First-principles Study of UO₂ Lattice Thermal-Conductivity: A Simple Description

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Received: 16 May 2020 / Accepted: 2 July 2020 / Published online: 20 August 2020
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Abstract
Modeling the high-$T$ paramagnetic state of bulk UO₂ by a non-spin-polarized calculation and neglecting the Hubbard-U correction for the $f$ electrons in U atoms, the lattice thermal conductivity of bulk UO₂ is investigated by the exact solution of the Boltzmann transport equation for the steady-state phonon distribution function. The resulting phonon dispersion shows good agreement with experiment and when the non-analytical correction of the dynamical matrix was added, this agreement is enhanced. Analysis of the results shows that TA branches corresponding to U-atoms vibrations have the largest lifetimes and therefore have dominant role in thermal conductivity, while the optical branches corresponding mainly to O-atoms vibrations have the shortest lifetimes. Using this simple model, our results for the thermal conductivity show a very good agreement with the experiments. The calculations are repeated for bulk UO₂ with different U-235 concentrations of 3%, 5%, 7% and 20%, and the results show a small decrease in thermal conductivity which arises from scattering of phonons by impurities.

Keywords
Uranium dioxide · Lattice thermal conductivity · Boltzmann transport equation · Acoustic branch · Optical branch · Phonon lifetime · Density-functional perturbation theory

1 Introduction
One of the vastly used fuels in nuclear power reactors is uranium-dioxide, UO₂. The performance of a nuclear fuel is highly correlated with its thermal conductivity, and therefore, studying the thermal conductivity of nuclear fuel and understanding the mechanisms behind it is one of the most active fields of research in nuclear industry. Due to the fission processes of the uranium atoms, large amounts of heat are released, leading to large temperature gradients throughout the fuel rod. Having an efficient thermal conductivity, the generated temperature-gradients in the fuel are immediately balanced and the heat is easily extracted by the coolant so that the fuel system does not meet any safety problems because of any temperature increase or thermal stresses.

Experiments have determined the crystal structure of UO₂ as a 3k-order antiferromagnet (AFM) at $T < 30^\circ$ K, and paramagnetic at higher temperatures (Amoretti et al. 1989; Faber et al. 1975). The uranium atoms sit on the sites of an FCC structure with lattice constant $a = 5.47 \, \text{Å}$, while the oxygen atoms are positioned at sites with $Pa\bar{3}$ symmetry (Idiri et al. 2004). Uranium-dioxide is electrically an insulator material (the so-called Mott insulator), and because of the localized partially filled $f$-orbitals on U atoms, it is a strongly correlated electron system. Theoretical description of electronic properties of such a system by ordinary density-functional theory (DFT) (Hohenberg and Kohn 1964; Kohn and Sham 1965) approximations usually leads to incorrect metallic behavior, and for a correct prediction, one has to somehow take into account the “localized” behavior of the $f$-electrons in U atoms. Two methods that are commonly used for this purpose are the DFT+U (Dorado et al. 2009; Freyss et al. 2012) and using orbital-dependent hybrid functional for the exchange-correlation (XC) part of the energy (Sheykhi and Payami 2018). Since in the bulk UO₂, there is no delocalized electrons, the thermal properties depends only on lattice
dynamics of the system. The properties of lattice dynamics are characterized by phonon dispersion, phonon density of states (PhDOS) and anharmonic behaviors.

