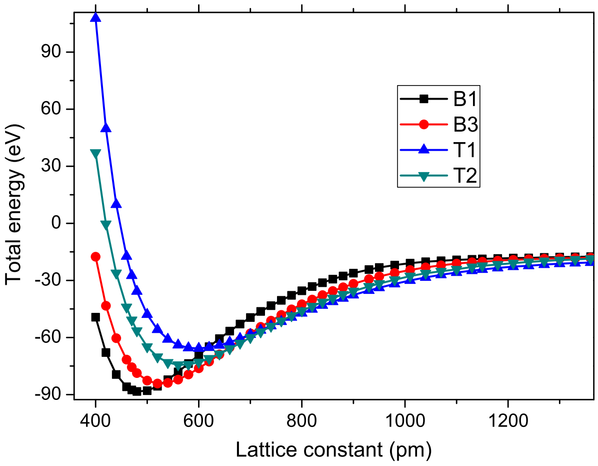

Fig. 2. Total energy versus lattice constant α of the NU polymorph from the VASP calculation.

2.2. Chen–Möbius lattice inversion

With the identical lattice constant α, the difference between B1 and B3 structures is only about the U^{+}–N^{-} distance. Then the total-energy difference $E_{B1}-E_{B3}$ between B1 and B3 only depends on the U^{+}–N^{-} interaction, and can be rewritten as:

$$E_{B1}-E_{B3}=\frac{1}{2}\left(\sum_{B1}\phi_{+-}(r_{ij})-\sum_{B3}\phi_{+-}(r_{ij})\right). \tag{1}$$

where ϕ_{+-} is the cation–anion pair potential and r_{ij} is the separation between ions at lattice site i and j ($i \neq j$). Then ϕ_{+-} can be solved from Eq. (1) by Chen–Möbius lattice inversion [8,9]. For the anion–anion potential, since the B1 and T1 structures have the same U sublattice for the lattice constant α, the total-energy difference $E_{B1}-E_{T1}$ between B1 and T1 should be independent of the cation–cation spacing and can be express as

$$E_{B1}-E_{T1}=\frac{1}{2}\left(\sum_{B1}\phi_{+-}(r_{ij})+\sum_{B1}\phi_{--}(r_{ij})-\sum_{B3}\phi_{+-}(r_{ij})-\sum_{T1}\phi_{--}(r_{ij})\right). \tag{2}$$

Using the above inverted U–N pair potential, we can calculate the U–N interaction in B1- and T1-UN crystals, respectively. Then the N–N pair potential ϕ_{--} can be obtained from Eq. (2). By the similar method for N–N pair potential, the U–U pair potential can also be obtained. In terms of the curve shape, Morse functions were selected for U–U, N–N and U–N pair potentials. The final potential parameters are listed in Table 1. The Morse function is :

$$\phi(r_{ij})=D_0\{exp[-2\alpha(r_{ij}-r_0)]-2exp[-\alpha(r_{ij}-r_0)]\}. \tag{3}$$

2.3. Molecular dynamics calculation

One motivating feature for classical molecular dynamic simulation is its ability to simulate finite temperature atomistic properties with no further computational cost, that would be extremely time consuming via first principle approaches. Our MD calculations were carried in a constant temperature–constant volume thermodynamic ensemble (NVT) using LAMMPS package [16]. The MD calculation for UN is performed for a system of 512 ions (U: 256; N: 256) initially arranged in the B1 type crystal structure with periodic boundary conditions applied to reproduce bulk environment. The calculation was made in the temperature range 0–2500 K, and in the pressure range of 0–1.5 GPa. All MD calculations were performed for at least 10,000 time steps, where one time step was 1×10^{-15} s and r_{cutoff} = 15 Å.

Table 1
Interionic pair potential parameters obtained in this work. The symbols + and – represent cation and anion, respectively.

