Thermal conductivity of UO₂ and PuO₂ from first-principles

Bao-Tian Wang,⁎, Jing-Jing Zheng, Xiaotian Qu, Wei-Dong Li, Ping Zhang

⁎ Corresponding author. Tel.: +86 351 701 1081.
E-mail address: wbz11129@sxu.edu.cn (B.-T. Wang).

Contents lists available at ScienceDirect
Journal of Alloys and Compounds

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

ARTICLE INFO

Article history:
Received 14 October 2014
Accepted 27 December 2014
Available online 3 January 2015

Keywords:
First-principles
Thermal conductivity
UO₂
PuO₂

ABSTRACT

Based on our previously calculated phonon spectra from first-principles, in the present work, we have applied the Slack relation to obtain the thermal conductivity of UO₂, PuO₂, (Th, Pu)O₂, and (U, Pu)O₂ in temperature range of 300–1500 K. Also, the mode Grüneisen parameters of PuO₂ and UO₂ were presented to analyze the anharmonic properties. Rapid decrease of the thermal conductivity for UO₂ at low-temperature zone was observed. As for PuO₂, its larger phonon group velocity results in better thermal transfer ability than ThO₂, UO₂, and AmO₂ at high-temperature zone.


1. Introduction

Considering the importance of actinide dioxides (AnO₂) and actinide-mixed oxides (MOX) as potential fuels for nuclear reactors, plenty of works have probed into their electronic, mechanical, magnetic, vibrational, and thermal properties [1–10]. Within those properties, the thermal stability and the thermal conductivity have attracted various experiments [11–18] and theoretical calculations [4,9,17,19–31] over last five decades.

In experiments, Gibby et al. [14] reported that the thermal conductivities of UO₂, PuO₂, and U-MOX with PuO₂ contents from 0 to 9 wt.% decrease upon heating in temperature range of 100–1200 K; Cozzo et al. [16] also measured the thermal conductivities of ThO₂, PuO₂, and Th-MOX with PuO₂ contents from 0 to 30 wt.% in temperature range of 450–1600 K. In theoretical aspect, Kurosaki et al. [22] simulated the thermal conductivities of UO₂, PuO₂, and (U, Pu)O₂ by the molecular dynamics (MD) method in 2001; Yin et al. [24] reported lattice dynamical properties of UO₂ and PuO₂ and uncovered various contributions to their thermal conductivities by using a combination of local density approximation and Dynamical Mean-Field Theory (LDA + DMFT) in 2008. Colbert et al. [29] analyzed the impact of defect on the thermal conductivity of UO₂ by using the Phonon Interface Thermal Conductivity (PITHON) model in 2014; Kim et al. [30] also predicted that the thermal conductivity of UO₂ is reduced by the presence of pores and grain-boundary scattering, by employing the MD method in 2014. In a recent combination work of Inelastic Neutron Scattering (INS) experiment and first-principles simulations, Pang et al. [17] investigated the anharmonicity and thermal conductivity of UO₂ at 295 K and 1200 K.

In our previous works, we have reported the dynamic and thermodynamic properties of ThO₂ [26,32], UO₂ [9], PuO₂ [4], and AmO₂ [28]. Recent inelastic X-ray scattering [33] and INS [34] experiments indicated that their phonon density of states of PuO₂ and UO₂ are considerably consistent with our results [4,9] from density functional theory (DFT). Our calculated thermal conductivities of ThO₂ and AmO₂ also accord well with experiments [35–37]. In the present study, based on the phonon spectra of UO₂ and PuO₂ [4,9], we calculate not only the Grüneisen parameters of them, but also the thermal conductivity of PuO₂, UO₂, (Th, Pu)O₂, and (U, Pu)O₂, where the Slack method [38] is employed. The rest of this paper is arranged as follows. We will detail the simulation method of lattice thermal conductivity in Section 2. Then, in Section 3, we will report the mode Grüneisen parameters of PuO₂ and UO₂ in part A and the thermal conductivity for PuO₂, UO₂, (Th, Pu)O₂, and (U, Pu)O₂ in parts B and C. In Section 4 we summarize the conclusions of this work.

