**Anisotropic thermophysical properties of U3Si2 fuel: An atomic scale study**

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**Abstract**

Due to renewed interest in uranium silicide compounds as a candidate for nuclear reactor fuels, there is a need for extensive investigations of their thermophysical properties as a function of temperature. In this work, we calculate the thermophysical properties of the U3Si2 compound within the framework of molecular dynamics (MD) using a semi-empirical modified Embedded-Atom Method (MEAM) potential and density functional theory (DFT). Thermal expansion, thermal conductivity, heat capacity, and elastic properties are presented as a function of temperature from 300 to 1800 K. The thermal conductivity of U3Si2 increases with temperature due to the electronic contribution while the phonon contribution decreases with increasing temperature. The phonon contribution to the thermal conductivity at 300 K is estimated at 2.03 W/mK and 1.41 W/mK using non-equilibrium molecular dynamics (NEMD) and equilibrium molecular dynamics (EMD), respectively. The electronic contribution is estimated to be 8.56 W/mK using the semi-classical Boltzmann transport theory at 300 K. Furthermore, we compared the thermal conductivity in two different crystallographic directions to shed light on the spatial anisotropy using NEMD and EMD methods. The inherent anisotropic thermophysical properties can be used to parametrize phase field models to incorporate anisotropic thermal conductivity and thermal expansion, allowing for a more accurate description of microstructural evolution under variable temperature and irradiation conditions.

***Keywords:*** *Uranium silicide; Anisotropy; molecular dynamics; thermophysical; MEAM.*

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**1. Introduction**

Uranium dioxide (UO2) is the standard fuel in today’s Light Water Reactors (LWRs). The nuclear accident at Fukushima in 2011 provided motivation for fuel vendors, in collaboration with national and international regulatory agencies, to consider an alternative fuel that can withstand the loss of coolant for a considerably longer time in the case of an accident. Alternate fuel types must maintain high safety and reliability during normal operation, and it would be preferable if major changes to the present design of the LWRs are not required [1,2]. Binary uranium-silicon compounds such as U3Si2 have attracted a lot of attention as a nuclear fuel material because of some more favorable characteristics when compared to UO2. For instance, U3Si2 has a higher thermal conductivity and higher fissile material density [3]. The enhanced heat removal capabilities make uranium silicide fuel a promising potential fuel for generation *IV* reactors. However, until recently there has been limited study on the thermal properties of uranium silicide [4] compared to properties such as oxidation behavior [5,6], structural information [7,8], and radiation resistance [9,10].

According to experiments [7,8], U3Si2 has a tetragonal crystal structure (space group 127) with U occupying *2a* and *4h* Wyckoff positions while Si occupies the *4g* site as shown in Figure 1. Using a particle swarming optimization code, Noordhoek *et al*., predicted a new U3Si2 phase with space group number 2 which has not been experimentally synthesized [11].

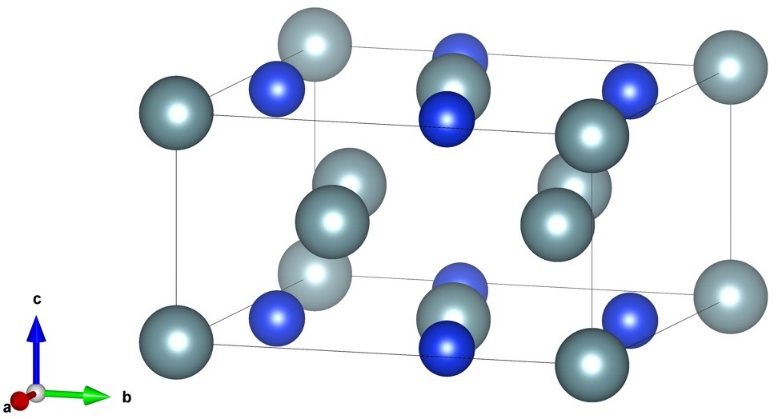


Figure 1: Unit cell of ordered uranium silicide containing 2 formula units of U3Si2 (10 atoms). (Color scheme: U=grey, Si=blue)

Due to the growing interest in Accident Tolerant Fuels (ATFs) in the last few years, some work has been conducted on U-Si alloys focused on U3Si2. Density functional theory (DFT) calculations by Wang *et al.* provided detailed data on the electronic structure [12] and work by Middleburgh *et al.* modeled the formation energies of point defects [13]. White *et al*. developed a feasible powder metallurgy method of preparation and measured the thermophysical properties of U3Si2 [3]. More recently, Obbard *et* *al.* used *in-situ* neutron diffraction to collect the temperature dependence of lattice parameters and the lattice thermal expansion coefficient was calculated. They observed anisotropy in lattice expansion at ~1000 oC, corroborating the dilatometry measurement of White *et al*. [3, 14] . Our recent work within the framework of DFT explores the mechanism of oxidation from an atomistic perspective [15], while work by Wood *et al*., experimentally showed the oxidation kinetics in the presence of air and steam [16–18]. Furthermore, these authors investigated the possibility of reducing oxidation by alloying of U3Si2 with aluminium, exploring formation of an Al2O3 passivation layer for preventing further oxidation [19]. Recent *in-situ* TEM observation of Xe ion irradiated U3Si2 indicates that, at normal reactor operation conditions, uranium silicide is stable and no radiation-induced amorphization was reported [20]. In a similar experiment using Kr ions, Miao *et al*. noticed that U3Si2 is oxidized forming a mixture of nanocrystalline UO2 and a Si-enriched amorphous phase, raising concern for radiation assisted corrosion issues [10]. Beyond the properties of pristine U3Si2, it is essential to understand the underlying behavior in an extreme environment typical for a nuclear reactor. The radiation-induced defects and fission products in nuclear reactor fuel result in microstructural changes which in turn alters the fuel’s thermophysical properties [21]. This has a significant effect on the thermal conductivity which decreases as radiation dose increases due to the contribution from phonon scattering. Such behavior is difficult to determine from experiment due to the limitation and cost of irradiation experiments. Beeler *et al*. developed a MEAM potential to model the formation of point defects, and calculated formation energy and thermophysical properties of U3Si2 [22]. The interatomic potential reported in Beeler’s paper will be used in this work to calculate various thermophysical properties of U3Si2.

