

**First Principle based Thermal Conductivity Modeling of Metal Alloys with
Applications on Uranium Alloys**

by

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Abstract

Thermal conductivity is an important materials property related to heat transport, which is essential to many applications, ranging from thermoelectrics to nuclear reactor materials. High-quality thermal conductivity data is critical to these materials and their associated technologies, including the nuclear fuel materials like traditional oxide fuels and metallic uranium (U) fuels, e.g. U-Zr and U-Mo alloys. And thermal conductivity modeling is widely used to interpolate or extrapolate experimental data, to obtain high-quality thermal conductivity data over wide temperature and composition range, and to understand the impacts of different factors including defects and microstructures. However, a general thermal conductivity model for metal alloys which can work regarding different phase components is still missing. Also, for U alloys, a thermal conductivity model working with different phases is needed. Therefore, in this work, we developed thermal conductivity models for metal alloys, based on ab-initio calculations, semi-classical physics rules, and limited experimental data. The goals of these models are to help obtain high-quality thermal conductivity data within a little experimental input as possible, have models that are extendable to varying microstructures, including different types of irradiation effects, and provide mechanistic understanding of heat transfer in the modeled alloys.

In this work, our model solves several challenges in the development. The DFT-BTE approach is applied to decrease the reliance on experimental data and make the model extendable to composition changes and defects. A practical and efficient way to combine the DFT inputs with physics rules is pointed out in this work too. A staged approach, which starts from simple cases of elemental metals, then extends to solid solutions, different compound phases, and multi-phase mixtures, is presented to work with the metal alloys in different phase components.

Our models are demonstrated respectively on α U for elemental metal model, on U-Zr and U-Mo alloys in α U temperature range for multi-phase mixture model, on high-temperature U-Zr, U-Nb, and U-Mo alloys in the body-centered cubic phase for concentrated solid solution model, and on irradiated U-Mo alloys for irradiated metal alloy model. All models show great agreement with experimental data.

In these demonstrations, our model shows its advantages compared to previous empirical fitting model. Our model requires fewer experimental data, due to the inputs from DFT. The quantitative insights into the different physical factors are provided in our model, as it incorporates the electron and phonon scattering mechanisms. Our model also can be extended to incorporate the contributions of point defects, grain boundaries, and noble gas bubbles, to integrate their effects on heat transfer. This model can serve as both a foundation for understanding the more complex thermal conductivity of realistic U alloy fuels and a useful tool to guide further modeling of thermal conductivity to aid materials and device design.

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List of Abbreviations

ATAT: Alloy Theoretic Automated Toolkit

BCC: Body-centered cubic

BTE: Boltzmann transport equation

CDW: Charge density wave

DFT: Density functional theory

DOS: Density of states

EMT: Effective medium theory

GB: Grain boundary

GGA: Generalized gradient approximation

GGA+ U : Generalized gradient approximation with Hubbard U correction

ME: Mean error

PAW: Projector augmented wave

PBE: Perdew-Burke-Ernzerhof pseudopotential

PD: Point defect

RMSE: Root-mean-square error

RRR: Residual resistivity ratio

RTA: Relaxation time approximation

SQS: Special quansirandom structure

VASP: Vienna ab-initio simulation package

Chapter 1 : General Introduction

1.1 Overview of the Thesis

This thesis is comprised of seven chapters. Chapter 1 provides a brief introductory summary of the work contained here, which introduces the background of current research in thermal conductivity modeling and uranium alloys and states our research motivation and objectives in developing a first-principle based thermal-conductivity model for metal alloys. Chapter 2 provides an in-depth description of the theoretical and computational background of this work, including the concepts, mechanisms, and approaches. Chapter 2 includes the transport properties in metal with a focus on the thermal conductivity and resistivity in terms of electron and phonon scattering mechanisms, the Boltzmann transport theory as a semiclassical transport theory, the Density Functional Theory (DFT) as an advanced computational theory, the Density Functional Theory–Boltzmann Transport Equation approach as a computational approach to calculate transport properties from atomic ab-initio calculations, and a staged approach designed to model the metal alloys with different phase compositions. In Chapter 3 through Chapter 6, the thermal conductivity models for metal alloys with different phase compositions are presented and demonstrated using several uranium alloys. Chapter 3 focuses on the thermal conductivity model for elemental metals and its demonstration on alpha-uranium (α U); Chapter 4 expands the elemental model to include multiphase mixtures with demonstrations on U-Zr and U-Mo alloys for their multiphase regions below 900 K; Chapter 5 describes our thermal conductivity model on concentrated binary metal alloys and presents the modeling results on concentrated U-Zr, U-Nb, and U-Mo alloys in the body-centered cubic (BCC) phase. In Chapter 6, the irradiation effects are discussed and added into our thermal conductivity model for metal alloys, with applications to the

irradiated U-Mo alloys. Finally, Chapter 7 summarizes the study with a plan for possible future work.

1.2 Background

1.2.1 Current Thermal Conductivity Modeling

Thermal conductivity is defined as the transport rate of heat energy across a temperature gradient, which is widely used to describe how fast the heat is transferred at a given temperature gradient in a material. Heat transport is essential to many applications, ranging from thermoelectrics to nuclear reactor materials. High-quality, thermal conductivity data is critical to these technologies and materials, including the nuclear fuel materials like traditional oxide fuels and metallic uranium fuels, e.g. U-Zr and U-Mo alloys. To obtain the thermal conductivity data, one natural and direct way is by experimental measurements. To establish a good database, the measurements are needed under different conditions with varying temperatures, compositions, etc. However, experimental thermal conductivity data is usually difficult to obtain over a range of temperatures and compositions, due to the high cost and time required of traditional thermal conductivity measurement techniques [1,2]. Therefore, thermal conductivity modeling is widely used to interpolate or extrapolate thermal conductivity data from experimental measurements and to understand the impact of different factors, including temperature, compositions, defects, and microstructures on the thermal conductivity.

Different approaches have been used for thermal conductivity modeling. The traditional empirical interpolation formulae directly interpolate between measured experimental data. It can conveniently produce thermal conductivity results under various conditions but relies on the existence of relatively large amounts of experimental data covering all the relevant conditions and

providing little physical insight. For example, Abu-Eishah collected the experimental data for thermal conductivity in 56 elements in different phases and provided their parameters in empirical interpolation formulae [3].

Some recent thermal conductivity models use density functional theory (DFT) calculations to explore the electron and phonon properties of the materials and feed the results into the Boltzmann transport equations (BTE) to calculate the transport properties. This method is based on the fundamental equations of quantum mechanics and the physics of heat transport, thereby requiring little or even no experimental data. More specifically, for phonon dominated materials, the DFT calculations can produce phonon properties, including the interatomic force constants and phonon spectra; based on DFT calculated phonon properties, phonon BTEs can be used to calculate the phonon transport properties, including thermal conductivity. This approach, which is known as the DFT-BTE approach, had been applied to many phonon-dominated materials, including semiconductors like Si [4], thermoelectric materials like PbSe [5], and multiple zincblende-type compounds [6]. For electron-dominated materials, the DFT-BTE approach is analogous but focused on electrons. The DFT calculations can obtain electron properties, including electron group velocities, and spectra, which are used in BTE as inputs to calculate electron transport properties. This approach had also been applied to multiple elemental metals [7]. However, DFT only models can struggle to obtain quantitative predictions, particularly for higher temperatures [8], and rarely treat alloys. Furthermore, most previous works only focus on either electrons or phonons. An integrated model for metal alloys with varying compositions, which integrates both electrons and phonons and which makes optimal use of limited experimental data, has been missing and is the focus of the work in this thesis.

1.2.2 Metallic Uranium Alloy Fuels

Metallic uranium (U) alloy fuels have a long history of use, which can stretch from the Clementine reactor in 1946 to many other test and research reactors. The U alloys that have been used in the reactors include uranium aluminum (U-Al), uranium zirconium (U-Zr), uranium silicon (U-Si), uranium molybdenum (U-Mo), and uranium zirconium hydride (U-ZrH). Metallic U alloys possess multiple advantages compared to the traditional UO_2 -based fuels that are widely used in current thermal reactors, including: higher thermal conductivity, high burn-up capability, ease of recycling, and a lower radiotoxicity of nuclear waste [9,10]. These advantages make metallic U alloys promising materials for use as fuels in fast reactors, which is a leading concept for Generation IV nuclear reactor designs [11] and attracts a lot of research interests.

Although U alloys have higher thermal conductivities than UO_2 -based fuels, the melting temperature of U alloys are lower than U oxides, which leads to lower operating temperatures and more rigorous temperature control. Consequently, understanding the magnitude of change in thermal conductivity, due to temperature changes and compositions, becomes a critically important issue, as it is essential for the heat management and temperature control of fuel reactors using metallic U alloys. Developing a thermal conductivity model for metallic U alloy fuels that covers wide temperature and composition ranges and can provide semiquantitative insights regarding the contributions of different scattering effects will help improve temperature control and guide the use of metallic U alloys in reactor environments.

1.2.3 Thermal Conductivity Data and Models of Metallic Uranium Alloys

Before we develop the thermal conductivity models for metal alloys and demonstrate them on U alloys, the current state-of-the-art thermal conductivity data and models of metallic U alloys

are important to review. It is critical to collect the thermal conductivity data for inputs and validation and to compare with previous models to learn the advantages and shortcomings of the models.

As an elemental metal, a large amount of thermal conductivity data has been collected for pure U. Since 1950, the thermal conductivity of pure U has been measured in numerous experiments. In particular, the experimental data available before 1970 has been summarized by Touloukian et al. [12]. Since 1970, the main experimental data has been reported by Takahashi et al. [13], Hall et al. [14], and Kaity et al. [15]. The thermal conductivity data for pure U reported from ten different research groups has two main gaps. The thermal conductivity reported at high temperature, e.g. β U and γ U whose stable temperatures are both higher than 935 K, are rare. Only one set of thermal conductivity data from Ho et al. [16] exists at this temperature range. What's more, as the crystal structures of α U and β U are anisotropic, the anisotropy in the thermal conductivity data of these phases is missing.

Among metallic U alloys, U-Zr and U-Mo are the most interesting, due to their technological relevance, and they have the most abundant experimental data on thermal conductivity. For U-Zr, the experimental data available before 1970 has been summarized by Touloukian et al. [17] and Madelung et al. [18]. The experimental data after 1970 has been reported by Takahashi et al. [19], Kaity et al. [20], and Cheon et al. [21] for the temperature regime of α U, and by Argonne National Laboratory [22] for the BCC phase (the phase of γ U). For U-Mo, the experimental data available before 1991 has been summarized by Madelung et al. [18], as well as summarized by Rest et al. [23] in 2006. After that, the main experimental data is from Creasy et al. [24] for metastable U-Mo in the BCC phase. However, the experimental thermal conductivity data of U alloys are still limited in terms of both sufficiency and accuracy, due to the difficulties

and high cost of measurements. The composition is limited, as U-Mo data only exists for which the Mo at% is $< 30\%$. And the accuracy is also limited, e.g., the experimental thermal conductivity data for U-21.6at%Mo have $\sim 50\%$ difference between different measurements. And the experimental thermal conductivity data of these U alloys at high temperatures, or the BCC phase, are limited, due to the difficulties and high cost of measurements at high temperatures. Accordingly, only one set of data exists for stable BCC phase U-Mo.

The current model for U alloys are either purely fitting models like Kim et al.'s model for U-Zr [25] and for U-Mo [26] or have some physical terms but ignore some major physical processes like Chen et al.'s model for U-Zr [27], which does not include the effects of phase separation. Like the traditional methods we mentioned above, these models rely heavily on experimental data and do not explicitly consider mechanistic scattering processes and phase mixture physics. Therefore, due to the rarity of the experimental data of these BCC U alloys, the current empirical models like Kim et al.'s pure fitting model for U-Zr [25] and for U-Mo [26] cannot be used in the temperature range of the BCC phase at high temperatures.

1.3 Motivation for the current investigation

As discussed in Section 1.2.1, the previous empirical fitting models for thermal conductivity are very convenient, both to develop and to use. The developers choose appropriate formulae to fit the experimental data, and the users feed the temperature and composition conditions as inputs to obtain the thermal conductivities as outputs. However, the accuracy and efficiency of such a model critically depends on the amount of data. An accurate empirical model is only possible when a large amount of experimental thermal conductivity data covering wide ranges of temperature and composition are available. As mentioned in Section 1.2.1, obtaining

high-quality thermal conductivity data for metal alloys is very expensive in terms of time and costs, therefore, high-quality data are rare for most metal alloys, e.g. metallic U alloys as introduced in Section 1.2.2. Additionally, empirical fitting models are not able to extend to other conditions that are not explored by experiments, such as when the temperatures and compositions exceed the range of experimental data and/or extra mechanisms affecting thermal conductivity, like defects come into play. Also, the empirical fitting models don't provide physical understanding about the sources and contributions in the thermal transport.

The recent thermal conductivity models based on ab-initio calculations, as mentioned in Section 1.2.1, can overcome the disadvantages of the empirical fitting model. The calculation results from DFT can benefit the model in two ways. First, the DFT calculations can provide inputs as a function of composition, thereby reducing the need to rely on experimental data. Furthermore, DFT calculations can help uncover the unknown mechanisms of how different features, such as lattice defects, may affect thermal transport, allowing for the extrapolation of models to conditions where few or no experimental data are available. Besides the ab-initio calculations, the physics rules are also useful in modeling extension. The physics rules combine the terms of different physical mechanisms together, which serve as the basis of modeling. Therefore, one just follows the physics rules while adding new mechanisms into the system (e.g., from DFT calculations), which helps the model to have consistent physical senses. Also, by physics rules, the model has the ability to present quantitative physical insights. As a summary, by combining DFT calculations and physics rules, the thermal conductivity models can be developed with a reduced reliance on the amount of experimental data needed and with better transferability, overcoming the shortcomings of previous empirical fitting models and yielding a better thermal conductivity model.

In addition to the motivation from modeling, the demonstration of this model is motivated by the research interests in the thermal conductivity of metallic U alloy fuels. The high-quality thermal conductivity data are critical for nuclear fuel materials. Among the nuclear fuel materials, U alloys have attracted the research interests in recent years, due to their multiple advantages compared to traditional oxide fuels and their possible deployment in next generation reactors as mentioned in Section 1.2.2. However, their experimental thermal conductivity data are still rare as mentioned in Section 1.2.3. Their thermal conductivity values are highly dependent on microstructures in the reactor, which is changing through the process of reaction. Therefore, a model which relies on little experimental data, and can be extended to different microstructures, will improve the temperature control and guide the use of metallic U alloys in reactor environments

1.4 Thesis Objectives

Motivated by the modeling needs of extendable thermal conductivity models for different microstructures and the applied needs of an efficient thermal conductivity model of U alloys, this thesis presents an accurate and extendable model of thermal conductivity in metal alloys and add to the knowledge of physical insights of scattering mechanisms of heat transport in metals. In our research, this model is based on physical mechanisms, which are combined using physics rules. The DFT calculation results are used as inputs in this mechanistic model where applicable, and the empirical fitting based on physical rules are used as inputs when it's necessary. Based on this modeling philosophy, the developed model is as accurate as the empirical fitting models but requires fewer fitting parameters and less fitting data. Also, this model provides mechanistic insights for understanding potential limitations and natural framework of physics rules for

extension to new conditions. If this approach is practical, we can obtain a model that is better than empirical fitting by every metric except for the effort needed for model development.

The overall objectives of this thesis are to 1) develop a best-practice thermal conductivity model for metal alloys, based on ab-initio calculations, semiclassical physics rules, and experimental data and 2) demonstrate this model on metallic U alloys including U-Zr, U-Nb, and U-Mo and yield the physical insights of scattering mechanisms in these alloys.

Chapter 2 : Theory and Computational Methods

2.1 Thermal Conductivity of Metals

As mentioned in Section 1.2.1, thermal conductivity is defined as the transport rate of heat energy across a temperature gradient, given by

$$\kappa = -\frac{Q}{\nabla T}, \quad (2.1)$$

where Q is the heat flux and T is the temperature. For the simplest case of ideal gases, if c is the heat capacity of each particle, n is the concentration of the particles, and $\mathbf{v}$ is the velocity vector of one particle, the energy change rate of this particle of a temperature gradient ∇T is:

$$\frac{\partial E}{\partial t} = c\mathbf{v}\nabla T. \quad (2.2)$$

If the average distance this particle travels before being scattered is $v\tau$, where τ is the relaxation time, the average total heat flux over all particles is

$$Q = -nc\tau\langle\mathbf{v} \cdot \mathbf{v}\rangle\nabla T = -\frac{1}{3}ncv^2\tau\nabla T, \quad (2.3)$$

The thermal conductivity of ideal gases is given by Eqs. (2.1) and (2.3):

$$\kappa = -\frac{1}{3}ncv^2\tau = \frac{1}{3}Cv^2\tau, \quad (2.4)$$

where C is the total heat capacity of the particles. This equation represents the classical model of how thermal conductivity, due to particle motions, depends on particle velocity and relaxation time.

2.1.1 The Heat Carriers in Metals

Heat energy can be transmitted through solids via different heat carriers, including electrons, holes, phonons, spin waves, or other excitations. In metals, the conduction electrons are

not only transporting charges but also carrying heat. And like other crystalline solids, the vibrations of the crystalline lattice also support the heat transfer. While both electrons and phonons can transfer heat in metals, their contributions are varying in different metals. In pure metals, such as gold, silver, copper, and aluminum, the heat current carried by electron far exceeds the one associated with phonons; and in other metals like transition metals, especially transition metal alloys, the electronic term is less dominant, while the phonon contribution has to be taken into account to properly assess the heat conducting process [28].

Therefore, generally, the heat in metal alloys is transported by electrons and phonons. An implicit and essential assumption is usually made for metals that the electrons and phonons are independent entities in heat transfer. Therefore, in metal alloys, the thermal conductivity κ is the sum of electron thermal conductivity κ_e and phonon thermal conductivity κ_{ph} :

$$\kappa = \kappa_e + \kappa_{ph}. \quad (2.5)$$

There are some certain cases, in which other possible excitations like spin waves also play a small additional role in heat transfer in metals. However, for the most cases, these contributions by other carriers are small and often conjectured [28].

As for electrons and phonons, their motions or relaxations are influenced by multiple scattering processes between themselves and each other. Electrons can scatter with electrons and phonons, and similarly, phonons can scatter with phonons and electrons. As for realistic scenarios, defects including point defects, defect clusters, dislocations, and grain boundaries can also scatter electrons and phonons, which all change the thermal conductivity of the materials.

2.1.2 The Wiedemann-Franz Law

As the electrons carry both charge current and the heat flux, there is an empirical relation, which was discovered in metals about 150 years ago, called the Wiedemann-Franz Law [29]. The Wiedemann-Franz Law states that, at a given temperature, the electronic thermal conductivity is directly related to the resistivity:

$$\kappa_e = \frac{LT}{\rho}. \quad (2.6)$$

where L is the Lorenz number. The Lorenz numbers for various metals are approximately constants over temperature and are closed to the theoretical value $L_0 = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.44 \times 10^{-8} W\Omega K^{-2}$ but may vary for different metals [30]. The approximation of constant Lorenz numbers can allow for a fairly accurate estimate of the electronic thermal conductivity for many metals; on the other hand, some electronic scattering processes, like inelastic scattering, can cause the deviations from the Wiedemann-Franz Law by influencing the electron dynamics [28].

2.2 Resistivity of Metals

As the electronic thermal conductivity is directly related to resistivity in metals by the Wiedemann-Franz Law (Eq.(2.6)), a brief introduction of resistivity in metals is also presented here. Electrical resistivity quantifies how strongly a material resists electric current, and it is defined by the ratio of the electric field $\mathbf{E}$ to the current density $\mathbf{J}$:

$$\rho = \frac{E}{J}. \quad (2.7)$$

As the electron scattering processes with electrons, phonons, defects, etc. can influence the thermal conductivity, these scatterings also affect the resistivity in materials. In most metals, especially the simple metals like silver, gold, and aluminum, the electron scattering with phonons dominates the resistivity; and in some other metals, like transition metal alloys, the electron-electron scattering

also plays an important role. The Matthiessen's Rule states that the total resistivity can be approximated by adding up different scattering terms, which works well for simple metals [31].

2.2.1 The Bloch-Gruneisen Formula

In this section, the Bloch-Gruneisen formula is presented as a semiclassical description of the temperature dependence of resistivity in metals. In general, electrical resistivity of metals increases with temperature. Mathematically, the temperature dependence of the resistivity ρ of a metal is given by the Bloch-Gruneisen formula [31]

$$\rho(T) = \rho(0) + A \left(\frac{T}{\theta_R} \right)^n \int_0^{\frac{\theta_R}{T}} \frac{x^n}{(e^x - 1)(1 - e^{-x})} dx, \quad (2.8)$$

where $\rho(0)$ is the residual resistivity due to defect scattering, which is equal to the resistivity at 0 K, where A is a constant and θ_R is the Debye temperature from resistivity measurements. n is an integer that depends on the interactions: $n = 5$ implies the resistivity caused by electron-phonon scattering in simple metals; $n = 3$ implies the resistivity caused by s-d electron scattering in transition metals; and $n = 2$ implies the resistivity caused by electron-electron scattering [31]. At high temperatures $T \gg \theta_R$, the resistivity increases linearly with temperature $\rho(T) \propto T$, and at low temperatures $T \ll \theta_R$, the resistivity follows a power law function $\rho(T) \propto T^n$.

2.2.2 The Resistivity Saturation

There are some other effects which can also affect the temperature dependence of resistivity, among which is the resistivity saturation effect. Resistivity saturation is observed in many metallic systems with large resistivities. When the temperature increases, the resistivity increases along with the increasing temperature and, after it reaches a critical value, its further

increase is substantially reduced. This effect typically happens when the apparent mean free path of electron is comparable to the interatomic separations (or lattice constants for crystalline metals) [32]. In the semiclassical theory, the increasing resistivity refers to decreasing the electron mean path and, when the electron mean path is smaller than interatomic separations, the semiclassical theory breaks down, which is known as the Ioffe-Regel condition [32]. Although many theoretical works were performed to explain the resistivity saturation effect, none is widely accepted by the community. The resistivity saturation effect is also observed in U alloys like α U [33]. An empirical formula of resistivity saturation, Wiesmann et al.'s parallel resistor formula [32], is observed to accurately describe the experimental resistivity data such as Nb₃Sb [32]:

$$\rho = \{\rho_{id}^{-1} + \rho_{sat}^{-1}\}^{-1}, \quad (2.9)$$

where the saturation resistivity ρ_{sat} is assumed to be a temperature-independent constant.

2.3 Boltzmann Transport Equation (BTE)

The Boltzmann transport equation describes the statistical transport behaviors of particles (which includes the carriers of classical particles, electrons, and phonons [31]). Assuming there exists a distribution function $f_k(\mathbf{r})$, which measures the number of particles in the k th state in the neighborhood of $\mathbf{r}$, the general equation of how $f_k(\mathbf{r})$ changes with time is [31]:

$$\frac{df_k}{dt} = \left(\frac{\partial f_k}{\partial t}\right)_{force} + \left(\frac{\partial f_k}{\partial t}\right)_{diff} + \left(\frac{\partial f_k}{\partial t}\right)_{scatt}, \quad (2.10)$$

where the term “force” corresponds to the external forces exerted on the particles, the term “diff” corresponds to the diffusion process of the particles, and the term “scatt” is the influence of scattering processes on the distribution of the particles. The difficulty with solving the BTE is the

complexity of the scattering term. One approximation, which is widely used to simplify the BTE, is that the distribution relaxes exponentially in time to the equilibrium form when the field is switched off, in which case

$$\left(\frac{\partial f_k}{\partial t}\right)_{scatt} = -\frac{f_k - f_0}{\tau_k}, \quad (2.11)$$

where τ_k is the relaxation time which varies with the magnitude of k . This is called the relaxation time approximation (RTA) [31]. RTA is quite rigorous for elastic scattering and spherical Fermi surface for electrons [34].

2.4 Density Functional Theory (DFT)

2.4.1 The foundation of DFT and the N-electron problem

The Schrödinger equation was developed by Erwin Schrödinger in the early 20th century to describe the motion of quantum particles. The Schrödinger equation, when written independent of time and assuming non-relativistic quantum particles, assumes the form of:

$$\hat{H}\Psi(\vec{r}) = E\Psi(\vec{r}), \quad (2.12)$$

where E is the energy level of the particle, $\Psi(\vec{r})$ is the wavefunction of the particle, and $\hat{H}$ is the Hamiltonian (total energy) operator:

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r}). \quad (2.13)$$

In Eq. (2.13), the first term is the kinetic energy, where $\hbar$ is the reduced Planck's constant, m is the particle mass, and ∇^2 is the Laplacian ($\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$). The second term $V(\vec{r})$ represents the total potential energy. Analytic solutions to the Schrödinger equation exist for only a small number of physical systems, e.g. a potential energy well or a hydrogen atom. If the system contains

more than one electron, e.g. in a helium atom, a fully analytic solution for the wavefunction cannot be obtained, due to the electron correlations [35]. Therefore, for many-body systems which contain numerous electrons and/or elements, the fully analytic solution of the Schrödinger equation is not practical. DFT specifically addresses this need to develop a mathematical method to solve the Schrödinger equation for these complicated systems with given approximations.

2.4.2 The Kohn-Sham equations

The groundwork of DFT was laid by Pierre Hohenberg and Walter Kohn [36], which was later expanded by Kohn and Lu Jeu Sham [37]. In brief, DFT maps the problem of solving the Schrödinger equation of an unsolvable N-electron wavefunction into the N one-electron wavefunctions with the Kohn-Sham equations, which are solved for individual electrons that are influenced by all other electrons in an average way via the charge density. The Kohn-Sham equation is given by [38]:

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r}) \right] \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r}), \quad (2.14)$$

where $\varphi_i(\vec{r})$ are the one-electron wavefunctions and ε_i are the Kohn-Sham electron energy levels. In Eq. (2.14), the first term corresponds to the electron kinetic energy, where $V(\vec{r})$ is the electrostatic interaction potential between the electron and the collection of atomic nuclei, $V_H(\vec{r})$ is called the Hartree potential and is the Coulomb repulsion between the electron considered in the Kohn-Sham equation with the charge density of all electrons in the system, and $V_{xc}(\vec{r})$ is the potential that includes the exchange and correlation effects of the electron with the total charge density and the Hartree potential. The electron kinetic energy and electrostatic potential energies

$V(\vec{r})$ and $V_H(\vec{r})$ in the Kohn-Sham equation can be solved exactly. The major source of approximations in DFT comes from the exchange and correlation term $V_{XC}(\vec{r})$, which is discussed in Section 2.4.3.

DFT calculations of solids usually use periodic boundary conditions for spatially periodic systems, where the one-electron wavefunctions can be represented as a linear combination of periodic planewaves. For example, a widely used choice of the planewave basis is the Fourier functions, and its one-electron wavefunctions thus have the form:

$$\varphi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{\vec{k}+\vec{G}} \exp(i(\vec{k} + \vec{G}) \cdot \vec{r}), \quad (2.15)$$

where $\exp(i(\vec{k} + \vec{G}) \cdot \vec{r})$ is a plane wave, $\vec{k}$ is the reciprocal lattice coordinate, $\vec{G}$ is a reciprocal lattice vector, and $c_{\vec{k}+\vec{G}}$ are the Fourier coefficients. The number of $\vec{G}$ vectors are restricted by the energy cutoff.

The electron charge density $n(\vec{r})$ is obtained by summing over the probabilities of all electrons|:

$$n(\vec{r}) = 2 \sum_i \varphi_i^*(\vec{r}) \varphi_i(\vec{r}), \quad (2.16)$$

where $\varphi_i^*(\vec{r})$ is the complex conjugate of the wavefunction $\varphi_i(\vec{r})$ and the factor of 2 is present, due to the Pauli-exclusion principle[129]. Also, solving $\varphi_i(\vec{r})$ simultaneously solves electron energy levels, which provide the electronic band structure and the ground state energy of the system.

2.4.3 Exchange and Correlation functionals

As DFT solves a series of one-electron wavefunctions, which do not have electron exchanges and correlations, these effects are considered explicitly using a potential term. The electron correlations include the interactions between electrons that occupy the same orbital or different orbitals and approximations for the interaction strength of electrons in localized, spatially overlapping orbitals. These correlation effects cannot be solved for analytically, making approximating $V_{xc}(\vec{r})$ a challenge for accurate DFT formulations [38]. In this work, we focus on using the Generalized Gradient Approximation (GGA) for the exchange and correlation functional $V_{xc}(\vec{r})$. GGA utilizes the local charge density and its gradient to calculate $V_{xc}(\vec{r})$ and is generally viewed as an improvement over the older Local Density Approximation (LDA) [39,40]. The GGA exchange and correlation energy functional E_{xc}^{GGA} is calculated as [41]:

$$E_{xc}^{GGA}[n(\vec{r})] = \int n(\vec{r}) \varepsilon_{xc}(n(\vec{r}), \vec{\nabla}(n(\vec{r}))) d^3r, \quad (2.17)$$

where $n(\vec{r})$ is again the charge density, $\vec{\nabla}(n(\vec{r}))$ is the gradient in the charge density, and ε_{xc} is the GGA exchange and correlation energy. In GGA, ε_{xc} is a function of both the charge density and its gradient. $V_{xc}(\vec{r})$ is obtained by taking the functional derivative of E_{xc}^{GGA} with respect to $\vec{r}$.

