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A comment on the thermal conductivity of (U,Pu)O_2 and (U,Th)O_2 by molecular dynamics with adjustment for phonon-spin scattering

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Abstract

A new approach for adjusting molecular dynamics results on UO_2 thermal conductivity to include phonon-spin scattering has been used to improve calculations on $U_xPu_{1-x}O_2$ and $U_xTh_{1-x}O_2$. We demonstrate that by including spin scattering a strong asymmetry as a function of uranium actinide fraction, x, is obtained. Greater degradation is shown for $U_xTh_{1-x}O_2$ than $U_xPu_{1-x}O_2$. Minimum thermal conductivities are predicted at $U_{0.97}Pu_{0.03}O_2$ and $U_{0.58}Th_{0.42}O_2$, although the degradation in $U_xPu_{1-x}O_2$ is negligible relative to pure UO_2.

1. Introduction

Nuclear fuel has been UO_2-based for several decades due to its radiation tolerance, high melting point and ability to accommodate the significant chemical changes that it undergoes during reactor operation. UO_2 can also be blended with PuO_2 [1, 2] or ThO_2 [3] to form mixed oxide (MOX) fuels. Alternatively, transmutation of U to Pu during reactor operation creates a (U,Pu)O_2 solid solution as the host lattice. (U,Pu)O_2 is also used as MOX fuel in fast breeder reactors and pressurized water reactors, providing a route for recycling Pu stockpiles that have built up over decades of nuclear reactor operation. By mixing the fertile isotope Th^{232} with fissile species, such as U^{235}, the relatively abundant Th deposits can be incorporated into the fuel cycle. Advanced fuel cycles such as these would greatly improve the longevity and sustainability of nuclear power as an energy resource.

To underpin performance for advanced MOX fuels or for higher burn up conventional fuel it is important to understand how the thermophysical properties of these solid solutions deviate from the end members. Many important properties, such as elastic constants, thermal conductivity, fission gas mobility and specific heat, are temperature dependent. Thermal conductivity, therefore, plays a particularly important role as the primary factor in determining fuel pellet temperatures. Knowledge of the thermal conductivity is crucial to avoiding centerline pellet melting such that safety cases for MOX or high burn up fuel require a strong understanding of this property [1, 4]. Consequently, there have been significant efforts to investigate the thermal conductivity of nuclear fuel experimentally [5–10] and computationally [11–14, 16, 17]. Using the same many-body potential employed here Qin *et al.* [16] predicted a strong degradation in UO_2 thermal conductivity due to disorder on the anion sublattice. To identify the role of the mixed cation lattice in MOX fuel, Arima *et al.* [11, 12] and Ma *et al.* [13] investigated the thermal conductivity of $(U_xPu_{1-x})O_{2-y}$ as a function of $0 \leqslant x \leqslant 0.3$ and $0 \leqslant y \leqslant 0.25$. It was predicted that the oxygen to metal ratio has a much stronger effect on thermal conductivity than the mixed cation sublattice. Similarly, Ma *at al.* [14] calculated the thermal conductivity of $(Th_xU_{1-x})O_2$ and $(Th_xPu_{1-x})O_2$ for $0 \leqslant x \leqslant 0.3$ indicating a greater impact on thermal conductivity due to the addition of Pu or U to the ThO_2 lattice compared to the addition Pu to UO_2 [11–13, 15].

A recent MD study by Cooper *et al.* [18], using a many-body potential developed by Cooper, Rushton and Grimes (CRG) [19], predicted the thermal conductivity of $U_xPu_{1-x}O_2$ and $U_xTh_{1-x}O_2$ over the full compositional range ($0 \leqslant x \leqslant 1$) and from 300 K to 2000 K. The results indicated a stronger scattering effect due to the mixed cation lattice in $U_xTh_{1-x}O_2$ compared to $U_xPu_{1-x}O_2$. However, it has been shown that classical MD using the CRG potential significantly overestimates thermal conductivity of pure UO_2 compared to experiment data [16, 18, 20], something widely reported for a range of UO_2 empirical potentials [11–14, 16, 17]. Recent work [10] has identified spin scattering as the primary reason for low UO_2 thermal conductivity. This cannot be included directly in MD, however a method

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has been developed [20, 21] to include the experimentally determined spin scattering effects with MD results through the Callaway model [22]. It shows that spin scattering fully accounts for the discrepancy between the CRG potential and experiment. Here we used CRG UO_2 data that has been adjusted for spin scattering [20] to update the description of solid solution scattering in $U_xPu_{1-x}O_2$ and $U_xTh_{1-x}O_2$, which was also derived using the CRG potential [18].

