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A molecular dynamics study of the thermal conductivity of uranium mononitride

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Abstract

The thermal conductivity of uranium mononitride (UN) in the temperature range of 300–2000 K was estimated by molecular dynamics (MD) calculation on the basis of Green-Kubo relation. The Morse-type added to the Busing-Ida type function was adopted as the interatomic potential function. The parameters of the interatomic potential were determined by fitting the changes in the lattice parameters with temperature and pressure to experimental values in the literature. The temperature dependence of the calculated thermal conductivity followed a $1/T$ law, suggesting that the lattice contribution to the thermal conductivity (λ_{lat}) was evaluated by the molecular dynamics calculation. The electronic contribution to the thermal conductivity (λ_{el}) was conjectured by Wiedemann-Franz law using the electrical resistivity data in the literature, and the temperature dependence of $\lambda_{lat}+\lambda_{el}$ was compared with the reported experimental data. The values of $\lambda_{lat}+\lambda_{el}$ obtained in the present study agreed with the literature values of the thermal conductivity. In the present study it was found that the MD simulation technique was useful and applicable to estimate the lattice thermal conductivity of UN.

Keywords: Uranium mononitride, Molecular dynamics; Thermal conductivity

1. Introduction

Uranium–plutonium mixed nitride (U,Pu)N, is under consideration as a fast breeder reactor fuel because of several desirable properties, for instance, high melting point, high fuel density and high thermal conductivity [1]. Physico-chemical properties such as thermal and mechanical properties of uranium mononitride (UN) are required 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. For oxide fuel several molecular dynamics (MD) studies [2–6] of uranium dioxide (UO_2), plutonium dioxide (PuO_2), and uranium–plutonium mixed oxide (MOX) have been performed to estimate the various physico-chemical properties, and the calculated results almost agreed with the experimentally measured values. For nitride fuel, however, only one study about the heat capacity of UN has been reported by the present authors [7].

In the present study, the MD calculation for UN has been performed to evaluate the thermal conductivity in the temperature range of 300–2000 K, and the applicability of the MD method to evaluation of the thermal properties of UN was examined.

2. Molecular dynamics calculation

The MD calculation for UN is performed for a system of 512 ions (U^{3+}, 256; N^{3-}, 256) initially arranged in the NaCl type crystal structure. In the present study the calculation was performed by the molecular dynamics program based on MXDRTO [8]. The standard constant pressure–temperature (NPT) calculation on thermodynamic equilibrium was performed. The quantum effect [9] was taken into account in the present calculation. Fig. 1 shows the MD cell used in the present calculation. The lattice containing a fixed number of atoms was assumed to

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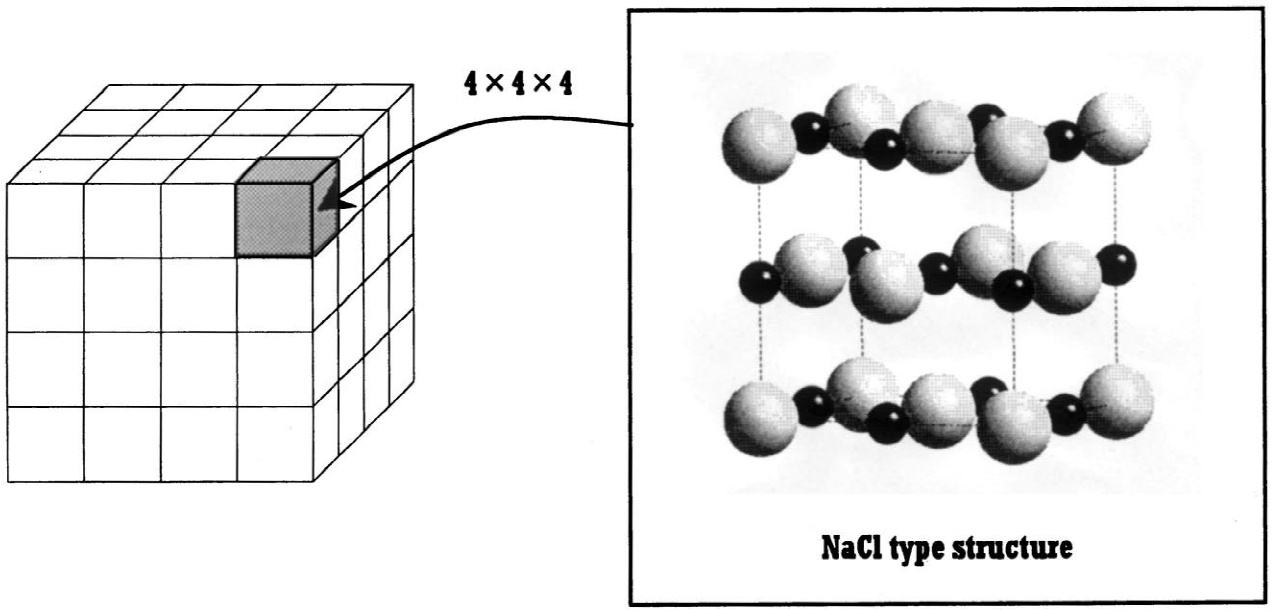

Fig. 1. MD cell used in the present calculation.

be repeated periodically throughout the material, and there was no edge or surface effect.