The thermophysical properties such as specific heat, the coefficient of thermal expansion, density and the thermal conductivity of the fuel as a function of temperature are important and must be known in order to effectively model and predict fuel behavior under normal and unusual irradiation conditions. In this work, we calculated these properties and evaluate the results obtained by comparing them with the experimental data available in the existing literature.

**2. Computational details**

*2.1 Phonon assisted thermal conductivity calculation*

Molecular Dynamics (MD) simulations, employing a set of interatomic potentials for U3Si2 derived previously by Beeler *et al*. [22] are adopted in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [23]. In the proposed model the potential energy , of an atom *i* with respect to all other atoms has two components which are: i) a pair potential description of each system and ii) an angular dependent many-body embedding function contribution. The detailed formalism of the modified many-body embedded atom method (MEAM) is well described in references [24,25].

The phonon assisted thermal conductivity () of a material is determined by several scattering mechanisms which include isotopic scattering, point defect scattering, three-phonon scattering and grain boundary scattering to name just a few. The value of can be calculated in different ways [26] including the relaxation time approximation [27], Callaway model [28], Slack model [26], Non-Equilibrium Molecular Dynamics (NEMD) [26], Equilibrium Molecular Dynamics (EMD) with Green-Kubo formalism [29,30] and by solving Boltzmann transport equation iteratively [31]. In this work, we calculated using the MD-based methods and the electronic thermal conductivity () was approximated using the Wiedemann–Franz lawrelationship [32]. In this work, the calculation of was done using both EMD and NEMD methods for comparison.

*2.1.1 Equilibrium Molecular Dynamics method*

In the EMD approach, the Green-Kubo method relates the equilibrium fluctuations of the heat current vector, S, to the thermal conductivity tensor via the fluctuation-dissipation theorem. The phonon assisted thermal conductivity ( in the α-direction is given by Eq.1 [29,30]

|  |  |
| --- | --- |
| α = *x*, *y* or *z* direction | (1) |

where is the Boltzmann constant, t is time, T is temperature, is the ensemble average of in the *α*-direction, usually called the heat current autocorrelation function (HCACF). denotes the heat current in the *α*-direction which can be computed by Eq.2 [33,34]:

|  |  |
| --- | --- |
| , | (2) |

where and are the total energy and velocity of atom *i,* respectively, is the force exerted by atom *j* on atom *i*, and is the instantaneous and equilibrium interatomic separation vectors between atoms *i* and *j*. The EMD simulations were performed using the LAMMPS code [23]. The starting structures of size were first run for 4,000,000 time steps using an isothermal-isobaric (NPT) ensemble to allow the volume to expand, and then equilibrated under a constant volume and energy ensemble (NVE) for 4,000,000 time steps at temperatures of interest. A time step of 0.25 fs was deemed suitable to maintain energy conservation. To avoid statistical noise during heat flux collection, NVE was run for an additional 2,000,000 time steps. Correlation functions were evaluated from the heat current time series.

*2.1.2 Non-Equilibrium Molecular Dynamics method*

In the NEMD simulations, the systems were initially equilibrated using an NPT ensemble with a Nosé-Hoover thermostat and barostat with a damping time of 0.1 ps and 0.5 ps respectively at zero external pressure. Equilibration is achieved when there is convergence in total energy and volume of the system.

These structures are equilibrated for 2 ns for temperatures between 300 K and 1800 K at 15 K intervals with the thermophysical properties (lattice parameter and enthalpy) obtained from averages taken over the final 0.25 ns of the simulation.

The equilibrated structures were also used for thermal conductivity simulations by means of the non-equilibrium MD method. A time step of 1 fs was used throughout the simulation. In the NEMD method [35], kinetic energy can be transferred between atoms from one region of the supercell to another. Here, we used a rectangular supercell (slab) of five different lengths including 100, 125, 150 and 175 unit cells in the *z*-direction. The supercell is split into several bins with a constant heat flux , generated by heat exchange of atoms between the hot and cold region, respectively, as shown by the schematic illustration in Figure 2 (inset). The temperature gradient, , is established between the two extreme temperatures due to the kinetic energy exchange. Eventually, a steady state in thermal gradient is reached where is equal and opposite to the kinetic energy exchange so that the temperature profile remains constant. In Figure 2 (main), a steady state temperature distribution, along the direction of heat transfer, is plotted for the largest system (5 × 5 × 175 unit cells) studied with the cold region at both ends and the hot region at the middle of U3Si2 This shows that the temperature at the center of the supercell is higher than that at the edge. The slope of the profile is the temperature gradient of the system, . Temperature control can be simulated by addition or subtraction of the non-translational kinetic energies in the heat bath such that momentum is conserved.