2. Methodology

Previous work calculated the thermal conductivity of $U_xPu_{1-x}O_2$ and $U_xTh_{1-x}O_2$ from 300 K to 2000 K over the full compositional range of each actinide. These results were determined by non-equilibrium MD using the many-body potential developed by CRG [19, 23]. Note that for PuO_2 the modified potential parameter set was used [24]. Full calculation details can be found in Ref. [18]. Analytic expressions describing the thermal conductivity of the mixed oxides were developed by fitting equation 1 [25–27] to the MD data.

$$k = \frac{1}{xw_A + (1-x)w_B + x(1-x)C_{AB}} \tag{1}$$

where C_{AB} is the scattering strength associated with the mixed cation lattice. w_A and w_B are the thermal resistivities of the end members A and B respectively:

$$w_A = a_A + b_A T$$
$$w_B = a_B + b_B T$$

where b_A and b_B are the phonon-phonon scattering parameters and a_A and a_B represent temperature independent scattering processes in end member A and B respectively. We use a_{PuO_2}, b_{PuO_2}, a_{ThO_2}, a_{ThO_2}, C_{UTh} and C_{UPu} reported by Cooper *et al.* [18]. Due to the problem of reproducing UO_2 thermal conductivity with classical MD alone we use the a_{UO_2} and b_{UO_2} reported by Liu *et al.* [20], which were fitted to spin scattering adjusted MD data also using the CRG potential and fully account for discrepancies with experiment. The parameters used in equation 1 are reported in Table 1. This allows us to predict the thermal conductivity of $U_xPu_{1-x}O_2$ and $U_xTh_{1-x}O_2$, while taking into account the effect of spin scattering due to UO_2. This approach assumes that spin scattering is proportional to the uranium content. Testing this assumption should be the focus of future quantum mechanical or experimental work and is beyond the scope of this paper.

Table 1: Parameters (see equation 1) used for calculating the thermal conductivity of $U_xTh_{1-x}O_2$ and $U_xPu_{1-x}O_2$, where the pure UO_2 parameters include spin scattering from Ref. [20]. The remaining parameters are taken from Ref. [18]. The results using these parameters are also reported in Figure 2.

End member parameters	
a_{ThO2} [18]	-1.65×10^{-2} mKW^{-1}
b_{ThO2} [18]	2.19×10^{-4} mW^{-1}
a_{UO2} [20]	3.11×10^{-2} mKW^{-1}
b_{UO2} [20]	2.08×10^{-4} mW^{-1}
a_{PuO2} [18]	-1.96×10^{-2} mKW^{-1}
b_{PuO2} [18]	2.13×10^{-4} mW^{-1}
Mixing parameters	
C_{UTh} [18]	2.59×10^{-1} mKW^{-1}
C_{UPu} [18]	5.21×10^{-2} mKW^{-1}

3. Results and discussion

Figure 1 shows the previous results of Cooper *et al.* [18] for the thermal conductivity of $U_xPu_{1-x}O_2$ and $U_xTh_{1-x}O_2$ using classical MD without adjustment for spin scattering. Defect scattering due to the mixed cation lattice is far more significant in $U_xTh_{1-x}O_2$ than $U_xPu_{1-x}O_2$ due to the large mismatch in lattice parameter for UO_2 and ThO_2.

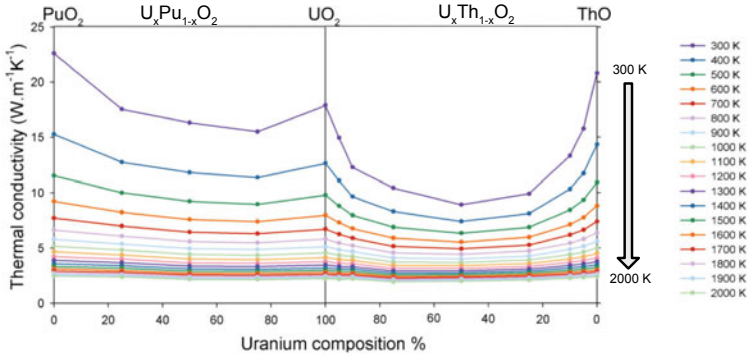

Figure 1: MD study of the thermal conductivity of $U_xPu_{1-x}O_2$ and $U_xTh_{1-x}O_2$ as a function of actinide composition ($100x$ at.%). This figure is a modified version of two figures in Ref. [18].