The lattice dynamics and thermal conductivity of bulk UO$_2$ have been studied by many researchers both experimentally and theoretically. For example, Dolling et al. (1965), using the neutron inelastic-scattering technique, were the first ones that experimentally determined the phonon dispersion and density-of-states curves of UO$_2$; Godfrey et al. (1965) have used a radial heat flow technique and measured the thermal conductivity of polycrystalline UO$_2$ in the range $-57^\circ$ to $1100^\circ$C; Goldsmith and Douglas (1973) using the laser-flash method have measured the thermal conductivity of porous stoichiometric and hyper-stoichiometric uranium dioxide in the temperature range of 670–1270$^\circ$K; Fink and coworkers in two separate works (Fink et al. 1981; Fink 2000) have reviewed the experimental data on thermodynamic and transport properties of solid and liquid UO$_2$, and by analyzing the data have obtained consistent equations for the thermophysical properties. On the other hand, in theoretical investigations, Motoyama et al. (1999) resorting to nonequilibrium classical molecular dynamics (MD) have calculated the thermal conductivity of UO$_2$ pellet; Arima et al. (2005) using the Born-Mayer-Huggins interatomic potential with the partially ionic model have performed equilibrium MD simulations and investigated the thermal properties of UO$_2$ and PuO$_2$ between 300 and 2000$^\circ$K; Kaur et al. (2013) within DFT+U method in generalized gradient approximation (GGA) (Perdew et al. 1996) and applying an external hydrostatic pressure of 7 GPa have optimized the geometry of UO$_2$ crystal in AFM 1k-order configuration, and then using the resulted lattice parameters have studied the thermal properties using the density functional perturbation theory (DFPT) (Baroni et al. 2001) in conjunction with the quasi-harmonic approximation (QHA); Pang et al. (2013), in a joint experimental and theoretical investigation, using high-resolution inelastic neutron scattering, have measured phonon lifetimes and dispersion of UO$_2$ at 295 and 1200$^\circ$K, and then analyzing the calculated result of thermal conductivity within the relaxation-time approximation (RTA), have concluded that longitudinal optical (LO1) branch of phonons carries the largest amount of heat; Resnick et al. (2019) have used an MD simulation to study the thermal transport of plutonium dioxide and uranium dioxide with point defects; Torres and Kaloni (2019) had performed the solution of BTE on top of a DFT+U calculation with 1k-order AFM configuration for UO$_2$, but because of the diversity of their work, they had not provided a satisfactory analysis of the problem.

One of the ways to investigate the heat transport in solids is using the Boltzmann transport equation (BTE). The earlier BTE studies on lattice thermal conductivity of UO$_2$ were based on the relaxation-time approximation (RTA). Although the RTA gives good results in cases where the “umklapp” scattering processes are dominant, the exact solution of the BTE is needed whenever the “normal” processes dominate. In this work, we have obtained the exact solution of BTE for phonons’ distribution from which the lattice thermal conductivity is calculated. Our results show a very good agreement with the experiments.

In nature, uranium is found as U-238 (99.2739%), U-235 (0.7198%) and a very small amount of U-234 (0.0050%). Since in different nuclear fuels, the relative abundances of U-238 and U-235 are different, the scattering rates by “impurities” differs from one fuel to other and this affects the thermal conductivity of the fuel. We have therefore repeated the procedure for the cases U-235 (3%), (5%), (7%) and (20%), and the results showed a small decrease in thermal conductivity by increasing the impurity level.

The organization of this paper is as follows. In Sect. 2, we present the computational details; in Sect. 3, the results are presented and discussed; Sect. 4 concludes this work. Finally, in “Appendix,” the convergency issues of our calculations are detailed.

2 Computational Details

Since the simulation of the high-$T$ paramagnetic state of UO$_2$ system with randomly oriented magnetic moments requires a very large supercell, it is computationally very prohibitive, and it is common to model it with a 1k-order AFM. However, in this work, we model the paramagnetic state of bulk UO$_2$ by a non-spin-polarized calculation, and neglect the Hubbard-U correction for the localized orbitals in the study of lattice dynamics. It has already been observed that although not using the Hubbard correction in the DFT calculations gives incorrect metallic ground state for UO$_2$, but surprisingly the phonon properties are comparable with experiment (Wen et al. 2013).

2.1 Geometry and Harmonic Lattice Dynamics

For the electronic structure calculations, we have used the first-principles DFT method as implemented in the Quantum-ESPRESSO code package (Giannozzi et al. 2009) and used Ultra-soft pseudopotentials with the rev-PBE XC-functional (Zhang and Yang 1998). The reason for choosing the rev-PBE method is that, among the other exchange-correlation functionals used here, it gives the best
agreement with experiment for the lattice constant. Specifically, comparing the results for functionals LDA (Kohn and Sham 1965), PBE (Perdew et al. 1996), PW91 (Perdew and Wang 1992) and rev-PBE; we obtained the values of 5.27, 5.36, 5.36 and 5.39 Å for the lattice constants, respectively. The kinetic-energy cutoffs for the expansion of the Kohn–Sham (KS) (Kohn and Sham 1965) orbitals and charge densities were chosen as 60 and 600 Ry, respectively. For the integrations over the Brillouin-zone (BZ), a Γ-centered 8 × 8 × 8 grid were used. The optimization of the geometry was performed with a maximum 10−5 Ry/au of residual force on each atom. The convergence tests with respect to the parameters are detailed in “Appendix”.