Ion pair	D_0 (eV)	α (Å^{-1})	r_0 (Å)
ϕ_{++}	1.1192	1.1000	3.5547
ϕ_{--}	0.2790	1.3950	2.5594
ϕ_{+-}	0.4250	1.1430	3.1602

3. Results and discussion

By means of MD, we calculated the structural and elastic properties of UN. The first important information we can deduce from the results is the thermal expansion, which provides a test of the anharmonicity of the interaction as described by the potentials, since an entirely harmonic crystal has no thermal expansion. The change in the lattice parameter for UN with temperature obtained by the MD calculation controlled at 0.1 MPa are shown in Fig. 3, together with the experimental data [17,18]. From Fig. 3, it can be found that the calculated changes in the lattice parameter of UN with temperature agree well with the reported values.

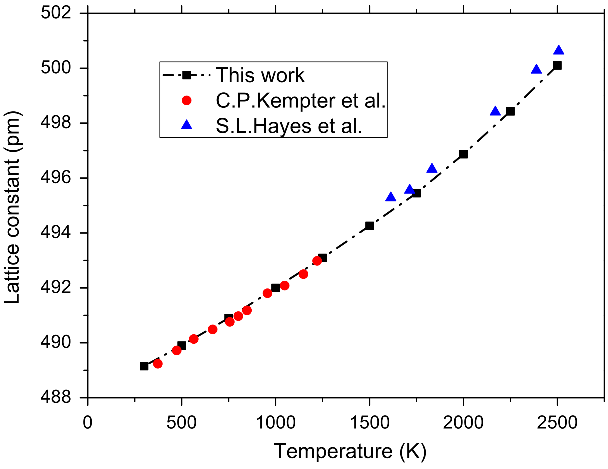

Fig. 3. Change in the lattice constant of UN with temperature.

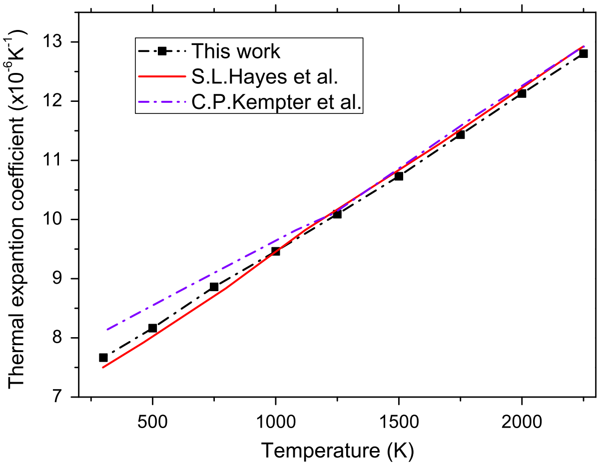

Fig. 4. Calculated linear thermal expansion coefficient of UN as a function of temperature.

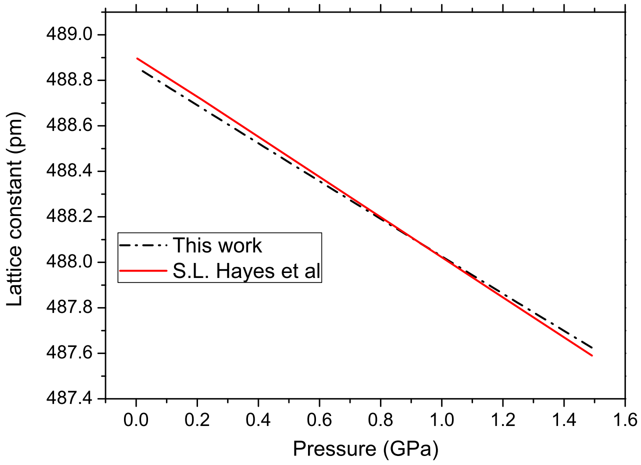

Fig. 5. Change in the lattice parameter of UN with pressure.

The thermal expansion coefficients were computed using the lattice parameter variation versus temperature at zero pressure and the thermodynamic expression:

$$\epsilon(T) = \frac{1}{\alpha_0}\left(\frac{d\alpha}{dT}\right)_{p=0}. \qquad (4)$$

where ϵ is the linear thermal expansion coefficient. The change in the linear thermal expansion coefficient with temperature is shown in Fig. 4, together with the experiment data [17,18]. One can see that the linear thermal expansion coefficient can be well reproduced by this potentials.