We employed the potential function proposed by Ida [10] for cation–anion interactions. This potential was a partially ionic model including a covalent contribution,

$$U_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + (b_i + b_j)\exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) + D_{ij}\{\exp[-2\beta_{ij}(r_{ij} - r_{ij}^*)] - 2\exp[-\beta_{ij}(r_{ij} - r_{ij}^*)]$$

where Z_i and Z_j are the effective partial electronic charges on the ith and jth ions, r is the atom distance, r_{ij}^* is the bond length of cation–anion pair in vacuum, and a and b are the characteristic parameters depending on the ion species. D_{ij} and β_{ij} describe the depth and shape of this potential, respectively. The first term is the Coulomb interaction, the second term denotes the core repulsion, and the third term which is called Morse-type [11] potential corresponds to the covalent contribution. The equations of motion were integrated with Verlet's algorithm [12] using an integration time step of 2.0×10^{-15} s. At the start of the calculation the initial velocity of each atom was assumed to take random velocities, which was about 0.01 Å fs^{-1}.

The simulation technique and conditions were the same as those in our previous study [7]. The parameters (Z, a, b, D_{ij}, β_{ij} and r_{ij}^*) and the shape of the effective interatomic potential used in the present study were also the same of the our previous study [7] in which the interatomic potential parameters were determined by trial and error to fit in the experimental values of the thermal expansion coefficient and compressibility [13–17]. To control the pressure and temperature, a combination of the methods introduced by Andersen [18] and Nose [19] was used.

The thermal conductivity of the system was calculated based on the Green–Kubo relation. Because the Green–Kubo theory is a statistical method, the NPT calculation was performed using the methods introduced by Andersen [18] and Nose [19]. The detail of the Green–Kubo relation has been described in the literature [20].

The thermal conductivity of the system has a form based on the following integrated heat flux [$S(t)$] autocorrelation function,

$$K = \frac{V}{3k_B T^2}\int_0^\infty \langle S(t)\cdot S(0)\rangle \, dt$$

where

$$S = \frac{1}{V}\left[\sum_j e_j v_j - \frac{1}{2}\sum_j\sum_{j=i} r_{ij}(f_{ij}\cdot v_{j)}\right]$$

The instantaneous excess energy of atom j, e_j, is described by

$$e_j = \left\{\frac{1}{2}m_j v_j^2 + \frac{1}{2}\sum_{i=j} u(r_{ij})\right\} - e_{av}$$

where e_{av} is the mean energy of the system.

The calculation was made in the temperature range of 300–2000 K at the pressure of 0.1 MPa.

3. Results and discussions

The values of the interatomic potential function parameters used in the present study are summarized in Table 1. By using the interatomic potential function parameters we have succeeded in evaluation of the thermal expansion coefficient (α), compressibility (β), and heat capacity at

Table 1
The potential parameters used in the present calculation

	z	a	b		D	B	r*
N^{3-}	−1.450	1.797	0.080	N^{3-}–U^{3+}	7.00	1.25	2.364
U^{3+}	1.450	1.228	0.080				

constant pressure (CP) for UN [7]. In the present study the thermal conductivity of UN was evaluated by molecular dynamics with the interatomic potential function. In molecular dynamics calculations only the lattice contribution of the thermal conductivity (λ_{lat}) can be calculated. The lattice thermal conductivity is obtained as the plateau value of the time integral of the auto-correlation function (ACF) of the energy current, $\langle S(t)\cdot S(0)\rangle$. Fig. 2 reveals the ACF at each temperature, indicating that the ACF converges on zero and its time integral attains a plateau value. By integrating ACF with respect to time, the thermal conductivity can be calculated. The values of the thermal conductivity at each temperature obtained by conversion from the ACF are illustrated in Fig. 3.