The phonon thermal conductivity, , is computed using Eq. 3:

|  |  |
| --- | --- |
| , | (3) |

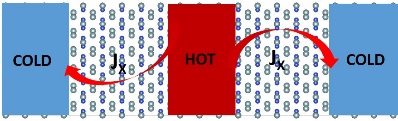
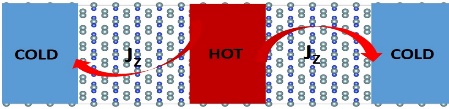
where the heat flux, is given by Eq. 4:

|  |  |
| --- | --- |
| , | (4) |

is the amount of transferred kinetic energy calculated over all exchanges during the simulation time t in the z-direction. and are the supercell lengths of the area through which the heat is transferred. The temperature gradient,, is given by Eq. 5:

|  |  |
| --- | --- |
| , | (5) |

where T is the temperature in Kelvin and is the length of the supercell in the *z*-direction.



(a)

(b)

Figure 2: A steady-state temperature profile for a (a) 175 × 5 × 10 (b) 5 × 5 × 175 unit cell system with the cold region at both ends and the hot region at the middle of U3Si2. The inset is a schematic illustration of the NEMD simulation setup used to study thermal conductivity of U3Si2. (Color scheme: U=grey, Si=blue).

Due to the spatial difference in the *x* and *z* directions of tetragonal U3Si2 structure, we expect difference in phonon transport in both directions. To investigate the spatial anisotropy in , we applied the same methods discussed above to the *x* direction of the crystal.

*2.2 Electronic thermal conductivity calculation*

The electronic thermal conductivity () at a given temperature T, can be calculated from electrical conductivity tensor () of a material using Wiedemann-Franz law [32]:

|  |  |
| --- | --- |
| = σLT, | (6) |

where L is the Lorenz number which equals L = 2.44 × 10−8 W Ω K−2.

The electron-electron contribution to electrical resistivity () which is related to can be obtained using the Eq. (7):

|  |  |
| --- | --- |
| , | (7) |

where is the electronic relaxation time for electron-electron scattering, τ is the total electronic relaxation time and is calculated using the Semi-Classical Boltzmann Theory with the relaxation time approximation and the rigid band approximation as implemented in the BoltzTraP code [36] . The full tensor of σ is calculated from the conductivity distributions:

|  |  |
| --- | --- |
| , | (8) |

Where *f* is the Fermi-Dirac distribution function, ɛ is the band energy, µ is the Fermi level and is defined as:

|  |  |
| --- | --- |
| , | (9) |

Where k is a set of k-points elements in reciprocal space, N is the number of k-points sampled, *i* is the band index and is given by:

|  |  |
| --- | --- |
| , | (10) |

where e is the elementary charge and is the group velocity of the electrons. Based on Eqs. 6–10, the full tensor of σ is calculated using and the electronic band structure data is calculated within the framework of DFT as implemented in the Quantum ESPRESSO code [37]. The exchange and correlation effects were described by the generalized gradient approximation (GGA) in the Wu-Cohen (GGA-WC) formulation [38]. The norm-conserving Wu-Cohen (WC) pseudopotentials (where these potentials treat 7p0 6d1 5f3 7s1 as valence electrons for U and 3s2 3p6 as valence electrons for Si) was used in this calculation. The strong on-site Coulomb repulsion among the localized uranium 5f electrons is described by the DFT + U formalism formulated by Liechtenstein *et al*. [39]. The Hubbard U parameter of 1.5 eV was utilized in this work in line with an earlier valued reported by Noordhoek *et al.* [11]. The Fermi surface effects were treated by the smearing technique of Methfessel-Paxton [40], using a smearing parameter of 0.02 Ry (0.27 eV). An energy threshold defining self-consistency of the electron density was set to 10-8 eV and a beta mixing factor of 0.3. Brillouin zone integration was performed using Monkhorst-Pack [41] k-point grids centred at the point. Structural relaxation was carried out to minimize the energy using the conjugate gradient method within the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [42], until the magnitude of the residual Hellmann-Feyman force on each relaxed atom reached 0.01 eV Å-1.

**3. Results and discussion**

*3.1 Lattice parameter and thermal expansion*

As a preliminary step, we calculate the lattice parameter ‘*a*’ and ‘*c*’ as a function of temperature. Not only is it required for all simulations, but also the thermal expansion coefficient α is a simple characteristic that depends directly on the anharmonic terms in the potential. Therefore, it gives a quick indication of how appropriate the interatomic potential is for studying thermal conductivity. The total energies, lattice parameters and volumes were determined by averaging over the last 50 ps of the simulations. The linear thermal expansion coefficient (LTEC) and volumetric thermal expansion are then given by the relationship respectively:

|  |  |
| --- | --- |
| = | (11a) |
| = | (11b) |

where L is the lattice parameter in *x* and *z* direction while *v* is volume. The derivative of the lattice parameter with respect to temperature, and were calculated by fitting a straight line to the lattice parameters and volume respectively at a specific temperature, T, and the points within 15 K on either side (See supplementary material for detailed plots from which lattice gradients are extrapolated) in order to reduce numerical fluctuations. The calculated lattice parameters *a*, *c* and cell volume at 0 K are presented in Table 1. Our results are in good agreement with the work by Beeler *et al.* given that the same interatomic potential is used in this work. There is a variation between our MD results and previous DFT + U and experimental measurements. For instance, a comparison with DFT + U calculations from Noordhoek *et al.* showed that *a* is underestimated by ~2.1 % and *c* overestimated by ~4 %.