However, one major problem of GGA is that the strong interactions between d -electrons are underestimated, as DFT calculations with GGA tend to over delocalize these d -electrons. This means that, in GGA calculations, the transition metal d -electrons are spatially extended in their nuclei more than in reality. To combat this, the GGA+ U method was developed, where the “+ U ” is a Hubbard-like term added to $V_{xc}(\vec{r})$ as an added on-site Coulomb repulsion for d -electrons of the transition metal elements [42,43]. The Hubbard “+ U ” term in GGA+ U adds an energy term for the on-site Coulomb repulsion between the d -electrons (or f -electrons if needed) of the transition metal elements, to enhance the localization of these d -electrons to the nuclei [42,43].

2.4.4 The DFT calculation scheme

The self-consistent solution scheme of the Kohn-Sham equation is introduced in this section. The positions and symmetry of the atoms of interest are first needed as inputs. The first step of setting up the Kohn-Sham equation is to provide an initial guess of what the charge density looks like by guessing an initial set of wavefunctions. From this initial charge density, the effective potential is generated. This effective potential is the sum of the potential terms in Eq. (2.14), including the exchange and correlation functional. The Kohn-Sham equation is then solved with this initial guess of the wavefunctions, and the new charge density is calculated from the resulting new wavefunctions. If the charge density differs from the previous guess, this process will be iterated to update the charge density, and calculating the new wavefunctions via the Kohn-Sham equation will be repeated until the charge density is self-consistent. This overall process is called the electronic self-consistency loop.

Once the first electronic self-consistency loop is completed, the positions of the ions are updated according to some specific numerical minimization schemes, e.g. the conjugate gradient relaxation algorithm. This process is called the ionic relaxation loop. Once the ion positions are updated, the electronic self-consistency iteration described above is repeated. The DFT calculation is completed once the ionic relaxation loop results in the convergence of the total energy. That is, the change in the total energy is smaller than the predefined tolerance, e.g., 1 meV per supercell. At this point, the wavefunctions, and thus charge density, are self-consistent solutions to the Kohn-Sham equation with the total energy converged and information on the charge density, energies, electronic structure, atom positions, and other data are outputted for post-processing.

2.4.5 The Vienna Ab-initio Simulation Package (VASP)

DFT is a powerful and versatile computational technique, and it is the leading method of quantum mechanical simulation in the solid state physics and materials science communities [44]. There are several computational codes available to perform DFT calculations, including: ABINIT [45] (freely available), Quantum Espresso [46], Wien2k [47], Gaussian [48], SIESTA [49], and the Vienna Ab-initio Simulation Package (VASP) [50]; VASP is used throughout in this work. VASP is a planewave-based DFT code written in the Fortran programming language and is designed to run in a UNIX operating environment. VASP calculations are typically run in parallel across numerous compute nodes and processors, greatly enhancing the speed of calculation.

2.5 Density Functional Theory–Boltzmann Transport Equation (DFT-BTE) Approach

The DFT-BTE approach combines the electron and phonon properties calculated by DFT with BTE and RTA to calculate the transport properties, which has been widely applied in recent calculation works on phonon thermal conductivity [51,52] and electric resistivity [8,53]. The DFT-BTE approach will be introduced in the following sections.

2.5.1 DFT-BTE Approach for Phonons

DFT calculations can produce phonon spectra and interatomic force constants. Then, the phonon thermal conductivity κ_{ph} can be calculated using the phonon BTE given by [54]:

$$\kappa_{ph} = \frac{1}{3\Omega N_k} \sum_{k\lambda} c_{k\lambda} v_{k\lambda} \Lambda_{k\lambda}, \quad (2.18)$$

where k represents the wavevector, λ represents the different phonon branches, N is the total number of discrete k-points, and Ω is the volume of the unit cell. The quantities inside the summation consist of $c_{k\lambda}$, $v_{k\lambda}$, and $\Lambda_{k\lambda}$, which are the heat capacity, phonon group velocity, and phonon mean free path for each wavevector and phonon branch respectively. The $c_{k\lambda}$ values are evaluated from the phonon density of states using the Bose-Einstein distribution. The $v_{k\lambda}$ values are obtained by calculating the gradient of the phonon dispersion relation. Finally, the $\Lambda_{k\lambda}$ values are equal to phonon group velocity $v_{k\lambda}$ multiplied by the phonon relaxation time τ_{ph} . The phonon DFT-BTE approach can be performed with computational tools like Phono3py [55]. Considering different phonon scattering contributions, the phonon relaxation time τ_{ph} for each wavevector, and phonon branch can be divided into three contributions, e.g. phonon-phonon, phonon-electron, and phonon-(point defect) scattering, using Matthiessen's rule [56]:

$$\frac{1}{\tau_{ph}} = \frac{1}{\tau_{ph-ph}} + \frac{1}{\tau_{ph-gb}} + \frac{1}{\tau_{ph-pd}}, \quad (2.19)$$

where τ_{ph-ph} , τ_{ph-e} and τ_{ph-pd} are the relaxation time of phonon-phonon, phonon-electron, and phonon-(point defect) scattering contribution, respectively. The relaxation times of different phonon scatterings are needed as inputs into the BTE to calculate phonon thermal conductivity.

2.5.2 DFT-BTE Approach for Electrons

DFT calculations can produce electron bands and density of states (DOS), and the contributions of different electron scattering mechanisms to resistivity are assumed to be independent with each other. If ρ_{e-i} is the resistivity contribution of electron scattering with particle type i , ρ_{e-i} can be obtained from the electrical conductivity tensor σ , total electronic relaxation time τ , and the electronic relaxation time for electron-electron scattering τ_{e-i} :

$$\rho_{e-i} = \frac{1}{\sigma_{e-i}} = \frac{1}{\frac{\sigma}{\tau} \tau_{e-i}} = \frac{1}{s \tau_{e-i}}, \quad (2.20)$$

$s \equiv (\frac{\sigma}{\tau})$, which is defined as electrical conductivity over relaxation time, is calculated using the BTE with RTA with the rigid band approximation as follows [57]. The full tensor of σ can be calculated from the conductivity distributions:

$$\sigma_{\alpha\beta} = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\varepsilon) \left[-\frac{\partial f_{\mu}(T; \varepsilon)}{\partial \varepsilon} \right] d\varepsilon, \quad (2.21)$$

where $\sigma_{\alpha\beta}$ is the full tensor denoted as just σ in Eq. (4) (and will be denoted as just σ throughout this paper when convenient), f is the Fermi-Dirac distribution function, Ω is the volume system, T is the temperature, ε is the band energy, μ is the Fermi level, and $\sigma_{\alpha\beta}(\varepsilon)$ is the transport distribution given by:

$$\sigma_{\alpha\beta}(\varepsilon) = \frac{1}{N} \sum_{i,k} \sigma_{\alpha\beta}(i, k) \frac{\delta(\varepsilon - \varepsilon_{i,k})}{d\varepsilon}, \quad (2.22)$$

where k represents elements of a set of k -points in reciprocal space, N is the number of k -points sampled, and i is the band index. Finally, $\sigma_{\alpha\beta}(i, k)$ is the conductivity tensor, which depends on the electron group velocity v_{α} , the elementary charge e , and the relaxation times $\tau_{i,k}$:

$$\sigma_{\alpha\beta}(i, k) = e^2 \tau_{i,k} v_{\alpha}(i, k) v_{\beta}(i, k), \quad (2.23)$$

Therefore, the input parameters for calculating the electrical conductivity tensor σ are the relaxation times $\tau_{i,k}$ and the electronic band structure information calculated by DFT. Here, we simplify the input of $\tau_{i,k}$ by assuming that it is constant with no dependences on the band index i and the wave direction k , which has been shown to be a satisfactory assumption for many metals [58,59]. With this approximation, $s \equiv (\frac{\sigma}{\tau})$ depends on only the electronic band structure through Eqs. (2.21)–(2.23) and its value can be obtained from DFT-BTE calculations, which is already implemented by computational tools like BoltzTrap [57]. Still, the electron relaxation time of each electron scattering process considered is needed in the calculations.

2.6 Staged Approach based on Phase Compositions and Phases

Based on the DFT-BTE approach, the electron and phonon thermal conductivity can be calculated for single-phase bulk materials. However, as alloy systems are considered, information on the elemental metals, compositions, and phase fractions are all needed to estimate the thermal conductivity and needed as inputs in the model. Here, the models are developed with incremental complexity: we first build models for fixed compositions, followed by solid solutions and phase mixtures, and eventually lattice defects. A staged computational model, shown in the schematic diagram in **Figure 2.1**, is developed based on this rule, which extends from modeling fixed compositions to solid solutions and multi-phase mixtures:

- Stage 1: model solid solutions at fixed compositions (referenced as the anchor structures). Stage 1 focuses on a physics-based model [8] for the thermal conductivity of anchor structures. This model incorporates different electron and phonon scattering processes using the DFT-BTE approach, aided by using experimental thermal and electrical conductivity data.
- Stage 2: model the solid solutions with varying compositions. For general cases, Stage 2 deals with solid solutions with linear interpolation or extrapolation of two anchor structures modeled in Stage 1. Besides the general case, one edge case of dilute alloying is modeled by DFT-BTE approach.
- Stage 3: model the multiphase mixtures. Stage 3 models systems in multiphase regions by combining the thermal conductivities of phases at the boundaries of these regions using appropriate averaging schemes. The conductivities of the boundary phases are described by models developed in Stage 1 and 2.

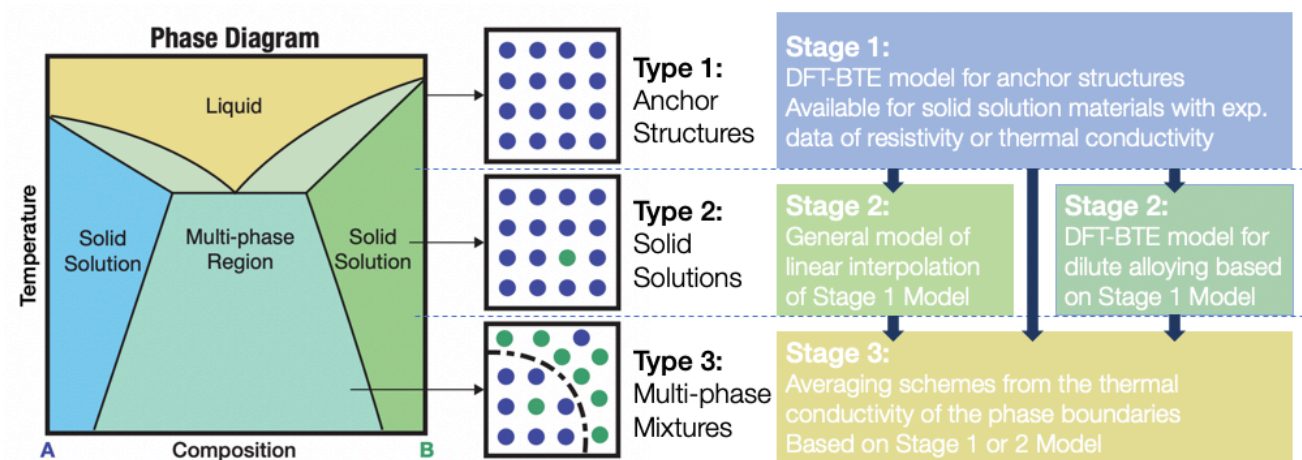


Figure 2.1. The schematic diagram of the three-stage modeling approach of thermal conductivity of metal alloys.

Chapter 3 : Thermal Conductivity Modeling for Elemental Metals: Demonstration on α U

3.1 Chapter Abstract

The future deployment of nuclear reactors using metallic U-based fuels hinges on the quantitative understanding of thermal transport characteristics of the fuel. In this work, we developed a computational model of metallic α -U thermal conductivity based on DFT calculations and all known experimental resistivity and thermal conductivity data. The model incorporates both phonon and electron scattering contributions, and displays good agreement with experimental data over the temperature range where α -U is stable. It provides insight into the different physical factors that govern the thermal conductivity under different temperatures, and serves as a first step in understanding the thermal transport behavior of metallic U alloys. We also extended our thermal conductivity model for α -U to U-rich U-Zr and U-Mo alloys. Moving forward, this model can incorporate more complex effects like additional alloying species, defects, transmutation products and noble gas bubbles to predict the behavior of more realistic metallic U-alloy fuel systems.

3.2 Introduction

Metallic uranium (U) alloys possess multiple advantages compared to the UO_2 -based nuclear fuels that are widely used in both current thermal and fast nuclear reactors, including higher thermal conductivity, high burn-up capability, ease of recycling, and lower radiotoxicity of nuclear waste [60]. These advantages make metallic U alloys promising materials for use as nuclear fuels in thermal reactors and especially in the future deployment of fast reactors as Generation IV nuclear reactor designs [61]. While metallic U alloys have higher thermal conductivities than

UO₂-based fuels, they also have much lower melting temperatures. Consequently, temperature control of reactors containing metallic U alloy fuels becomes a critically important issue. Thus, the thermal conductivity of metallic U alloys is an essential property influenced by many factors, including alloying, impurities, and point and extended defects. Developing a physical understanding of the thermal conductivity of metallic U alloy fuels will help improve temperature control and guide its use in reactor environments.

Since 1950, the thermal conductivity of α -U has been measured in numerous experiments. In particular, the experimental data available before 1970 has been summarized by Touloukian et al. [12]. Since 1970, the main experimental data has been reported by Takahashi et al. [13], Hall et al. [14], and Kaity et al. [15]. While there is extensive experimental data on the thermal conductivity of α -U, a physics-based computational model that includes the fundamental factors contributing to the thermal conductivity of α -U under different temperature conditions has not been established. In metals, the conduction of heat is a complicated phenomenon which involves different interactions between phonons and electrons, including phonon-phonon, electron-phonon, and electron-electron scattering, but it is not known which scattering processes dominate under different temperature conditions.

The goal of the present study is to develop a physics-based computational model of thermal conductivity in pure α -U as a foundation for understanding the more complex thermal conductivity of realistic U alloy fuels. Here, we use all known experimental data of thermal conductivity and electrical resistivity in α -U combined with a density functional theory (DFT)-based computational framework to construct a model of the phonon and electron contributions to the thermal conductivity in pure α -U. This physics-based computational model provides an understanding of the dominant mechanisms for thermal conductivity and, importantly, is extensible to more realistic

metallic alloy fuels that include physical effects resulting from alloying elements, impurities, transmutation products, radiation-induced defects and noble gas bubbles. As an example, we have extended the present model of thermal conductivity for pure α -U to binary U-rich alloys containing Zr and Mo to calculate the thermal conductivities of U-Zr and U-Mo alloy fuels.

3.3 Methods

3.3.1 Computational model of thermal conductivity in pure α -U and U-rich alloys

3.3.1.1 Models for pure α U

In metals like α -U, the thermal conductivity κ is the sum of electron and phonon thermal conductivities [62]:

$$\kappa = \kappa_e + \kappa_{ph} , \quad (3.1)$$

where κ_e is controlled by electron-electron, electron-phonon and electron-defect scattering, the relative strengths of which are material- and environment-dependent, and κ_{ph} is controlled by phonon-phonon, phonon-grain boundary and phonon-defect scattering. A physics-based computational model that separately includes electron and phonon contributions and their relative scattering mechanisms (phonon-phonon, phonon-defect, electron-phonon, electron-electron and electron-defect) cannot be obtained from the available experimental data. Therefore, DFT calculations were used to calculate the structural, electronic and vibrational properties of α -U to analyze the phonon scatterings and electron-electron scattering processes. We combined these results with semi-empirical analytic models of electron-phonon, phonon-defect and phonon-grain boundary scattering fitted to available experimental electrical resistivity data of α -U to form our full model. In the following paragraphs, we describe how each term is modeled.

The electronic thermal conductivity κ_e can be evaluated from electrical resistivity using the Wiedemann-Franz law [56]:

$$\kappa_e = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 \frac{T}{\rho}, \quad (3.2)$$

where T is the temperature and ρ is the electrical resistivity. It is useful to treat the resistivity as having an ideal contribution, which is modeled accurately with the semi-classical BTE approach, and then modify this ideal contribution with a saturation effect, which occurs due to the breakdown of the semi-classical approach for electrons with wavelengths approaching the interatomic separation [33]. We will take this approach in the present work and first we consider the ideal contribution, ρ_{id} , to the electrical resistivity. ρ_{id} can be divided into two scattering contributions using Matthiessen's rule [56]:

$$\rho_{id} = \rho_{e-e} + \rho_{e-ph}, \quad (3.3)$$

where ρ_{e-e} is the electron-electron scattering contribution and ρ_{e-ph} is the electron-phonon scattering contribution. ρ_{e-e} can be obtained from the electrical conductivity tensor σ , total electronic relaxation time τ , and the electronic relaxation time for electron-electron scattering τ_{e-e} :

$$\rho_{e-e} = \frac{1}{\sigma_{e-e}} = \frac{1}{\frac{\sigma}{\tau} \tau_{e-e}}. \quad (3.4)$$

$\left(\frac{\sigma}{\tau} \right)$ is calculated using the Boltzmann transport equation (BTE) with the relaxation time approximation (RTA) and the rigid band approximation as follows [57]. The full tensor of σ can be calculated from the conductivity distributions:

$$\sigma_{\alpha\beta} = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\epsilon) \left[-\frac{\partial f_{\mu}(T; \epsilon)}{\partial \epsilon} \right] d\epsilon, \quad (3.5)$$

where $\sigma_{\alpha\beta}$ is the full tensor that we denote as just σ in Eq. (3.4) (and will denote as just σ throughout this paper when convenient), f is the Fermi-Dirac distribution function, Ω is the volume system, T is the temperature, ε is the band energy, μ is the Fermi level, and $\sigma_{\alpha\beta}(\varepsilon)$ is the transport distribution given by:

$$\sigma_{\alpha\beta}(\varepsilon) = \frac{1}{N} \sum_{i,k} \sigma_{\alpha\beta}(i, k) \frac{\delta(\varepsilon - \varepsilon_{i,k})}{d\varepsilon}, \quad (3.6)$$

where k represents elements of a set of k -points in reciprocal space, N is the number of k -points sampled, and i is the band index. Finally, $\sigma_{\alpha\beta}(i, k)$ is the conductivity tensor, which depends on the electron group velocity v_α , the elementary charge e , and the relaxation times $\tau_{i,k}$:

$$\sigma_{\alpha\beta}(i, k) = e^2 \tau_{i,k} v_\alpha(i, k) v_\beta(i, k). \quad (3.7)$$

Therefore, the input parameters for calculating the electrical conductivity tensor σ are the relaxation times $\tau_{i,k}$ and the electronic band structure information calculated from DFT. Here, we simplify the input of $\tau_{i,k}$ by assuming it is constant which neither depends on band index i nor direction k , which has been shown to be a satisfactory assumption for many metals [58,59]. With this approximation ($\frac{\sigma}{\tau}$) depends on only the electronic band structure through Eqs. (3.5)-(3.7) and its values can be obtained from DFT-BTE calculations using VASP for the band structure and the BoltzTrap code to solve the equations [57]. In metals, the electron-electron scattering relaxation time τ_{e-e} is dependent on temperature T and can be approximated by:

$$\tau_{e-e} = AT^{-2}, \quad (3.8)$$

where A is typically assumed to be a constant [63–65].

For the electron-phonon scattering contribution ρ_{e-ph} , we use semi-empirical models and fit the unknown terms using available experimental data. We note that ρ_{e-ph} can be predicted from DFT calculations. However, the approaches for realistic systems generally follow those taken in,

e.g., Savrasov et al.'s calculation [66] and Verstraete's calculation [67]. In these approaches, anharmonicity effects are not taken into account at high temperature, thus the temperature range is limited by $T < 2\theta_{tr}$, where θ_{tr} is the average phonon frequency [66,68]. For α -U, $\theta_{tr} \approx 150K$ from our phonon calculations, thus these DFT-based approaches to calculate ρ_{e-ph} don't cover the reactor working temperature near 600K. Although some approaches can calculate the phonon anharmonicity like Phono3py [55] and phonon Monte Carlo [69], a robust approach that includes phonon anharmonicity into the calculation of ρ_{e-ph} is not presently available. Therefore, we did not pursue this path and instead fit semi-empirical models to the available experimental data and phonon spectrum calculation results. Bloch-Gruneisen formula is a classic theory to describe the resistivity of electron-phonon scattering for spherical Fermi surface and Debye phonon spectrum [56]:

$$\rho_{e-ph} \propto \left(\frac{T}{\theta_D}\right)^5 \int_0^{\frac{\theta_D}{T}} \frac{x^5}{(e^x-1)(1-e^{-x})} dx, \quad (3.9)$$

where θ_D is the Debye temperature obtained from resistivity measurement. Instead of using Debye phonon spectrum, we use phonon spectrum for α -U obtained by DFT:

$$\rho_{e-ph} = BT^2 \sum_{k\lambda} \frac{(\hbar\omega_{k\lambda}/k_B T)^3}{(e^{\hbar\omega_{k\lambda}/k_B T} - 1)(1 - e^{-\hbar\omega_{k\lambda}/k_B T})}, \quad (3.10)$$

where k represents the wavevector, λ represents the different phonon branches, ω is the phonon frequency and B is a constant which, in general, depends on crystallographic direction.

Within the framework described above the ideal resistivity ρ_{id} given in Eq. (3.3) grows linearly with temperature T at high temperature due to the dominance of electron-phonon scattering [33]. However, in some metals, including α -U (see Figure 3.3), the resistivity at high temperature is not a linear function of T due to the resistivity saturation effect mentioned

above [33]. We model the total resistivity ρ in the presence of saturation using Wiesmann et al.'s parallel resistor formula [32]:

$$\rho = \{\rho_{id}^{-1} + \rho_{sat}^{-1}\}^{-1}, \quad (3.11)$$

where the saturation resistivity ρ_{sat} is assumed to be a temperature-independent constant. This approach has been successfully applied to multiple A15 compounds, e.g. Nb₃Sn [32].

As the final component of our resistivity model we include the electron-defect scattering for pure α -U, which is assumed to arise from point defects and dislocations, and to some extent the impurities that occur in even the purest material. The electron-defect scattering is approximately temperature independent [56], so we can model its contribution by adding a constant residual resistivity term ρ_0 to the total electrical resistivity. We directly use an experimentally extracted residual resistivity value of $\rho_0 = 0.8 \times 10^{-8} \Omega$ [14,70] to represent the typical scale of the effect of these defects. To summarize, for each crystallographic direction, the electrical resistivity ρ in our model is given by:

$$\rho = \left\{ \left[\left(\frac{\sigma}{\tau} \frac{A}{T^2} \right)^{-1} + BT^2 \sum_{k\lambda} \frac{(\hbar\omega_{k\lambda}/k_B T)^3}{(e^{\hbar\omega_{k\lambda}/k_B T} - 1)(1 - e^{-\hbar\omega_{k\lambda}/k_B T})} \right]^{-1} + \rho_{sat}^{-1} \right\}^{-1} + \rho_0, \quad (3.12)$$

where $\left(\frac{\sigma}{\tau}\right)$ is obtained from the DFT electronic density of states and associated BTE calculations (electronic DFT-BTE calculations). The values of A , B , ρ_{sat} and θ_D are obtained by fitting to experimental resistivity data. The values of B and ρ_{sat} depend on crystallographic direction, while A and θ_D are direction-independent.

The phonon thermal conductivity κ_{ph} can be calculated using the phonon Boltzmann transport equation (BTE) given by [54]:

$$\kappa_{ph} = \frac{1}{3\Omega N_k} \sum_{k\lambda} c_{k\lambda} v_{k\lambda} \Lambda_{k\lambda}, \quad (3.13)$$

where k represents the wavevector, λ represents the different phonon branches, N is the total number of discrete k-points, and Ω is the volume of the unit cell. The quantities inside the summation consist of $c_{k\lambda}$, $v_{k\lambda}$, and $\Lambda_{k\lambda}$, which are the heat capacity, phonon group velocity and phonon mean free path for each wavevector and phonon branch, respectively. The $c_{k\lambda}$ values are evaluated from the phonon density of states using the Bose-Einstein distribution. The $v_{k\lambda}$ values are obtained by calculating the gradient of the phonon dispersion relation. Finally, the $\Lambda_{k\lambda}$ values are equal to phonon group velocity $v_{k\lambda}$ multiplied by the phonon relaxation time τ_{ph} . Considering different phonon scattering contributions, the phonon relaxation time τ_{ph} for each wavevector and phonon branch can be divided into three contributions, one each for phonon-phonon, phonon-grain boundary and phonon-defect scattering, using Matthiessen's rule [56]:

$$\frac{1}{\tau_{ph}} = \frac{1}{\tau_{ph-ph}} + \frac{1}{\tau_{ph-gb}} + \frac{1}{\tau_{ph-def}}, \quad (3.14)$$

where τ_{ph-ph} , τ_{ph-gb} and τ_{ph-def} are the relaxation time of phonon-phonon, phonon-grain boundary and phonon defect scattering contribution, respectively.

The phonon relaxation time for phonon-phonon scattering τ_{ph-ph} is calculated from Fermi's Golden rule using the harmonic and third-order anharmonic force constants [55]. The phonon relaxation time for phonon-grain boundary scattering τ_{ph-gb} can be estimated by [56,71]:

$$\tau_{ph-gb} = \frac{L}{v}, \quad (3.15)$$

where L is the grain size and v is the phonon group velocity. We directly evaluate the value of L by experimental data and in this work use a grain size of ~ 0.015 mm in diameter [70]. The phonon relaxation time for phonon-defect scattering can be approximated by [56,71]:

$$\tau_{ph-def}^{-1} = C\omega^4, \quad (3.16)$$

where ω is the phonon frequency and C is a constant. In our model C is assumed an isotropic fitting parameter obtained from fitting to low temperature thermal conductivity data. Thus, calculating κ_{ph} requires calculation of the harmonic and third-order anharmonic force constants and the associated phonon dispersion relations and couplings. All of these phonon-related quantities can be determined from DFT calculations using the Vienna Ab initio Simulation Package (VASP) code [50,72]. This approach for phonon-phonon scattering has been successfully applied to calculate the phonon contribution to the thermal conductivity in a number of systems, such as PbTe and PbSe materials [73]. To summarize, κ_{ph} is calculated using Eq. (3.13), where the contributions of different phonon scatterings are combined using Eq. (3.14).

The total thermal conductivity κ is then given by:

$$\kappa = \kappa_{ph} + \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 \frac{T}{\rho}, \quad (3.17)$$

where κ_{ph} and ρ is the results from Eq. (3.13) and Eq. (3.12), respectively. In total, we have five fitting parameters in our model for α -U thermal conductivity, which are A , B , ρ_0 , ρ_{sat} for the electronic contributions and C for the phonon contributions, and where B and ρ_{sat} are potentially anisotropic, i.e., can have directional dependence.

3.3.1.2 Anisotropy Approximation for U-rich alloys

In dilute alloys, the total resistivity must include the residual resistivity ρ_{res} produced by scattering due to alloy atoms. The total resistivity can be represented using Matthiessen's rule [56]:

$$\rho_{total} = \rho_{pure} + \rho_{res}, \quad (3.18)$$

where ρ_{pure} is the resistivity of pure α -U using Eq. (3.12), and the ρ_{res} in the binary alloy can be estimated using Nordheim's rule [56]:

$$\rho_{res} = Dc(1 - c), \quad (3.19)$$

where c is the alloying concentration and D is a constant. If we assume the impact of alloying elements on the phonon thermal conductivity is small, the thermal conductivity of dilute U-rich alloys can be calculated using our α -U model of Eq. (3.16), and the only difference is to add ρ_{res} to the total resistivity formula:

$$\rho = \left\{ \left[\left(\frac{\sigma}{\tau} \frac{A}{T^2} \right)^{-1} + BT^2 \sum_{k\lambda} \frac{(\hbar\omega_{k\lambda}/k_B T)^3}{(e^{\hbar\omega_{k\lambda}/k_B T} - 1)(1 - e^{-\hbar\omega_{k\lambda}/k_B T})} \right]^{-1} + \rho_{sat}^{-1} \right\}^{-1} + \rho_0 + Dc(1 - c), \quad (3.20)$$

We apply this model as an approximation for binary U-rich U-Zr and U-Mo alloys in which the U at% is $> 78\%$, and fit parameter D using Eq. (3.17) with Eq. (3.20) for U alloys with different concentrations. This approach is supported by the fact that our calculated results fit experimental thermal conductivity data of U-Zr and U-Mo alloys well at 300-933K, which we show in Section 3.4.4.