To calculate the second-order (2nd) interatomic force constants (IFCs) and phonon frequencies, we have employed the DFPT method implemented in QE package for the optimized geometry of 3-atom primitive cell using a Γ-centered 12 × 12 × 12 uniform grid in the reciprocal space (The convergency test is presented in “Appendix”). To ensure the translational invariance of the symmetrized dynamical matrix, the acoustic sum-rule was applied. We have obtained the phonon frequencies by diagonalizing the calculated dynamical matrix. The effect of different atomic masses of the uranium isotopes on the phonon frequencies was checked and no meaningful differences obtained, and therefore, in subsequent calculations, all phonon frequencies were calculated with the mass of U-238 isotope.

### 2.2 Thermal Conductivity

The lattice thermal conductivity of bulk UO₂ is calculated by solving the linearized-BTE (Peierls 1997; Ziman 1960) for the steady-state phonon distribution function \( f_\lambda \):

\[
\nabla T \cdot \mathbf{v}_\lambda = \frac{\partial f_\lambda}{\partial T} = \frac{\partial f_\lambda}{\partial \mathbf{q}} \left|_{\text{scattering}} \right.,
\]

where the left-hand side of the equation corresponds to the phonon diffusion due to temperature gradient, and the term in the right-hand side is the time rate of change of phonon distribution due to all allowed scattering processes. Here, \( \mathbf{v}_\lambda \) is the group velocity of phonon in mode \( \lambda \) and \( \lambda \equiv (s, \mathbf{q}) \) with \( s \) and \( \mathbf{q} \) being the phonon branch index and wave vector in reciprocal space, respectively. In the linearized-BTE, the distribution \( f_\lambda \) differs from the equilibrium Bose-Einstein distribution function \( \xi_\lambda = 1/(\exp(\beta \omega_\lambda) - 1) \) by a linear term in \( \nabla T \). Here \( \beta = 1/k_B T \) and \( \omega_\lambda \) is the phonon frequency in mode \( \lambda \). The solution of the BTE is done using a full iterative algorithm (Omini and Sparavigna 1995; Lindsay et al. 2010; Li et al. 2012; Mingo et al. 2014) employing ShengBTE code package (Li et al. 2014). To calculate the thermal conductivity, the third-order (3rd) IFCs were computed up to the second shell of neighbors in a 3 × 3 × 3 supercell with a Γ-centered 2 × 2 × 2 uniform mesh of \( k \) points. The 3rd-IFCs corresponding to the displacements of \( (i, j, k) \) atoms along directions \( (x, \beta, \gamma) \) were computed using a three-point finite-difference method. To ensure the translational invariance, we have imposed the constraint \( \sum_{\lambda} \Phi_{\lambda} = 0 \) according to the prescription given by Esfarjani and Stokes (2008) and Li et al. (2012).

For the scattering contributions, which is treated within perturbation theory, we have considered scattering by isotopes (Tamura 1983, 1984) and all the three-phonon processes satisfying the energy and quasi-momentum conservation:

\[
o_\lambda \pm o_{\lambda'} = o_{\lambda''}, \quad (2)
\]

\[
\mathbf{q} \pm \mathbf{q}' = \mathbf{q}'' + \mathbf{Q}, \quad (3)
\]

where \( \mathbf{Q} \) is a reciprocal lattice vector. The linearized-BTE may be recasted in a form expressed in terms of a set of coupled equations for the phonon lifetimes, \( \tau_\lambda^{(s)} \) as (Omini and Sparavigna 1995; Lindsay et al. 2010; Li et al. 2012; Mingo et al. 2014):

\[
\tau_\lambda^{(s)} = \tau_\lambda^{(0)} (1 + \Delta_\lambda^{(s)}), \quad (4)
\]

where \( \tau_\lambda^{(0)} \), the phonon lifetime in the single-mode relaxation-time approximation (RTA), is defined by:

\[
\tau_\lambda^{(0)} = \frac{1}{N} \left( \sum_{\lambda', \lambda''} \Gamma_{\lambda', \lambda''}^{+} + \frac{1}{2} \sum_{\lambda', \lambda''} \Gamma_{\lambda', \lambda''}^{-} + \sum_{\lambda'} \Gamma_{\lambda', \lambda'} \right), \quad (5)
\]