Table 1: Structural properties (lattice parameter a, c (Å) and volume (Å3)) of U3Si2 calculated at 0 K using MEAM U-Si potential and compared to DFT + U calculations as well as experiment.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | a | c | Volume/atom | c/a |
| This work (MD) | 7.078 | 4.064 | 20.355 | 0.574 |
| Beeler (MD) *et al.* [22] | 7.078 | 4.064 | 20.355 | 0.574 |
| Noordhoek (DFT+U) *et al*. [11] | 7.230 | 3.891 | 20.339 | 0.538 |
| Wang (DFT+U) *et al.* [12] | 7.320 | 3.890 | 20.844 | 0.531 |
| Jossou (DFT+U) *et al.* [15] | 7.210 | 3.860 | 20.066 | 0.535 |
| Zachariasen (Expt.) [7] | 7.315 | 3.893 | 20.831 | 0.532 |
| Obbard (Expt.) *et al.* [14] | 7.324 | 3.882 | 20.832 | 0.530 |

The average lattice parameters *a*, *c* and cell volume *v* as a function of temperature obtained from the MD simulation for U3Si2 are shown in Figure 3a-c. Experimental values are also plotted in the range from 298 K to 1872 K. The lattice parameter *a* and cell volume *v* are underestimated while *c* is overestimated but it is clear that the MD results follow the experimental trend. Some disagreement with experiment is understandable since the interatomic potential model was not fitted to this data. In Figure 3a-c the behavior of the lattice parameters and cell volume can be seen to be almost linear in the range of 298-1800 K. Finally, Figure 3d-f shows thermal expansion ΔL/L0 as a function of temperature where L is lattice parameters *a*, *c* and cell volume *v* for U3Si2 structure. There is a subtle change in the thermal gradient at temperature points which coincidentally marks the onset of change in the LTEC calculated for U3Si2 in Fig. 4. The underestimation of the LTEC in comparison with experimental data is predictable as the individual components of the thermal expansion are also underestimated, especially after ~500 K.



(f)

(e)

(d)



(a)

(b)

(c)

Figure 3: (a-c) Shows variation of lattice parameter and cell volume (d-f) Thermal strain in lattice parameters and in cell volume as a function of temperature. The experimental lattice constants and lattice strain data were obtained from Refs. [14].

We compared the LTEC computed from the volumetric strain, (LTEC = and is the volumetric thermal expansion) with experimental measurements and the previous MD result. A fairly good agreement is observed with the data calculated here and the work of Loch *et al*. [43] and Shimizu [44] especially at temperatures above 900 K, while underestimation is noticed in comparison to the recent measurement by White *et al*. [3] and Taylor *et al*. [45]. The average LTEC from 300 to 1200 K is 11.81 10-6 K-1, in excellent agreement with the result of Beeler *et al.* [21].



(a)

(b)

Figure 4: (a) Linear thermal expansion coefficients of U3Si2 calculated from volumetric strain (b) anisotropy in linear thermal expansion coefficient in a and c direction as a function of temperature. The experimental linear thermal expansion coefficient data were obtained from Refs. [3, 43-45].

Beeler *et al.* [21] calculated an average LTEC but did not report unique *a*/*c* expansion coefficients. Additionally, this work utilizes a more refined temperature sampling, which allows for a more intricate analysis of the nature of anisotropic thermal expansion. This work is performed in order to compare with the experimental results from Obbard *et al.* [14]. We looked at the directional dependence of LTEC and it is interesting to note that there are three transition regimes in the *a* direction at 500, 1300 and 1700 K, with a LTEC of 9.86, 12.54 and 13.86 × 10-6 K-1,respectively. As shown in Figure 4b, there is a transition in the *c* direction at 600 K and a comparison with a recent study where a transition point is established at ~1300 K [14] shows agreement with one of the transition points observed in our calculation. These differences might be due to the nature of the MEAM potential since it was not developed for calculating thermophysical properties [22]. It is also well known that thermal expansion can be made up of lattice, electronic, magnetic and vacancy/interstitial compo­nents, depending upon the material and temperature range. The MD model does not account for all of these factors, and the electronic contribution could be especially important given the metallic nature of U3Si2 [46]. To further investigate the observed anisotropy, we compute the *c*/*a* ratio which is a measure of the tetragonality of the structure. The change in *c*/*a* with temperature is important, because it has a direct influence on the evolution of the LTEC.



Figure 5: The temperature dependence of the *c*/*a* ratio of U3Si2. The experimental *c*/*a* data were derived from Ref. [14].

The non-uniform expansion of the *a* and *c* lattice parameters is responsible for the change in the *c*/*a* ratio with temperature as shown in Figure 5, which in turn results in the anisotropic nature of the LTEC in U3Si2. The *c*/*a* ratio is overestimated in our calculation but none the less follows the experimental trend.