2. Computational method

In our previous study of UO₂ [9] and PuO₂ [4], we have presented their phonon spectra as well as temperature dependences of lattice parameter, bulk modulus, and heat capacity by the local density approximation (LDA) plus Hubbard U method [39] as implemented in Vienna ab initio simulation package (VASP) [40]. After critically testing our results with respect to available experiments and also other calculations, an effective Hubbard U parameter of 4 eV was used for both UO₂ and PuO₂. For a more detailed overview of the computational details, we redirect the reader to Refs. [4,9]. Based on these data, in the present study, we further calculate their group velocities vj, Grüneisen parameter γj, and lattice thermal conductivity κL.
For the fluorite-type actinides dioxides, including ThO$_2$ [32], UO$_2$ [9], PuO$_2$ [4], and AmO$_2$ [28], the efficient heat carriers were believed to be their acoustic branches [24]. Thus, we predict the lattice thermal conductivity $\kappa_l$ here by employing the Slack theory [38], i.e.,

$$\kappa_l = A \frac{\theta^2}{\omega_0^2} \left( \frac{T}{\theta} \right)^2 \left( \frac{T}{\theta} \right)^2$$

(1)

where $A$ is a physical constant with the value of $3.1 \times 10^{-3}$, $M$ is the average mass per atom in the crystal, $\theta(T)$ is the Debye temperature, $\beta$ is the cubic root of the average volume per atom, $n$ is the number of atoms in the primitive unit cell, and $\gamma(T)$ is the acoustic Grüneisen parameter. The units of $\kappa_l$ and $\beta$ in Eq. (1) are W m$^{-1}$ K$^{-1}$ and $A$, respectively. With reasonable expressions for the Debye temperature and acoustic Grüneisen parameter to describe the harmonic phonons and the anharmonic interactions between different phonon branches, Eq. (1) can provide accurate predictions for a material’s thermal conductivity [38]. Note that the Slack theory is only valid at temperature $T > \theta$.

Firstly, the Debye temperature $\theta$ can be determined from the elastic constants within the Debye theory, in which the vibrations of the solid are considered as elastic waves, and the Debye temperature of the solid is related to an averaged sound velocity [18]. Within the isotropic approximation, the Debye temperature $\theta$ can be expressed as [41]

$$\theta(T) = \frac{h}{k_B} \frac{1}{\beta} \frac{M}{n \nu} \left( \frac{T}{\theta} \right)^2 \left( \frac{T}{\theta} \right)^2$$

(2)

where $M$ stands for the molecular mass per formula unit, $B(T)$ is the bulk modulus, $\nu$ is the material’s Poisson ratio, and $f(v)$ can be calculated by

$$f(v) = \frac{3}{2} \left[ \frac{2 + \nu}{3 - 2\nu} \right]^{3/2} + \left[ \frac{1 + \nu}{3 - 2\nu} \right]^{3/2}$$

(3)

Secondly, the mode Grüneisen parameter $\gamma_j(q)$ describing the phonon frequency shift with respect to the volume can be calculated by

$$\gamma_j(q) = \frac{d \ln \omega_j(q, v)}{d \ln V}$$

(4)

The acoustic Grüneisen parameters $\gamma_j(T)$ defined as the weighted average of the mode Grüneisen parameters for all acoustic phonon branches is calculated to be

$$\gamma_j(T) = \frac{\gamma_j(T) \omega_j(T) \nu_s(T)}{C_V(T)}$$

(5)

where $\nu_s(T)$ is the thermal expansion coefficient and equals $\frac{1}{3} \frac{d V}{d T}$; $V_s(T)$ is the volume per mole of material, and $B(T)$ and $C_V(T)$ are the bulk modulus and specific heat, respectively.

In the present work, the $v$, $\omega_j(q, V)$, $B(T)$, and $C_V(T)$ can be directly read from Refs. [49], while the $V_s(T)$ and $\omega_j(T)$ can be deduced from the temperature dependence of the lattice constant $a(T)$ as presented in our previous studies [49].