in which \( N \) is the number of unit cells, and \( \tau_\lambda^{(s)} \) corresponds to phonon modes propagating in \( x \) direction. The “+” and “−” symbols denote the sums are over two different types (“combination” and “decay” processes, respectively) of three-phonon processes defined by Eqs. (2) and (3) including both “normal” \( (\mathbf{Q} = 0) \) and “umklapp” \( (\mathbf{Q} \neq 0) \) processes. The quantities \( \Gamma_{\lambda', \lambda''}^{+} \) and \( \Gamma_{\lambda', \lambda''}^{-} \) are, respectively, the three-phonon and phonon-impurity scattering rates. The quantity \( \Delta_\lambda^{(s)} \) in Eq. (4) is defined by:

\[
\Delta_\lambda^{(s)} = \frac{1}{N} \left( \sum_{\lambda', \lambda''} \Gamma_{\lambda', \lambda''}^{+} \left( \xi_{\lambda', \lambda''}^{(s)} \tau_{\lambda'}^{(n)} - \xi_{\lambda', \lambda''}^{(s)} \tau_{\lambda'}^{(0)} \right) \right)
\]

\[
+ \frac{1}{2} \sum_{\lambda', \lambda''} \Gamma_{\lambda', \lambda''}^{-} \left( \xi_{\lambda', \lambda''}^{(s)} \tau_{\lambda'}^{(1)} + \xi_{\lambda', \lambda''}^{(s)} \tau_{\lambda'}^{(2)} \right) + \sum_{\lambda'} \Gamma_{\lambda', \lambda'} \xi_{\lambda', \lambda'}^{(s)} \tau_{\lambda'}^{(3)} \right), \quad (6)
\]

where \( \xi_{\lambda', \lambda''}^{(s)} = v_{\lambda'}^2 \omega_{\lambda''}/v_{\lambda'}^2 \omega_{\lambda'} \). The solution of Eq. (4) is achieved by the iterative process of \( \tau_\lambda^{(n)} \) being the phonon branch index and wave vector in reciprocal space, respectively. In the linearized-BTE, the distribution \( f_\lambda \) differs from the equilibrium Bose-Einstein distribution function \( \xi_\lambda = 1/(\exp(\beta \omega_\lambda) - 1) \) by a linear term in \( \nabla T \). Here \( \beta = 1/k_B T \) and \( \omega_\lambda \) is the phonon frequency in mode \( \lambda \). The solution of the BTE is done using a full iterative algorithm (Omini and Sparavigna 1995; Lindsay et al. 2010; Li et al. 2012; Mingo et al. 2014) employing ShengBTE code package (Li et al. 2014).
self-consistent $\tau^{(z)}_k$ is determined, the thermal conductivity tensor is calculated from:

$$\kappa^{\beta\beta} = \frac{1}{V k_B T^2} \sum_k (\hbar \omega_k)^2 f_{\beta}^0 \left( \tau^{(\beta)}_k + 1 \right) v^{\beta}_{\beta} \tau^{(\beta)}_k.$$  \hspace{1cm} (7)

Having 2nd- and 3rd-IFCs at hand, the iteration of Eq. (4) is started by calculating the scattering rates $\Gamma^{\alpha}_{\beta\beta}$ and $\Delta^2_k$ from Eq. (5), and continued by computing $\Delta_k$ from Eq. (6). At each step of iteration, the conductivity is calculated from Eq. (7), and the iteration continues until the relative change of the conductivity norm $\sqrt{\sum_k \sum_\beta |\kappa^{\beta\beta}|^2}$ is less than $10^{-5}$. To calculate the thermal conductivity form Eq. (7), we have used an appropriate BZ sampling density of $10 \times 10 \times 10$ and Gaussian smearing of 0.1, which gives almost equal conductivity values obtained using $30 \times 30 \times 30$ and Gaussian smearing of 1.0.

3 Results and Discussions

3.1 Geometry and Harmonic Lattice Dynamics

Using a non-spin-polarized calculation, we have first fully optimized the geometry of the UO$_2$ primitive unit cell with space group 225 and obtained the optimized value of lattice constant for the FCC structure as 5.396 Å.