*3.2 Enthalpy and Specific heat*

In this work we determine the enthalpy increment (increase in enthalpy with respect to standard temperature and pressure as a function of temperature, using the relationship. Just like the lattice parameter, the enthalpy increment increases approximately linearly with temperature as shown in Figure 6a. The first derivative of the enthalpy increment with respect to temperature is used to calculate the specific heat capacity at constant pressure due to phonon scattering, , (including both harmonic and anharmonic contributions) using the following relationship,

|  |  |
| --- | --- |
| = | (12) |

where n is the number of moles. The first derivative of the enthalpy was calculated by fitting a straight line to the enthalpy (see supplementary material for detailed plots from which enthalpy gradients are extrapolated) at a given temperature T and the data at T±15 K on either side. The molar heat capacity of a metal is the summation of the dilatational, harmonic and anharmonic lattice (phonon), and electronic terms. The total molar heat capacity, is estimated by addition of the and the electronic heat capacity, given by:

|  |  |
| --- | --- |
| , | (7) |

where is the electronic specific heat coefficient (experimentally determined as 52.0 mJ/mol-K2 [3] and estimated to be 13.2 mJ/mol-K2 from DFT+U calculations [47]) and T is the temperature in Kelvin. The calculated values agree with the Dulong Petit Law value above the Debye temperature. The sum of and components of heat capacity give the total heat capacity, , shown as the red and black data points in Figure 6b. In comparison to previous work [3,48], there is a good agreement from 300 to 900 K especially with the experimentally determined. The electronic contribution to heat capacity is quite significant since the Dulong-Petit limit for phonon specific contribution is ~125 J/mol-K. This is consistent with work by Beeler and coworkers who determined at 400 K to be 134 J/mol-K [22] which agrees with recently measured value by Antonio *et al*. at 300 K as 149 J/mol-K [4].



(a)

(b)

Figure 6: (a) The change in enthalpy relative to the enthalpy at 300 K (b) molar heat capacity at constant pressure as a function of temperature. The experimental heat capacity at constant pressure data were obtained from Refs. [3, 48].

*3.3 Elastic constants*

Elasticity describes the physical and internal changes of solid material under the application of stress and strain. The elastic coefficients and moduli can be also linked to the atomic bonding, deformation characteristics and mechanical and structural stability. To investigate the mechanical stability of the intermetallic U3Si2, we computed the elastic constants from the ground-state elastic tensor using structures optimized at 0 and 300 K using the scripts provided with LAMMPS code [23]. Temperatures considered here allow for comparison with DFT results (0 K) and experimental data at 300 K. The calculated elastic constants of a single crystal of U3Si2 are listed in Table 2 along with the reported values from DFT calculations [11,12,47] and experiment [49]. For tetragonal symmetry, there are six independent elastic constants, that is, C11, C12, C13, C33, C44 and C66. The calculated elastic constants of U3Si2 fulfil the Born criteria for mechanical stability [50]. Therefore, it can be said that U3Si2 is mechanically stable at ambient conditions.

While DFT calculations are believed to be more accurate than MD simulations, their high computational cost strongly limits the length and time scales used in such calculations. The bulk and shear moduli here are estimated using the Hill’s model which is an average of the Voigt and Reuss bounds [51] while Beeler *et al.* used only the Voigt bound, hence the difference in bulk modulus. As shown in Table 2, there is a general softening in the elastic constant as we increased the temperature from 0 to 300 K, and a look at the experimental measurements which are done at room temperature shows that Young's modulus is overestimated in our MD calculation by ~15–20% at 300 K, while comparison at 0 K shows that our result is underestimated by ~3–17% [12, 47]. There are various deviations in the calculated Bulk moduli in comparison to the measured values of 68.3 and 64.3 GPa, which are from the different sets of U3Si2 samples prepared at Los Alamos National Laboratory [49]. It is also important to mention that theoretical calculations assume a single crystal during simulations while experimental measurements were conducted on polycrystalline U3Si2 samples with the possible presence of porosity, grain boundaries and microcracks, which might account for the general overestimation in DFT and MD data. The external defects can significantly reduce the magnitude of the elastic properties [52].

The elastic and thermophysical properties of solids are related through the Debye model. Furthermore, the Debye temperature, is related to many physical properties such as specific heat, elastic constants, and melting point, [53]. The is estimated using elastic constant data which is related to the mean sound velocity, from the following equation [46]:

|  |  |
| --- | --- |
| , | (13) |

where ħ is the Planck's constant, k is Boltzmann’s constant, is Avogadro's number, n is the number of atoms per formula unit, and is the density. The mean sound velocity, , in polycrystalline materials is approximated by [54]:

|  |  |
| --- | --- |
| , | (14) |

where the transverse velocity and the longitudinal velocity.

The calculated elastic constants can be used to estimate the of solids based on a correlation derived by Fine *et al*. from studying many cubic and tetragonal structures [55]. This is given by:

|  |  |
| --- | --- |
| , | (15) |

Using Eqs. 13–15, the polycrystalline properties of U3Si2 are calculated and are presented in Table 3. These results are also compared to recent DFT result from Wang *et al*. [12]. The calculated value of the from data at 0 K and 300 K are 1300 and 1198.300 K, respectively. Furthermore, DFT work by Szpunar *et al.* reports for paramagnetic and ferromagnetic U3Si2 phases as 1796 and 1250 K respectively [56]. These values are reasonably close to the experimental value of 1938 K [57] and the MD result of 1775 K especially when the upper limit is considered. This relation provides a quick method for estimating the using the elastic constants calculated in this work. The calculated value of the Debye temperature of U3Si2 agrees well with the reported theoretical value of 280.92 K [4]. Although it is overestimated by approximately 76 (81) K in comparison to a recent experimental measurement of 200 K, this is still considered excellent agreement.

Table 2: Elastic constants (GPa) and elastic moduli (GPa) of U3Si2 at 0 and 300 K. Experimental U3Si2 specimens labelled a= set A (samples1 – 5) and b= set B (samples 6 – 7) were prepared from different feedstocks [49].