The calculated results of the change in the lattice parameter of UN with pressure in the range of 0–1.5 GPa at 300 K are shown in Fig. 5. The calculated lattice parameters were in agreement with the experimental values in the literature [18]. The compressibility (β) at the pressure from 0 to 1.5 GPa was evaluated up to 1800 K, and the temperature dependence of the calculated β for UN is shown in Fig. 6, together with the experimental data [18]. The calculated values of compressibility agreed with the experimental data. These results indicated that the potential function used in the present calculation well describes the changes in the lattice parameter of UN with both temperature and pressure.

Although there have been many interionic potentials for UN [2–4], the scheme in this work has features as as follows. Our interatomic pair potentials cover much larger phase space including not only the B1 phase, but also B3 and two P4/mmm structures with nonequilibrium states. Second, this work is a parameter-free method to derive interionic potentials. The potential functions could be selected in terms of the shapes of the inverted potential curves.

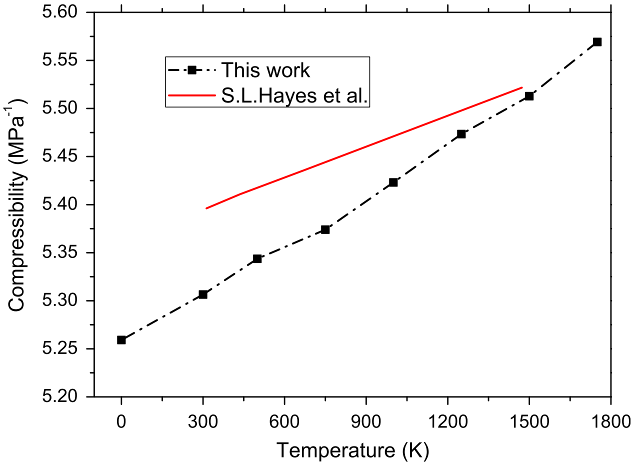

Fig. 6. Temperature dependence of compressibility of UN.

4. Conclusions

In this paper, we carried out density functional theory (DFT) based first principle calculations, using the projected augmented plane-wave (PAW) method in order to determine the total energies of four type UN crystals. The interionic potentials for UN was derived from total energies with multiple-lattice inversion techniques. Based on the potentials, we have applied MD method to examine this interionic potentials. Comparing with the experimental data, the thermal expansion coefficient and the compressibility were well reproduced by this potentials, indicating that the multiple-lattice inversion technique is useful and applicable to estimate the physio-chemical properties of nuclear fuels.

Acknowledgement

This work was supported in part by the Science and Technology Foundation of China Academy of Engineering Physics (No. 2008A0301013).

References

[1] A.A. Bauer, Reactor Technol. 15 (1972) 87.
[2] K. Kurosaki, K. Yano, K. Yamada, M. Uno, S. Yamanaka, J. Alloy. Compd. 297 (2000) 1.
[3] J.G. Rodeja, M. Meyer, M. Hayoun, Model. Simul. Mater. Sci. Eng. 9 (2001) 81.
[4] Y. Ida, Phys. Earth Planet. Inter. 13 (1976) 97.
[5] M. Prencipe, A. Zupan, R. Dovesi, E. Apra, V. Saunders, Phys. Rev. B 51 (1995) 3391.
[6] C.R.A. Catlow, K.M. Diller, M.J. Norgett, J. Phys. C 10 (1977) 1395.
[7] A.E. Carlsson, C.D. Gelatt, H. Ehrenreich, Philos. Mag. A 41 (1980) 241.
[8] N.X. Chen, Z.D. Chen, Y.C. Wei, Phys. Rev. E 55 (1997) R5.
[9] N.X. Chen, N.X. Chen, X.J. Ge, W.Q. Zhang, F.W. Zhu, Phys. Rev. B 57 (1998) 14203.
[10] S. Zhang, N.X. Chen, Phys. Rev. B 66 (2002) 064106.
[11] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558.
[12] G. Kresse, J. Furthmuller, Phys. Rev. B 54 (1996) 11169.
[13] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
[14] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.
[15] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.
[16] S.J. Plimpton, J. Comp. Physiol. 117 (1995) 1.
[17] C.P. Kempter, R.O. Elliott, J. Chem. Phys. 30 (1959) 1524.
[18] S.L. Hayes, J.K. Thomas, K.L. Peddicord, J. Nucl. Mater. 171 (1990) 262.