Using the optimized geometry lattice parameter, the 2nd-IFCs were calculated employing the DFPT method. To this end, we first performed an scf calculation using the optimized lattice parameter with kinetic energy cutoffs of 60 and 600 Ry for the wavefunction and density expansion in terms of plane waves with a $\Gamma$-centered $8 \times 8 \times 8$ mesh in $k$ space with a tighter convergency threshold of $10^{-12}$ Ry. Using the resulting wavefunctions and eigenvalues as unperturbed quantities, the inhomogeneous KS equations in DFPT were solved in $q$-space self-consistently for the potential and density variations, and thereafter, the dynamical matrix is calculated using the atomic mass of U-238 isotope. The threshold for self-consistency of the potential variation was taken as $10^{-14}$. Diagonalizing the dynamical matrix, the phonon frequencies were obtained. In Fig. 1, the experimental and the calculated phonon dispersion curves along the high-symmetry directions in the BZ as well as the PhDOS are shown.

In Fig. 1a, among the nine calculated branches, the lowest three belong to transverse acoustic (TA) and longitudinal acoustic (LA) that correspond to the vibrations of heavy U atoms. The higher frequency branches belong to the transverse optical (TO) and longitudinal optical (LO) modes that correspond to vibrations of lighter O atoms. As is seen, the agreement between experiment and our calculation is excellent for the acoustic branches. However, because in this step, we have not included the non-analytical terms in the dynamical matrices in our simplified model, near the $\Gamma$ point in the $M - \Gamma - X$ and $\Gamma - L$ paths we see no splittings of LO-TO branches.

In the second step, in our simple model, the “exact dispersion” showing LO-TO splitting is obtained just by applying the non-analytic correction to the phonon dispersion. In the correction, the dielectric constant was chosen as 5.2, and the Born charges of U and O as 4.7 and -2.35 units, respectively. The result is shown in Fig. 2. As is seen from Fig. 2a, the non-analytic term correction applied on the second-order force constants in our simple model, could reproduce the LO-TO splitting around the $\Gamma$
point which leads to excellent agreement with experimental results. As we can see, these fine structures does not spoil the calculated lattice thermal conductivity which is a sum over all branches.

In Figs. 1b and 2b, the plotted PhDOS shows that the states in acoustic branches belong to the vibrations of the heavy U atoms whereas the states of optical branches are comprised from the vibrations of the lighter O atoms. It should be mentioned that the calculated phonon frequencies using the atomic mass of U-235 isotope did not result in a meaningful differences in the phonon dispersion, and therefore, we use the same phonon frequencies obtained from U-238 in the calculations of thermal conductivities of bulk UO2 with different isotope abundances.

3.2 Thermal Conductivity

From Eq. (7), to calculate the thermal conductivity, we need phonon frequencies, equilibrium distribution function, group velocities and phonon lifetimes. All needed quantities, but phonon lifetimes were determined from our harmonic calculations. To calculate the phonon lifetimes, we have solved the equation Eq. (4) by iteration until self-consistency. The calculated phonon lifetimes at 300°C are shown in Fig. 3.

As seen from Fig. 3, the TA branches have the largest lifetimes and therefore have dominant role in thermal conductivity. On the other hand, we expect that the optical branches having the shortest lifetimes (corresponding to the vibrations of O atoms) to have smaller contributions in the total conductivity. This result contradicts the result reported in Pang et al. (2013) which claims the optical phonons have the largest contributions in thermal conductivity. However, the experimental results reported in Pang et al. (2013) that show the dominant role is played by optical phonons should be verified in another theoretical study using DFT+U or other methods.

In Fig. 4, we show the lifetimes of the phonons at two temperatures of 300 and 1000°C. It is evidently seen that the phonon lifetimes decrease with temperature.

In Fig. 5, the calculated thermal conductivities in both RTA and full-iterative schemes are compared with experimental data. As is seen, the agreement between full-iterative results and experiment is very good at relatively lower temperatures. This is because, in experiment at lower temperatures, the four- and higher-phonon processes are not activated and the dominant contribution comes from the three-phonon processes which is consistent with our calculations.

In Fig. 6, the thermal conductivity is resolved into the elemental contributions and as is seen, the contributions from U atoms are dominant at all temperatures. This is consistent with the PhDOS plot of Fig. 1b in which all contributions of acoustic branches comes from the U atoms.