The variation in the calculated thermal conductivity with temperature is shown in Fig. 4 with the previous reported experimental values [21–29]. These experimental data were corrected to 100% of the theoretical density (100% T.D.). The calculated thermal conductivity was significantly lower than the experimental values including the electronic contribution (λ_{el}). The temperature dependence of the calculated thermal conductivity followed a $1/T$ law, suggesting that the λ_{lat} was evaluated by the molecular dynamics calculation.

In order to estimate the validity of the results of the calculated lattice thermal conductivity, the values of $\lambda_{lat}+\lambda_{el}$ were compared with the reported experimental values. The electronic contribution (λ_{el}) can be conjectured by the Wiedemann-Franz law.

$$\frac{\lambda_{el}}{\sigma} = LT$$

where σ is the electrical conductivity and L is the Lorenz number:

$$L = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right) = 2.45\times 10^{-8} \quad (\mathrm{W\,\Omega\,K^{-2}})$$

where k_B is the Boltzmann constant and e is the elementary electric charge. In the present study the λ_{el} of UN was calculated from the electrical conductivity of UN reported by Hayes [30]. Fig. 5 shows the temperature dependence of $\lambda_{lat}+\lambda_{el}$ for UN compared with the reported experimental data [21–29]. The values of $\lambda_{lat}+\lambda_{el}$ obtained in the present study agree with literature values, although they are slightly lower than the experimental data around room temperature. From this study it was found that the MD simulation technique is useful and applicable to estimate the lattice thermal conductivity of UN. This MD simulation technique appears to be applicable to evaluate properties of TRU compounds.

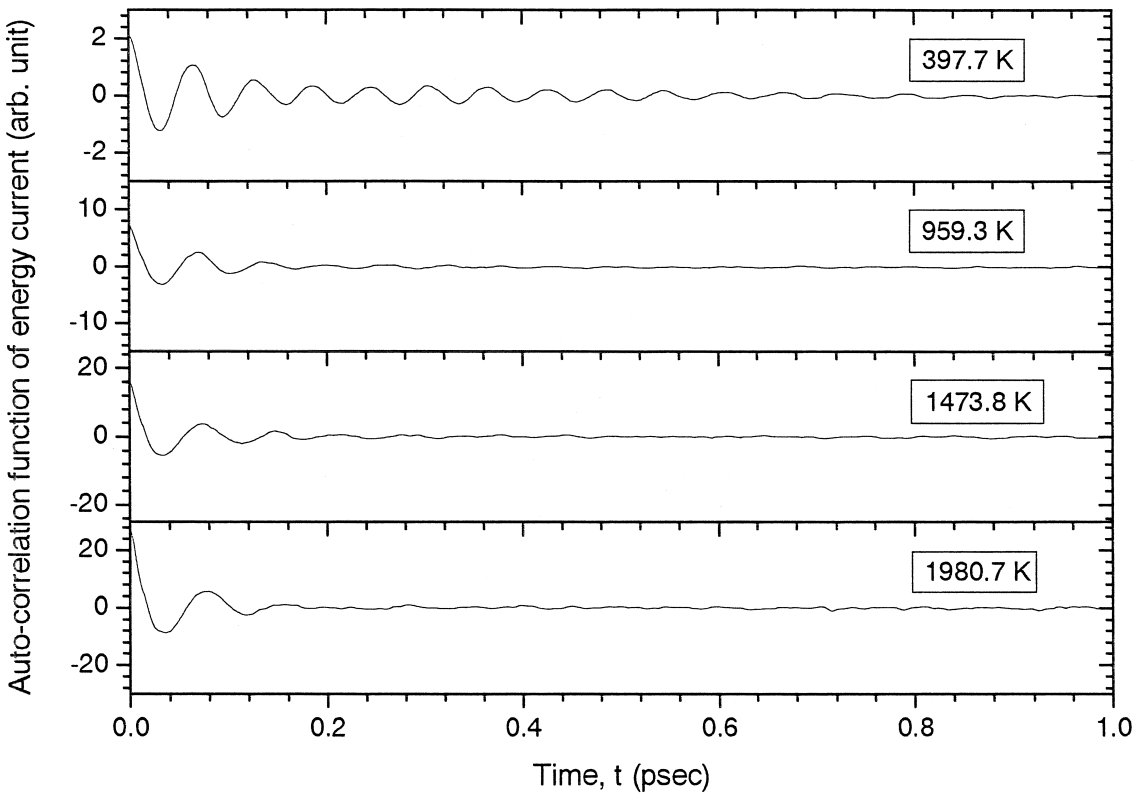

Fig. 2. Auto-correlation function (ACF) of energy current, $\langle S(t)\cdot S(0)\rangle$.