3.3.2 Structural characteristics of α -U

3.3.2.1 Anisotropy

Bulk α -U crystallizes in an orthorhombic structure (Space group: $Cmcm$, No. 63) [74]. Due to its anisotropic properties, we have evaluated our computational model for three different crystalline directions: [100], [010] and [001]. For each crystallographic direction, we used Eq. (3.12) to fit experimental data of single crystal α -U resistivities, then calculated the anisotropic thermal conductivity with Eq. (3.17). We note here that the parameter B and θ_D are isotropic, while the other two fitting parameters, ρ_{sat} and C , are anisotropic. To make comparisons with

polycrystalline experimental data, we calculated the trace of the electrical and thermal conductivity tensors. Thus, for the total thermal conductivity κ_{total} :

$$\kappa_{total} = \frac{1}{3}(\kappa_{100} + \kappa_{010} + \kappa_{001}), \quad (3.21)$$

and for the resistivity ρ_{total} , which is equal to the inverse of electric conductivity:

$$\frac{1}{\rho_{total}} = \frac{1}{3} \left(\frac{1}{\rho_{100}} + \frac{1}{\rho_{010}} + \frac{1}{\rho_{001}} \right). \quad (3.22)$$

3.3.2.2 Phase stability

We note here there are other U phases that are stable at temperatures below 43 K and above 933 K. A series of three low-temperature charge density wave (CDW) structural phase changes occur below 43K [75,76], and the phase transition to β -U occurs at 933K [77]. Therefore, the valid temperature range of our model is between 43 K to 933 K, which is the temperature range where α -U is stable. The typical operating temperature of a fast nuclear reactor is about 600 K, which is well within the temperature range our model can accurately capture. For the remainder of this work, all models are evaluated and all results are plotted using this relevant temperature range of 43 K to 933 K.

3.3.2.3 Perfect crystal approximation

In this study, our DFT calculations model α -U as an ideal crystalline material. Therefore, our phonon DFT calculations of α -U do not directly include effects on the thermal conductivity due to point and extended (dislocation and grain boundary) defects, and the effects of these defects (electron-defect, phonon-grain boundary and phonon-defect scattering) are counted in our model separately, as mentioned in Section 3.3.1.1. The magnitude of the effect depends on the defect

concentration present in the experimental samples. However, since the electrical resistivity in our model is fit to single-crystal resistivity data [78], [79], the effects of electron-grain boundary scattering are not included in our model.

With respect to the effect of electron-grain boundary scattering, we will also show in Section 3.4.1 by comparing the single-crystalline and polycrystalline resistivity data, that both types of samples display the same temperature dependence with a small difference ($\sim 5\%$) in resistivity values, at least for a typical grain size that is $\sim 0.015\text{mm}$ in diameter [70]. These results indicate that structural differences between single crystal and polycrystalline samples produce only a small difference in the resistivity. Thus the effect of electron-grain boundary scattering on the thermal conductivity is expected to be small at high temperature. Our model can therefore be considered accurate within 5-10% near 600K for materials with defects concentrations and grain sizes similar to those used in our fitting and the above discussion describes how each term might be affected if significantly different defect levels are considered.

3.3.3 DFT calculations of α -U

All DFT calculations were performed with periodic boundary conditions with a plane-wave basis set using the Vienna Ab-Initio Simulation Package (VASP). Initial atomic coordinates for α -U were obtained from the orthorhombic structure (Space group: *Cmcm*, No. 63) in Ref. [74,80]. The electron-ion interaction of U uses the projector augmented wave (PAW) method [81] as implemented by Kresse and Joubert [82]. The valence electron configuration for the U pseudopotential was $6s^2 6p^6 7s^2 5f^3 6d^1$. The exchange correlation functional parameterized in the generalized gradient approximation (GGA) [83] by Perdew, Burke, and Ernzerhof (PBE) [84] was used. The plane wave cutoff energy was set to 450 eV, and the stopping criteria for self-consistent

loops were 1 meV per cell for electronic and ionic relaxation. For phonon calculations, the phonon band structure was simulated with a $4 \times 4 \times 4$ supercell (128 atoms) and a $4 \times 4 \times 2$ Monkhorst-Pack [85] k-point grid. Anharmonic force constant calculations were performed using the small displacement method [86] with a $2 \times 2 \times 2$ supercell (16 atoms) and a $10 \times 10 \times 10$ Monkhorst-Pack k-point grid. The phonon contribution to the thermal conductivity (phonon-phonon scattering) was obtained by calculating the phonon BTE using Phono3py [55] with a $13 \times 13 \times 13$ q-point mesh, resulting in a convergence error of phonon thermal conductivity of $< 10\%$. For electron calculations, band structure calculations were performed with a $2 \times 2 \times 2$ supercell (16 atoms) and a $23 \times 23 \times 12$ Monkhorst-Pack k-point grid. The electron-electron scattering portion of the electronic contribution to the thermal conductivity was obtained using the BoltzTraP [57] software to conduct BTE calculations in the RTA with a convergence error of $< 5\%$.

3.4 Summary

3.4.1 Electron contribution to U thermal conductivity

Figure 3.1 contains a plot of $(\frac{\sigma}{\tau})$ (electrical conductivity divided by relaxation time) of electrons along different crystallographic directions in α -U over the temperature range of 43K to 933K, as determined from the electronic BTE of Eq. (3.5). Overall, the value of $(\frac{\sigma}{\tau})$ shows a very weak temperature dependence of $< 10\%$ change over the entire range of 43K to 933K.

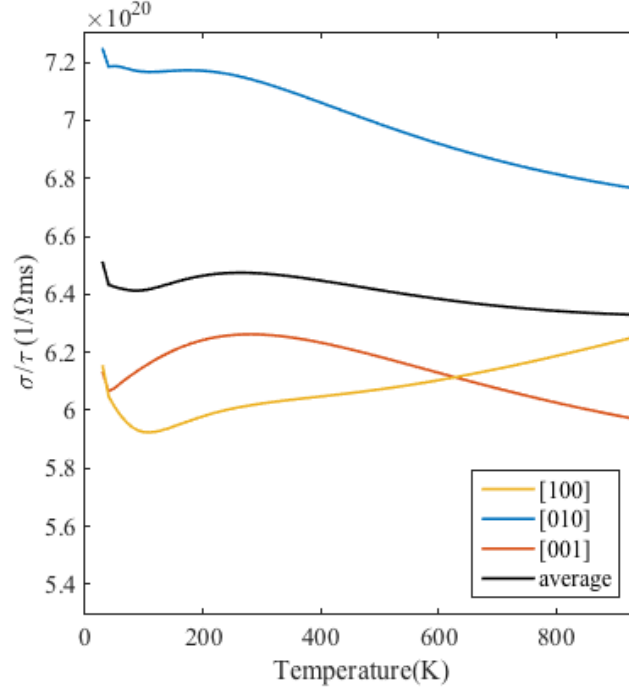


Figure 3.1. Plot of $(\frac{\sigma}{\tau})$ (electrical conductivity divided by relaxation time) of electrons in α -U over the temperature range of 43K to 933K. The curves with different colors indicate the value of $(\frac{\sigma}{\tau})$ along different crystallographic directions and the black curve indicates the average over the different directions.

Now that $(\frac{\sigma}{\tau})$ has been determined, we can fit A , B , ρ_{sat} and θ_D to model single crystal electrical resistivity data using the complete resistivity model in Eq. (3.12). Fitting parameters are calculated by minimizing the root-mean-square error (RMSE) between model and all experimental data for single crystal resistivity, and the standard deviations of the fitting parameters are obtained from the coefficient covariance matrix from fitting [87]. The fitted parameter values and their standard deviations are given in Table 3.1. Figure 3.2 contains single crystal α -U experimental resistivity data along different crystallographic directions together with our full resistivity model of Eq. (3.12) fitted to these data. From the standard deviations of all fitting parameters the standard deviations of the predicted single crystal resistivity are calculated via propagation of error formula [88], providing an estimate of the uncertainty of the model predictions. One standard

deviation for all the model predictions is shown in Figure 3.2 as shaded areas, from which the model uncertainties are all within 10% of the calculated single crystal resistivity. However, this uncertainty is large enough that almost all experimental data are within the uncertainty of our model.

Table 3.1. Fitting parameters obtained from fitting Eq. (3.12) to anisotropic single crystal α -U experimental resistivity data.

	[100]	[010]	[001]
$B(10^{-16}\Omega\text{m} \cdot \text{K}^{-2})$	14.8 ± 0.5	8.3 ± 0.2	11.5 ± 0.3
$\rho_{sat}(10^{-7}\Omega\text{m})$	7.3 ± 0.4	8.5 ± 0.9	9.7 ± 0.7
$A(10^7\text{s} \cdot \text{K}^2)$	0.3 ± 0.2		

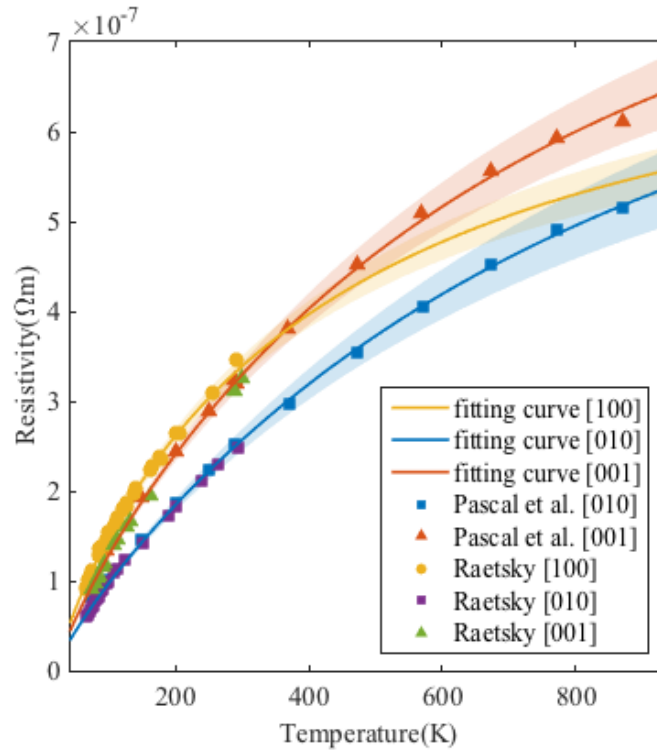


Figure 3.2. Plot of fitted resistivity model (using Eq. (3.12), solid curves) of α -U resistivity from 43K to 933K, compared with single crystal α -U experimental resistivity data (symbols). The curves with different colors represent the fitted resistivity along different crystallographic directions, and the shade areas represent the error ranges. The experimental data for the [010] and [001] directions were obtained from Pascal, et al. [79] and Raetsky [78], and the [100] data was from Raetsky [78].

We use Eq. (3.22) to estimate the electrical resistivity of polycrystalline α -U. The calculation results of resistivity are shown in Figure 3.3, together with a comparison to experimental data. The filled circles represent experimental data of single crystal α -U, and the open circles represent experimental data of polycrystalline α -U. The solid black curve (ρ_{total}) is the calculated resistivity of α -U, and the dashed orange (ρ_{e-ph}), purple (ρ_{e-e}) and blue (ρ_0) curves are the electron-phonon, electron-electron, electron-defect scattering contributions, respectively (the equations used to estimate ρ_{e-ph} , ρ_{e-e} and ρ_0 are shown in Section 3.7.5). The shade area is the error range of calculated resistivity. The polycrystalline and single crystal α -U resistivity data have the same temperature dependence. The average of the single crystal data over different directions falls within the spread of the polycrystalline data. This result suggests grain boundary effects are smaller than the uncertainty introduced by different experiments and by our averaging over the single crystal data. Here and in some later sections of the paper we will calculate errors between model and experimental data where the experimental data is often clustered in certain temperature ranges. In such comparisons, when possible we extrapolate the experiments through linear interpolation onto an approximately uniform temperature grid so that errors represent uniform sampling over temperature. These temperature grids can be found for each case in the Appendices. The mean average error (MAE) and root-mean-square error (RMSE) between our model and average polycrystalline data are $0.01 \pm 0.03 \times 10^{-7} \Omega m$ and $0.14 \times 10^{-7} \Omega m$, respectively, which are $<5\%$ of the total resistivity value. The model RMSE appears to be within the experimental uncertainty and generally shows good agreement with experimental data. To estimate the magnitude of the effect of grain boundaries on resistivity, we should calculate the RMSE between single- and polycrystalline resistivity data. However, due to the lack of resistivity along [100] direction at 300-935K, we can't directly calculate the average of single crystal resistivity data. As our resistivity

model is fitting to single crystal data, we use the RMSE value between our model and average polycrystalline data to estimate the RMSE between single- and polycrystalline resistivity data, which is <5%. Such a small difference of the resistivity between single crystal and polycrystalline samples suggests that the effects of grain boundaries are small and our estimation of averaging the resistivity (and electronic contributions to thermal conductivity) along different crystallographic directions as a proxy for a polycrystalline resistivity (and electronic contributions to thermal conductivity) value is reasonable. All values of resistivity from our calculation results (Section 3.7.1, **Table A3.1**) and the known experimental measurements (Section 3.7.2, **Table A3.3**) are provided in the appendices.

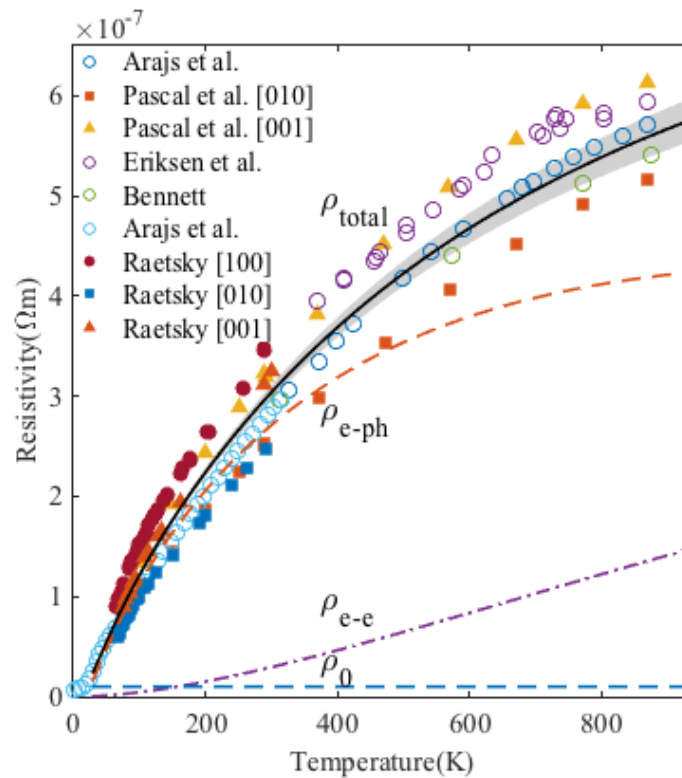


Figure 3.3. Calculation results of α -U resistivity from 43K to 933K (curves), compared with experimental data (symbols). The filled circles represent experimental data of single crystal α -U from Ref. [78,79], and the open circles represent experimental data of polycrystalline α -U from

Refs. [70,89–91]. The solid black curve (ρ_{total}) is the calculated resistivity of α -U, and the dashed orange, purple and blue curves, labeled $\rho_{\text{e-ph}}$, $\rho_{\text{e-e}}$ and ρ_{o} , respectively, are the electron-phonon, electron-electron scattering contributions and residual resistivity due to electron scattering with point defects.

3.4.2 Phonon contribution to U thermal conductivity

The phonon DFT calculation results for α -U are plotted in Figure 3.4 and Figure 3.5. Figure 3.4 illustrates the calculated α -U phonon dispersion curves along [100], [010] and [001] directions at equilibrium calculated by VASP and Phono3py using the small displacement method. The dots in the figure show Crummett et al.'s experimental data for inelastic neutron scattering at room temperature [92]. Our calculation results agree well with Bouchet's calculation [93] and Yang et al.'s calculation [94]. In addition, Bouchet and Yang et al.'s work suggested that the discrepancies between calculations and experiments of the optical branches of [010] and [001] directions are due to the large uncertainties of the experimental measurements for these modes and the temperature difference between the DFT calculations (which are at zero temperature) and experiments conducted at room temperature.

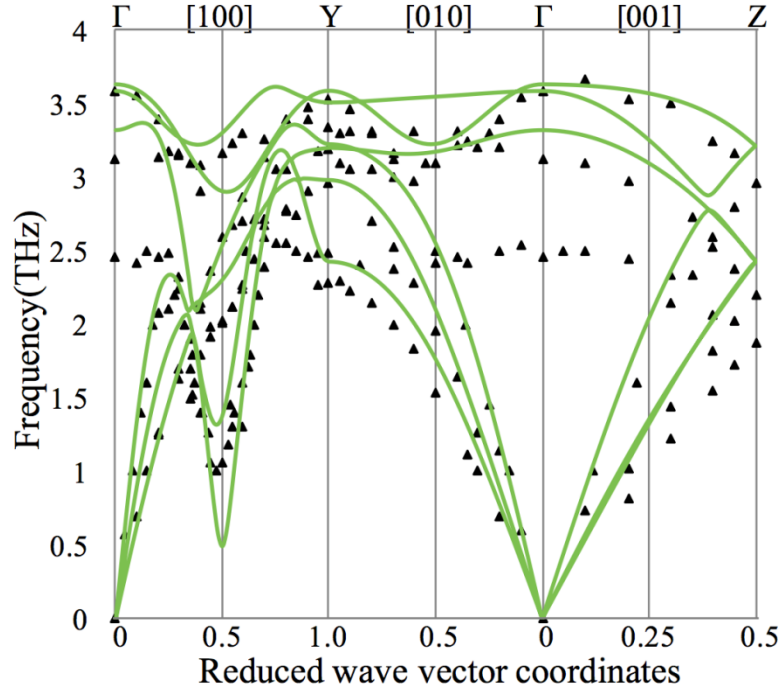


Figure 3.4. The calculated phonon dispersion curves along [100], [010] and [001] directions for α -U. The dots represent Crummett et al.'s experimental data [92] obtained from inelastic neutron scattering.

Figure 3.5 illustrates the phonon-phonon scattering contribution for α -U in the temperature range of 43K to 933K calculated using the phonon dispersion data of Figure 3.4 and the phonon BTE in Eq. (3.13), where for the phonon relaxation time τ_{ph} in Eq. (3.14) only the phonon-phonon scattering contribution τ_{ph-ph} is included. The curves with different colors correspond to the phonon contribution to the thermal conductivity along different crystallographic directions in the anisotropic α -U structure. For all crystallographic directions, the calculated phonon portion of thermal conductivity decreases with increasing temperature.

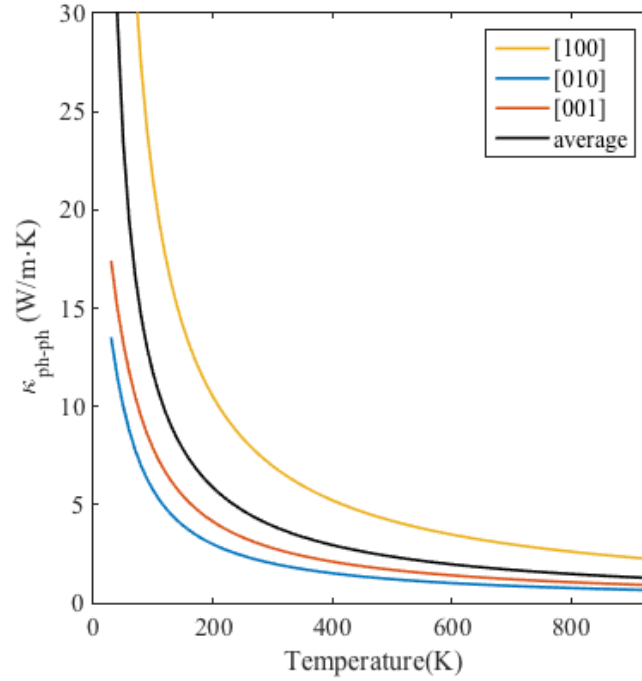


Figure 3.5. Plot of the phonon contribution to the α -U thermal conductivity in the temperature range of 43K to 933K. The different curves correspond to the phonon contribution to the thermal conductivity along different crystallographic directions and the black curve indicates the average over the different directions. Only the phonon-phonon scattering is included in these values.

Then phonon-grain boundary and phonon-defect scattering contributions are added into τ_{ph} using Eq. (3.14), Eq. (3.15) and Eq. (3.16). As discussed in Section 3.3.1, the values of grain size used is $L=0.015\text{mm}$. C is fit to the experimental phonon thermal conductivity data at 54K: $\kappa=32.3\text{ W/m-K}$ from Hall et al. [14], $\rho = 0.60 \times 10^{-7} \Omega\text{m}$ in our model, therefore $\kappa_e=22.0\text{ W/m-K}$ from Eq. (3.2), and finally $\kappa_{ph}=10.3\text{ W/m-K}$ at 54K from Eq. (3.1). Using this data point, C is fit to be $C = 1.0 \times 10^{-2} (ps)^3$, and the calculated phonon scattering contributions for polycrystalline α -U are shown in Figure 3.6. The different curves correspond to the different phonon scattering contributions to the thermal conductivity and the black curve indicates the phonon thermal conductivity obtained from Eq. (3.13).

From room temperature to 933K, the phonon thermal conductivity decreases to about 1 W/m-K. At the fast reactor working temperature near 600K, the phonon contribution to the thermal

conductivity is only about 1 W/m-K from Figure 3.6, and the experimentally measured thermal conductivity of α -U is ≈ 30 W/m-K near 600K [12]. Therefore, the phonon contribution to the total thermal conductivity at reactor operating conditions in relatively pure α -U is likely negligible for most considerations, although this could change in more realistic fuels. However, it is still of interest to evaluate which scattering dominates the phonon thermal conductivity. Although some parameters in our model are only accurate for specific samples in specific experiments, e.g. the grain size L and the constant A , which depends on defect concentration, the model can still get the typical scales of these effects in different temperature regions. Examination of the results in Figure 3.6 shows that phonon-defect scattering dominates when $T < 80$ K while for $T > 80$ K, phonon-phonon scattering dominates and is $\sim 70\%$ of phonon thermal conductivity near 600K. Also at temperatures above about 600K, where the phonon thermal conductivity is $< 5\%$ of total thermal conductivity, the influence of phonon defects on the total thermal conductivity are $< 1.4\%$ and can be considered negligible for most applications.

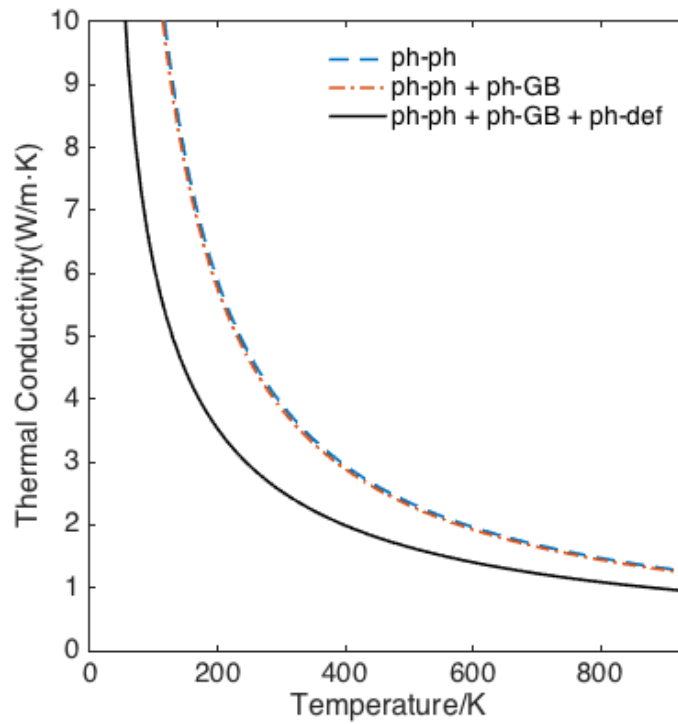


Figure 3.6. Plot of the phonon scattering contributions to the α -U thermal conductivity in the temperature range of 0K to 933K. The different curves correspond to the different phonon scattering contributions to the thermal conductivity and the black curve indicates the phonon thermal conductivity obtained from Eq. (3.13).

3.4.3 Total model for U thermal conductivity

Using Eq. (3.17), Eq. (3.21), our calculated phonon thermal conductivity and fitted resistivity results, the thermal conductivity of α -U was calculated. The values are tabulated in Section 3.7.1, along with all available experimental values from the literature in **Table A3.4** of Section 3.7.2. Figure 3.7 shows the anisotropic thermal conductivity results of α -U compared with experimental polycrystalline thermal conductivity data. To our knowledge, no thermal conductivity data of single crystal α -U exists in the literature. Almost all of the experimental polycrystalline data points are within our predicted α -U thermal conductivity curves. In Figure 3.7 and 8, the solid black curve (κ_{total}) is the thermal conductivity of polycrystalline α -U, estimated

using an average of different crystallographic directions (Eq. (3.21)). And in Figure 3.8, the dashed orange (κ_{ph}) and purple (κ_e) curves illustrate the phonon contribution and electronic contribution, respectively. For the entire temperature range, the mean average error (MAE) and root-mean-square error (RMSE) between our model and experimental thermal conductivity data are 0.20 ± 0.10 W/m-K and 2.08 W/m-K, respectively. Our model is within the range of reported experimental data and shows good overall agreement.

Despite the good overall agreement of our model with the experimental data, we obtain slightly higher thermal conductivity values than some experimental data for 300-700K, slightly lower thermal conductivity values for 750-933K (see errors in **Table A3.2** of Section 3.7.2), and show some dramatic errors below about 300K for Tyler et al.'s data [12] and below about 100K for Hall et al.'s data [14]. To explain the discrepancy with Tyler et al.'s data we note that at low temperatures, defects (point defects, impurities and dislocations) can significantly decrease the thermal conductivity of α -U due to their influence on both the phonon and electronic component of the thermal conductivity. It is shown by our calculation results that phonon-defect scattering dominates the phonon thermal conductivity at low temperature. It also has been shown experimentally by Hall et al.'s experiments [14] that the α -U thermal conductivity values increase more than 40% at low temperature after annealing. The fact that annealing tends to remove defects from a material suggests that the samples used by Tyler et al. contain a sizeable number of defects, which decrease both the phonon and electronic contributions to the thermal conductivity. This hypothesis is also supported by the residual-resistance ratio (RRR) of the Hall and Tyler samples, which is 28 for Hall et al.'s, and 10 for Tyler et al.'s [95]. RRR is the ratio of the resistivity at 300K and at temperature close to 0K, and usually a higher RRR value indicates a sample with lower residual resistivity and fewer defects. Therefore, Tyler et al.'s sample may have a higher

concentration of defects. Although the origin of the discrepancy between our model and Hall et al.'s data is the clear, we note that the latter shows complex temperature dependence at low temperature, which is not supported by the basic theory of thermal conductivity of metals that underlies our modeling [56]. Therefore, we exclude both Tyler et al's and Hall et al's data in our RMSE calculations. Only one data point from Hall et al's data is used, $\kappa=32.3$ W/m-K at 54K, which is used to estimate the correct scale of phonon-defect scattering.

For the slight discrepancies at 300-933K, they may due to the missing physics in the model, or due to the inaccuracy of the model results on [100] direction, and we discuss both here. a potentially significant piece of missing physics in the model is that our phonon band structures are calculated in 0K and ignore the physics of thermal expansion. Thermal expansion effects will decrease the density of materials and therefore decrease phonon thermal conductivity [96]. Thus, thermal expansion effects may make our predicted thermal conductivity slightly higher than actual values, particularly at lower temperatures where the phonon contributions are more significant. DFT or experimental thermal expansion could be added to a future iteration of the model to reduce any errors associated with these effects. Another source of error between the predicted thermal conductivity and the measured values is that the resistivity prediction for the [100] direction may be inaccurate from 300K to 933K, due to less resistivity data being available in this direction. As the electronic contribution is the majority of the thermal conductivity at high temperature, this inaccuracy in the [100] resistivity data could lead to the discrepancies of the thermal conductivity.

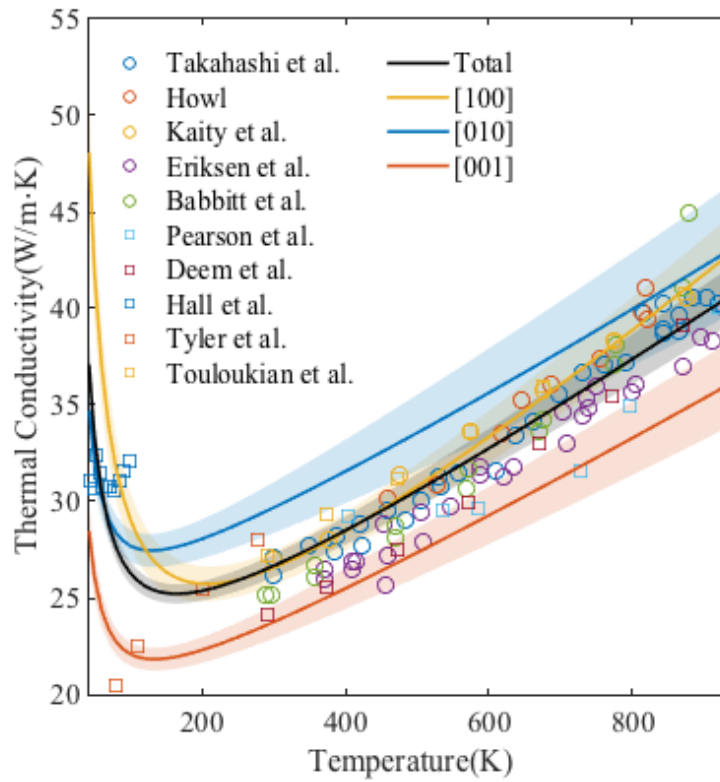


Figure 3.7. Plot of our thermal conductivity model from 43K to 933K (solid curves), compared with polycrystalline α -U experimental thermal conductivity data (symbols). The curves with different colors represent the calculated thermal conductivity along different crystallographic directions. The experimental thermal conductivity data were obtained from the following references: [12–15,89,97,98].