Finally, in Fig. 7, we have plotted the thermal conductivities for fuels with different abundances of U-235 isotope. Inspecting the values for different abundances, we observe that with increasing the concentration of U-235, the thermal conductivity decreases, which is due to the increasing the scattering rates due to impurities, $\Gamma_{\text{imp}}$. This argument is confirmed by looking at Fig. 8. However, the decrease in thermal conductivity is not significant because the phonon lifetime, which is determined from the combination of anharmonic and isotopic scattering rates through Matthiessen’s rule (Matthiessen and Vogt 1864), does not change significantly.
Fig. 3 Phonon lifetimes in ps at 300° K. The red, green and blue symbols correspond to TA, LA and optical branches, respectively.

Fig. 4 Calculated phonon lifetimes in ps. The red and green symbols correspond to 300° K and 1000° K, respectively.

Fig. 5 Lattice thermal conductivity of UO$_2$, in W/mK, as a function of temperature. The red solid squares and red open triangles correspond to this work with full-iterative method and RTA calculations, respectively, which are compared with experimental data.

Fig. 6 Elemental resolution of total thermal conductivity. Blue and violet bars correspond to U and O contributions, respectively.

Fig. 7 Thermal conductivities in W/mK as functions of temperatures for fuels with different abundances of U-235.

Fig. 8 Phonon scattering rate due to isotopic mass disorder in ps$^{-1}$ with respect to frequencies for different U-235 concentrations at $T = 300$ K. The lower scattering rates correspond to lower U-235.
4 Conclusions

In this work, the lattice thermal conductivity of bulk UO\(_2\) is studied by the exact solution of the BTE equation for the steady-state phonon distribution function. In this lattice-thermal-conductivity study, we have modeled the high-\(T\) paramagnetic state of bulk UO\(_2\) by a non-spin-polarized calculation, and neglected the Hubbard-U correction for the localized \(f\)-electrons in the U atoms. The computed phonon spectra showed that among the nine branches, the lowest three belonging TA and LA, corresponding to U atoms, were in excellent agreement with experimental data. However, applying a correction due to non-analytical term in the dynamical matrix enhanced the quality of the phonon phonon lifetimes at 300\(^\circ\) K showed that the TA branches had the largest lifetimes and therefore had dominant role in thermal conductivity. On the other hand, the optical branches having the shortest lifetimes (corresponding to the vibrations of O atoms) had smaller contributions in the total conductivity. Due to the fact that nuclear power reactors may use fuels with different relative concentrations of U-235 and U-238, we had also repeated the thermal-conductivity calculations for the cases with U-235 concentrations of 3\%, 5\%, 7\% and 20\%, and observed a small decrease in thermal conductivity by increasing the impurity level. This fact was explained to be due to the increase in the phonon scattering rates from the impurity atoms (U-235).

Acknowledgements This work is part of research program in School of Physics and Accelerators, NSTRI, AEOL.

Data Availability Statement The raw or processed data required to reproduce these results can be shared with anybody interested upon sending an email to M. Payami.

Appendix: Convergenc Tests

In the course of thermal conductivity calculations, at each step, we have to ensure the convergency of the calculated quantities with respect to relevant parameters. These steps include the DFT calculations, harmonic lattice-dynamic calculations, 3rd-IFCs calculations and the solution of the BTE. First, we ensure the convergency of lattice constant with respect to basis-set kinetic-energy cutoffs and \(k\)-grid for structural optimization. The results are tabulated in Table 1:

| \(k\)-mesh | \(E\_c\) |
|---------|---------|
| 40      | 5.4007  |
| 50      | 5.4011  |
| 60      | 5.4010  |
| 70      | 5.4014  |
| 80      | 5.4015  |
| 2 \times 2 \times 2 | 5.3993  |
| 3 \times 3 \times 3 | 5.3994  |
| 4 \times 4 \times 4 | 5.3937  |
| 5 \times 5 \times 5 | 5.3979  |
| 6 \times 6 \times 6 | 5.3956  |
| 7 \times 7 \times 7 | 5.3965  |
| 8 \times 8 \times 8 | 5.3965  |
| 10 \times 10 \times 10 | 5.3965  |

The cutoff for density expansion is taken as 10 times of \(E\_c\). The chosen parameters for \(k\)-mesh and \(E\_c\) are 8 \times 8 \times 8 and 60 Ry, respectively; and the corresponding lattice constant is 5.3968 Å.