3. Results

3.1. Grüneisen parameters of UO$_2$ and PuO$_2$

The mode Grüneisen parameters, describing the phonon frequency shift with respect to the volume, can be used to discuss the anharmonic effects. By expanding or compressing the equilibrium volume by 1%, we calculate the mode Grüneisen parameters $\gamma_j(q)$ for all nine phonon branches according to Eq. (4). Based upon the phonon spectra of our calculations on UO$_2$ [9] and PuO$_2$ [4], we plot the mode Grüneisen parameters along $\Gamma-X-K-\Gamma-L-X-W$ directions in Figs. 1 and 2 for UO$_2$ and PuO$_2$, respectively.

From Fig. 1, one can see that the three acoustic modes of the Grüneisen parameters for UO$_2$ show some negative values near the $\Gamma$ point. All other branches are positive in the whole Brillouin zone (BZ). At X point, the largest value of the mode Grüneisen parameter appears on the first transverse optical (TO1 and TO2) and longitudinal optical (LO) branches, close to 5. The second transverse optical (TO1 and TO2) and longitudinal optical (LO) branches distribute in range from 1 to about 3 in the whole BZ. To quantitatively analyze the anharmonic effects along typical crystallographic directions, we present the calculated average mode Grüneisen parameters $\gamma_j = \frac{1}{3} \sum_j \gamma_j(q)$, referred to along the $[001]$, [011], and [1 1 1] orientations of the UO$_2$ unit cell in Table 1. It is clear that the values on TO branches are wholly larger than that on LO, transverse acoustic (TA), TO, LO, and longitudinal acoustic (LA) branches. The largest average value appears on TO, along the [001] direction. Due to the fact that the lattice anharmonicity strength can be reflected by the Grüneisen parameters, our calculated $\gamma_j$ illustrate the anomalously large anharmonicity of the TO modes. We note that Yin et al. [24] have calculated $\gamma_j(q)$ at $T$ and $X$ points by employing the LDA + DMFT method. They found that the LO mode possesses anomalously large anharmonicity. However, according to our present Grüneisen parameter spectrum, the TO modes may also exhibit large anharmonicity.

As shown in Fig. 2, the TO1 and TO2 branches of PuO$_2$ own the same largest Grüneisen parameter value at the X point, with a value of 11 or so. For other branches, the $\gamma_j$ mainly vary from 0 to 6 in the BZ, with some TA and LA branches exhibiting some negative values near the $\Gamma$ point. Same with UO$_2$, we also list the $\gamma_j$ along the [001], [011], and [1 1 1] directions of the PuO$_2$ unit cell in Table 1. From these data, one can clearly see the following features: (i) among all modes, the two TO modes hold the largest values along all three typical directions and (ii) the TA mode along the [001] direction exhibits larger values than that in UO$_2$.

After summarizing the Grüneisen parameters values on nine branches and along the three typical crystalline directions of UO$_2$ and PuO$_2$, we obtain $\gamma$(UO$_2$) $= 46.06$ and $\gamma$(PuO$_2$) $= 61.86$. Thus, we can say that the anharmonic effect of PuO$_2$ is larger than that of UO$_2$. This result can be used to explain the temperature-dependent behaviors of the thermal conductivity.

3.2. Thermal conductivity of UO$_2$ and PuO$_2$

Due to the important role the thermal conductivity of actinides playing in nuclear industries, it is necessary for ones to explore it. To study thermal conductivity, we should firstly analyze the phonon group velocities $v_j$, $v_j = \frac{\omega_j(q)}{\Delta q_j}$, since their tight relationship
Table 1
Calculated average mode Grüneisen parameters $\tilde{\gamma}_j$ and group velocities $v_j$ (× 10^2 m/s) of UO$_2$ and PuO$_2$ along [001], [011] and [111] directions at 0 K. Since that the symmetry along [001] and [111] directions is high, the two transverse vibration branches are degeneracy, thus, they are presented as one value. For comparison, available theoretical group velocities from Ref. [24] are presented within parentheses.