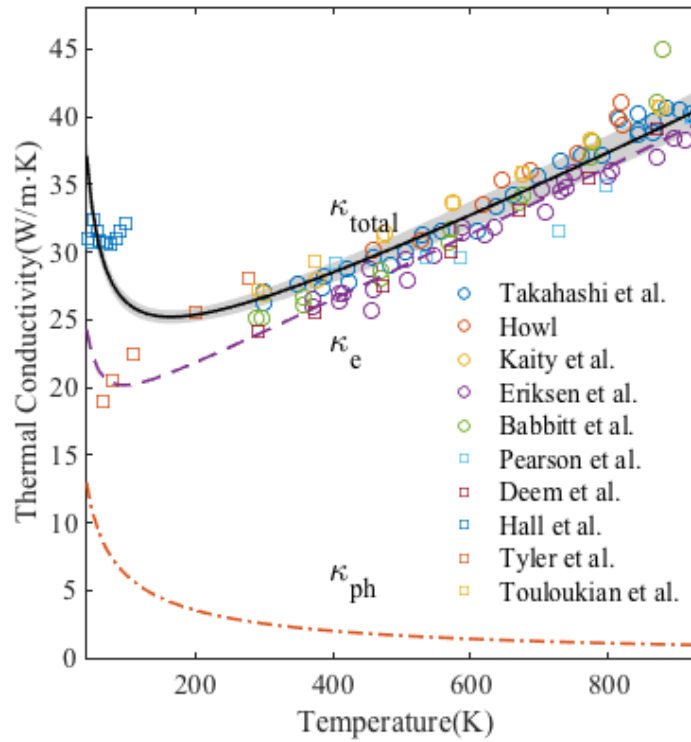


Figure 3.8. Calculation results of α -U thermal conductivity from 43K to 933K (curves), compared with polycrystalline α -U experimental thermal conductivity data (symbols). The solid black curve (κ_{total}) is the calculated thermal conductivity of α -U, and the dashed orange and purple curves, labeled κ_{ph} and κ_{e} , respectively, are the phonon contribution and electronic contribution to the thermal conductivity, respectively. The experimental thermal conductivity data were obtained from the following references: [12–15,89,97,98].

3.4.4 Extended thermal conductivity model for binary U-rich alloys

The thermal conductivities of binary U-rich U-Zr and U-Mo alloys from 300K to 933K were calculated by fitting the full thermal conductivity equation (Eq. (3.17)) with alloy resistivity equation (Eq. (3.20)) to experimental data. The thermal conductivity values are tabulated in **Table A3.5** and **Table A3.6** of Section 3.7.3, and experimental data of thermal conductivity for alloys is tabulated in **Table A3.7** and **Table A3.8** of Section 3.7.4. Figure 3.9 and Figure 3.10 contain U-Zr and U-Mo experimental thermal conductivity data with our alloy thermal conductivity model fitted to these data, respectively. The fitting parameters are the same as values in Table 3.1 except

for the addition of the parameter D in Eq. (3.20). The values of D obtained from the fit are: $D_{U_{Zr}} = (0.97 \pm 0.08) \times 10^{-6} \Omega m$, $D_{U_{Mo}} = (1.51 \pm 0.13) \times 10^{-6} \Omega m$. The overall RMSE values in our fits are 1.3 W/m-K and 1.6 W/m-K for U-Zr and U-Mo, respectively. The overall MAE values in our fits are (0.15 ± 0.18) W/m-K and (0.29 ± 0.24) W/m-K for U-Zr and U-Mo, respectively. We note here that in theory this model only applies for dilute U alloys. However, the agreement between our fitted model results and experimental data shows that despite the alloy composition being somewhat out of the dilute regime (we consider U at% > 78%) this model is still a good approximation for U-Zr and U-Mo alloys. We also note that the typical alloy components in actual fuels are U-22at%Zr in the Experimental Breeder Reactor-II in Idaho, USA [99], and U-15.7at%Mo in the Belgian Reactor 2 in Mol, Belgium [100]. These Zr and Mo composition ranges are covered by our model. Based on experimental data, Kim et al. developed empirical formulas for the thermal conductivity of the U-Zr [101,102] and U-Mo alloys [103,104] applicable to any composition, which are shown as dashed curves in Figure 3.9 and Figure 3.10, respectively. Comparing to the same data, the overall RMSE values for Kim et al.'s empirical formulas are 1.6 W/m-K and 1.6 W/m-K for U-Zr and U-Mo, respectively. Thus, based only on the RMSE values, for U-Zr our model is slightly better than Kim et al.'s formula, and for U-Mo our model is as good as Kim et al.'s formula. However, while both our and Kim et al.'s models are based on the thermal conductivity of pure α -U, Kim et al.'s formulas use five parameters to fit the thermal conductivity of alloys, whereas we only use one. This suggests that our model may give a more complete physics-based representation of the contributions to the thermal conductivity, and that our modeling approach can be easily extended to complex materials like U alloys. The current alloying model is quite approximate. Specifically, we don't include the impact of alloying elements on phonon thermal conductivity and use a one-parameter fitting formula for residual resistivity with

only up to quadratic concentration dependence and with no temperature dependence. Adding the effects of alloying on the phonon thermal conductivity and incorporating a more complex alloying resistivity formula, e.g., with temperature dependence and/or higher order terms in concentration, could produce a more accurate model compared to experimental data for U alloys, including U-Zr and U-Mo. Developing such a model will be the subject of the future work.

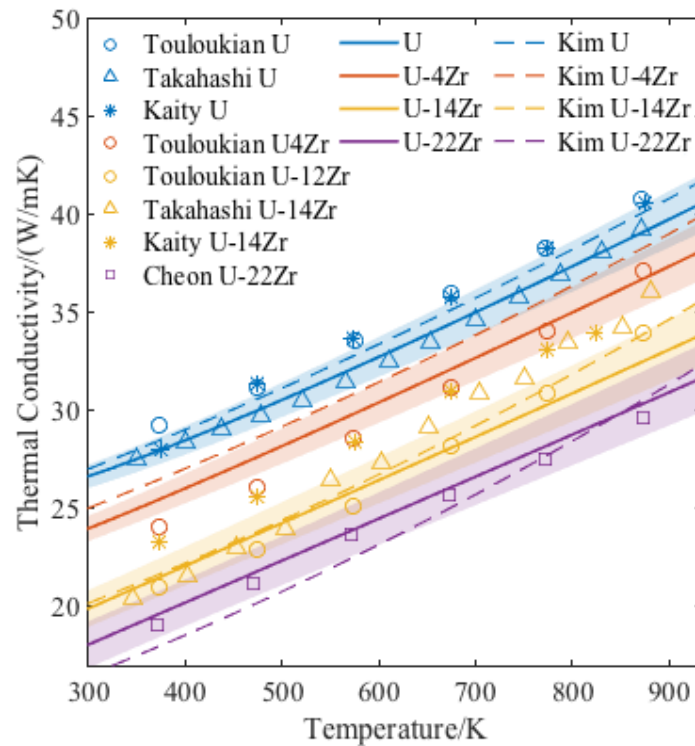


Figure 3.9. Calculation results of U-rich U-Zr alloys thermal conductivity from 300K to 933K (solid curves), compared with U-Zr experimental thermal conductivity data (symbols). The dashed lines are values based on empirical models developed by Kim, et al. [102]. The curves and symbols with different colors represent the U-Zr thermal conductivities in different Zr at%. The experimental thermal conductivity data were obtained from the following references: [12,13,15,101,105].

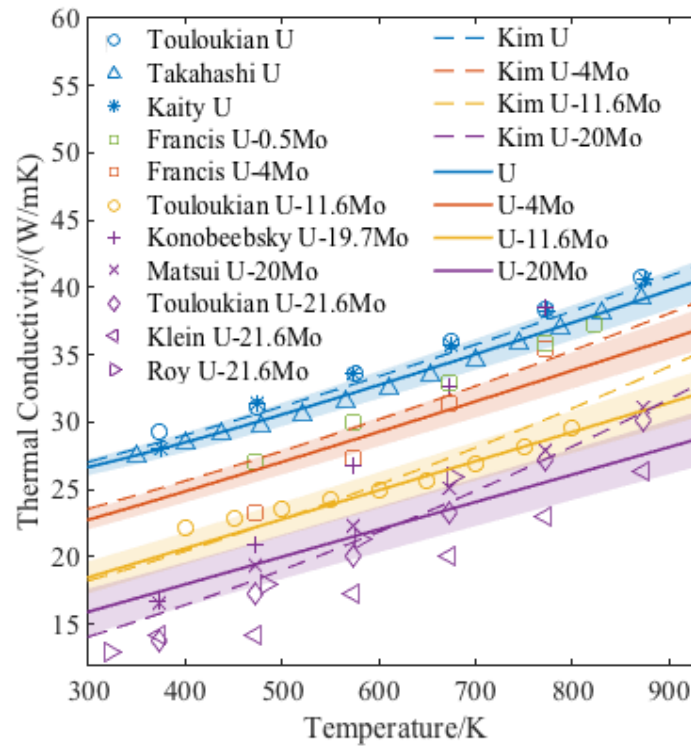


Figure 3.10. Calculation results of U-rich U-Mo alloys thermal conductivity from 300K to 933K (solid curves), compared with U-Mo experimental thermal conductivity data (symbols). The dashed lines are values based on empirical models developed by Kim, et al. [104]. The curves and symbols with different colors represent the U-Mo thermal conductivities in different Mo at%. The experimental thermal conductivity data were obtained from the following references: [12,13,15,95,103,106–109].

3.5 Discussions

From the results of our anisotropic single crystal resistivity model, we predicted that the resistivity along [100] direction goes lower than the resistivity along [001] direction when $T > 370\text{K}$, and nearly identical to the resistivity along [010] direction at $\sim 930\text{K}$, although all experimental data of [100] direction has larger values than other two directions in the range 43–300K. These results show that the relative value of the [100] resistivity changes dramatically with temperature, going from the largest to tie for the smallest value among the three directions. Such large changes in relative values is not unprecedented in materials exhibiting resistivity saturation,

e.g., yttrium and WO_2 also show significant changes in the relative values of resistivity along different directions with increasing temperatures [110].

From the results of our fitted thermal conductivity model, we can clearly see which physical contribution dominates the thermal conductivity of α -U under different temperature regimes. In Figure 3.3, the electron-phonon scattering contribution of resistivity is larger than both the electron-electron scattering part and residual resistivity, and dominates the temperature dependence of resistivity from 43 to 933K. In Figure 3.8, the electronic thermal conductivity is larger than the phonon thermal conductivity from 43K to 933K, and dominates the temperature dependence of thermal conductivity. Thus, electrons are the major heat carriers, and electron-phonon scattering is the dominant interaction of thermal conductivity of α -U, including at the expected working temperature of U-based metallic fuels of around 600K. However, the electron-electron scattering contribution and the phonon contribution (mainly controlled to phonon-phonon and phonon-defect scattering) play an important (~ 10 -20% of the total thermal conductivity), although not dominant, role in setting thermal conductivity values near 800K and 100K, respectively.

Besides temperature, anisotropy also influences the contributions of different scattering mechanisms to the thermal conductivity. From Figure 3.2, the electrical resistivity along the [010] direction is smaller than along [100] and [001] directions. This directly leads to the result in Figure 3.7 that the thermal conductivity along [010] direction is much larger than along the [100] and [001] directions from 150-933K. Also, as shown in Figure 3.5, the phonon-phonon scattering contribution along the [100] direction is much larger than along the other two directions for $T < 100\text{K}$. This leads to the result in Figure 3.7 that for $T < 100\text{K}$, although the resistivity along [100]

direction is slightly larger than [001] and [010] direction, the thermal conductivity along the [100] direction is still the largest among three directions.

3.6 Conclusions

A computational, physics-based model of α -U thermal conductivity has been constructed which is based on DFT calculations and experimental data, and which incorporates both phonon and electron scattering contributions, including phonon-phonon, phonon-grain boundary, phonon-defect, electron-phonon, electron-electron and electron-defect scatterings. This is the first model of α -U thermal conductivity that incorporates all known experimental resistivity and thermal conductivity data and separates out contributions from different mechanisms. This model provides insight into the different physical factors that govern the thermal conductivity of α -U under different temperature ranges. At 43-933K, electrons are the major heat carriers and the conductivity is generally dominated by electron-phonon scattering.

Overall, this work serves as a first step to understanding the complex behavior of thermal conduction in metallic U alloy nuclear fuels. Now that a model of pure α -U has been established, it can be used to incorporate more physically realistic and complex effects, such as intentional alloying elements, transmutation products, radiation-induced defects and noble gas bubbles. For example, the thermal conductivity of U-rich U-Zr and U-Mo alloys can be calculated simply by adding a residual resistivity term, with results that agree well with the available experimental data. The usage and extension of this thermal conductivity model of α -U to more complex systems is an important step to gaining a deeper understanding of the thermal conduction characteristics of metallic U-alloy nuclear fuels. This understanding will in turn enable the improved design of

temperature control in the future construction of nuclear reactors powered by metallic U-alloy fuels.

3.7 Appendices

3.7.1 Model and experimental data of resistivity and thermal conductivity of α -U.

Table A3.1. Calculation results of α -U resistivity from 43K to 933K. Both single- and polycrystalline results are listed.

T (K)	Resistivity ($\times 10^{-7} \Omega m$)								Error ²
	Calculations				Experiments				
	[100]	[010]	[001]	Total	Arajs ¹	Eriksen ¹	Bennett ¹	Avg ¹	
43	0.55	0.35	0.46	0.44	0.46	-	-	0.46	-0.02
100	1.49	0.97	1.29	1.21	1.08	-	-	1.08	0.13
150	2.11	1.43	1.88	1.76	1.57	-	-	1.57	0.19
200	2.61	1.84	2.41	2.24	2.02	-	-	2.02	0.22
250	3.03	2.22	2.87	2.66	2.46	-	-	2.46	0.20
300	3.39	2.57	3.30	3.04	2.86	-	-	2.86	0.18
350	3.70	2.89	3.68	3.38	3.21	-	3.17	3.19	0.19
400	3.97	3.19	4.03	3.69	3.57	4.11	3.44	3.71	-0.02
450	4.21	3.47	4.35	3.97	3.88	4.33	3.72	3.98	-0.01
500	4.42	3.73	4.64	4.22	4.19	4.62	4.00	4.27	-0.05
550	4.61	3.97	4.91	4.46	4.47	4.88	4.27	4.54	-0.08
600	4.77	4.19	5.17	4.68	4.72	5.14	4.50	4.79	-0.11
650	4.93	4.40	5.40	4.87	4.95	5.47	4.68	5.03	-0.16
700	5.06	4.60	5.61	5.06	5.15	5.62	4.86	5.21	-0.15
750	5.19	4.78	5.81	5.23	5.36	5.77	5.04	5.39	-0.16
800	5.30	4.95	6.00	5.39	5.51	5.78	5.20	5.49	-0.10
850	5.41	5.12	6.17	5.53	5.65	5.91	5.34	5.63	-0.10
900	5.50	5.27	6.34	5.67	-	-	-	-	-
933	5.56	5.36	6.44	5.75	-	-	-	-	-
The average (Mean Average Error (MAE)) and standard deviation of error									0.01±0.03
The Root Mean Square Error (RMSE)									0.14

¹ Experimental resistivity values are calculated using linear interpolation of experimental data from Arajs et al. [70,90], Eriksen et al. [89], and Bennett[45]. Average experimental resistivity values are the mean values of interpolated values. All original data is given in **Table A3.3**.

² The error is defined as $\Delta\rho_{error} = \rho_{total} - \rho_{exp(avg)}$.

Table A3.2. Calculation results of α -U thermal conductivity from 43K to 933K. Both single- and poly-crystalline results are listed.

T (K)	Thermal conductivity (W/m-K)					
	Calculations				Exp (Avg) ¹	Error ²
	[100]	[010]	[001]	Total		
43	47.92	34.60	28.37	36.96	-	-
54 ³	40.01	31.37	25.44	32.27	32.31	-0.04
100	29.09	27.70	22.09	26.29	-	-
150	26.35	27.53	21.86	25.25	-	-
200	25.73	28.06	22.30	25.36	-	-
250	25.94	28.82	22.97	25.91	-	-
300	26.56	29.68	23.75	26.66	26.19	0.47
350	27.43	30.60	24.60	27.54	27.02	0.52
400	28.45	31.56	25.49	28.50	28.05	0.45
450	29.58	32.54	26.41	29.51	29.02	0.49
500	30.78	33.55	27.35	30.56	30.04	0.52
550	32.04	34.58	28.31	31.64	31.03	0.61
600	33.35	35.63	29.28	32.75	32.20	0.55
650	34.70	36.69	30.27	33.88	33.55	0.33
700	36.07	37.77	31.26	35.03	34.92	0.11
750	37.47	38.86	32.27	36.20	36.18	0.02
800	38.88	39.97	33.29	37.38	37.68	-0.30
850	40.32	41.09	34.31	38.57	38.83	-0.26
900	41.77	42.21	35.35	39.78	39.95	-0.17
933	42.73	42.96	36.03	40.58	41.13	-0.55
The average (Mean Average Error (MAE)) and standard deviation of error						0.20±0.10
The Root Mean Square Error (RMSE)						2.08

1 Experimental thermal conductivity values are calculated using linear interpolation of experimental data from Hall et al. [14] for $T \leq 100\text{K}$, and from Ref [12,13,15,89,97,98] for $T \geq 300\text{K}$. The results of linear interpolation are not listed, but average values are given. All original data is given in **Table A3.4**. We exclude Tyler et al.'s data [12] and Hall et al.'s data [14] as discussed in Section 3.4.3.

2 The error is defined as $\Delta\kappa_{error} = \kappa_{total} - \kappa_{exp(avg)}$.

3 This data point ($\kappa=32.31$ W/m-K at 54K from Hall et al's [14]) is used to estimate the proper scale of phonon-defect scattering and to fit the parameter C in Eq. (3.16).

3.7.2 All experimental data of resistivity and thermal conductivity of α -U.

Table A3.3. Experimental α -U resistivity data.

T (K)	R ($10^{-8}\Omega\text{m}$)	T (K)	R ($10^{-8}\Omega\text{m}$)	T (K)	R ($10^{-8}\Omega\text{m}$)	T (K)	R ($10^{-8}\Omega\text{m}$)
Raetsky ¹ [100]		Raetsky ¹ [010] cont.		Pascal et al. ¹ [001] cont.		Arajs et al. ³ cont.	
67	9.2	97	9.8	200	24.4	45	4.6
69	9.7	99	10.0	250	28.8	51	5.2
70	10.0	108	10.9	288	32.3	58	5.8
73	10.4	113	11.3	369	38.1	65	6.5
73	10.6	125	12.4	472	45.2	77	7.8
76	11.2	150	14.1	569	51.0	88	8.9
85	12.8	191	17.3	672	55.7	97	9.8
86	13.0	201	18.2	772	59.2	107	10.8
87	13.5	239	21.0	871	61.2	116	11.6
89	13.7	263	22.9			127	12.7
95	14.0	293	24.8	Eriksen et al. ²		137	13.6
95	14.5			369	39.5	147	14.4
98	15.0	Raetsky ¹ [001]		409	41.6	157	15.3
101	15.3	80	9.7	458	43.8	168	16.3
104	15.7	84	10.3	463	44.3	177	17.1
107	16.1	84	10.5	504	46.3	188	18.1
109	16.5	91	11.5	546	48.6	198	18.8
113	17.1	93	11.9	585	50.7	209	19.7
120	17.8	109	13.9	592	51.1	219	20.5
121	18.0	114	14.6	623	52.4	229	21.3
126	18.3	128	16.0	633	54.2	241	22.2
127	18.7	133	16.6	702	56.3	250	23.0
137	19.6	163	19.4	712	55.9	261	23.8
141	20.2	288	31.2	729	57.7	272	24.6
164	22.3	300	32.5	738	56.7	283	25.5
166	22.8			746	57.7	295	26.4
177	23.8	Pascal et al. ¹ [010]		803	58.1	304	27.1
178	23.6	99	10.1	870	59.4	315	27.8
202	26.4	150	14.5			326	30.7
206	26.4	200	18.6	Bennett ²		373	33.5

257	30.9	251	22.4	312	29.6	398	35.5
291	34.7	289	25.2	574	44.0	425	37.2
		372	29.8	774	51.2	499	41.8
Raetsky ¹ [010]		473	35.4	876	54.1	543	44.4
69	6.3	571	40.6			590	46.8
72	6.6	672	45.2	Arajs et al. ³		657	49.8
75	7.0	772	49.2	7	0.8	679	50.8
77	7.3	869	51.6	14	0.9	699	51.4
80	7.8			20	1.1	728	52.9
82	8.1	Pascal et al. ¹ [001]		24	1.6	758	53.8
84	8.3	73	10.9	29	2.4	790	54.8
89	8.8	98	13.3	35	3.2	832	56.0
91	9.1	149	19.3	40	3.9	869	57.1

1 Values read from the plot of Ref. [111]

2 Values read from the plot of Ref. [91]

3 Values read from the plot of Ref. [90]

Table A3.4. Experimental α -U thermal conductivity data.

T (K)	K (W/m-K)	T (K)	K (W/m-K)	T (K)	K (W/m-K)
Hall et al. ¹		Babbitt et al. ¹ Sample1		Deem et al. ¹ cont.	
50	32	293	25	473	27.5
60	32	360	26.5	573	30
80	32	473	28.5	673	33
100	33	573	31.5	773	35.5
		680	34	873	39
Tyler et al. ¹		780	38		
66	19	880	45	Pearson et al. ¹	
80	20.5			407	29
110	22.5	Babbitt et al. ¹ Sample2		540	29.5
200	25.5	293	25	589	29.5
278	28	360	26	735	31.5
		473	28	800	35
Eriksen et al. ¹		540	29.5	926	40
373	26	573	30.5		
473	28.5	680	33.5	Takahashi et al. ⁴	
573	31	780	37	300	27

673	33	880	41	400	28.5
773	35.5			500	30.5
873	38	Kaity et al. ²		600	32.5
Howl ³		300	27	700	35
		373	28	800	38
		473	31.5	900	40.5
422	30.5	573	33.5	Touloukian et al. ^{3,5}	
526	31	673	36		
614	33.5	773	38.5		
648	35.5	873	40.5	373	29.5
685	36	Deem et al. ¹		473	31
754	37.5			573	33.5
823	39.5			673	36
812	40	293	24	773	38.5
		373	25.5	873	41

1 Values read from Ref. [46]

2 Values read from Ref. [15]

3 Values read from Ref. [12]

4 Values read from Ref. [13]

5 Recommended data

3.7.3 Model and experimental data of thermal conductivity of U-Zr and U-Mo.

Table A3.5. Calculation results of U-Zr thermal conductivity(W/m-K) from 373K to 873K.

T (K)	U 4at%Zr			U 12at%Zr		
	Calc	Touloukian ¹	Error	Calc	Touloukian ¹	Error
323	24.6	23.2	1.4	21.0	19.8	1.2
373	25.6	24.1	1.5	22.1	21.0	1.1
423	26.6	25.1	1.5	23.2	22.0	1.2
473	27.7	26.1	1.6	24.3	22.9	1.4
523	28.8	27.3	1.5	25.4	24.0	1.4
573	29.9	28.6	1.3	26.5	25.1	1.4
623	31.0	29.8	1.2	27.6	26.6	1.0
673	32.2	31.1	1.1	28.7	28.1	0.6
723	33.3	32.6	0.8	29.8	29.5	0.3
773	34.5	34.1	0.4	30.9	30.9	0.1

823	35.7	35.6	0.8	32.1	32.4	0.3		
873	36.8	37.2	-0.3	33.2	34.0	-0.8		
T (K)	U 14at%Zr					U 22at%Zr		
	Calc	Takahashi ₁	Kaity ₁	Exp(Avg) ₁	Error	Calc	Cheon ¹	Error
323	20.4	19.7	22.3	21.0	-0.6	18.6	18.6	0.0
373	21.5	21.0	23.3	22.1	-0.6	19.6	19.1	0.5
423	22.6	22.2	24.4	23.3	-0.7	20.7	20.2	0.5
473	23.7	23.4	25.5	24.5	-0.8	21.8	21.2	0.5
523	24.8	25.0	26.9	26.0	-1.2	22.8	22.5	0.4
573	25.9	26.9	28.3	27.6	-1.7	23.9	23.7	0.2
623	27.0	28.1	29.6	28.9	-1.9	25.0	24.7	0.3
673	28.1	29.9	30.9	30.4	-2.3	26.1	25.7	0.4
723	29.2	31.2	32.0	31.6	-2.4	27.1	26.6	0.5
773	30.3	32.6	33.1	32.8	-2.5	28.2	27.6	0.6
823	31.4	33.9	34.0	33.9	-2.5	29.3	28.6	1.2
873	32.5	35.6	-	35.6	-3.1	30.4	29.7	0.7
The average (Mean Average Error (MAE)) and standard deviation of error (for all concentrations)								0.15±0.18
The Root Mean Square Error (RMSE) (for all concentrations)								1.3

¹ Experimental thermal conductivity values are calculated using linear interpolation of experimental data from Touloukian et al. [12] for U4Zr, from Takahashi et al. [13] and Kaity et al. [15] for U14Zr (and the average experimental values for U14Zr), and from Cheon et al. [105] for U22Zr. All original data is given in **Table A3.7**.

Table A3.6. Calculation results of U-Mo thermal conductivity(W/m-K) from 373K to 873K.

T (K)	U 0.5at%Mo			U 4at%Mo			U 11.6at%Mo		
	Calc	Francis ¹	Error	Calc	Francis ¹	Error	Calc	Touloukian ₁	Error
323	26.5	-	-	23.2	-	-	19.0	-	-
373	27.4	-	-	24.3	-	-	20.0	-	-
423	28.4	-	-	25.4	-	-	21.1	22.4	-1.3
473	29.5	27.0	2.5	26.4	23.2	3.2	22.2	23.1	-0.9
523	30.5	28.5	2.1	27.5	25.3	2.3	23.3	23.8	-0.6
573	31.6	29.9	1.7	28.7	27.3	1.4	24.3	24.5	-0.2
623	32.8	31.4	1.4	29.8	29.3	0.5	25.4	25.2	0.2
673	33.9	32.9	1.0	30.9	31.4	-0.4	26.5	26.2	0.3

723	35.1	34.3	0.7	32.1	33.4	-1.3	27.6	27.5	0.1
773	36.2	35.8	0.4	33.2	35.4	-2.2	28.7	28.8	-0.2
823	37.4	37.3	0.1	34.4	-	-	29.8	-	-
873	38.6	-	-	35.5	-	-	30.8	-	-
T (K)	U 20at%Mo			U 21.6at%Mo					
	Calc	Matsui ¹	Error	Calc	Touloukian ₁	Klein ¹	Roy ₁	Exp(Avg) ₁	Error
323	16.4	15.2	1.2	16.0	12.7	12.8	13.0	12.8	3.2
373	17.4	16.6	0.8	17.0	13.8	14.2	14.5	14.2	2.9
423	18.4	18.0	0.4	18.0	15.6	14.2	16.1	15.3	2.8
473	19.4	19.4	0.0	19.1	17.3	14.2	17.6	16.4	2.7
523	20.5	20.9	-0.4	20.1	18.7	15.7	19.3	17.9	2.2
573	21.5	22.3	-0.8	21.1	20.1	17.2	21.1	19.5	1.6
623	22.5	23.7	-1.2	22.1	21.7	18.7	23.4	21.2	0.9
673	23.5	25.1	-1.6	23.1	23.3	20.1	25.7	23.0	0.0
723	24.5	26.5	-2.0	24.1	25.3	21.6	-	23.4	0.7
773	25.5	27.9	-2.4	25.1	27.2	23.0	-	25.1	0.0
823	26.6	29.5	-2.9	26.1	28.7	24.7	-	26.7	-0.6
873	27.6	31.1	-3.5	27.1	30.1	26.4	-	28.3	-1.1
The average (Mean Average Error (MAE)) and standard deviation of error (for all concentrations)									0.29±0.24
The Root Mean Square Error (RMSE) (for all concentrations)									1.6

¹ Experimental thermal conductivity values are calculated using linear interpolation of experimental data from Francis et al. [95] for U0.5Mo and U4Mo, from Touloukian et al. [12] for U11.6Mo, from Matsui et al. [107] for U20Mo, and from Ref. [12,108,109] for U21.6Mo (and the average experimental values for U21.6Mo). All original data is given in **Table A3.8**. We exclude Konobeevsky et al.'s data [106] for U19.7Mo due to its significant error near 800K.

3.7.4 Experimental data of thermal conductivity of U-Zr and U-Mo alloys.

Table A3.7. Experimental thermal conductivity data of U-Zr alloys in at%.