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | C11 | C33 | C12 | C13 | C44 | C66 | G | B | E | ν |
| MEAM at 0K (This work) | 210.23 | 160.20 | 178.90 | 65.75 | 103.10 | 35.40 | 51.09 | 126.67 | 135.13 | 0.32 |
| MEAM at 0K [22] | 210.2 | 160.2 | 178.9 | 65.8 | 103.1 | 35.4 |  | 134 | – | – |
| DFT at 0K [11] | 149 | 139 | 49 | 48 | 63 | 46 | 53 | 81 | 130 | 0.23 |
| DFT at 0K [12] | 167.26 | 205.31 | 45.63 | 50.34 | 67.49 | 74.09 | 67.68 | 92.01 | 163.06 | 0.20 |
| DFT at 0K [47] | 155 | 142 | 47 | 50 | 65 | 46 | 57 | 83 | 139 | 0.22 |
| MEAM at 300K (This work) | 208.57 | 145.79 | 144.9 | 67.01 | 90.99 | 47.1 | 60.00 | 118.70 | 154.04 | 0.28 |
| Experiment [49] | 137.90 | – | – | – | 53.75 | – | – | 68.30±0.5a 64.30±0.3b | 130.40±0.5a 122.90±2.4b | 0.182±0.003a 0.179±0.007b |

Table 3: Theoretical sound velocities (m/s), Debye and melting temperatures (K) of U3Si2 predicted using the elastic properties at 0 and 300 K

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Temperature (K) |  |  |  |  |  |
| 0 | 4174.17 | 2295.05 | 2558.19 | 276.19 | 1224.300 |
| 300 | 4125.83 | 2338.76 | 2600.55 | 280.76 | 1300 |
| DFT at 0 [12] | 3865.04 | 2355.32 | 2601.53 | 280.92 | 1300 |

*3.4 Thermal conductivity*

*3.4.1. Phonon contribution to the thermal conductivity*

The thermal conductivity of nuclear fuel pellets is an important thermophysical property in nuclear reactors. It is argued in the literature that the high thermal conductivity of metallic systems is mainly contributed by the electrons (*el*) while the phonon (*ph*) contribution is small, and hence neglected in some cases [32]. However, our work on uranium diboride (UB2) which is a metallic system, showed significant phonon contribution [58], which implies the scattering centers that contribute to thermal conductivity depends on the nature of the material. Phonon scattering occurs in three phonon interactions, which result from anharmonicities in the interatomic potential. The other phonon scattering center which contributes to thermal conductivity includes impurities, grain boundaries or local distortions of the lattice. These contributions are not accounted for in this work, as their effects are expected to be statistically insignificant in U3Si2.

The total thermal conductivity of metallic nuclear fuel is determined by the combination of the contribution to the thermal conductivity both from electronic and phonon transport as follows:

|  |  |
| --- | --- |
| , | (16) |

The is the electronic contribution to the thermal conductivity that is calculated below using the Wiedemann-Franz law [32]. We have calculated the of U3Si2 at temperatures from 300 to 1500 K by both the NEMD and the EMD methods. The size of the supercell has a considerable effect on the thermal conductivity calculated using both methods. Therefore, rigorous convergence testing for a finite simulation cell size was carried out for the two methods.

In the EMD approach, the convergence of with respect to the HCACF integral and finite simulation cell size are key sensitivity tests that are needed to achieve converged values of thermal conductivity. The HCACF integral is directly proportional to the thermal conductivity (see Eq. 4). Convergence in HCACF is achieved by varying the correlation length (truncation time) until it has decayed to zero. The normalized HCACF (main figure) and its integral (inset) at 300 and 1200 K are shown in Figure 7a. The HCACF integral converged after 0.90 ns, hence we specify the converged value of the HCACF integral by averaging its value between times of 0.90 and 1.25 ns (the shaded region of the inset).

The number of phonons needed to capture the *ph–ph* scattering in the bulk material is dependent on the simulation cell size. This effect is reduced by increasing the simulation cell length until the thermal conductivity reaches a size independent value. In this work, we investigated system sizes of , and (12000, 20160, 31360, and 46080 atoms, respectively) all at a temperature of 300 K. These systems correspond to lengths of 4.68, 5.46, 6.24, and 7.02 nm respectively. In Figure 7b we show the computed thermal conductivity obtained by direct integration for 1.25 ns of the HCACF for different choices of simulation cell. We see that the 12000 atom (3.90 nm) system results in the lower value of 0.73 W/mK, compared to the simulations in a larger system size of 46080 atoms (7.02 nm). However, it is apparent from Figure 7b that the results for are well converged by 31360 atoms (6.24 nm) with a value of 1.37 W/mK. See supplementary material (Figure S3) for convergence of HCACF with respect to supercell size and the dependence of on collection time (t) calculated for cell sizes of , and . The same finite size convergence tests have been used in a previous work [59].



(a)

(b)



Figure 7: (a) Normalized heat current autocorrelation function (body) and its integral (inset) for U3Si2 at 300 and 1200 K. The HCACFs are normalized by their initial values. The shaded region in the inset indicates the time range over which the HCACF integral is averaged to predict the phonon assisted thermal conductivity . Note that the time scale of the inset is 50 times that of the body (b) Thermal conductivity plotted against lateral simulation box dimensions at 300 K. Results converged at supercell length of 6.24 nm.