We have chosen a \(\Gamma\)-centered 8 \times 8 \times 8, 60 Ry, and 600 Ry for the \(k\)-mesh, wavefunction cutoff and density cutoff, respectively, for our DFT calculations and obtained the converged value of 5.3968 Å for lattice constant.

In the DFPT calculations, we have started with a \(q\)-grid of 8 \times 8 \times 8 and calculated the phonon frequencies and the 2nd-IFCs. To calculate the 3rd-IFCs, we have used the supercell approach. In this step, we determine the appropriate supercell size, magnitude of atomic displacement, and the number of neighboring shells. The appropriate supercell size is intimately connected to the range of forces (McGaughey et al. 2019). We have displaced one atom in a 3 \times 3 \times 3 supercell with 81 atoms from its equilibrium position by 0.2 Bohr. Then, we determined the magnitude of forces acting on each of 81 atoms in the supercell and plotted with respect to the distance from the displaced atom (see Fig. 8).

As shown in Fig. 9, the forces drop to \(~0.01\) of the maximum force at a distance of 4 Å which encloses up to second neighbor atomic shells. This estimate indicates that the adopted supercell size of 3 \times 3 \times 3 is appropriate for our 3rd-IFCs calculations. Using this force cutoff as an initial guess for the cubic cutoff, we have then determined the appropriate magnitude for the atomic displacements. To this end, considering all the symmetries of the system, we have generated sets of 108 displacements sufficient for calculating 3rd-IFCs for each magnitude of 0.005, 0.01, 0.03, 0.05 and 0.1 Å. Testing the thermal conductivities obtained from these trial 3rd-IFCs (see Fig. 10), we found that the appropriate magnitude of 0.03 Å gives stable value for the thermal conductivity at 300\(^\circ\) K.

Next, we have tested the convergency of thermal conductivity with respect to the number of interaction shells in...
Finally, we have tested the convergency of thermal conductivity with respect to the $q$-mesh in the DFPT calculations, and found that the $q$-mesh of $12 \times 12 \times 12$ leads to converged result.

References

Amoretti G, Blaise A, Caciuffo R, Fournier JM, Hutchings MT, Osborn R, Taylor AD (1989) 5f-electron states in uranium dioxide investigated using high-resolution neutron spectroscopy. Phys Rev B 40:1856

Arima T, Yamasaki S, Inagaki Y, Idemitsu K (2005) Evaluation of thermal properties of UO$_2$ and PuO$_2$ by equilibrium molecular dynamics simulations from 300 to 2000 K. J Alloys Compd 400:43

Baroni S, de Gironcoli S, Dal Corso A, Giannozzi P (2001) Phonons and related crystal properties from density-functional perturbation theory. Rev Mod Phys 73:515

Dolling G, Cowley R, Woods A (1965) The crystal dynamics of uranium dioxide. Can J Phys 43(8):1397

Dorado B, Amadon B, Freyss M, Bertolus M (2009) DFT+U calculations of the ground state and metastable states of uranium dioxide. Phys Rev B 79:235125

Esfarjani K, Stokes HT (2008) Method to extract anharmonic force constants from first principles calculations. Phys Rev B 77:144112

Faber J, Lander GH, Cooper BR (1975) Neutron-diffraction study of UO$_2$: observation of an internal distortion. Phys Rev Lett 35:1770

Fink J (2000) Thermophysical properties of uranium dioxide. J Nucl Mater 279(1):1

Fink J, Chasanov M, Leibowitz L (1981) Thermophysical properties of uranium dioxide. J Nucl Mater 102(1):17

Freyss M, Dorado B, Bertolus M, Jomard G, Vathonne E, Garcia P, Amadon B (2012) First-principles DFT+U study of radiation damage in UO$_2$: $f$ electron correlations and the local energy minima issue. No. 113 in Scientific Highlight of the Month. https://psi-k.net/highlights/

Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C, Ceresoli D, Chiarotti GL, Cococcioni M, Dabo I et al (2009) QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. J Phys Condens Matter 21(39):395502

Godfrey T, Fulkerson W, Kollie T, Moore J, McElroy D (1965) Thermal conductivity of uranium dioxide from $57^\circ$ to $1100^\circ$ C by a radial heat flow technique. J Am Ceram Soc 48(6):297

Goldsmith L, Douglas J (1973) Measurements of the thermal conductivity of uranium dioxide at 670–1270 K. J Nucl Mater 47(1):31