<table>
<thead>
<tr>
<th>Branch</th>
<th>UO$_2$</th>
<th></th>
<th></th>
<th>PuO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[001]</td>
<td>[011]</td>
<td>[111]</td>
<td></td>
</tr>
<tr>
<td>$\tilde{\gamma}_j$</td>
<td>1.56</td>
<td>1.83/1.42</td>
<td>0.88</td>
<td>5.80 (6.76)$^a$</td>
</tr>
<tr>
<td>TA</td>
<td>0.61</td>
<td>1.51</td>
<td>1.43</td>
<td>11.17 (11.23)$^a$</td>
</tr>
<tr>
<td>LA</td>
<td>3.74</td>
<td>2.38/2.06</td>
<td>2.16</td>
<td>$-1.22$ (-0.55)$^a$</td>
</tr>
<tr>
<td>TO</td>
<td>2.42</td>
<td>1.64</td>
<td>1.14</td>
<td>$-10.68$ (-9.53)$^a$</td>
</tr>
<tr>
<td>LO</td>
<td>1.27</td>
<td>1.62/1.17</td>
<td>1.32</td>
<td>$0.77$ (-0.31)$^a$</td>
</tr>
<tr>
<td>TO</td>
<td>1.52</td>
<td>1.37</td>
<td>2.08</td>
<td>$1.99$ (2.95)$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_j$</td>
<td>[001]</td>
<td>[011]</td>
<td>[111]</td>
<td></td>
</tr>
<tr>
<td>TA</td>
<td>3.09</td>
<td>2.38/2.17</td>
<td>1.98</td>
<td>6.38 (6.67)$^a$</td>
</tr>
<tr>
<td>LA</td>
<td>1.18</td>
<td>0.89</td>
<td>2.21</td>
<td>10.76 (11.48)$^a$</td>
</tr>
<tr>
<td>TO</td>
<td>5.36</td>
<td>4.15/2.90</td>
<td>2.72</td>
<td>$-10.84$ (1.84)$^a$</td>
</tr>
<tr>
<td>LO</td>
<td>2.27</td>
<td>1.88</td>
<td>1.79</td>
<td>$-12.91$ (-11.10)$^a$</td>
</tr>
<tr>
<td>TO</td>
<td>1.49</td>
<td>1.76/1.46</td>
<td>1.80</td>
<td>$-2.28$ (-1.02)$^a$</td>
</tr>
<tr>
<td>LO</td>
<td>1.29</td>
<td>1.33</td>
<td>1.32</td>
<td>$-0.07$ (2.46)$^a$</td>
</tr>
</tbody>
</table>

$^a$ Ref. [24].

$\kappa_T \propto \nu_0^2$.

We deduce the $v_j$ of UO$_2$ and PuO$_2$ along the [001], [011], and [111] crystalline directions from the phonon spectra data $\omega_j(q)$ in our previous DFT studies [4,9] and report them in Table 1.

For UO$_2$, as seen in Table 1, the TA, LA and LO branches of UO$_2$ possess larger phonon group velocities than other branches, especially along the [001] direction. As a result, the TA, LA and LO modes can be regarded as the best heat carriers. However, considering that the LO branch holds large mode Grüneisen parameters [24], the LO mode may contribute limitedly to the thermal conductivity of UO$_2$, especially in high temperature domain.

As for PuO$_2$, only LO branch exhibits relatively small phonon group velocities. All other branches can be viewed as good heat carriers at low temperature. After increasing temperature, the anharmonic effects may constrain the heat transfer ability in some branches, like TO.

From Table 1, we can summarize the total phonon group velocities of UO$_2$ and PuO$_2$ along the [001], [011] and [111] directions. For UO$_2$, they equal to 39.42 × 10^2, 26.60 × 10^2, and 20.90 × 10^2 m/s, respectively. For PuO$_2$, the results are 62.87 × 10^2, 39.6 × 10^2, and 25.73 × 10^2 m/s, respectively. These data clearly indicate that PuO$_2$ shows larger phonon group velocities than UO$_2$, and the direction-dependent property of $v_j$ for PuO$_2$ is more pronounced than that for UO$_2$. Therefore, the fact that the thermal conductivity of PuO$_2$ is larger than that of UO$_2$ in high temperature zone is understandable.