In the NEMD, it has been shown in the previous study that the finite size of the system can limit phonon mean free path, hence underestimating the thermal conductivity. Furthermore, it is well known that the supercell dimension in the and directions (perpendicular to heat flux) have a small effect on the thermal conductivity, but changes along the (direction of heat flux) are more significant [59]. Therefore, we estimated the minimum used in the NEMD simulation with the relationship derived by Sellan *et al*. [60]:

|  |  |
| --- | --- |
| , | (17) |

where is the maximum that can be accurately predicted by linear extrapolation with a minimum used in the NEMD simulation, is Boltzmann constant, and are the longitudinal and transverse velocities, respectively, from Table 3 while *a* and *c* are the simulation cell parameters at 300 K. As a rule of thumb, the minimum is increased until ~ predicted by linear extrapolation approach or Eq. 3. A quick check shows that the results are converged at an of 100 unit cells, which is a necessary condition for accurate prediction within the NEMD formalism. The same supercell sizes are applied to the *x* direction, since the size of has a minimal effect on the thermal conductivity values.



(a)

(b)

Figure 8: The variation of the reciprocal of thermal conductivity as a function of the reciprocal of supercell length for perfect U3Si2 at a range of temperatures in (a) *x* (b) *z* directions respectively. The y-intercept indicates the reciprocal of bulk thermal conductivity.

The linear relationship between and is well described in Ref. [35] and plotted in Figure 8 for the perfect U3Si2 structure for a number of temperatures with supercell sizes of, , , and unit cells with heat flow in the *z* direction while simulation systems containing , , , and unit cells were used for heat exchange in the *x* direction. The y-intercept is used to determine the thermal conductivity of the bulk U3Si2 as shown in Figure 8a-b. The data points at 1500 K deviate slightly from linearity due to statistical noise which accounts for the unusual increase in at 1500 K.

Having computed the thermal conductivity of U3Si2 using the NEMD and the EMD method, we are now in a position to directly compare the results. For the NEMD at 300 K, extrapolation to = 0 yields a value of of 2.37 and 1.37 W/mK (crystallographically averaged is 2.04 W/mK) in the *x* and *z* directions respectively while the EMD method gives a result of 1.50 and 1.23 W/mK (crystallographically averaged is 1.41 W/mK) for a system at 300 K in the *x* and *z* directions, respectively. The predicted thermal conductivities from the two methods are plotted against temperature from 300 –1500 K in Figure 9a. In the temperature range of study, it is reasonable to think that Umklapp process (phonon-phonon interactions) dominates; hence should decrease like 1/T which is not obvious from the calculated values of Figure 9a. These values were therefore fitted with a function of the form *c*/T + *k* to highlight the 1/T dependence.



(a)

(b)

(c)



Unlike the Boltzmann Transport Equation (Lattice dynamics and MD) prediction methods, there are no major assumptions inherent to the EMD and NEMD methods other than the choice of the interatomic potential and the damping parameters, which are consistent here. The predicted thermal conductivity values from the EMD are underestimated compared to NEMD results but generally within about ~18–30%. Previous work by others have also found that EMD and NEMD thermal conductivity predictions are consistent [59,61]. Our MD results compare reasonably well with recent work by Antonio *et al.*,who predicted a from 0 – 350 K, with a value of 1.99 W/mK at 300 K, which is overestimated by ~29% compared to our EMD (1.41 W/mK) while in excellent agreement with NEMD (2.03 W/mK) results, respectively [4]. This provides evidence that either method can be applied to compute bulk thermal conductivity in perfect crystalline U3Si2. It is important to note that the many-body MEAM potential used here is not developed with a special focus on thermal properties of U3Si2.

We further explored the directional dependence of as presented in Figure 9b-c, which shows the variation in and as a function of temperature in both methods. The exhibits significant directional anisotropy. In order to track the trend, we fitted the data to a quadratic equation which points to a moderate decrease in from 0.76 at 300 K and 0.50 at 1500 K in the EMD data. NEMD results also follow similar trend except at 1500 K due to the unusual increase in the thermal conductivity which can be ascribed to thermal fluctuations and the system size which unfortunately we cannot afford to increase due to computational limitations. To reduce the effect of thermal fluctuation, we computed thermal conductivity at 1200 and 1500 K by averaging 2 independent simulations. This anisotropic behavior may be attributed to differences in group velocity, anharmonicity, and scattering phase space along the different directions [62]. It is well known that the longitudinal sound velocity () and the transverse sound velocity () are primarily harmonic parameters while their ratio is an anharmonic quantity which depends on the ratio between the axial and shear rigidities of interatomic bonds [63]. We find that the value of is 1.76 which is a deviation from unity (isotropic behavior). This implies that the anisotropy in the of U3Si2 should be ascribed to its anisotropic sound velocities amongst other factors that have not been explored in this work.

It is important to note that both methods give similar results within statistical uncertainty especially in the *z* direction, which implies that EMD and NEMD methods are fundamentally reliable. The difference in the *x* direction might be due to the difficulty in converging the HCACF in the *x*-*y* direction during our simulation even after convergence of the simulation size, integration procedure, and the total simulation duration. Even at that, the in plane thermal conductivity using the EMD is overestimate by ~37% at 300 K compared to the NEMD technique. This disparity between the results in the in-plane direction from both methods reduces especially at higher temperature.

In metallic system like U3Si2, it has been shown that at the low temperature i.e. T , only phonon scattering, *ph–ph*, plays a role in the thermal conductivity calculation [32,64] while in the T regime, *el–el* interaction is the main contribution, hence it is not surprising to have low at 300 K given the fact that the has been determined to be ~200 K [3,4,65]. Low contribution means that as temperature increases, degradation in phonon-based thermal conductivity is not a big concern in U3Si2 fuel, since is the dominant component of and increases with increasing temperature.