Hohenberg P, Kohn W (1964) Inhomogeneous electron gas. Phys Rev 136(3B):B864

Idiri M, Le Bihan T, Heathman S, Rebizant J (2004) Behavior of actinide dioxides under pressure: UO$_2$ and ThO$_2$. Phys Rev B 70(1):014113

Kaur G, Panigrahi P, Valsakumar MC (2013) Thermal properties of UO$_2$ with a non-local exchange-correlation pressure correction: a systematic first principles DFT+U study. Modell Simul Mater Sci Eng 21:065014

Kohn W, Sham LJ (1965) Self-consistent equations including exchange and correlation effects. Phys Rev 140(4A):A1133

Li W, Lindsay L, Broido DA, Stewart DA, Mingo N (2012) Thermal conductivity of bulk and nanowire Mg$_2$Si$_{1-x}$Sn$_x$ alloys from first principles. Phys Rev B 86:174307
Li W, Carrete J, Katcho NA, Mingo N (2014) ShengBTE: a solver of the Boltzmann transport equation for phonons. Comput Phys Commun 185(6):1747
Lindsay L, Broido DA, Mingo N (2010) Diameter dependence of carbon nanotube thermal conductivity and extension to the graphene limit. Phys Rev B 82:161402
Matthiessen A, Vogt C (1864) IV. On the influence of temperature on the electric conducting-power of alloys. Philos Trans R Soc Lond 154:167
McGaughy AJ, Jain A, Kim HY, Fu B (2019) Phonon properties and thermal conductivity from first principles, lattice dynamics, and the Boltzmann transport equation. J Appl Phys 125(1):011101
Mingo N, Stewart D, Broido D, Lindsay L, Li W (2014) Ab initio thermal transport. In: Length-scale dependent phonon interactions. Springer, New York, pp 137–173
Motoyama S, Ichikawa Y, Hiwatari Y, Oe A (1999) Thermal conductivity of uranium dioxide by nonequilibrium molecular dynamics simulation. Phys Rev B 60(1):292
Omini M, Sparavigna A (1995) An iterative approach to the phonon Boltzmann equation in the theory of thermal conductivity. Physica B 212(2):101
Pang JWL, Buyers WJL, Chernatynskiy A, Lumsden MD, Larson BC, Philippot SR (2013) Phonon lifetime investigation of anharmonicity and thermal conductivity of UO$_2$ by neutron scattering and theory. Phys Rev Lett 110:157401
Peierls R (1997) On the kinetic theory of thermal conduction in crystals. In: Dalitz RH, Peierls R (eds) Selected scientific papers of Sir Rudolf Peierls: (With Commentary). World Scientific, Singapore, pp 15–48
Perdew JP, Wang Y (1992) Accurate and simple analytic representation of the electron-gas correlation energy. Phys Rev B 45:13244
Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approximation made simple. Phys Rev Lett 77:3865
Resnick A, Mitchell K, Park J, Farfán EB, Yee T (2019) Thermal transport study in actinide oxides with point defects. Nucl Eng Technol. https://doi.org/10.1016/j.net.2019.03.011
Sheykh S, Payami M (2018) Electronic structure properties of UO$_2$ as a Mott insulator. Physica C (Amsterdam, Neth) 549:93
Tamura S (1983) Isotope scattering of dispersive phonons in Ge. Phys Rev B 27:858
Tamura S (1984) Isotope scattering of large-wave-vector phonons in GaAs and InSb: deformation-dipole and overlap-shell models. Phys Rev B 30:849
Torres E, Kaloni T (2019) Thermal conductivity and diffusion mechanisms of noble gases in uranium dioxide: a DFT+U study. J Nucl Mater 521:137
Wen XD, Martin RL, Henderson TM, Scuseria GE (2013) Density functional theory studies of the electronic structure of solid state actinide oxides. Chem Rev 113(2):1063. https://doi.org/10.1021/cr300374y PMID: 23252457
Yamada K, Kurosaki K, Uno M, Yamanaka S (2000) Evaluation of thermal properties of uranium dioxide by molecular dynamics. J Alloys Compd 307:10
Zhang Y, Yang W (1998) Comment on generalized gradient approximation made simple. Phys Rev Lett 80:890
Ziman J (1960) Electrons and phonons: the theory of transport phenomena in solids. Clarendon, Oxford