The new results, which incorporate spin scattering in UO_2, are shown in Figure 2. Comparison of Figures 1 and 2 shows that for $U_xPu_{1-x}O_2$ the inclusion of spin scattering has a dramatic effect. Rather than UO_2 thermal conductivity being degraded by the addition of Pu, there is no noticeable effect until $x < 0.85$ with further additions of Pu actually increasing thermal transport. This indicates that the removal of spin scattering out weights the additional defect scattering for $x < 0.85$. Conversely, the significantly greater defect scattering in $U_xTh_{1-x}O_2$ (represented by $C_{UTh} > C_{UPu}$) has a greater negative impact on thermal conductivity than the positive effect of removing spin scattering. Thus the $U_xTh_{1-x}O_2$ thermal conductivity reaches a minimum at around $U_{0.58}Th_{42}O_2$ for 300 K at which point further additions of Th begin to increase thermal conductivity. Figure 2 shows that for both mixed oxide systems the relationship between thermal conductivity and actinide composition becomes strongly asymmetric when including spin scattering compared to Figure 1.

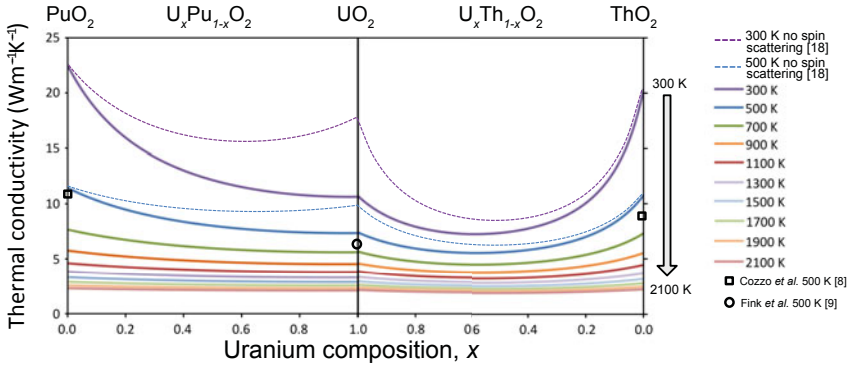

Figure 2: The spin scattering adjusted thermal conductivity of $U_xPu_{1-x}O_2$ and $U_xTh_{1-x}O_2$ calculated by combining the results of MD calculations on the mixed oxides [18] with spin scattering adjusted MD data for pure UO_2 [20]. The parameters used are reported in Table 1. The previous MD data [18] at 300 K, not adjusted for spin scattering, is included for comparison.

These results indicate that scattering due to the mixed cation lattice presents a more important consideration for the development of $(U,Th)O_2$ than $(U,Pu)O_2$ MOX fuels. In order to achieve a noticeable increase in thermal conductivity compared to conventional UO_2 fuel it may be necessary to use high

concentrations of Th, however, this has the negative effect of limiting the reactivity of the fuel. Alternatively, defect scattering due to the mixed cation lattice could be limited by developing heterogeneous (U,Th)O_2 fuels with separate grains of UO_2 and ThO_2. However, this may have negative consequences for other fuel properties and eventually the transmutation of Th^{232} to U^{233} will nonetheless lead to defect scattering. (U,Pu)O_2 MOX fuels on the other hand are predicted to benefit from higher thermal conductivity than conventional UO_2 if Pu is greater than 15 % of the actinide composition. Furthermore, Pu is fissile and does not significantly alter the reactivity of the fuel in the same way as Th, so even greater thermal conductivities may be attainable by using high Pu content fuel. Similarly, our results indicate that transmutation of U to Pu will not significantly change conventional fuel thermal conductivity, instead radiation damage, fisssion products or non-stoichiometry are probably more important at high burn-up [20].

4. Conclusions

Previous MD work has been used to combine phonon-spin scattering adjusted UO_2 data [20, 21] with results for $U_xTh_{1-x}O_2$ and $U_xPu_{1-x}O_2$ [18]. The results show a strong asymmetry in thermal conductivity as a function of actinide composition. Little to no degradation is predicted for $U_xPu_{1-x}O_2$, in fact for compositions where $x < 0.85$ Pu increases the thermal conductivity with respect to pure UO_2 through the reduction of spin scattering. On the other hand, high defect scattering in $U_xTh_{1-x}O_2$ has a significant effect, with the minimum thermal conductivity occurring for $U_{0.58}Th_{42}O_2$. Although ThO_2 has a much higher thermal conductivity than UO_2, $U_xTh_{1-x}O_2$ only has a greater thermal conductivity than UO_2 for $x < 0.2$. These results indicate that transmutation of U to Pu is not a significant factor for high burn-up conventional fuel but transmutation of Th to U in (U,Th)O_2 MOX fuel may be important.

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