T (K)	K (W/m-K)	T (K)	K (W/m-K)	T (K)	K (W/m-K)
Touloukian et al. U-4Zr ¹		Takahashi et al. U-14Zr ²		Kaity et al. U-14Zr ³	
293	22.6	300	18.8	300	21.8
373	24.1	350	20.4	373	23.3
473	26.1	400	21.6	473	25.6
573	28.6	450	23.0	573	28.4

673	31.1	500	24.0	673	31.0
773	34.1	550	26.5	773	33.1
873	37.2	600	27.4	823	34.0
		650	29.2		
Touloukian et al. U-12Zr ¹		700	30.9	Cheon et al. U-22Zr ⁴	
293	19.2	750	31.6	293	18.2
373	21.0	800	33.5	373	19.1
473	23.0	850	34.2	473	21.2
573	25.1	880	36.1	573	23.7
673	28.2			673	25.7
773	30.9			773	27.5
873	34.0			873	29.7

1 Values read from Ref. [12]

2 Values read from the plot of Ref. [13]

3 Values read from the plot of Ref. [15]

4 Values read from the plot of Ref. [105]

Table A3.8. Experimental thermal conductivity data of U-Mo alloys in at%.

T (K)	K (W/m-K)	T (K)	K (W/m-K)	T (K)	K (W/m-K)
Francis et al. U-0.5Mo ¹		Touloukian et al. U-11.6Mo ² cont.		Matsui et al. U-20Mo ³	
473	27.0	750	28.2	293	14.3
573	29.9	800	29.5	373	16.6
673	32.9			473	19.4
773	35.8	Touloukian et al. U-21.6Mo ²		573	22.3
823	37.3	293	12.1	673	25.1
		373	13.8	773	27.9
Francis et al. U-4Mo ¹		473	17.3	873	31.1
473	23.2	573	20.1		
573	27.3	673	23.3	Konobeebsky et al. U- 19.7Mo ³	
673	31.4	773	27.2	373	16.7
773	35.4	873	30.1	473	20.9
				573	26.8
Touloukian et al. U- 11.6Mo ²		Klein et al. U-21.6Mo ³		673	32.6
400	22.1	296	12.1	773	38.5

450	22.8	373	14.2	Roy et al. U-21.6Mo ³	
500	23.5	473	14.2		
550	24.2	573	17.2	323	12.97
600	24.9	673	20.1	485	17.99
650	25.6	773	23	581	21.34
700	26.9	873	26.4	677	25.94

1 Values read from Ref. [95]

2 Values read from Ref. [12]

3 Values read from Ref. [103]

3.7.5 The equations to separate electron-electron and electron-phonon contribution for total resistivity.

The resistivity for each direction is calculated using (as same as Eq.(3.12)):

$$\rho^X = \left\{ [\rho_{e-e}^{X,id} + \rho_{e-ph}^{X,id}]^{-1} + (\rho_{sat}^X)^{-1} \right\}^{-1} + \rho_0, \quad (\text{A.34})$$

where X represents a direction (100), (010), or (001), $\rho_{e-e}^{X,id}$ is calculated using Eq.(3.5) and Eq.(3.9), and $\rho_{e-ph}^{X,id}$ is calculated using Eq.(3.10). We approximately separated electron-electron and electron-phonon contribution by weighting the total resistivity along a direction by the fraction of the ideal resistivity due to each contribution, as show here:

$$\rho_{e-e}^X = \left\{ [\rho_{e-e}^{X,id} + \rho_{e-ph}^{X,id}]^{-1} + (\rho_{sat}^X)^{-1} \right\}^{-1} \times \frac{\rho_{e-e}^{X,id}}{\rho_{e-e}^{X,id} + \rho_{e-ph}^{X,id}}, \quad (\text{A.35})$$

$$\rho_{e-ph}^X = \left\{ [\rho_{e-e}^{X,id} + \rho_{e-ph}^{X,id}]^{-1} + (\rho_{sat}^X)^{-1} \right\}^{-1} \times \frac{\rho_{e-ph}^{X,id}}{\rho_{e-e}^{X,id} + \rho_{e-ph}^{X,id}}. \quad (\text{A.36})$$

We used Eq.(3.21) to calculated total resistivity from anisotropic resistivities of each direction and this equation mixes contributions of ρ_{e-e}^X and ρ_{e-ph}^X in ways that do not allow for a rigorous separation of ρ_{total} into electron-electron and electron-phonon components. Therefore, we instead use a simple average to calculate the total contribution of electron-electron and electron-phonon scattering:

$$\rho_{e-e/e-ph} = \frac{1}{3} \times (\rho_{e-e/e-ph}^{100} + \rho_{e-e/e-ph}^{010} + \rho_{e-e/e-ph}^{001}). \quad (\text{A.37})$$

This average means that ρ_{total} is not rigorously equal to $\rho_{e-e} + \rho_{e-ph}$, although the difference is small than 3% at all temperatures.

Chapter 4 : Thermal Conductivity Modeling for Multi-phase Mixtures: Demonstration on U-Zr and U-Mo

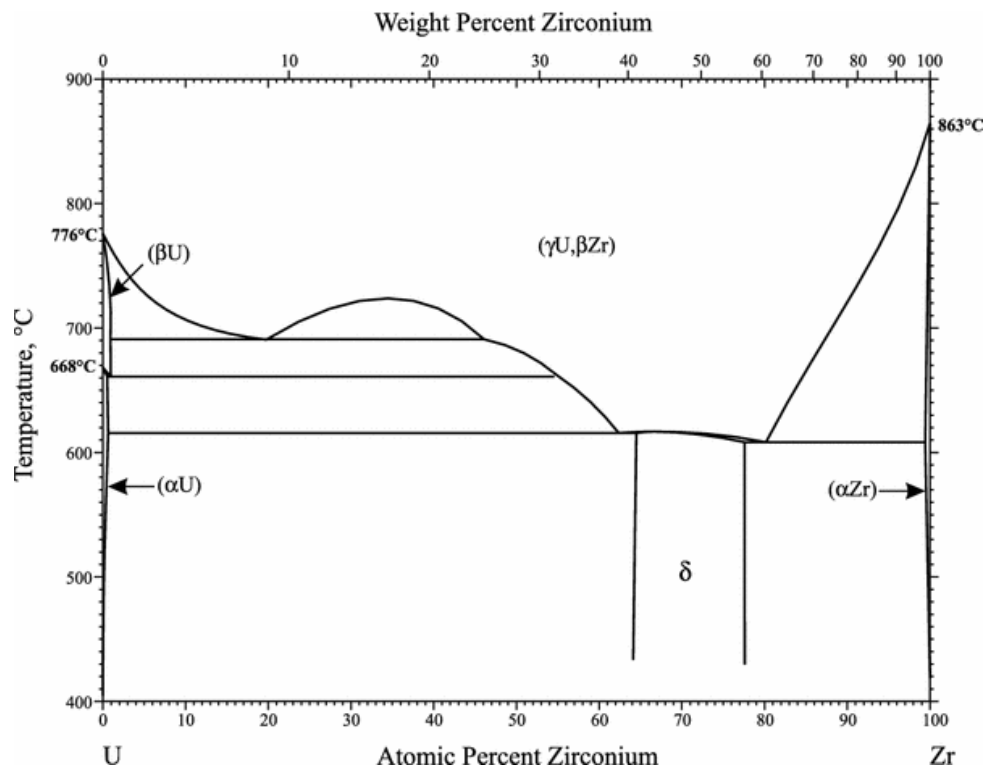
4.1 Chapter Abstract

In this work, we developed a thermal conductivity model based on density functional theory calculations, physics rules, and experimental data, for different types of metal alloys: anchor structures, solid solutions, and multi-phase mixtures. The model contains three stages to incorporate with different types of metal alloys: Stage 1: model for anchor structures with fixed compositions at a range of temperatures; Stage 2: model for solid solutions across a range of compositions; and Stage 3: model for multi-phase mixtures. The model is demonstrated on U-Zr and U-Mo alloys and displays good agreement with experimental data, which has a root-mean-square error of about 1.3 W/m-K ($\approx 10\%$ error versus experiment) over the typical operating temperature for all phases of U-Zr. Compared with previous models for U-Zr and U-Mo, this model reduces the reliance on experimental data by utilizing density functional theory calculations and physics rules, while giving comparable accuracy. Providing insights on the physics of various electron and phonon scattering mechanisms, this model is a powerful tool for semi-quantitative predictions of thermal conductivity in both single-phase alloys and alloys with phase mixtures.

4.2 Introduction

As mentioned in Section 1.2, the thermal conductivity modeling is an useful tool to obtain high-quality data, i.e. the DFT-BTE approach which is developed in recently years which relies on few experimental data and is extendable to different conditions. One example of our model is demonstrated on α U, shown in Chapter 3. However, this model did not solve the problem how thermal conductivity changes as a function of alloying compositions. In our previous α U work in

Chapter 3, we tried to use the Nordheim's rule as an approximation to demonstrate that our model can be extended for metal alloys like U-Zr and U-Mo alloys. Although the extension results show quantitatively good agreement at low concentration for U-Zr and U-Mo, Nordheim's rule is highly approximated, which does not even work for many solid solution systems [112]. And Nordheim's rule is qualitatively incorrect for complex metal alloy systems containing multiple phases. As examples, the phase diagrams of U-Zr and U-Mo [113,114] are presented in **Figure 4.1**. For U-Zr system at 900°C, it has only one phase, (γ U, β Zr). However, for U-Zr system at 600°C, it has three single-phase regions, α (U), δ (U,Zr), and α (Zr), and two two-phase regions between them. Multiple phases also exist in U-Mo system, and is common for various metal alloy systems.



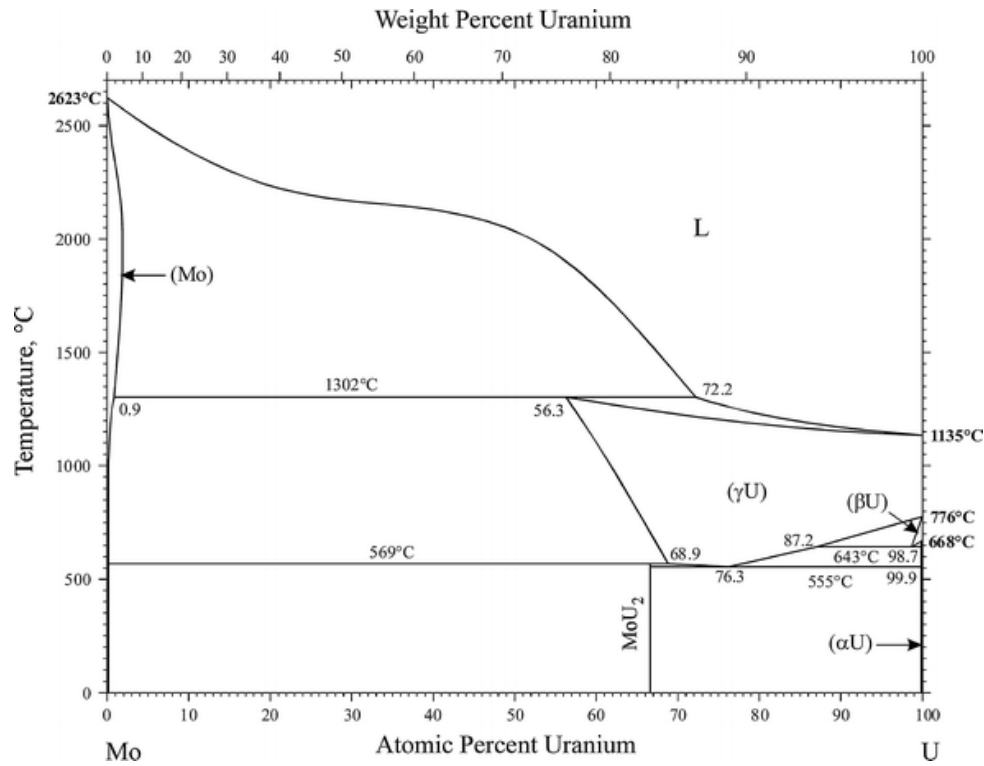


Figure 4.1. Phase diagrams of (a) U-Zr and (b) U-Mo [113,114].

Therefore, to model the thermal conductivity for metal alloys across wide ranges of compositions, a physics-based model is needed that can provide quantitative descriptions of thermal conductivity for anchor structures at specific compositions, solid solutions with varying compositions, and multi-phase mixtures, as mentioned in Section 2.6. Such a model of thermal conductivity may be developed via a three-stage approach as shown in the schematic diagram **Figure 4.2** (as same as **Figure 2.1**) and described with more details in the following:

- Stage 1: model for anchor structures with specific compositions. Stage 1 is to construct a physics-based model for single phase alloys at fixed compositions. By incorporating the various phonon and electron scattering mechanisms, this provides a foundation for extension in Stage 2 for solid solutions with varying composition. For this purpose, our physics-based approach [115] is used to model the thermal conductivity which incorporates

with different electron and phonon scattering processes. However, experimental data of electrical or thermal conductivity is needed to fit key scattering terms like electron-phonon scattering. This stage is available for the single phase alloys which have experimental data and are achievable in DFT calculations, which are called as “anchor structures” throughout this work. The approach will be presented in Section 2.1.

- Stage 2: model the solid solutions with varying compositions. For a solid solution phase, if it contains multiple anchor structures with different compositions, which are modeled by Stage 1, the solid solution can be modeled approximately by linear interpolation or extrapolation of these modeled anchor structures. For dilute alloying case, which usually does not fit the condition above, the thermal conductivity is modeled by reusing a lot of data from the anchor structure modeled by Stage 1 and adding new scattering terms due to the dilute alloying. The approach of Stage 2 will be presented in Section 2.2.
- Stage 3: model for multi-phase mixtures. Stage 3 is modeling the thermal conductivity in multi-phase regions by combining the thermal conductivity at phase boundaries (which may be either line compounds or solid solutions) through an appropriate averaging scheme. Several empirical formulae (i.e. the Series Model, the Parallel Model, and the Effective Medium Theory (EMT) [116]) have been established for different microstructures.

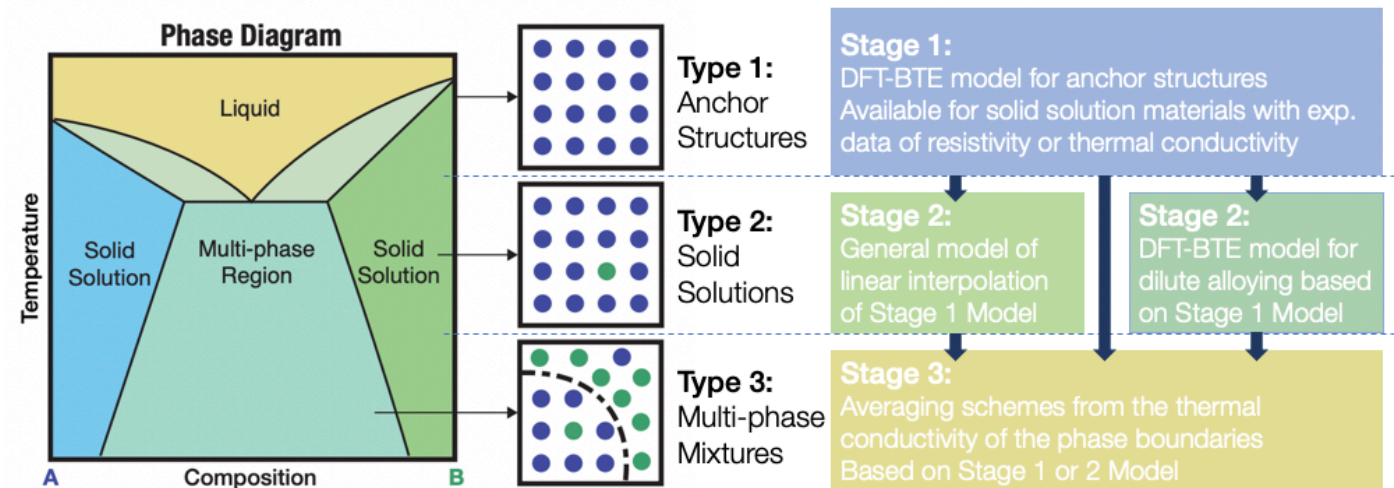


Figure 4.2. The schematic diagram of the three-stage modeling approach of thermal conductivity of metal alloys, and the three types of metal alloys this approach works for.

Although this approach is general, the specific systems for which we demonstrate this modeling approach are U-Zr and U-Mo alloys. Among metallic U alloys, U-Zr and U-Mo are of the most interest due to their technological relevance and have the most abundant experimental data on thermal conductivity. For U-Zr, the experimental data available before 1970 has been summarized by Touloukian et al. [17] and Madelung et al. [18], and after 1970, reported by Takahashi et al. [19] (which we find a mistake in Takahashi et al.'s data and correct it in Appendix I), Kaity et al. [20], and Cheon et al. [21]. For U-Mo, the experimental data available before 2006 has been summarized by Rest et al. [23], as well as in our pervious paper [115]. However, the experimental thermal conductivity data of U alloys are still limited in terms of both sufficiency and accuracy due to the difficulties and high cost of measurements. E.g., U-Mo data only exist for which the Mo at% is $< 30\%$, and the experimental thermal conductivity data for U-21.6at%Mo have $\sim 50\%$ difference between different measurements.

The current model for U alloys are either purely fitting model like Kim et al.'s model for U-Zr [25] and for U-Mo [26], or having some physical terms but ignoring some major physical

processes like Chen et al.'s model for U-Zr [27] which does not have phase separation. Like the traditional methods we mentioned above, these models highly rely on the experimental data, and do not provide the mechanistic understanding of scattering processes and phase mixture physics. Therefore, in this work, we develop a physics-based computational model of thermal conductivity in metal alloys, which incorporates physics rules of scattering processes and phase mixtures, DFT calculations, and empirical fitting, where DFT calculations are used to provide input information and decrease the number of fitting parameters, and the physics rules ensure our model have a reasonable physics basic. The demonstration of this model on U-Zr and U-Mo alloys can serve as both a foundation for understanding the more complex thermal conductivity of realistic U alloy fuels and a useful tool to guide further modeling of thermal conductivity to aid materials and device design.

4.3 Modeling Methods

In metal alloys, the thermal conductivity κ is the sum of electron thermal conductivity κ_e and phonon thermal conductivity κ_{ph} [29]:

$$\kappa = \kappa_e + \kappa_{ph}, \quad (4.1)$$

The electronic thermal conductivity κ_e is related to the electrical resistivity by the Wiedemann-Franz law [29]:

$$\kappa_e = \frac{LT}{\rho}. \quad (4.2)$$

where L is the Lorenz number. In the following sections 4.3.1, 4.3.2 and 4.3.3, we will present how we model the phonon thermal conductivity κ_{ph} and the resistivity ρ (thus κ_e) in Stage 1, 2,

and 3, respectively. The total thermal conductivity is given by summing κ_{ph} and k_e using Eqs. (4.1)-(4.2).

4.3.1 Stage 1: model for anchor structures with fixed compositions

The model for anchor structures with fixed compositions basically follows the DFT-BTE approach in our previous model [115], which was demonstrated using αU , with some improvements. This approach is available for the single-phase alloys, which have experimental electrical or thermal conductivity data and their structures are available to be used in DFT calculations (so called anchor structures). In the DFT-BTE approach, DFT calculations are used to calculate the structural, electronic, and vibrational properties of materials, and BTE calculations are used to calculate transport properties like electronic and thermal conductivity from the DFT calculations. The only missing term in this process is the relaxation time, which is separated into the relaxation times of different electron and phonon scattering processes; these relaxation times are modeled by either semi-classical physics formulae or empirical fitting. The separation of the relaxation times also separates the contributions of different scattering processes in thermal conductivity, which will be presented as below. For ordered compounds like elemental metals or line compounds, their crystal structures can be directly used in DFT calculations. As for disordered compounds in solid solution phase, the special quasicrystal structure (SQS) [117] can be used in DFT calculations as an approximation for their crystal structures in the phonon and electron band calculations.

The phonon thermal conductivity κ_{ph} can be calculated using the phonon Boltzmann transport equation (BTE) given by [6]:

$$\kappa_{ph} = \frac{1}{3\Omega N_k} \sum_{k\lambda} c_{k\lambda} \mathbf{v}_{k\lambda} \otimes \mathbf{v}_{k\lambda} \tau_{k\lambda}^{ph}, \quad (4.3)$$

which is already introduced in Section 2.5.1. Considering different phonon scattering contributions, the phonon relaxation time $\tau_{k\lambda}^{ph}$ for each wavevector k and phonon branch λ can be divided into four contributions, one each for phonon-phonon, phonon-electron, phonon-(grain boundary) and phonon-(point defect) scattering, using Matthiessen's rule [56]:

$$\frac{1}{\tau_{k\lambda}^{ph}} = \frac{1}{\tau_{k\lambda}^{ph-ph}} + \frac{1}{\tau_{k\lambda}^{ph-e}} + \frac{1}{\tau_{k\lambda}^{ph-gb}} + \frac{1}{\tau_{k\lambda}^{ph-pd}}, \quad (4.4)$$

where $\tau_{k\lambda}^{ph-ph}$, $\tau_{k\lambda}^{ph-e}$, $\tau_{k\lambda}^{ph-gb}$ and $\tau_{k\lambda}^{ph-pd}$ are the relaxation time of phonon-phonon, phonon-electron, phonon-(grain boundary) and phonon-(point defect) scattering contribution, respectively. There are other phonon scattering processes that are neglected in our model, for instance, phonon-dislocation scattering.

The phonon relaxation time for phonon-phonon scattering τ_{ph-ph} is calculated from Fermi's Golden rule using the harmonic and third-order anharmonic force constants from DFT calculations [55]:

$$\tau_{\lambda}^{ph-ph} = \frac{1}{2\Gamma_{\lambda}(\omega_{\lambda})}, \quad (4.5)$$

where the $\Gamma_{\lambda}(\omega)$ is the imaginary part of the phonon self-energy calculated by many-body perturbation theory [55]. The phonon relaxation time for phonon-electron scattering τ_{ph-e} can be approximated by the semi-classical formula [118]:

$$\tau_{k\lambda}^{ph-e-1} = \frac{A}{2\pi} \omega_{k\lambda}, \quad (4.6)$$

where ω is the phonon frequency (angular frequency) and A is a constant. In our model A is assumed to be a fitting parameter obtained by fitting to thermal conductivity data at different temperatures. The phonon relaxation time for phonon-(grain boundary) scattering τ_{ph-gb} can be estimated by the semi-classical formula [56,71]:

$$\tau_{k\lambda}^{ph-gb} = \frac{D}{v_{k\lambda}}, \quad (4.7)$$

where D is the grain size and $v_{k\lambda}$ is the phonon group velocity. The phonon relaxation time for phonon-(point defect) scattering can be approximated by [6,71,118]:

$$\tau_{k\lambda}^{ph-def}^{-1} = \frac{V}{4\pi v_{k\lambda}^3} \omega_{k\lambda}^4 \sum_i c_i \left(1 - \frac{m_i}{\bar{m}}\right)^2 = \frac{V}{4\pi v_{k\lambda}^3} \omega_{k\lambda}^4 g, \quad (4.8)$$

where V is the volume per atom, $g \equiv \sum_i c_i \left(1 - \frac{m_i}{\bar{m}}\right)^2$ is the mass variance parameter, where m_i is the mass of an atom, c_i is the mole fraction of atoms with mass m_i (if the atom i is one type of point defects, c_i is equal to the atomic concentration of this point defect), and $\bar{m}$ is the average mass of all atoms given by $\bar{m} = \sum_i c_i m_i$. For an ordered stoichiometric compound, the mass variance parameter is given by the isotopes of the elements and the impurities in the sample.

To summarize, calculating κ_{ph} requires calculations of the force constants and the associated phonon dispersion relations, which are obtained from DFT calculations, as inputs of Eq.(4.3). The other input needed in Eq.(4.3) is the phonon relaxation time, Eq.(4.4), which combines the contributions of different phonon scatterings, Eq. (4.5)-(4.8). There is only one fitting parameter, A for phonon-electron scattering, that is obtained by fitting κ_{ph} to experimental data.

The resistivity ρ consists of three components, the intrinsic resistivity ρ_{int} (which is the sum of the electron-phonon contribution ρ_{e-ph} and the electron-electron contribution ρ_{e-e}), the residual resistivity ρ_{res} due to point defects, and the saturation resistivity ρ_{sat} due to the saturation effect in metals [119], using Cote et al.'s formula [120]:

$$\rho = \left(1 - \frac{\rho}{\rho_{sat}}\right) \rho_{int} + \rho_{res} e^{-2W(T)}, \quad (4.9)$$

where the $e^{-2W(T)}$ term is the Debye-Waller factor, which is generally close to 1 [121–123]. For example, it was previously verified by Gomi et al. [121] using a Debye model that for Fe, $1 >$

$e^{-2W(T)} > 0.99$ below 1000K, and $1 > e^{-2W(T)} > 0.95$ below 5000K. Rearranging Eq. (9) and assuming $e^{-2W(T)} = 1$, the total resistivity ρ can be given by the equation:

$$\rho = \frac{\rho_{int} + \rho_{res}}{1 + \rho_{int}/\rho_{sat}} = \frac{\rho_{e-ph} + \rho_{e-e} + \rho_{res}}{1 + (\rho_{e-ph} + \rho_{e-e})/\rho_{sat}}. \quad (4.10)$$

Note that in pure elemental metals for which $\rho_{res} \approx 0$, this equation reduces to $\rho^{-1} = \rho_{int}^{-1} + \rho_{sat}^{-1}$, which is Wiesmann *et al.*'s parallel resistor formula [119,124]. The saturation resistivity ρ_{sat} is a constant at a given composition. The residual resistivity ρ_{res} is also approximately temperature-independent [29]. In this approach, ρ_{sat} and ρ_{res} are treated as two constants obtained by fitting to experimental resistivity data.

For these resistivity contributions ρ_{e-ph} and ρ_{e-e} , the DFT-BTE approach is applied, which is already introduced in Section 2.5.2. The resistivity can be readily calculated using the BTE method with the relaxation time approximation (RTA) approach with DFT-calculated electronic band structures [125]:

$$\rho_{e-ph,e-e} = \frac{1}{\sigma_{e-ph,e-e}} = \frac{1}{\left(\frac{\sigma}{s}\right)\tau_{e-ph,e-e}} = \frac{1}{s\tau_{e-ph,e-e}}, \quad (4.11)$$

where σ is the electrical conductivity and τ is the electronic relaxation time. ρ_{e-ph} and ρ_{e-e} can be calculated when τ take the values of the relaxation times of electron-phonon scattering τ_{e-ph} and electron-electron scattering τ_{e-e} , respectively. $s \equiv \frac{\sigma}{\tau}$ is calculated using the BTE-RTA and the rigid band approximation following the work of Madsen and Singh [125]. $\sigma(T)$ is calculated as the trace of the full electronic conductivity tensor, which can be calculated from the conductivity distributions:

$$\sigma_{\alpha\beta}(T) = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\varepsilon) \left[-\frac{\partial f_{\mu}(T, \varepsilon)}{\partial \varepsilon} \right] d\varepsilon, \quad (4.12)$$

where $f_\mu(T, \varepsilon)$ is the Fermi-Dirac distribution function, $\frac{\partial f_\mu(T, \varepsilon)}{\partial \varepsilon}$ is the temperature smearing, which is determined using the electronic density of states and the Fermi-Dirac distribution evaluated at the appropriate temperature, Ω is the system volume (taken as the DFT-calculated unit cell volume), T is the temperature, ε is the band energy, μ is the Fermi level, and $\sigma_{\alpha\beta}(\varepsilon)$ is the transport distribution given by:

$$\sigma_{\alpha\beta}(\varepsilon) = \frac{e^2}{N} \sum_{i,k} \tau_{i,k} v_\alpha(i, k) v_\beta(i, k) \frac{\delta(\varepsilon - \varepsilon_{i,k})}{d\varepsilon}, \quad (4.13)$$

where k represents elements of a set of k -points spanning reciprocal space in the Brillouin zone, N is the number of k -points sampled, i is the band index, v_α is the electron group velocity, e is the elementary charge, and $\tau_{i,k}$ are the relaxation times for each electron band i and k -point.

The input parameters for calculating the electrical conductivity tensor $\sigma_{\alpha\beta}(T)$ are the relaxation times $\tau_{i,k}$ and the electronic band structure information calculated from DFT. Here, we simplify the input of $\tau_{i,k}$ by assuming it is a constant which neither depends on band index i nor direction k , which has been shown to be a satisfactory assumption for many metals [126,127]. With this approximation, $s = \frac{\sigma}{\tau}$ depends on only the electronic band structure through Eqs. (4.12)-(4.13), whose values can be obtained from DFT-BTE calculations. This approach of assuming a constant, single τ value to obtain $\rho(T)$ from DFT-BTE calculated $s(T)$ has been successfully applied to Ag-Cu alloys [128] and W with vacancies [129].

The relaxation times of electron-phonon scattering τ_{e-ph} and electron-electron scattering τ_{e-e} can be approximated by the semi-classical formula:

$$\tau_{e-ph}^{-1} = BT, \quad (4.14)$$

$$\tau_{e-e}^{-1} = CT^2, \quad (4.15)$$

where B and C are typically assumed to be constants [63–65,130] and obtained from fitting to experimental resistivity data. Note Eqs. (4.14) works only for $T > \sim \theta_D$, where θ_D is the Debye temperature which is about 150K for metals.