After aforementioned analysis, one can believe that the acoustic branches of these two important nuclear materials play critical role in heat transfer no matter at low temperature or at high temperature. However, the optical modes may only contribute mainly to the heat transfer at low temperature. Their contribution at high temperature is limited by the anharmonic-induced shorter mean free path.

After ignoring the contribution from optical branches, we calculate the thermal conductivity of UO$_2$ and PuO$_2$ in temperature from 300 to 1500 K by the Slack relation. In temperature from 300 to 450 K, as shown in Fig. 3, our calculated thermal conductivity of UO$_2$ appears to be larger than the measured values [11–15,17], but still agrees with results predicted by Hyland et al. [21] and Pang et al. [17]. In temperature from 450 to 1500 K, our calculated thermal conductivity of UO$_2$ is comparable with available experiments [11–15,17] as well as previous analytical means [21] and DFT + MD [30], generalized gradient approximation plus U [17], and PITHON model [29] calculations. From our present results, we can see clearly the rapid decreasing behavior of the thermal conductivity of UO$_2$ in temperature range from 300 to about 680 K. Above temperature ($T$) = 680 K, the decrease behavior is slow down and our results are almost consistent with data by recent PITHON model [29].

In Fig. 4, we plot the temperature dependence of thermal conductivity for PuO$_2$ from 300 to 1500 K. For comparison, available
in the whole temperature range in some proportion decrease along with increasing temperature and in the temperature range of 300–1500 K, PuO₂ in this MOX, the and PuO₂ is almost consistent with that of UO₂ but smaller than that of PuO₂. The relatively large thermal conductivity of PuO₂ here is due to it’s large phonon group velocity. Actually, in one recent experimental report by Cozzo et al. [16], the thermal conductivity of ThO₂ in temperature range of about 500–1600 K is always smaller than that of PuO₂.

3.3. Thermal conductivity of (Th, Pu) O₂ and (U, Pu) O₂

According to the thermal conductivity result of four AnO₂ above, the thermal conductivity of (Th, Pu) O₂ and (U, Pu) O₂ over the temperature range of 300–1500 K, can be obtained by physically mixing the data of ThO₂ [26], PuO₂, and UO₂ in some proportions. By mixing ThO₂ with 3, 8 and 30 wt.% concentrations of PuO₂, the thermal conductivity of (Th, Pu) O₂ is achieved and is displayed in Fig. 6. In Fig. 7, we report the results of (U, Pu) O₂ with concentrations of UO₂ at 3, 6 and 9 wt.%. Meanwhile, the experimental results [16,42] related to corresponding materials are also shown for comparison.

From Fig. 6, one can see that all the thermal conductivity curves of (Th, Pu) O₂ decrease along with increasing temperature and cross at T ~ 600 K. Comparing with ThO₂, the variation of the thermal conductivity for (Th, Pu) O₂ is associated with the content of PuO₂. By increasing the concentration of PuO₂ in this MOX, the thermal transfer ability is enhanced over T ~ 600 K, but constrained below this point. Comparing with the experimental results [16], our calculated data are wholly agree with them. Slight difference may due to the electronic contribution to the thermal conductivity we ignored or the purity of the experimental samples they used. As for MOX of UO₂ and PuO₂, shown in Fig. 7, similar temperature-dependent behaviors as well as the doping effects can be observed. Good accordance with experiments [42] further guarantees the reliability of our present theoretical results.

4. Conclusion

In summary, based upon our published phonon spectra and correlated data from DFT [49,26,28], we have used the Slack relation to calculate the temperature-dependent thermal conductivity of some typical AnO₂ as well as their MOX. We have found that the thermal conductivity of AmO₂ is always smaller than that of ThO₂, UO₂, and PuO₂ over the temperature range 300–1500 K. The thermal conductivity curves of ThO₂, UO₂, and PuO₂ cross at T ~ 600 K. Below this temperature point, the thermal conductivity of UO₂ decreases rapidly. While above this point, since relatively larger phonon group velocity, the thermal transfer ability of PuO₂ is more pronounced than other AnO₂ we calculated.

Acknowledgments

This work was supported by NSFC under Grant Nos. 11104170, 11374197, and 51071032.

References