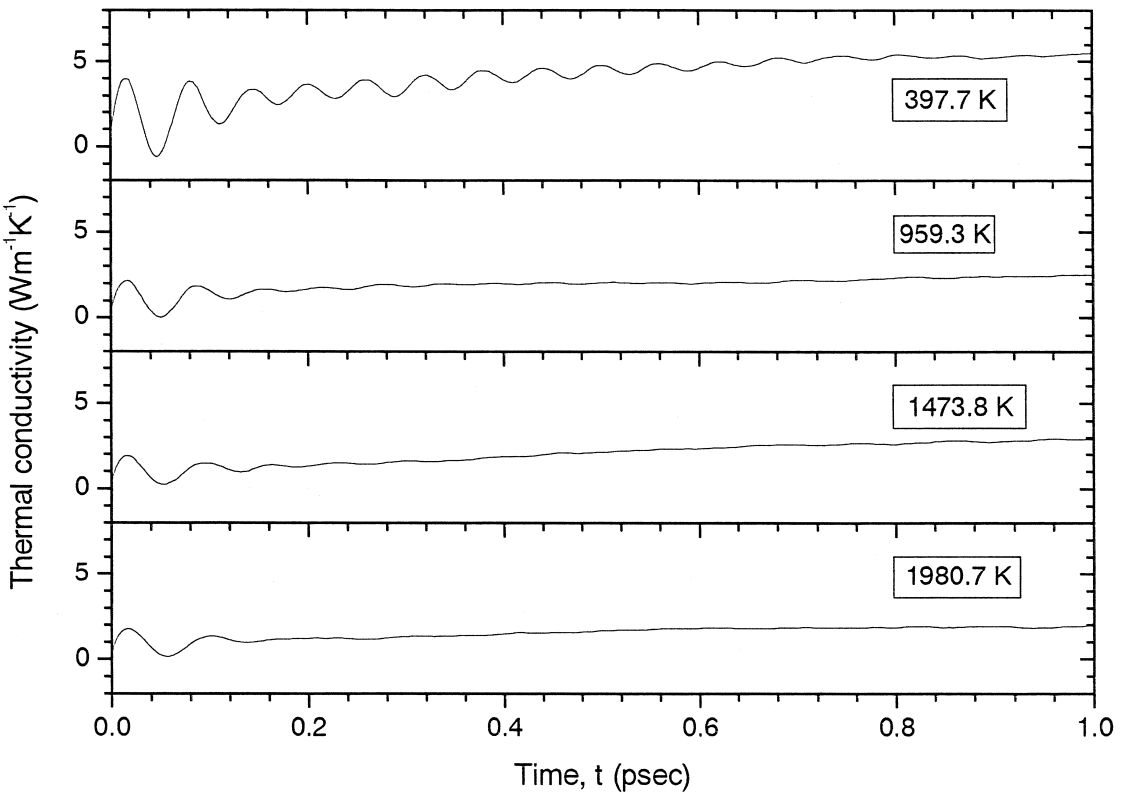

Fig. 3. Calculated thermal conductivity obtained by the conversion from ACF.