To summarize, calculating ρ requires calculation of $s = \frac{\sigma}{\tau}$, which are calculated by the DFT-BTE approach, Eqs. (4.12)-(4.13), and is given by combining Eqs. (4.10)-(4.11) and Eqs. (4.14)-(4.15):

$$\rho = \frac{(BT+CT^2)/s+\rho_{res}}{1+(BT+CT^2)/(s\rho_{sat})}, \quad (4.16)$$

where it has four fitting parameters in total, B in electron-phonon scattering time, C in electron-electron scattering time, ρ_{res} as the residual resistivity, and ρ_{sat} as the saturation resistivity. These four parameters are obtained from fitting ρ to experimental data. And the total thermal conductivity of one solid solution can be calculated by applying Eqs.(4.1)-(4.2) with calculated κ_{ph} and ρ .

4.3.2 Stage 2: model the solid solutions with varying compositions

As mentioned in Section 4.2, generally for solid solutions, the linear interpolation or extrapolation of two closest anchor structures modeled by the Stage 1 model, are used to model the thermal conductivity. This requires at least two anchor structures with different compositions in the solid solution region which have enough data to apply the Stage 1 model.

One case which cannot be solved by the interpolation or extrapolation method but is very common is the dilute alloying, where few atoms of an extra element are added into the anchor structures, e.g. the $\alpha(\text{U})$ and $\alpha(\text{Zr})$ regions in **Figure 4.1(a)** where the solubilities of Zr in $\alpha(\text{U})$ and of U in $\alpha(\text{Zr})$ are both $<1\text{at}\%$. Because the alloying is dilute, it is difficult to apply our Stage 1 approach on two compositions with accurate data. However, the dilute alloying can be viewed

as point defects. This approach, which reuses the data of different scattering contributions from our Stage 1 model and extends it to dilute alloying, will be presented as below.

For phonon thermal conductivity, the dilute alloying decreases the phonon thermal conductivity by decreasing the phonon relaxation time of phonon-(point defect) scattering:

$$\tau_{k\lambda}^{ph-def}(c)^{-1} = \frac{V}{4\pi v_{k\lambda}^3} \omega_{k\lambda}^4 g(c) \quad (4.17)$$

where c is the dilute alloying concentration and $g(c)$ is the mass variance parameter which contains the alloying and is obtained from its definition $g = \sum_i c_i \left(1 - \frac{m_i}{\bar{m}}\right)^2$. $g(c)$ has simpler math expression for elemental metals: if the metal element has average atomic mass m_0 and mass variance parameter g_0 (due to isotopes of the element or impurities in the sample), and it is alloyed with another element which has atomic mass m_A and dilute concentration c , then $g(c) = g_0 + cg_A$, where $g_A \equiv \left(1 - \frac{m_A}{m_0}\right)^2$. Therefore, the mass variance parameter $g(c)$ has a linear relationship with dilute concentration c .

The phonon thermal conductivity of dilute alloying can still be obtained using phonon BTE (Eq.(4.3)- (4.8)). The only difference is the phonon relaxation time of phonon-(point defect) scattering, Eq. (4.8), needs to be replaced by Eq.(4.17) due to alloying. This change can be regarded as the mass variance parameter g increases due to the dilute alloying. The values of other phonon relaxation times, Eq.(4.5)-(4.7), remain unchanged from the unalloyed anchor structure.

For electrical resistivity, as the extra element are added into the anchor structure with dilute alloying concentration, the total resistivity increases by the increase of residual resistivity, derived from Eq.(4.16):

$$\rho(c) = \frac{\rho_{int} + \rho_{res}(c)}{1 + \rho_{int}/\rho_{sat}} = \frac{(BT + CT^2)/s(0) + \rho_{res}}{1 + (BT + CT^2)/(s(0)\rho_{sat})}, \quad (4.18)$$

where the residual resistivity $\rho_{res}(c)$ are dependent on the alloying element and its dilute alloying concentration c , while the values of intrinsic resistivity ρ_{int} , and saturation resistivity ρ_{sat} are unchanged because the alloying is dilute.

For $\rho_{res}(c)$, assuming the residual resistivity arising from the dilute alloying is independent with the residual resistivity existed in the original anchor structure [131], and the residual resistivity arising from the dilute alloying is given by the DFT-BTE approach:

$$\rho_{res}(c) = \rho_{res}(0) + \frac{1}{s(c)\tau_{alloying}(c)}, \quad (4.19)$$

where $\rho_{res}(0)$ is the residual resistivity existed in the original anchor structure which takes the same value of ρ_{res} in Eq.(4.16), $s(c)$ is $\frac{\sigma}{\tau}$ values dependent on alloying concentration c , and $\tau_{alloying}(c)$ is the electronic relaxation time considering the electrons scattering with alloying atoms, which is calculated using the semi-classical formula [29]:

$$\tau_{alloying}(c) = \frac{V_{atom}}{cA_{cs}v_F} = \frac{V_{atom}}{cA_{cs}} \sqrt{\frac{m_e}{2E_F}}, \quad (4.20)$$

where V_{atom} is the volume per atom, A_{cs} is the electron scattering cross section, m_e is the electron mass, and E_F and v_F are the Fermi energy and Fermi velocity, respectively. V_{atom} , v_F and E_F can be calculated by DFT.

s (or $\frac{\sigma}{\tau}$) is calculated by the DFT-BTE approach by Eqs. (4.12)-(4.13). However, as the alloying concentration is dilute, at the dilute limit $c \ll 1$, $s(c)$ is approximately equal to $s(0)$ for the original anchor structure, which means the perturbation of electron band structure due to dilute alloying can be neglected in this work:

$$s(c, T) \approx s_0(T), \text{ for } c \ll 1. \quad (4.21)$$

To summarize, the resistivity with dilute alloying can be calculated by Eqs. (4.18)-(4.21), and the total thermal conductivity can be calculated by applying Eqs. (4.1)-(4.2) with calculated κ_{ph} and ρ .

4.3.3 Stage 3: model the multi-phase mixtures

After obtaining the thermal conductivity on phase boundaries by our Stage 1 and Stage 2 model, the thermal conductivity in multi-phase regions can be modeled by interpolating the thermal conductivities on phase boundaries using an appropriate averaging scheme. If the multi-phase mixture is mixed by phase 1, 2, ..., n, with volume fraction $v_1, v_2, \dots, v_n$, and thermal conductivity $\kappa_1, \kappa_2, \dots, \kappa_n$, respectively, the total thermal conductivity of the multi-phase mixtures can be given as a function of v s and κ s, $\kappa^{total} = f(v_1, v_2, \dots, v_n, \kappa_1, \kappa_2, \dots, \kappa_n)$. Different function forms for f have been proposed in the literature dependent on the microstructure of the mixture [116,132,133]:

$$\text{Series Model: } f = (\sum_{i=1}^n v_i / \kappa_i)^{-1}, \quad (4.22)$$

$$\text{Parallel Model: } f = \sum_{i=1}^n v_i \kappa_i, \quad (4.23)$$

Effective Medium Theory (EMT): κ^{total} is the solution

$$\text{of the function } \sum_{i=1}^n v_i \frac{\kappa_i - \kappa^{total}}{\kappa_i + 2\kappa^{total}} = 0. \quad (4.24)$$

The Series and Parallel Models are for the microstructures which the interfaces among the multiple phases are all perpendicular and parallel to the heat flow direction, respectively, and serves as lower and upper bounds to the conductivity of mixtures [116]. And the EMT is for the microstructure which all components are distributed randomly, with neither phase being

necessarily continuous or dispersed [116]. Therefore, EMT can be used to estimate the total thermal conductivity of an evenly mixed system, or thermal equilibrium.

Eqs. (4.22)-(4.24) can be directly used to many multi-phase systems individually and get good estimations for thermal conductivity. However, for some metal alloys like U-Zr, the mixture kinetics is slow due to the low inter-diffusivity [134,135]. For these metal alloys in a multi-phase region, the alloys usually require long time to reach their thermal equilibrium. If the conductivity measurements are performed before the thermal equilibrium, the conductivities measured are dependent on the processes of phase separation. Therefore, if we want best fits to these experimental data, different mixture rules should be applied to different multi-phase regions, or even to the same multi-phase region with different compositions. This can be confirmed from our observation on U-Zr alloys. In the two-phase region $\alpha(\text{U})$ - $\delta(\text{U,Zr})$, when the fractions of the two phases are comparable, its thermal conductivity agrees well with EMT, which means the measured alloys are likely in thermal equilibrium; and when the composition is near the phase boundaries of $\alpha(\text{U})$ and $\delta(\text{U,Zr})$, its thermal conductivity is close to the lower bound of the Series model, which means the measured alloys are likely in the process to the thermal equilibrium; also there should be transition regions between the two regions which agree well with EMT and the Series Model respectively. We express this mixture rule mathematically by:

$$f = \begin{cases} f_{EMT}, & \text{if } 0 \leq |v_1 - v_2| \leq t_1 \\ f_{series}, & \text{if } t_2 \leq |v_1 - v_2| \leq 1 \\ f_{series} t \left(\frac{|v_1 - v_2| - x_{t1}}{x_{t2} - x_{t1}} \right) + f_{EMT} \left[1 - t \left(\frac{|v_1 - v_2| - x_{t1}}{x_{t2} - x_{t1}} \right) \right], & \text{if } t_1 < |v_1 - v_2| < t_2 \end{cases}, \quad (4.25)$$

where v_1 and v_2 are the volume fractions of the two components and $v_1 + v_2 = 1$, t_1 and t_2 are the lower and upper boundaries of the transition region, and $t(x)$ is a transition function which

equals to 0 and 1 when x equals to 0 and 1, respectively. In this work the transition function used are $t(x) = \frac{e^{-\frac{1}{x}}}{e^{-\frac{1}{x}} + e^{-\frac{1}{1-x}}}$, to make all derivatives continuous when $0 < x < 1$. t_1 and t_2 are dependent on specific components and are different for different alloys. Even for some multi-phase alloys like the $\delta(\text{U,Zr})$ - $\alpha(\text{Zr})$ region of U-Zr alloy, the Series model always gives the best prediction for thermal conductivity, which is mathematically equivalent to the condition $t_1 = t_2 = 0$, and physically suggests that for the $\delta(\text{U,Zr})$ - $\alpha(\text{Zr})$ region, it's hard to reach their thermal equilibrium states. The reasons of why different mixture rules are needed for different compositions in U-Zr alloys will be discussed later in Section 4.4.1.3, as well as the parameters and averaging schemes we suggested for U-Zr alloys, based on experimental data of U-Zr alloys.

Note that, the averaging schemes of the Series Model, the Parallel Model, and EMT are still general to use, e.g. if one is only interested on the thermal conductivity of thermal equilibrium, EMT will serve as the best prediction. Our mixture rule, combining different average schemes to one multi-phase region, is trying to give the best prediction according to existed experiments. Although the sample preparation may vary, before some special techniques or processes are applied to help the sample reach its thermal equilibrium, our model serves as the best prediction of the experimental results. Also, this model is useful to check whether the sample is in thermal equilibrium.

4.3.4 Approximations in the approach and its demonstration on U-Zr and U-Mo

The general approach is presented in Section 4.3.1, 4.3.2, and 4.3.3, and will be demonstrated on U-Zr and U-Mo alloys in Section 4.4. Besides the approximations applied in the general approach, some further approximations are applied for U-Zr and/or U-Mo alloys. All these approximations are summarized in this section.

First, we list here the approximations applied in the general approach:

- Stage 1:
 - Crystal structures: the SQS structures are used for disordered alloys in DFT calculations.
 - Phonon calculations: the BTE method is used for phonon; the phonon relaxation times of phonon-electron, phonon- (grain boundary), and phonon- (point defect) scatterings are approximated by semi-classical formulae.
 - Electron calculations: The BTE method for electron with the relaxation time approximation (RTA) is used. The electron relaxation times of electron-phonon and electron-electron scattering are approximated by semi-classical formulae; the Cote et al.'s formula for the resistivity saturation effect; the residual resistivity and the saturation resistivity are approximated by constants.
- Stage 2:
 - General approach for Stage 2: solid solutions with varying compositions are approximated by linear interpolation or extrapolation of systems at fixed compositions calculated by the Stage 1 model.
 - Dilute alloying approach: The phonon band structure change and the phonon relaxation time changes of phonon-phonon, phonon-electron, and phonon-(grain boundary) due to the dilute alloying are negligible. The change of electron band structure, intrinsic resistivity, saturation resistivity and the electron relaxation time changes of electron-phonon, electron-electron scatterings due to the dilute alloying are negligible. The electron relaxation times of electron-(point defect) scattering are approximated by semi-classical formula.

- Stage 3: the averaging schemes are approximations which may not incorporate the actual microstructures in the alloy.

For U-Zr alloys, the Stage 1 approach will be applied to four anchor structures: αU , αZr , $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$, and $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$. Then the Stage 2 approach will be applied to three compositional regions: $\alpha(\text{U})$ from the Stage 1 results of αU using the dilute alloying approach, $\alpha(\text{Zr})$ from the Stage 1 results of αZr using the dilute alloying approach, and $\delta(\text{U,Zr})$ from the Stage 1 results of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ and $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ using the linear interpolation or extrapolation. Finally the Stage 3 approach will be applied to the two-phase regions $\alpha(\text{U})$ - $\delta(\text{U,Zr})$ and $\alpha(\text{Zr})$ - $\delta(\text{U,Zr})$ from the Stage 2 results of $\alpha(\text{U})$, $\alpha(\text{Zr})$, and $\delta(\text{U,Zr})$. These predicted thermal conductivity results will be compared to all available U-Zr experimental data. Some further approximations are applied in the approach demonstration on U-Zr alloys:

- Stage 1: the Lorenz numbers for αU and αZr are approximated by the theoretical Sommerfeld value $L_0 = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2$; the resistivity or thermal conductivity data which sample has a composition difference smaller than 3% of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ or $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ are used in fitting as an approximation for the data of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ or $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$; the resistivity contribution of electron-phonon scattering is neglected in $\delta(\text{U,Zr})$ (discussed in Section 4.4.1.1); the phonon thermal conductivities of $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ are approximated by the phonon thermal conductivity of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$, and the phonon-electron scattering contribution in phonon thermal conductivity of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ is neglected.

- Stage 2: the cross section A_{cs} of Zr in $\alpha(\text{U})$ is approximated by the A_{cs} of Mo in $\alpha(\text{U})$; the cross section A_{cs} of U in $\alpha(\text{Zr})$ is approximately calculated by the residual resistivities of other metal atoms in $\alpha(\text{Zr})$ (discussed in Section 4.3.2).

For U-Mo alloys, because experimental data only exists in $\alpha(\text{U})$ - U_2Mo region and no data is available in (Mo)- U_2Mo region, we only model the thermal conductivity in $\alpha(\text{U})$ - U_2Mo region (although our approach is general and can be applied to (Mo)- U_2Mo region). Therefore, the Stage 1 approach will be applied to two anchor structures: αU and U_2Mo , where αU results are as same as in our demonstration of U-Zr alloys. The Stage 2 approach will be applied to the solid solution $\alpha(\text{U})$ alloying with Mo from the Stage 1 results of αU using the dilute alloying approach. Finally the Stage 3 approach will be applied on the two-phase regions $\alpha(\text{U})$ - U_2Mo from the Stage 2 results of $\alpha(\text{U})$ and the Stage 1 results of U_2Mo . Note originally in our Stage 1 approach, the resistivity model of U_2Mo should be obtained by fitting with experimental resistivity data of U_2Mo . However, due to the lack of experimental resistivity data of U_2Mo , the resistivity of U_2Mo is calculated by a set of U-Mo alloy data using our Stage 3 approach (see in Section 4.3.1). Our predicted thermal conductivity results will also be compared to all available U-Mo experimental data as far as we know. Similar to the Stage 1 model for $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ and $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$, the electron-phonon scattering in resistivity and the phonon-electron scattering in phonon thermal conductivity are neglected in U_2Mo .

4.3.5 DFT details

And the DFT setups for electron and phonon calculations of Stages 1 models are presented below. All DFT calculations were performed with periodic boundary conditions with a plane-wave

basis set using VASP. Initial atomic coordinates for α U (orthorhombic structure, Space group: *Cmcm*, No. 63), δ (U,Zr) (hexagonal structure, Space group: *C6/mmm*, No. 191), α Zr (hexagonal close-packed structures, Space group: *P63/mmc*, No. 194), and U_2Mo (tetragonal structure, Space group: *I4/mmm*, No. 139) were obtained based on the work in Refs. [136–141]. The electron-ion interaction of U and Zr used the projector augmented wave (PAW) method [142] as implemented by Kresse and Joubert [82]. The valence electron configuration for the U, Zr, and Mo pseudopotential was $6s^2 6p^6 5f^3 6d^1 7s^2$, $4s^2 4p^6 4d^2 5s^2$, and $4s^2 4p^6 4d^5 5s^1$ respectively. The exchange correlation functional parameterized in the generalized gradient approximation (GGA) [83] by Perdew, Burke, and Ernzerhof (PBE) [84] was used. The plane wave cutoff energy was set to 450 eV, and the stopping criteria for self-consistent loops were 1 meV per cell for electronic and ionic relaxation. The Monkhorst-Pack [143] k -point grid was used in all DFT calculations.

Stage 1 includes the crystal relaxations, electron band calculations, and phonon (force constants) calculations for five anchor structures, α U, α Zr, $\delta(U_{0.33}Zr_{0.67})$, $\delta(U_{0.25}Zr_{0.75})$, and U_2Mo . The cell sizes and the k -point grids used in these calculations are listed in Table 1. Note the crystal structures for $\delta(U_{0.33}Zr_{0.67})$ and $\delta(U_{0.25}Zr_{0.75})$ were generated by SQS using Alloy Theoretic Automated Toolkit (ATAT) [144], the force constant calculations are performed following the small displacement method [145], and the electronic band calculations are performed by a selfconsistent calculation with a smaller k -points and a non-selfconsistent calculation with a larger k -points. With calculated electron and phonon bands, the electron and phonon BTE calculations are performed respectively with the BoltzTraP [125] and Phono3py [6] software with the RTA.

Table 4.1. The cell sizes (number of atoms per cell) and the k -point grids used in our DFT calculations.

Phase	Relaxation	Electron bands	Force constants
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	Cell size	k -point grid	Cell size	k -point grid (selfconsistent calculation)	k -point grid (non-selfconsistent calculation)	Cell size	k -point grid
α U	2	19×19×11	2	23×23×23	37×37×37	16	13×13×7
α Zr	2	17×17×11	2	23×23×23	37×37×37	16	11×11×7
$\delta(\text{U}_{0.33}\text{Zr}_{0.67})$	6	11×11×11	6	17×17×17	29×29×29	6	11×11×11
$\delta(\text{U}_{0.25}\text{Zr}_{0.75})$	12	7×7×7	12	13×13×13	21×21×21	-	
U_2Mo	3	19×19×13	3	23×23×23	37×37×37	12	11×11×7

4.4 Modeling Results and Discussions

4.4.1 U-Zr alloys

4.4.1.1 Stage 1: model at anchor structures (α U, α Zr, $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$, $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$)

As mentioned in Section 4.3.4, four compositions are modeled for U-Zr alloys as anchor structures: α U, α Zr, $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$, and $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$. The results for α U and α Zr will be presented first, followed by the results for $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ and $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$. For α U and α Zr, the setups of DFT calculations for electron bands are listed in **Table 4.1**, and $s(T)$ is calculated using Eqs.(4.12)-(4.13) from the electron bands. With calculated $s(T)$, our resistivity model of Eq. (4.16) is used to fit the experimental data and obtain the fitting parameters in resistivity, B , C , and ρ_{sat} , for α U and α Zr. For α U, the mean resistivity values from the resistivity experiments of Aaraj et al. [146,147], Eriksen et al. [148] and Bennett [149] for a given temperature grid from 43K to 850K are provided in our previous paper [115]. This mean resistivity data are used in the resistivity fitting for α U. For α Zr, the experimental resistivity data from Adenstedt, Potter, and White et al. are used in the resistivity fitting. These resistivity data of α Zr are all collected by Hellwege et al. [150]. The fitting results are tableted in Table 4.2(a). Note the residual resistivity (ρ_{res}) of α U and α Zr is approximately zero. As pointed out in our previous paper for α U [115], the residual resistivity of pure α U is <2% of total resistivity near 600K. The fitted resistivities of α U and α Zr

are shown in **Figure 4.3(a)**, compared with the experimental resistivity data used in the fitting. Note that we are not directly fit the experimental data using arbitrary models, instead we start with physical models and fit three parameters that have physical meanings.

There are three parameters that need to be determined for the phonon thermal conductivity: the grain size L , and the mass variance parameter g , and the constant A for phonon-electron scattering relaxation time. L for αU and αZr is estimated by the αU experimental value of $15\mu\text{m}$ [146]. g is dependent on the impurity compositions of the measurement samples. Arajs et al. [146] gave the impurity compositions of the three αU samples of resistivity measurement. Using the definition of the mass variance parameter with the given impurity compositions, the mass variance parameter $g = 0.6 \times 10^{-3}$, 5.0×10^{-3} , and 1.7×10^{-3} respectively for the three samples. The mean value of g for the three samples, $g = 2.5 \times 10^{-3}$, is used as an estimation for the g due to the impurities in the experimental samples for αU and αZr (represented as g_0 as below). This leaves A being the only parameter that needs to be fitted. For this purpose, we first obtain the *experimental* phonon thermal conductivity for αU and αZr , which is taken as the difference between the total experimental conductivity and the electronic conductivity, i.e., by Eqs. (4.1)-(4.2): $\kappa_{ph} = \kappa - \frac{LT}{\rho}$. In this equation, the experimentally measured thermal conductivity, which contains both phonon and electron contributions, is used for κ , and the resistivity ρ is calculated using our model Eq.(4.10). For αU , the mean values from the thermal conductivity experiments for a given temperature grid from 300K to 933K have also been summarized in our previous paper [115], and these data are used in the phonon thermal conductivity calculation. For αZr , Fink et al. [151] collected all available thermal conductivity measurement results before 1995 and gave their suggested values for αZr thermal conductivity, and their suggested values are used in the phonon thermal conductivity calculation. With DFT calculated phonon bands and force

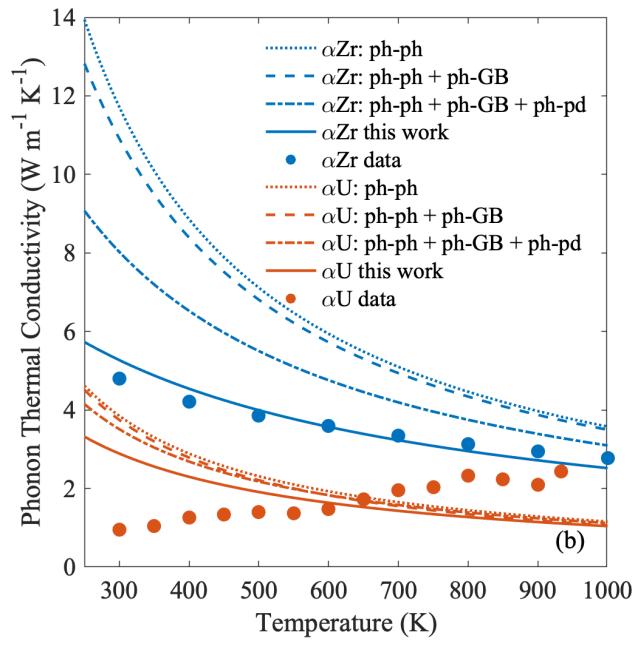
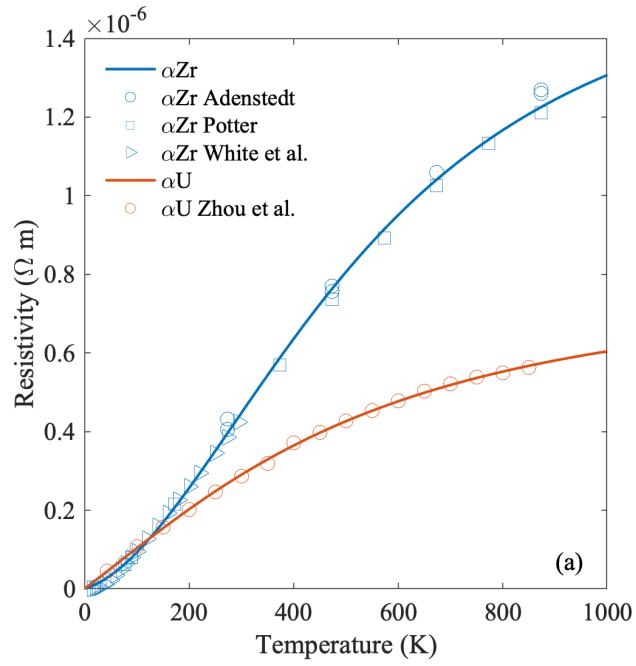
constants, the phonon thermal conductivity are calculated by Eqs.(4.3)-(4.8), where the only fitting parameter, A in Eq.(4.6), are obtained by fitting to the experimental phonon thermal conductivity data mentioned above. The fitted models of phonon thermal conductivity for αU and αZr are shown in **Figure 4.3(b)**, compared with the derived *experimental* phonon thermal conductivity data which are used in the fitting. The fitted values for the parameter A is listed in Table 4.2(a). The values of other two parameters in our phonon thermal conductivity model, grain size L in Eq.(4.7) and the mass variance parameter g in Eq.(4.8), are also given in Table 4.2(b). The fitted phonon thermal conductivity of αZr agree well with the *experimental* data. However, the derived *experimental* phonon thermal conductivity for αU increases with increasing temperature, while our modeled phonon thermal conductivity decreases with increasing temperature. Considering theoretically the phonon thermal conductivity should decrease with temperature [29], our derived *experimental* phonon thermal conductivity for αU has a wrong temperature dependence. This is likely due to the usage of a temperature independent Lorenz number, which may not be realistic for αU , in addition to possible errors in the experiments of resistivity and thermal conductivity measurements for αU . However, for αU , the root-mean-square error (RMSE) in the phonon thermal conductivity model is $0.96\text{W}/\text{mK}$, which is only $\sim 3\%$ of total thermal conductivity near 600K. Therefore, the approximation of constant Lorenz number is deemed as acceptable.

In addition to deriving the model for phonon thermal conductivity, the contribution of each individual scattering processes, namely phonon-phonon scattering, phonon-electron scattering, phonon-(grain boundary, GB) scattering, and phonon-(point defect, pd) scattering, can also be determined. This can be done by purposely excluding one or more scattering mechanisms in the model. Specifically, three case studies, 1) with only phonon-phonon scattering, 2) with phonon-phonon and phonon-GB scattering, and 3) with phonon-phonon, phonon-GB and phonon-pd

scattering, are performed. These results are shown in **Figure 4.3(b)** and compared with the results when all four phonon scattering mechanisms are considered. It can be found qualitatively each scattering decrease the thermal conductivity by different values. To quantitatively define the contribution of each scattering, the thermal resistivity W (the inverse of thermal conductivity) of each phonon scattering is calculated by only counting the phonon relaxation time of the given scattering in Eq. (4.4) (which means the other phonon scattering times are assumed to be infinite). The phonon thermal resistivities of different scattering processes are related with phonon total thermal resistivity by the Matthiessen approximation [29]: $W^{ph} = \frac{1}{\kappa_{ph}} \approx W^{ph-ph} + W^{ph-e} + W^{ph-GB} + W^{ph-pd}$. Therefore, the contribution of single phonon scattering process, phonon scattering with i , can be calculated by W^{ph-i}/W^{ph} . The values of the contributions at 600K are: for αZr , the phonon-phonon scattering contributes 60%, the phonon-electron scattering contributes 25%, the phonon-pd scattering contributes 13%, and the phonon-GB scattering contributes 2% of the total phonon thermal resistivity; for αU , they are 79%, 15%, 4%, and 2% in the same order, respectively. Therefore, the phonon-phonon scattering is the major contribution in the phonon thermal resistivity. Note here, this contribution value for phonon-pd scattering is based on the mass variance value $g = 2.5 \times 10^{-3}$, according to Araj et al.'s sample [146]. As examples, this g value can be produced by 0.28% C in αU , or 0.43% Fe in U. With increasing point defect concentration, the thermal resistivity produced by phonon-pd scattering increases.

With our modeled electronic and phonon thermal conductivity, the total thermal conductivity can be calculated with Eq.(4.1)-(4.2). The calculated total thermal conductivities are presented in **Figure 4.3(c)**, compared with our summarized mean values of the thermal conductivity experiments for αU [115], and Fink et al.'s summarized experimental values for αZr [151]. They also show good agreements. The Mean Error (ME) and RMSE are $0.02W/mK$

and $0.25W/mK$ respectively for αZr , and are $0.02W/mK$ and $0.96W/mK$ respectively for αU . The dashed curves in **Figure 4.3(c)** shows the electron contributions in total thermal conductivity, which contributes 81% and 95% of total thermal conductivity in αZr and αU respectively, and are the major contributions.