*3.4.2. Incorporation of the electronic contribution to the total thermal conductivity*

The electronic contribution to thermal conductivity is a consequence of the electrons presence at the Fermi energy. It is evident from both the band structure and partial density of states (PDOS) as shown in Figure 10 that U3Si2 is metallic with the bands crossing the Fermi level (0 eV in Figure 10). It can be seen in the PDOS that the conduction band is composed of a significant number of uranium 5*f* and a small number of 6*d* states, respectively. The U atoms act as the charge carriers and the 5*f* electrons as conduction electrons as observed in the region around the Fermi energy which is predominantly the uranium *f* electrons. A closer look at the band structure further corroborates our observation of appreciable band overlap between valence and conduction states, which is responsible for the metallic nature of U3Si2. The significant amount of electrons at the Fermi level implies that the electronic contribution to the heat capacity and thermal conductivity of U3Si2 is mainly due to the dominant U 5*f*  bands at the Fermi energy level.



Figure 10: Band structure and the total density of state of bulk U3Si2.

In the calculation of , the value σ/τ is determined from Eq. (8). Figure 11a is a plot of σ/τ of electrons along different crystallographic directions in U3Si2 over the temperature range of 300 to 1500 K. We observed that overall, the value σ/τ shows a very weak temperature dependence with a 10% change over the entire range of 300 to 1500 K. Additionally, in the z direction is \*much greater\* than in the x direction, which is an opposite relationship than that observed for . A plot of in *x* and *z* crystallographic directions is shown in Figure 11 b. Our result slightly overestimates in comparison to recent work by Srinivasu *et al.* [66]. This is not surprising since they used electrical resistivity data from Miyadai *et al.* [67] which is different from the value reported by Shimizu which is used in this work. Ranasinghe *et al.* [68] used the value from Shimizu, but the is slightly underestimated with reference to this work due to the fact that temperature dependent values of τ are used in the calculations. They assumed that the correlation of τ(T) for UN (τ(T)UN) and U3Si2 have similar forms which is the basis for scaling the coefficient of τ(T)UN for U3Si2. This assumption is not made in this work, and thus we have used a temperature independent τ in the calculations of .



(a)

(b)

Figure 11: (a) Plot of of electrons in U3Si2 (b) directional dependence over the temperature range of 300 to 1500 K. The theoretical thermal conductivity data were obtained from Refs. [66, 68].

A comparison between and (Figure 11a) clearly shows that the phonon thermal conductivity is relatively small compared to the electron thermal conductivity and its contribution at high temperature would be insignificant. Excellent agreement is observed for values from 300 K to 1000 K compared to recent theoretical [69] and experimental [3] data as shown in Figure 11b. Slight deviation becomes present once temperatures exceed 1000 K, with our predictions overestimating the value of . Similar trends have been reported for the thermal conductivity values of α-uranium where a similar method was used [70]. Furthermore, values reported by Shimizu are lower compared to our data which might be due to the defects in the structure and method of measurement [39].



(a)

(b)

Figure 11: (a) Comparison of and (b) over the temperature range of 300 to 1500 K. The experimental and theoretical thermal conductivity data were obtained from Refs. [3, 44, 69].

To further explain the underestimation in Shimizu’s data in comparison with recent works, we note that defects such as point defects, impurities, porosities and dislocations can significantly decrease the thermal conductivity of metallic systems such U3Si2 due to their influence on both the phonon and electronic component of the thermal conductivity [70].

**4. Conclusion**

In summary, we have performed a systematic atomistic study to investigate the anisotropic, temperature-dependent thermophysical properties of U3Si2 using a MEAM interatomic potential and first principles calculations. Based on the equilibrated structure of U3Si2, we obtain the values of thermal expansion coefficient, bulk modulus, and heat capacities at different temperatures, which are in good agreement with corresponding experimental measurements. A comparison of calculated molar heat capacity with experimental data also shows reasonable agreement with experiments. Due to the anisotropy in lattice expansion with temperature, we noticed a directional dependence in the linear thermal expansion coefficient which has also been experimentally observed. The agreement between our calculations and experiments emphasizes the validity of our methods and model, and the effectiveness of the MD method employed in this work.

In addition, we also calculated the phonon assisted thermal conductivity of U3Si2. Both the EMD (Green–Kubo) and the direct (NEMD) methods have been utilized to determine the phonon-based thermal conductivity. Both methods were also used for all predictions of the directional dependence of in U3Si2. The electronic thermal conductivity was determined from first principles band structure calculations and the Wiedemann-Franz law. The electronic contribution to the thermal conductivity in U3Si2 was confirmed to be the predominant component at temperatures of interest. Unlike other metallic fuel such as UB2 where there is significant[58], U3Si2 has a less than 2 W/mK, which means that above the Debye temperature, the thermal transport is mainly driven by which increases with temperature. Therefore, ‘ drag’ on the at reactor’s operating temperature is insignificant compared to UB2. The results also indicate an anisotropic behavior of the thermal conductivity in the *x* and *z* directions, in that the thermal conductivity is much higher in the *z* direction than in the *x* direction. The total thermal conductivity calculated is slightly overestimated compared to a recent experiment by White *et al.* [3], but generally shows excellent agreement across the entire temperature range.

Overall, this work serves as a first step towards understanding the complex anisotropic behavior of the thermophysical properties of metallic U3Si2 nuclear fuel. The calculated anisotropic thermophysical properties can be used to parametrize phase field models to incorporate anisotropic thermal conductivity and thermal expansion, allowing for more accurate description of microstructural evolution under variable temperature and irradiation conditions or in continuum models to understand how the thermal gradient and the centerline temperature evolve during normal operation and accident conditions.

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