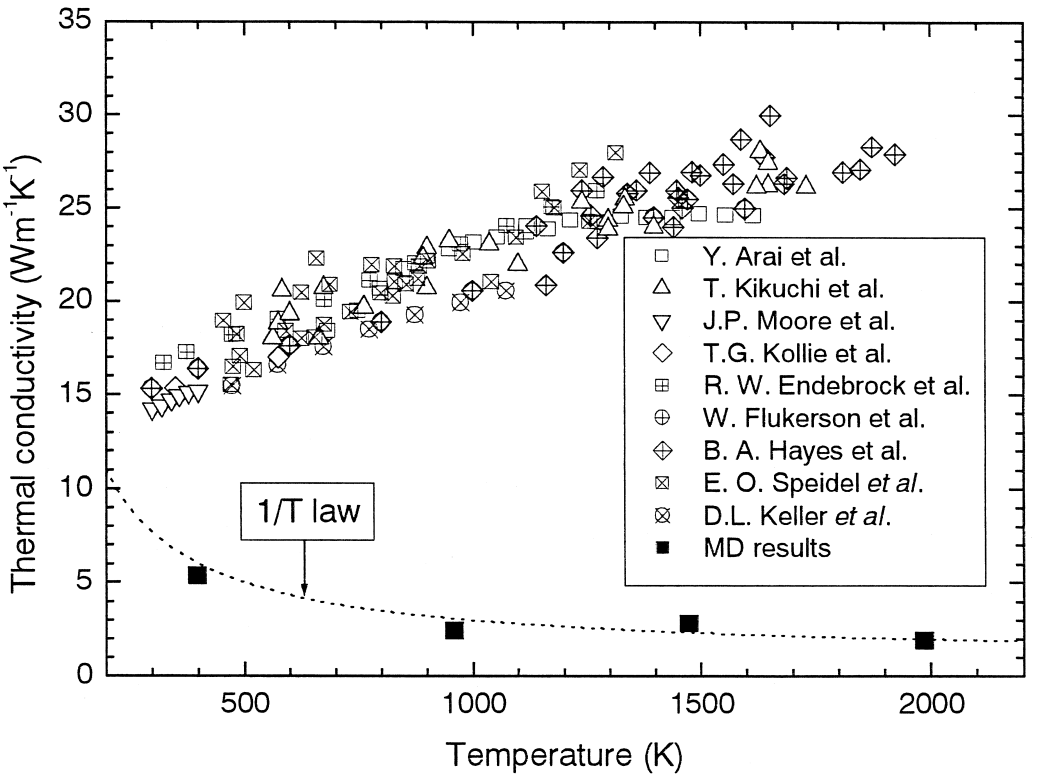

Fig. 4. Variation of the calculated thermal conductivity with temperature.

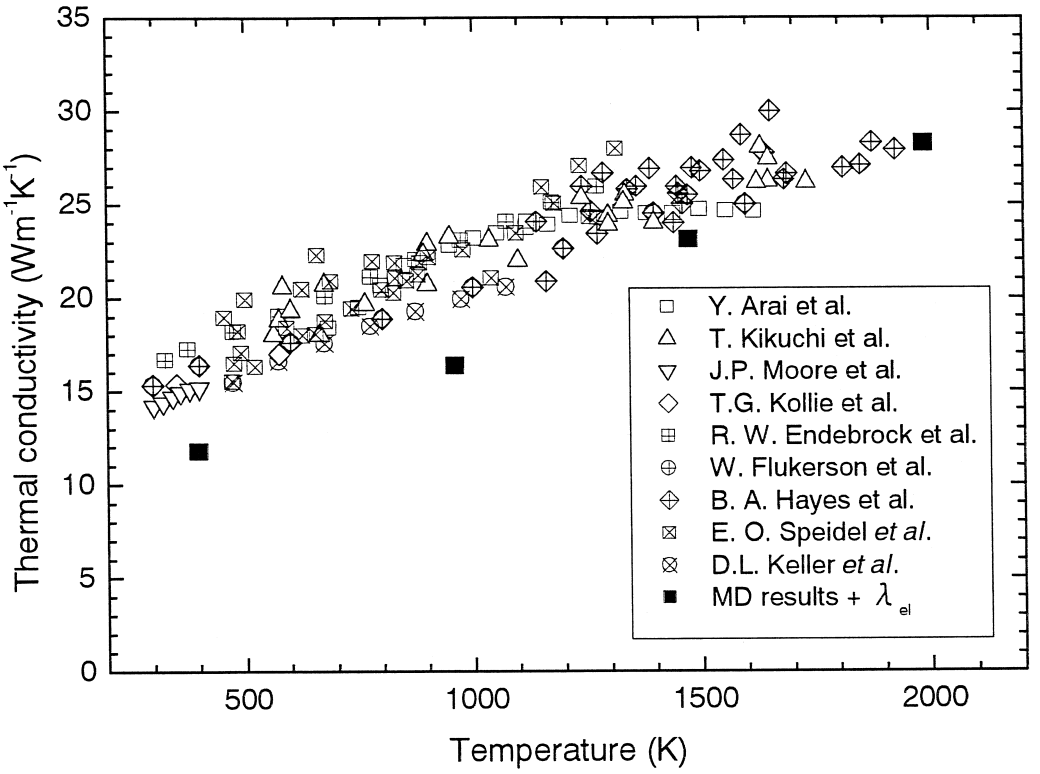

Fig. 5. Temperature dependence of $\lambda_{lat}+\lambda_{el}$.

4. Conclusion

The molecular dynamics calculation was performed for UN to evaluate the thermal conductivity in the temperature range of 300–2000 K. The temperature dependence of the calculated lattice thermal conductivity (λ_{lat}) of UN followed a $1/T$ law. The electrical contribution to the thermal conductivity (λ_{el}) of UN was estimated by using the Wiedemann-Franz law, and $\lambda_{lat}+\lambda_{el}$ was compared with the reported experimental data. The values of $\lambda_{lat}+\lambda_{el}$ obtained in the present study agree with literature values, indicating that the MD simulation technique is useful and applicable to estimate the lattice thermal conductivity of UN. The MD simulation technique will become a powerful method to estimate the physico-chemical properties of nuclear fuels.

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