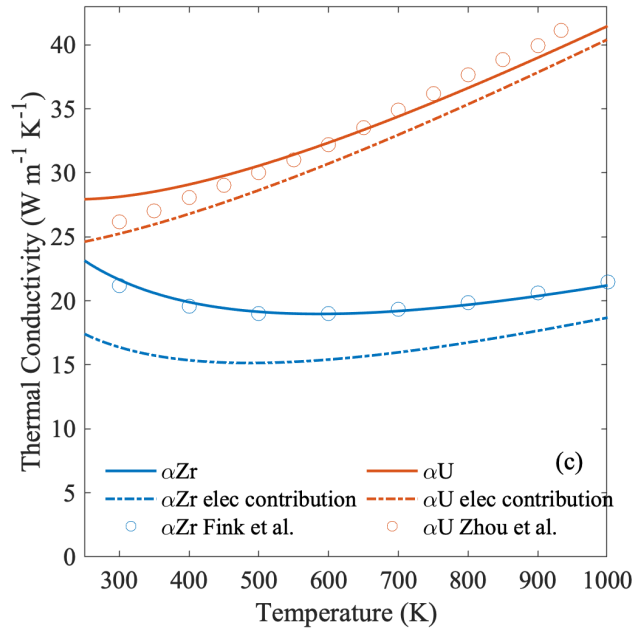


Figure 4.3. Plots of (a) resistivity over the temperature range of 0K to 1000K, (b) phonon thermal conductivity over the temperature range of 250K to 1000K, and (c) total thermal conductivity over the temperature range of 250K to 1000K for α U and α Zr. The curves with different styles indicate the different contributions. The symbols in plot (a) and (c) indicate the experimental resistivity from Refs. [115,150] and thermal conductivity data from Refs. [115,151], respectively, and the symbols in plot (b) indicate the calculated phonon thermal conductivity data from our modeled resistivity and experimental thermal conductivity data [115,151].

Table 4.2. The values of parameters used in this work.

(a) Fitting parameters

Parameters	α U	α Zr	$\delta(\text{U}_{0.33}\text{Zr}_{0.67})$	$\delta(\text{U}_{0.25}\text{Zr}_{0.75})$	U_2Mo	Note
A	4×10^{-2}	4×10^{-2}	-	-	-	The parameter in phonon-electron scattering in Eq.(4.1)
$B (s^{-1}K^{-1})$	6.46×10^{10}	2.28×10^{10}	-		-	The parameter in electron-phonon scattering in Eq.(4.1)
$C (s^{-1}K^{-2})$	4.61×10^7	3.33×10^8	1.36×10^6		2.32×10^9	The parameter in electron-electron scattering in Eq.(4.15)
$\rho_{sat} (\Omega m)$	9.03×10^{-7}	1.66×10^{-6}	6.19×10^{-7}	8.79×10^{-7}	8.12×10^{-7}	The saturation resistivity in Eq.(4.10)
$\rho_{res} (\Omega m)$	-	-	1.46×10^{-6}	1.72×10^{-6}	1.48×10^{-7}	The residual resistivity in Eq.(4.10)

(b) Other parameters

Parameters	Values (unit)	Note
D	15 (μm)	The average grain diameter in Eq. (4.7)
g_0	2.5×10^{-3}	The mass variance parameter in αU and αZr used in Eq. (4.8)
V_{atom}	20.06 ($\text{\AA}^3$) for αU 23.38 ($\text{\AA}^3$) for αZr	The cell volume, calculated by DFT, used in Eq. (4.20)
E_F	15.03 (eV) for αU 8.96 (eV) for αZr	The electron Fermi energy, calculated by DFT, used in Eq. (4.20)
A_{cs}	0.07 ($\text{\AA}^2$) for $\alpha(\text{U})$ 1.1 ($\text{\AA}^2$) for $\alpha(\text{Zr})$	The cross section of electron scattering with alloying atom, used in Eq. (4.20)
t_1	0.56	The parameter in the mixture rule Eq. (4.25)
t_2	0.72	The parameter in the mixture rule Eq. (4.25)

Before we present our modeled results for $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ and $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$, the reason why these two compositions are chosen among the δ phase, in which the at% of Zr varies from 64% to 78% (see in **Figure 4.1**), will be discussed. It has two reasons, from the point of view of calculations, and of experimental data. In DFT calculations, the composition of an alloy cannot be an arbitrary number due to the limited cell size. The Zr composition of 67% (actually 2/3) and 75% are chosen because they can be achieved in a $\delta(\text{U,Zr})$ cell with the smallest cell size of 12 atoms. The large cells, especially disordered cells, usually require significantly more time in phonon calculations. For the point of view of experimental data, the thermal conductivity data exist for $\delta(\text{U}_{0.36}\text{Zr}_{0.64})$ and $\delta(\text{U}_{0.28}\text{Zr}_{0.72})$ [17,19]. Although they are not exactly same with the compositions we used in the calculations, they are fairly close to the compositions we used. Therefore, these thermal conductivity data are used in the fitting progress to approximate the data of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ and $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$. Not only these thermal conductivity data, but also any resistivity or thermal conductivity data within a 3% difference range (e.g. for $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$, Zr at% varies from 72% to 78%) is used in fitting as an approximation for the data of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ or $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$, due to the rarity of both thermal conductivity and resistivity data in $\delta(\text{U,Zr})$ phase.

Although the data within a composition range are all used, some data needed in our approach is still lacking, i.e., no resistivity data near $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ above 500K. Therefore, some further approximations are made. The first approximation is the phonon-electron scattering in phonon thermal conductivity is neglected for $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ and $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$. If this approximation is applied on αU and αZr , the total thermal conductivity will be affected by 1% and 5%, respectively, which has already been discussed in this section above. Therefore, this approximation works for αU and αZr , and we assume it can also work for $\delta(\text{U,Zr})$, which will be justified in the next paragraph. The second approximation is the modeled phonon thermal conductivities of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ are used to approximate the phonon thermal conductivity of $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$. Theoretically they have same crystal structure with partially disordered sites, which should have similar phonon transport behaviors. And in practice the modeled phonon thermal conductivity of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ is close to both the derived *experimental* phonon thermal conductivity data of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ and $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ (see in the next paragraph). By applying this approximation, the *experimental* data we used for $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ are: thermal conductivity data of $\delta(\text{U}_{0.28}\text{Zr}_{0.72})$ from Takahashi et al. [19], resistivity data of $\delta(\text{U}_{0.26}\text{Zr}_{0.78})$ from Barnard [152] and Hellwege et al. [153] and of $\delta(\text{U}_{0.28}\text{Zr}_{0.72})$ from Rough [154], and phonon thermal conductivity data calculated by $\kappa_{ph} = \kappa - \frac{LT}{\rho}$, where κ uses linear interpolated Takahashi et al.'s data [19] and ρ uses linear interpolated Barnard's resistivity data [152] (these experimental data are linear interpolated to a temperature grid of 50K from 300K to 850K). The *experimental* data we used for $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ are: thermal conductivity data of $\delta(\text{U}_{0.36}\text{Zr}_{0.64})$ from Touloukian et al. [17], resistivity data of $\delta(\text{U}_{0.36}\text{Zr}_{0.64})$ from Rough [154] and from calculation via $\rho = \frac{LT}{\kappa - \kappa_{ph}}$, where κ uses Touloukian et al.'s data [17] and κ_{ph} uses our modeled phonon thermal conductivity of $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$, and phonon thermal

conductivity data calculated by $\kappa_{ph} = \kappa - \frac{LT}{\rho}$, where κ uses linear interpolated Touloukian et al.'s data [17] and ρ uses Rough's resistivity data [154] (these experimental data are linear interpolated to a temperature grid of two points, 295K and 373K, which are the temperature grids for Rough's data).

The phonon thermal conductivity of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ is calculated using the DFT-BTE approach (Eqs.(4.3)-(4.4)) with DFT calculated phonon bands and force constants with the setups given in **Table 4.1**, shown as dashed blue curve in **Figure 4.4(a)**. Note the disordered sites in $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ are occupied by 50% U and 50% Zr. Therefore, the mass variance parameter for these disordered sites is $g = 0.20$. As mentioned above, the calculated phonon thermal conductivity of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ are compared to the calculated phonon thermal conductivity data of both $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ and $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ from experiments. Our modeled phonon thermal conductivity of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ agree well with the derived *experimental* phonon thermal conductivity of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$, which the ME and RMSE are -0.45W/mK and 0.47W/mK respectively. This suggests our first approximation in the previous paragraph, the phonon-electron scattering in phonon thermal conductivity can be neglected, works for $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$. Furthermore, our modeled phonon thermal conductivity of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ has a good agreement with calculated phonon thermal conductivity data of $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$, for which the ME and RMSE are -0.34W/mK and 0.63W/mK respectively. This suggests our second approximation in the previous paragraph, the phonon thermal conductivities of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ and $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ are approximately identical, is also acceptable.

Then we move to the fitting of resistivity for $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ and $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$. As mentioned before, there is no resistivity data near $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ above 500K. The resistivity values calculated

by Eqs.(4.1)-(4.2) with our modeled phonon thermal conductivity of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ and Touloukian et al.'s thermal conductivity data of $\delta(\text{U}_{0.36}\text{Zr}_{0.64})$ [17] are used in the resistivity fitting of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$, shown as filled symbols in **Figure 4.4(b)**. Besides the calculated resistivity data, Rough's resistivity data of $\delta(\text{U}_{0.36}\text{Zr}_{0.64})$ [154] is also used in the resistivity fitting of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$, while Rough's resistivity data of $\delta(\text{U}_{0.28}\text{Zr}_{0.72})$ [154], Hellwege et al.'s data of $\delta(\text{U}_{0.26}\text{Zr}_{0.74})$ [153], and Barnard's data of $\delta(\text{U}_{0.26}\text{Zr}_{0.74})$ [152] are used in the resistivity fitting of $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$. These resistivity data show negative temperature dependence for both $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ and $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$. No resistivity saturations were observed in the high temperature data, resulting in significant uncertainty of ρ_{sat} while directly fitting with our model. With the observation that the resistivity difference between $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ and $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ is approximately constant over temperature, approximately $2.6 \times 10^{-7} \Omega m$, some further approximations are made. The parameters related to temperature dependence, B and C , are assumed to be the same for $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ and $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$. This assumption should be correct if the two compositions are close, which approximately work for $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ and $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$, considering the Zr at% has 8% difference. Then the resistivity difference is due to difference in ρ_{sat} and ρ_{res} . The ρ_{res} and ρ_{sat} , which respectively equals to the resistivity at 0K and at very high temperature (theoretically infinite temperature), should also have a difference of $2.6 \times 10^{-7} \Omega m$ between $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ and $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ if our observation holds at all temperatures. Therefore, the difference of ρ_{sat} between $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ and $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ is fixed to $2.6 \times 10^{-7} \Omega m$ in the fitting, as well as ρ_{res} . With these limitations we can fit our model to the resistivity data of $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ and $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$. Further in the fitting, the electron-phonon term is relatively negligible compared to electron-electron term, therefore, B is approximately zero, which we just fix it to zero as shown in **Table 4.2**. Again, these approximations in the resistivity are made due to the lacking in data, especially no data exhibits the resistivity saturation. This does

not mean our model is not general. If we don't apply these approximations, the direct fitting will still work and may still give good agreement with the limited data, however, the fitting parameters will have more significant uncertainty and may have unphysical values. These approximations are made based on the physical relationships in the data and are made to obtain the correct values of the fitting parameters in physical meanings as best as we can.

The fitting results are shown as the curves in **Figure 4.4(b)**, and the fitted parameters are tableted in **Table 4.2**. Our resistivity model has a good agreement with experimental data. With our modeled resistivity and phonon thermal conductivity for $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ and $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$, their total thermal conductivity can be calculated with Eq.(4.1)-(4.2), presented as solid curves in **Figure 4.4(a)** and compared with experimental data. The ME and RMSE are $-0.93W/mK$ and $1.22W/mK$ respectively for thermal conductivity of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$, and are $-0.77W/mK$ and $1.01W/mK$ respectively for $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$.

To summarize, we modeled the four anchor structures (αU , αZr , $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$, and $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$) following our approach in Section 4.3.1. These model separates thermal conductivity into different phonon and electron scattering contributions and shows good agreement to both resistivity and thermal conductivity data. The absolute values of ME and RMSE for these four anchor structures are all smaller than $1.3W/mK$. In next section we will extend these anchor structure models to model the solid solution regions.

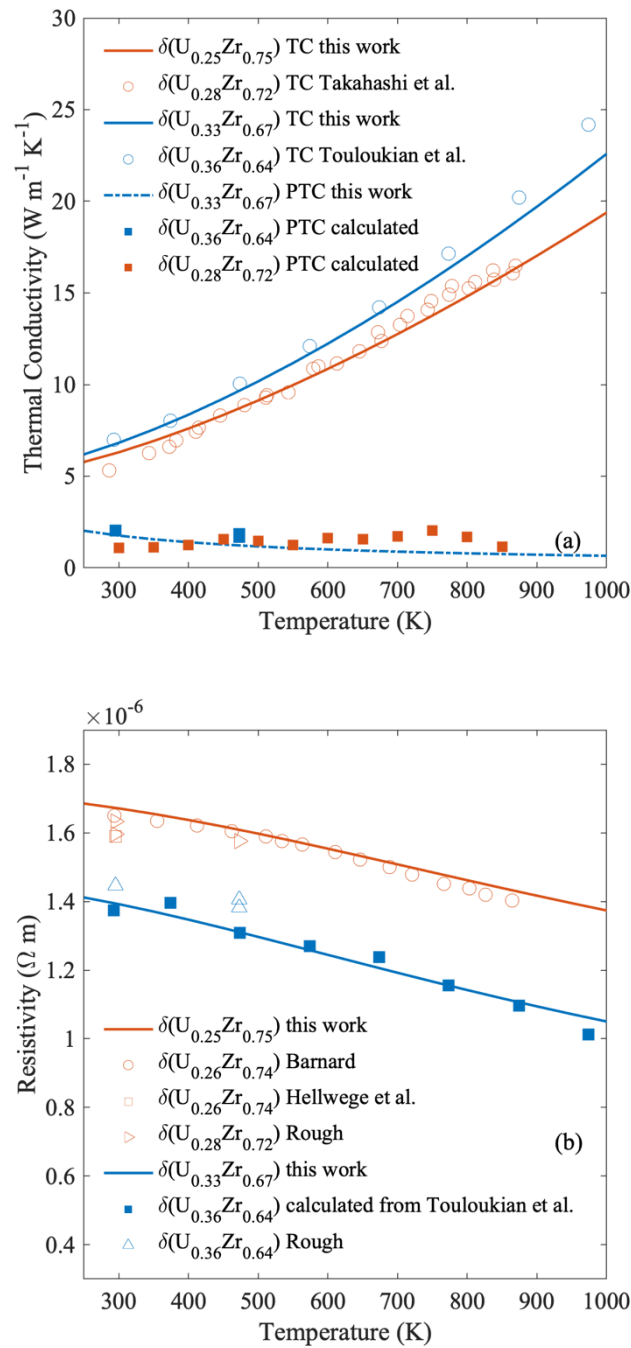


Figure 4.4. Plots of (a) thermal conductivity (TC) and phonon thermal conductivity (PTC), and (b) resistivity for $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ and $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ over the temperature range of 250K to 1000K, compared to experimental data. The curves with different colors indicate the different materials. The open symbols in (a) are experimental thermal conductivity data from Refs. [17,19], and the open symbols in (b) are experimental resistivity data from Refs. [152–154].

4.4.1.2 Stage 2: model the solid solutions with varying compositions ($\alpha(\text{U})$, $\alpha(\text{Zr})$, and $\delta(\text{U,Zr})$)

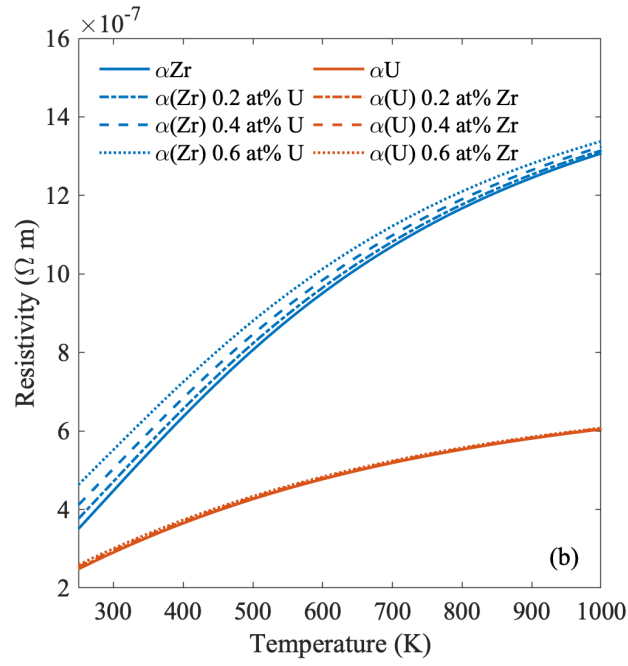
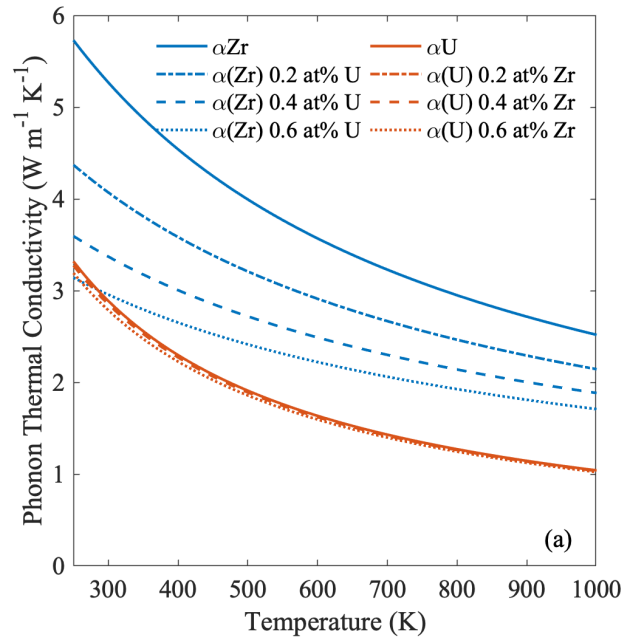
For $\delta(\text{U,Zr})$, two anchor structures, $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ and $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$, are modeled in Section 4.4.1.1. In our approach, the resistivity and phonon thermal conductivity of $\delta(\text{U,Zr})$ will be calculated by linear interpolation or extrapolation from our modeled resistivity and our modeled phonon thermal conductivity of $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$ and $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$, respectively, and the total thermal conductivity will be calculated by summing phonon and electron thermal conductivity (Eqs.(4.1)-(4.2)). We do not present this modeled thermal conductivity for $\delta(\text{U,Zr})$ individually by plots as no more thermal conductivity data exists for $\delta(\text{U,Zr})$ to compare, and these results will be presented in Section 4.4.1.2 and 4.4.1.3 together with the modeled two-phase thermal conductivities.

For $\alpha(\text{U})$ and $\alpha(\text{Zr})$, our approach for dilute alloying is presented in Section 4.3.2. For the phonon thermal conductivity, it can be obtained using phonon BTE (Eq.(4.3)-(4.8)), which the phonon relaxation time of scattering with point defects, Eq.(4.8), needs to be replaced by Eq.(4.17) due to the alloying. The alloying will increase the mass variance parameter and decrease the phonon thermal conductivity. E.g., if the $\alpha(\text{U})$ is alloying with 1 at% Zr atoms, the mass variance parameter due to the alloying is $g = 3.8 \times 10^{-3}$, and $g = 2.5 \times 10^{-2}$ if the $\alpha(\text{Zr})$ is alloying with 1 at% U atoms. Therefore, with $g_0 = 2.5 \times 10^{-3}$, the total mass variance parameter will increase to $g = 6.3 \times 10^{-3}$ for $\alpha(\text{U})$ with 1 at% Zr, and to $g = 2.7 \times 10^{-2}$ for $\alpha(\text{Zr})$ with 1 at% U. With the new total mass variance parameters, the phonon thermal conductivities for $\alpha(\text{U})$ alloying with Zr and $\alpha(\text{Zr})$ alloying with U, are calculated for alloying atomic concentration 0.2%, 0.4%, and 0.6%, shown in **Figure 4.5(a)**. Both for 0.5 at% alloying, the Zr in $\alpha(\text{U})$ only slightly decrease the phonon thermal conductivity ($\sim 3\%$ at 600K), while the U in $\alpha(\text{Zr})$ significantly decrease the phonon

thermal conductivity ($\sim 33\%$ at 600K). It has two reasons. First, with the same g value, the phonon- (point defect) scattering affects more in αZr than in αU . As the decrease of phonon thermal conductivity due to g_0 is calculated in Section 4.4.1.1, with the same value of g_0 , the phonon- (point defect) scattering affects 13% of phonon thermal conductivity in αZr , but only affect 4% in αU . The second reason is that for the same alloying concentration, U atoms in $\alpha(\text{Zr})$ lead to larger g values than Zr atoms in $\alpha(\text{U})$, which is about 6 times for 1 at% alloying as values given above, due to the mass difference of U and Zr atoms.

For resistivity change due to alloying, we need the scattering time to calculate the resistivity of dilute alloys using Eqs. (4.18)-(4.21). There are three parameters needed, V_{atom} , E_F , and A_{cs} , for the electron scattering time. The values of these parameters are listed in Table 4.2(b), in which the V_{atom} and E_F are calculated by DFT, and for A_{cs} , its value is calculated from experimental residual resistivity data per atomic percent impurity from Hellwege et al. [153]. For Zr in $\alpha(\text{U})$, there is no experimental data of its residual resistivity. However, the experimental data of Mo in $\alpha(\text{U})$ exists, so the A_{cs} for Mo in $\alpha(\text{U})$ can be calculated (see details in Section 4.4.2.2), and its value is used as an approximation for Zr in $\alpha(\text{U})$. For U in $\alpha(\text{Zr})$, the experimental data of residual resistivity doesn't exist, either. However, multiple metal atoms including Ag, Cd, and Gd, have the same values of residual resistivity per atomic present alloying for $\sim 2 \times 10^{-7} \Omega\text{m/at\%}$ [153]. This value is used as the best guess for U in $\alpha(\text{Zr})$. The calculated A_{cs} values are tableted in **Table 4.2(b)**. The modeled resistivity for alloying atomic concentration 0.2%, 0.4%, and 0.6% are shown in **Figure 4.5(b)**. For per 0.1 at% alloying at 600K, the Zr atoms in $\alpha(\text{U})$ increase $\sim 0.13\%$ resistivity, and the U atoms in $\alpha(\text{Zr})$ increase 0.67% resistivity. The modeled thermal conductivity, calculated by modeled resistivity and phonon thermal conductivity with Eqs.(4.1)-(4.2), are shown in **Figure 4.5(c)**. For 0.1 at% alloying at 600K, the Zr atoms in $\alpha(\text{U})$ decrease 0.12% thermal

conductivity, while the 0.1 at% U atoms in $\alpha(\text{Zr})$ decrease 2.5% thermal conductivity. Therefore, the effects of thermal conductivity decrease and resistivity increase due to Zr in $\alpha(\text{U})$ is negligible.



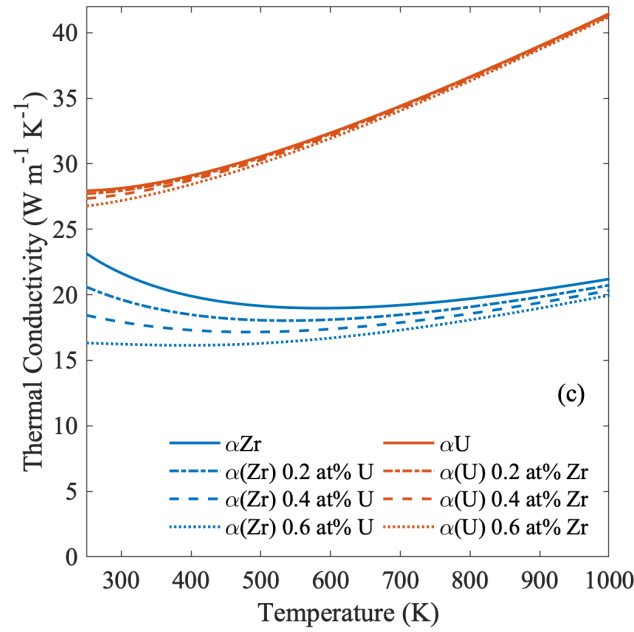


Figure 4.5. Plots of (a) phonon thermal conductivity, (b) resistivity, and (c) total thermal conductivity as functions of temperature from 250K to 1000K for $\alpha(U)$ and $\alpha(Zr)$. The curves with different styles indicate the different alloying concentration.

4.4.1.3 Stage 3: model the multi-phase mixtures ($\alpha(U)$ - $\delta(U,Zr)$ and $\alpha(Zr)$ - $\delta(U,Zr)$)

In Section 4.4.1.2, the resistivity and thermal conductivity of the three solid solution phases for U-Zr alloy are obtained. We can use our modeled thermal conductivity values at the phase boundary and our mixture rules Eq.(4.25) to model the thermal conductivity in the multi-phase regimes, $\alpha(U)$ - $\delta(U,Zr)$ and $\alpha(Zr)$ - $\delta(U,Zr)$. Two more things need to be clarified: the phase boundary of $\alpha(U)$, $\delta(U,Zr)$, and $\alpha(Zr)$, and the density of U-Zr alloy. According to the phase diagrams of U-Zr from Ref. [113,155]: the boundaries of $\delta(U,Zr)$ are Zr at% from 64% to 78% over the temperature range 300K to 900K; the solubility of Zr in $\alpha(U)$ increase approximately linearly with temperature, which has the minimum value of 0 at about 670K and the maximum value of 0.5 at% at about 900K; the solubility of U in $\alpha(Zr)$ increase approximately linearly with

temperature too, which has the minimum value of 0 at about 670K and the maximum value of 0.4 at% at about 900K. The density of U-Zr are given by Rough [154], which increase approximately linearly with Zr at%. The density values are used in our model to covert the mole fraction (or saying Zr at%) to volume fraction, to incorporate with Eqs.(4.25).

Using the Series Model (Eq.(4.22)) and EMT (Eq.(4.24)) with our modeled resistivity and thermal conductivity at phase boundaries, the resistivity and thermal conductivity in the two-phase regions, $\alpha(\text{U})-\delta(\text{U,Zr})$ and $\alpha(\text{Zr})-\delta(\text{U,Zr})$, can be calculated. The resistivity and thermal conductivity results at 295K are presented as the curves in **Figure 4.6(a)** and (b), respectively, compared with the experimental data as the symbols. Note the U-52at% Zr data from Takahashi et al. [19] shown in **Figure 4.6(b)** are our corrected data for U-52at% Zr (see details in **Figure 4.1**, as well as other data cited as “U-52at% Zr from Takahashi et al.” below). The thermal conductivity data at 295K shown as symbols in **Figure 4.6(b)** are the experimental data [17,19–21] linearly interpolated to 295K. The red curves in both **Figure 4.6(a)** and (b) are the results of EMT, while the yellow ones are for the Series Model. EMT gives higher conductivity and lower resistivity comparing to the Series Model. For $\alpha(\text{Zr})-\delta(\text{U,Zr})$ region, comparing experimental with EMT and the Series Model, the Series Model shows better agreements with both resistivity and thermal conductivity data; and for $\alpha(\text{U})-\delta(\text{U,Zr})$ region, EMT shows better agreements, which can be confirmed even by observation. This result shows that, for different multi-phase regions, the microstructure captured and measured by the experiments are different. If we assume that the sample preparation processes among these experiments for $\alpha(\text{Zr})-\delta(\text{U,Zr})$ and $\alpha(\text{U})-\delta(\text{U,Zr})$ are similar, then our results suggest that $\alpha(\text{Zr})-\delta(\text{U,Zr})$ needs longer time than $\alpha(\text{U})-\delta(\text{U,Zr})$ to finish the phase separation and reach the thermal equilibrium.

Then we consider whether these two two-phase regions need to combine multiple averaging schemes and use our mixture rule for a better thermal conductivity prediction. For $\alpha(\text{U})$ - $\delta(\text{U,Zr})$ region, the experimental data of resistivity from different sources distributed between the Series Model and EMT near 12 at% Zr and 52 at% Zr, while the experimental data of thermal conductivity from different sources also distributed between the Series Model and EMT near 12 at% Zr. This suggests that, the microstructures may differ among the different experimental samples near 12 at% Zr and 52 at% Zr, which leads to the different values of resistivity and thermal conductivity. Qualitatively, within the range 14 at% Zr to 50 at% Zr, the mixtures of the two phase are more close to thermal equilibrium, which the resistivity and thermal conductivity can be described by EMT; and within the range 0 at% Zr to 9 at% Zr and the range 55 at% Zr to 64 at% Zr, the mixtures of two phase are far from thermal equilibrium, leading their thermal conductivity and resistivity closed to the Series Model; And within the range 9 at% Zr to 14 at% Zr and the range 50 at% Zr to 55 at% Zr, the mixtures of two phase are likely in a transition process between the previous two states. This is equivalent to our mixture rule Eq.(4.25), with the parameter values $t_1 = 0.56$ and $t_2 = 0.72$, which are tableted in **Table 4.2(b)**. By applying Eq.(4.25) with these values t_1 and t_2 values for $\alpha(\text{U})$ - $\delta(\text{U,Zr})$ region, the results are shown as dashed blue curves in **Figure 4.6(a)** and (b). Quantitatively, the ME and RMSE of EMT are $0.86W/mK$ and $1.65W/mK$, respectively, comparing with the thermal conductivity data. And applying our mixture rule of Eq.(4.25) with the given parameters will decrease the ME and RMSE to $0.24W/mK$ and $1.10W/mK$, respectively. However for $\alpha(\text{Zr})$ - $\delta(\text{U,Zr})$ region, even near 50%-50% volume fraction point (equivalent to 89 at% Zr), which is the most possible point to reach an evenly distributed microstructure, the resistivity data of 91at% Zr from Hellwege et al. [153] and the thermal conductivity data of 91at% Zr from Takahashi et al. [19] have better agreements with

the Series Model. This means, comparing to EMT, the Series Model is always the best model at any Zr at% in $\alpha(\text{Zr})\text{-}\delta(\text{U,Zr})$ region. This is equivalent to the condition $t_1 = t_2 = 0$ in our mixture rule of Eq.(4.25).

Experimentally, these observations are supported by the slow transformation kinetics and low inter-diffusivity of U-Zr alloy system [134]. The experiments from Basak [135] shown that, for U-16 at% Zr and U-58 at% Zr samples, the cooling times affect the two-phase structures: the longer cooling time leads to more evenly distributed two-phase structures. Again, our results serve as the best prediction of the experimental results with similar sample preparation process. This suggests, when one takes the similar sample preparation process as previous experiments, whether the sample is in thermal equilibrium is depends on the composition of the sample. E.g. U-Zr alloys with Zr at% within 14% to 50% is easiest to reach thermal equilibrium. And our model has the ability to predict the thermal conductivity of thermal equilibrium at any composition in the multi-phase regions by applying EMT, e.g. the red curves in **Figure 4.6(a)** and (b) for the resistivity and thermal conductivity, respectively, for U-Zr.

One more thing we need to consider is what microstructure makes the conductivity following the Series Model. The Series Models are for the microstructures which the interfaces among the multiple phases are all perpendicular to the heat flow direction, and this means, each heat flow has to go through both high conductivity and low conductivity phases. Considering an early stage phase separation system, when one phase starts to grow as the interfaces between the another phase, the heat flow also has to go through both phases as the bulk and interface, respectively. This microstructure may cause the conductivity following the Series Model. Some other processes may also cause the thermal conductivity of an alloy lower than its equilibrium, including the decomposition of the high temperature phase is not fully complete, or the two mixture

phases are in oversaturated states rather than the states on the phase boundaries. These possible reasons can all lead to lower thermal conductivity (one example for oversaturated U-99at% Zr), and further research to distinguish and model the different effects needs comprehensive understanding of the phase compositions and microstructures of the samples used in conductivity measurements. However, at the current stage, this information is still lacking. E.g. the two major resources of U-Zr thermal conductivity data is Touloukian et al.'s and Takahashi et al.'s work. Touloukian et al.'s paper provided no such information. And in Takahashi et al.'s paper, only information provided is that no gamma phase U-Zr existed in the samples, and no information about whether the phases are oversaturated and what microstructure the sample is in is provided. We hope future experiments can verify the conductivity change in the process of phase separation, which is related to the alloy composition as our results shown.

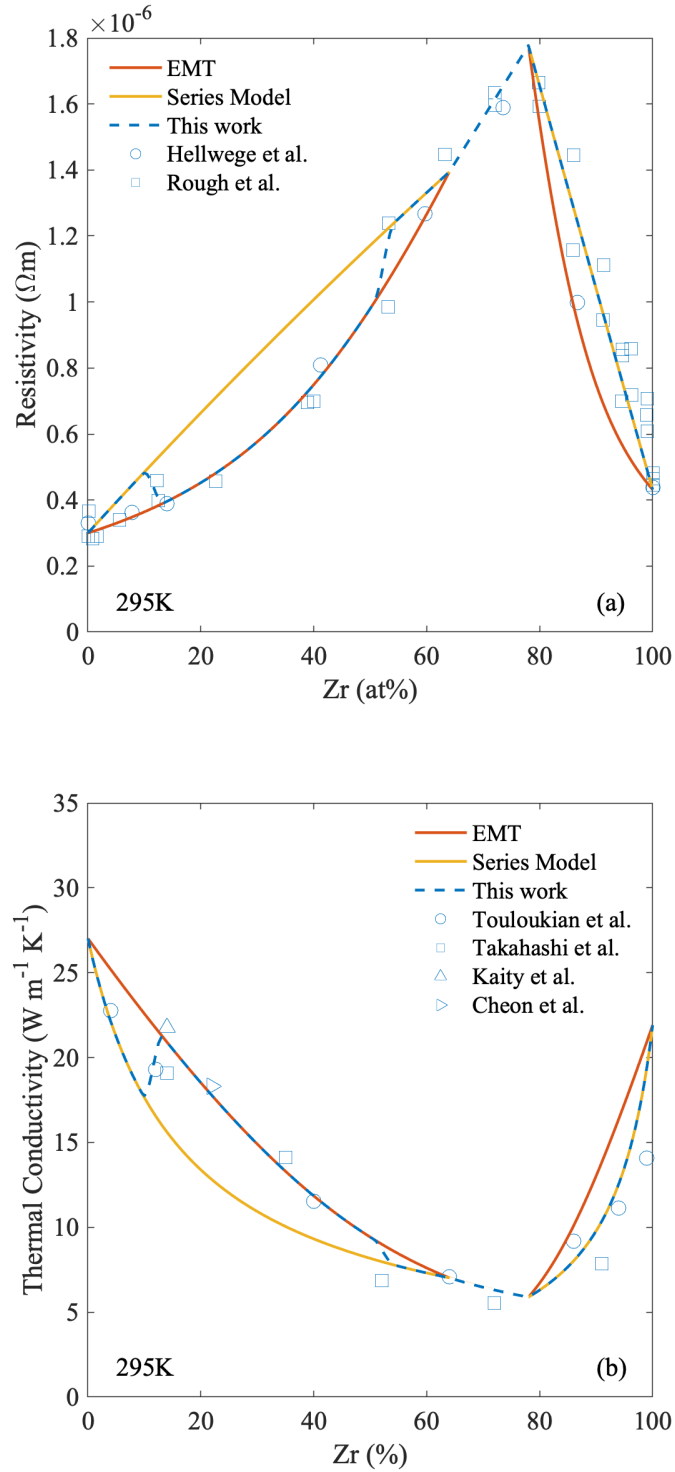
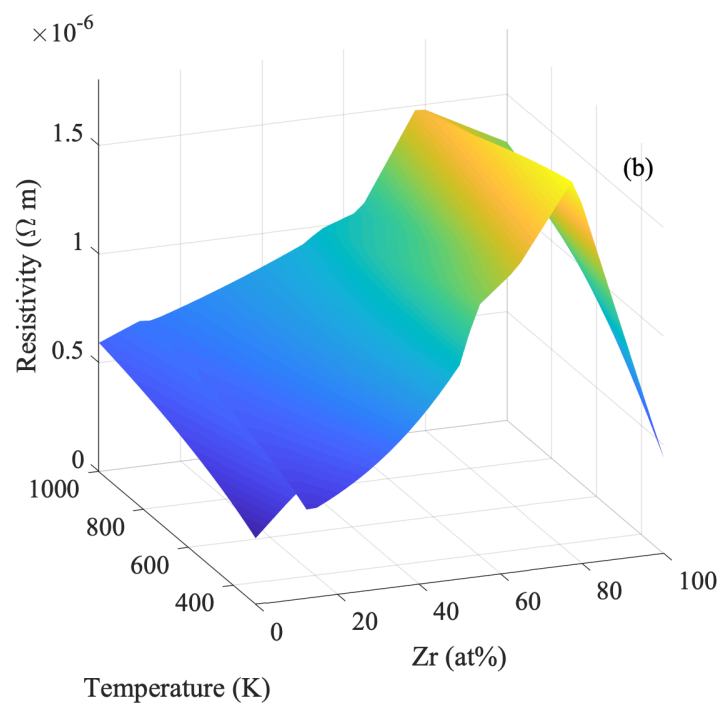
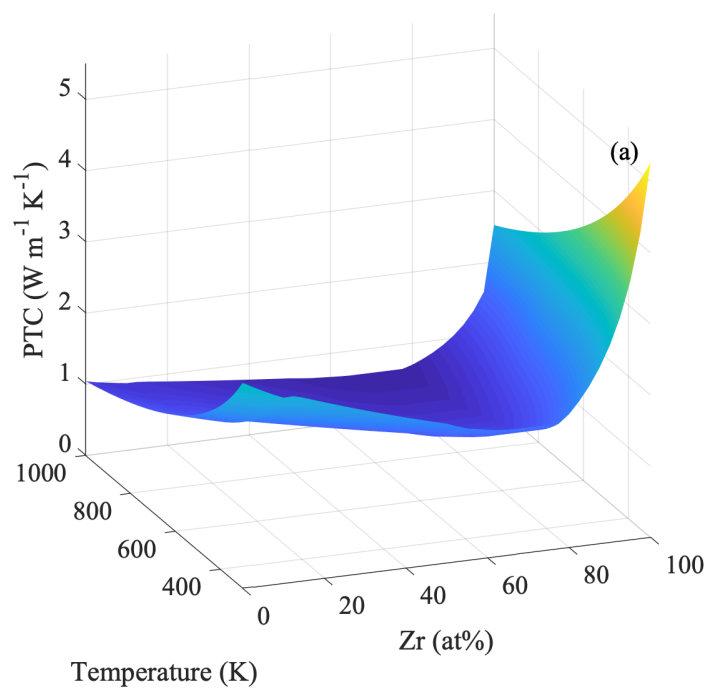


Figure 4.6. Plots of (a) resistivity and (b) thermal conductivity calculated from different averaging schemes for U-Zr alloy at 295K, compared with experimental data. The curves with different styles indicate the different averaging schemes. The symbols are (a) resistivity data from Ref. [153,154] and (b) linear interpolated thermal conductivity data of experiments from Ref. [17,19–21].

4.4.1.4 Results and error analyze for U-Zr alloy

Our Stage 1 model is applied to model four compositions of U-Zr alloy system. Based on the Stage 1 model, our Stage 2 model is applied to model the three solid solution regions of U-Zr. And based on the Stage 2 model, our Stage 3 model is applied to model the two two-phase mixture regions of U-Zr. Finally, these models together cover all the phases of U-Zr alloys below 900K. The calculated phonon thermal conductivity, resistivity, and total thermal conductivity are presented as a function of temperature and Zr at% in **Figure 4.7(a)**, (b), and (c), respectively. The phonon thermal conductivity decreases with increasing temperature, while resistivity and total thermal conductivity increase with increasing temperature. The $\delta(\text{U,Zr})$ phase gives the minimum values of thermal conductivities of the maximum values of resistivities.



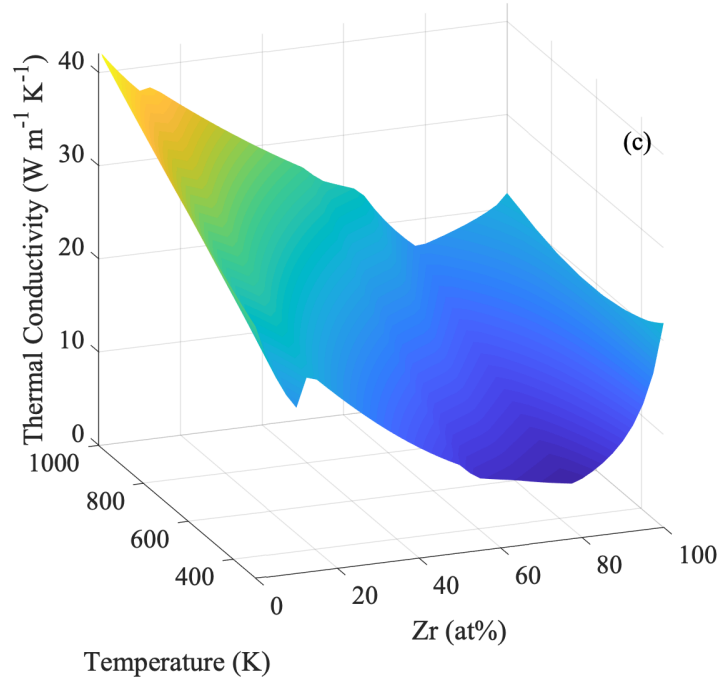


Figure 4.7. 3D Plots of (a) phonon thermal conductivity, (b) resistivity, and (c) thermal conductivity as a function of temperature and Zr at% over the temperature range 300-1000K and the composition range 0-100 at% Zr.

The modeled thermal conductivity compared with each set of experimental thermal conductivity data separately are presented in **Figure 4.8**. Generally, for each set of data except U-99 at% Zr, our modeled thermal conductivities have good agreements with experimental data. For U-99 at% Zr, we deduce that the low thermal conductivity is due to the sample contained oversaturated $\alpha(\text{Zr})$, which is presented in Section 4.6.2. Therefore, in following error analyze, we exclude the data of U-99 at% Zr from Touloukian et al. [17].

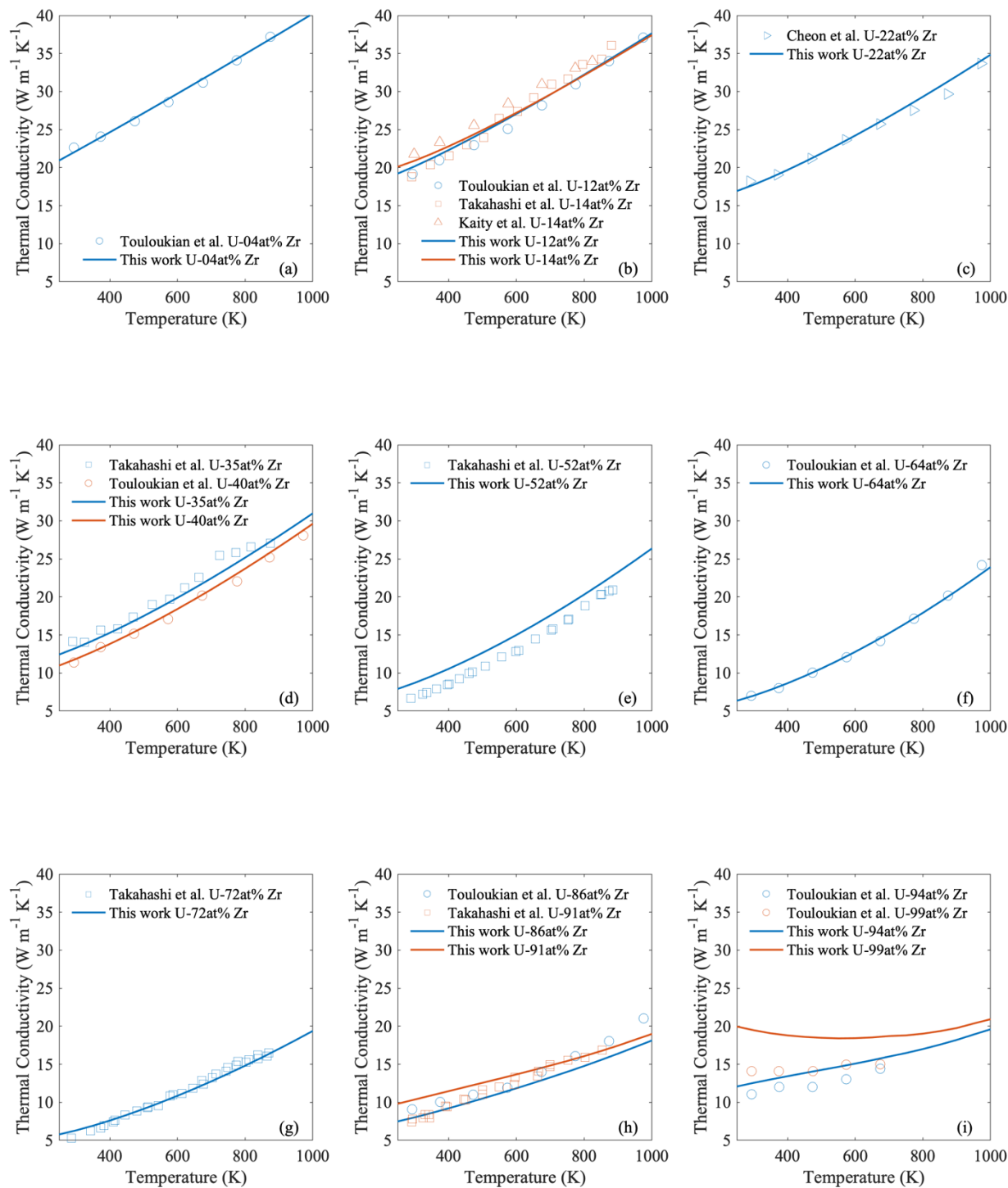


Figure 4.8. Plots of modeled thermal conductivity (curves) compared with experimental thermal conductivity data (symbols) for U-Zr alloys from Ref. [17,19–21]

To compare the accuracy of our model with previously established models from Kim et al. [25] and Chen et al. [27], the modeled thermal conductivity vs. experimental thermal conductivity is plotted in **Figure 4.9(a)**, and a bar plot which shows the numbers of data points at different errors (modeled values minus experimental values) is plotted in **Figure 4.9(b)**, where in **Figure 4.9(a)** and (b), the symbols and the bars with different colors represent the results from different models. In **Figure 4.9(a)**, the solid black line indicates the modeled values equals to experimental values, and the dashed black lines indicate $\pm 1W/mK$ for experimental uncertainty. It's hard to directly compare the modeled results from **Figure 4.9(a)**, so we plot **Figure 4.9(b)**, which can clearly show that our model has the most number of data points which has absolute error $< 0.5W/mK$ (shown as the medium bars). The ME and RMSE are $0.34W/mK$ and $1.24W/mK$ respectively for our model, are $-0.04W/mK$ and $1.28W/mK$ respectively for Kim et al.'s model, and are $-0.13W/mK$ and $1.53W/mK$ respectively for Chen et al.'s model. Our model gives the smallest RMSE. For ME, as both Kim et al.'s model and Chen et al.'s model are fitting models which directly fits to thermal conductivity data to minimum ME, they naturally have small values of ME. For our model, the most important reason for the large value of ME is the dataset of U-52 at% Zr from Takahashi et al.. Even after our correction, this data shows slightly lower thermal conductivity than U-64 at% Zr from Touloukian et al. (see in **Figure 4.6(c)** for the data at 295K, or in **Figure 4.8(e)** and (f)). U-64 at% Zr is on the boundary of $\delta(U,Zr)$ phase. If the U-52 at% Zr is in equilibrium and is a mixture of U-64 at% Zr and $\alpha(U)$, its thermal conductivity shouldn't be lower than both the thermal conductivity of U-64 at% Zr and $\alpha(U)$. This is conflicted with the data. Therefore, the thermal conductivity data of U-52 at% Zr from Takahashi et al. is likely not in equilibrium, or is affected by other factors that leads to the low thermal conductivity values. If we exclude U-52 at% Zr data from Takahashi et al. and re-calculate the ME and RMSE

for our model, their values are $0.08W/mK$ and $1.10W/mK$ respectively. Also here is a reminder of the RMSEs for each stage: for stage 1 the RMSE of the four are $< 1.3W/mK$; the RMSE for stage 2 is unknown due to no experiments to compare; the RMSE for stage 3 is $1.1W/mK$. Therefore, except no RMSE known for stage 2, our model shows stable accuracy which the RMSE is $< 1.3W/mK$ for each stage and the overall model, when demonstrated on U-Zr alloy system.

While our model has slightly better results of RMSE value, it's important to mention again that our model is different from Kim et al.'s and Chen et al.'s model. Kim et al.'s model is pure fitting model, which directly obtained by fitting their function with alloy data. Chen et al.'s model contains some physical terms and rules, like residual resistivity and Wiedemann-Franz law, but ignores some important physics processes including the phase separation in U-Zr alloys. However, our model is based on the physical rules for different type of materials: in stage 1 for alloys with fixed compositions, the thermal conductivity is combined from the contributions of multiple electron and phonon scattering processes; in stage 2 for dilute solid solutions, our model of stage 1 is extended to describe the contributions of dilute alloying by adding new electron and phonon scattering terms; in stage 3 for multi-phase regions, the thermal conductivity is obtained by using averaging schemes from the thermal conductivity of phase boundaries. Besides that, our model uses DFT calculations to provide as much input as we can for these physics bases. Developing such a physics-based computational model has multiple advantages. First and most directly, our model decreases the rely on experimental data and has less fitting parameters, due to the existence of physics rules and DFT inputs. A comparison of the numbers of fitting parameters from different models are given in **Table 4.3**. Basically the three model all follow the same path: fit the thermal conductivity for end components (αU and αZr) first then fit the thermal conductivity for alloys. For αU and αZr , our model contains 4 fitting parameters (A for phonon-electron scattering in

phonon contribution, B for electron-phonon scattering, C for electron-electron scattering, and ρ_{sat} for saturation resistivity in electron contribution, see in **Table 4.2(a)**), while Kim et al.'s model has 3 fitting parameters for αU , 4 for αZr , and Chen et al.'s model has 3 for αU and αZr . The numbers of fitting parameters for αU and αZr are close, but the numbers for alloys varies. In our model, 4 fitting parameters (C for electron-electron scattering, ρ_{sat} and ρ_{res} of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ for the saturation resistivity and residual resistivity respectively, and a fitted value for the difference of ρ_{sat} and ρ_{res} between $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ to $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$, see in Section 4.4.1.1 and **Table 4.2(a)**) are fitted with the data of two anchor structures, $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$ and $\delta(\text{U}_{0.25}\text{Zr}_{0.75})$. However, in Kim et al.'s and Chen et al.'s model, 6 and 12 fitting parameters, respectively, are fitted with the data of all available alloys. This exhibits that, our model relies on less data and have less fitting parameters in the entire model. What's more, each of our fitting parameters have specific physical meanings, which may be verified by experiments or by calculations if techniques allow. Second, our model can provide various physical insights about the thermal conductivity, including the quantitative results of the contributions of different scattering and carriers in thermal conductivity (see in Section 4.4.1.1) and the qualitative results of the microstructure changes in the two-phase region $\alpha(\text{U})$ - $\delta(\text{U,Zr})$ (see in Section 4.4.1.2). Finally, our model can be extended to incorporate other physical processes. One example is the dilute alloying model in Stage 2, where the phonon and electron scattering due to the dilute alloying are added in our model. Also for Stage 3, the averaging schemes can be adjusted to other schemes for specific mixture structures.

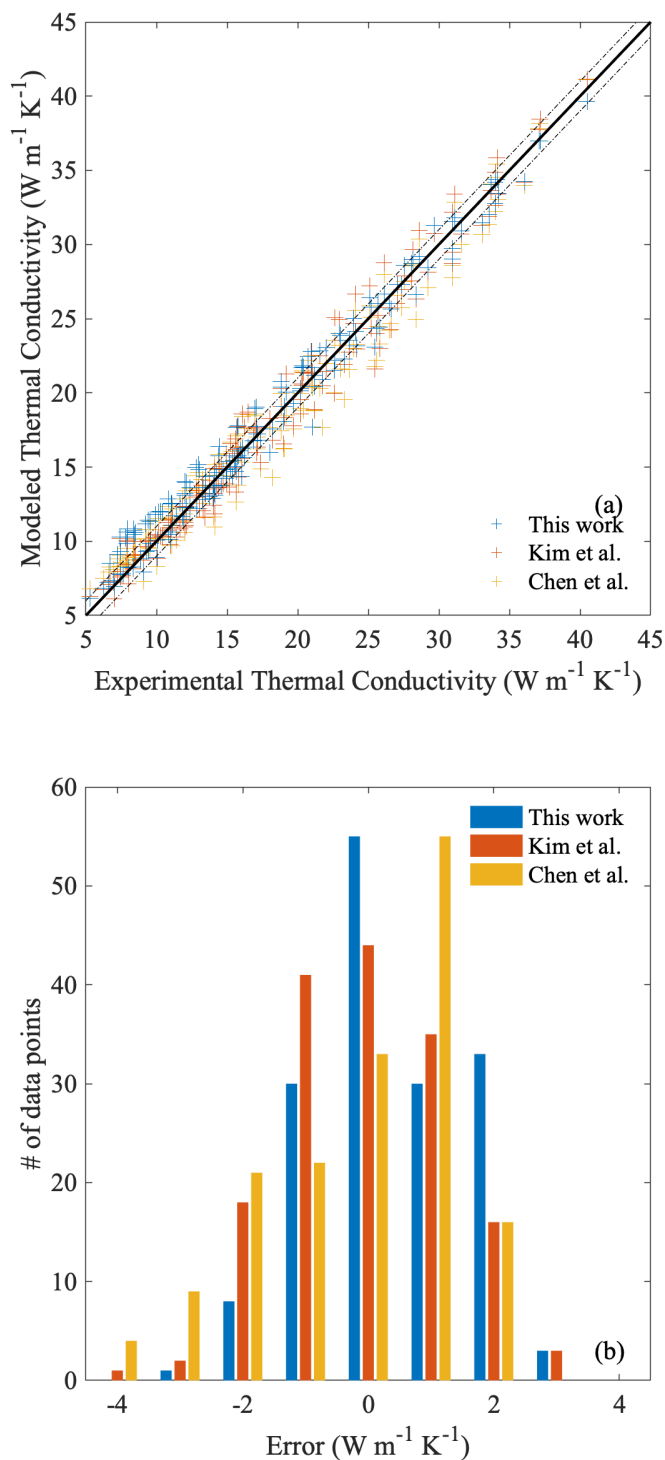


Figure 4.9. Plots of (a) modeled thermal conductivity vs. experimental thermal conductivity and (b) the numbers of data points with given errors. The symbols in (a) and the bars in (b) with different colors indicate the different models: the blue ones are for this work, the red ones are for Kim et al.'s model [25], and the yellow ones are for Chen et al.'s model [27].

Table 4.3. The comparison of number of fitting parameters used in different model.

# of fitting Parameters	αU	αZr	U-Zr alloys
This work	4 (3 in ρ , 1 in κ_{ph})	4 (3 in ρ , 1 in κ_{ph})	4 (in ρ of $\delta(\text{U,Zr})$)
Kim et al. [25]	3	4	6
Chen et al. [27]	3	3	12

4.4.2 U-Mo alloys

4.4.2.1 Stage 1: model at anchor structures (αU and U_2Mo)

We then demonstrate our model on U-Mo alloys for the region from αU to U_2Mo . In this region we will model two anchor structures, αU and U_2Mo , by our Stage 1 model, solid solutions with the $\alpha(\text{U})$ phase by our Stage 2 model of dilute alloying, and mixtures of $\alpha(\text{U})$ and U_2Mo phases by our Stage 3 model.

For αU , its phonon thermal conductivity, resistivity, and total thermal conductivity have already been presented in Section 4.4.1.1. For U_2Mo , the setups of DFT calculations are listed in **Table 4.1**, $s(T)$ can be calculated from DFT calculated electron bands, and the DFT phonon calculation results of phonon thermal conductivity are presented in **Figure 4.10(a)** as the dashed curve. Note as the same reason as of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$, the phonon-electron scattering in phonon thermal conductivity is neglected, due to it has small contribution on the total thermal conductivity. The calculated phonon thermal conductivity of U_2Mo , which is $< 0.15\text{W/mK}$ for temperature above 250K, is even smaller than it of $\delta(\text{U}_{0.33}\text{Zr}_{0.67})$.

Then in our approach, the resistivity model is needed to be fitted to the experimental data. However, no resistivity and thermal conductivity data exists for U_2Mo . We will use one set of thermal conductivity data of U-Mo alloy to calculate the resistivity data of U_2Mo , which means

we are actually fitting to one set of alloy data instead of U_2Mo data. The dataset chosen is the U-20at% Mo data from Matsui et al. [156]. It's chosen due to its wide temperature range (from 293K to 873K) and high Mo at%. The high Mo at% is needed as we use it to calculate the resistivity of U_2Mo . The closer is the Mo at% to that for U_2Mo , the more accurate is the estimate. As in our approach, if we have the resistivities and thermal conductivities of $\alpha(U)$ and U_2Mo , we can use the average schemes to calculate the thermal conductivity of U-20at% Mo. This process is reversed that we use the thermal conductivities of $\alpha(U)$ and of U-20at% Mo, to calculate the thermal conductivity and resistivity of U_2Mo , by the average scheme. Therefore, actually this step is finished after we obtain the modeled results for $\alpha(U)$, and decide which average scheme are best for U-Mo. However, the results are first presented in this section to make it consistent with our staged model. The results of $\alpha(U)$ will be presented in the next section. And the average scheme used for $\alpha(U)$ - U_2Mo region is the Series Model, which is decided by comparing the error of using EMT and the Series Model as the average scheme occurred in every process, see in Section 4.4.2.3. The calculated resistivities are presented as symbols in **Figure 4.10(b)**, as well as our fitted results of resistivity as the curve in the same figure. The fitting parameters are tableted in **Table 4.2(a)**. The calculated thermal conductivity by Eqs.(4.1)-(4.2) are presented as the solid curve in **Figure 4.10(a)**. Due to the lack of calculated resistivity data below 300K, the fitted residual resistivity ρ_{res} has large uncertainty. However, the predicted resistivity and thermal conductivity over the temperature range 300K-1000K still agree well with the calculated data. Note here this is the first estimation of resistivity and thermal conductivity of U_2Mo , and we appreciate any experimental validations of them.

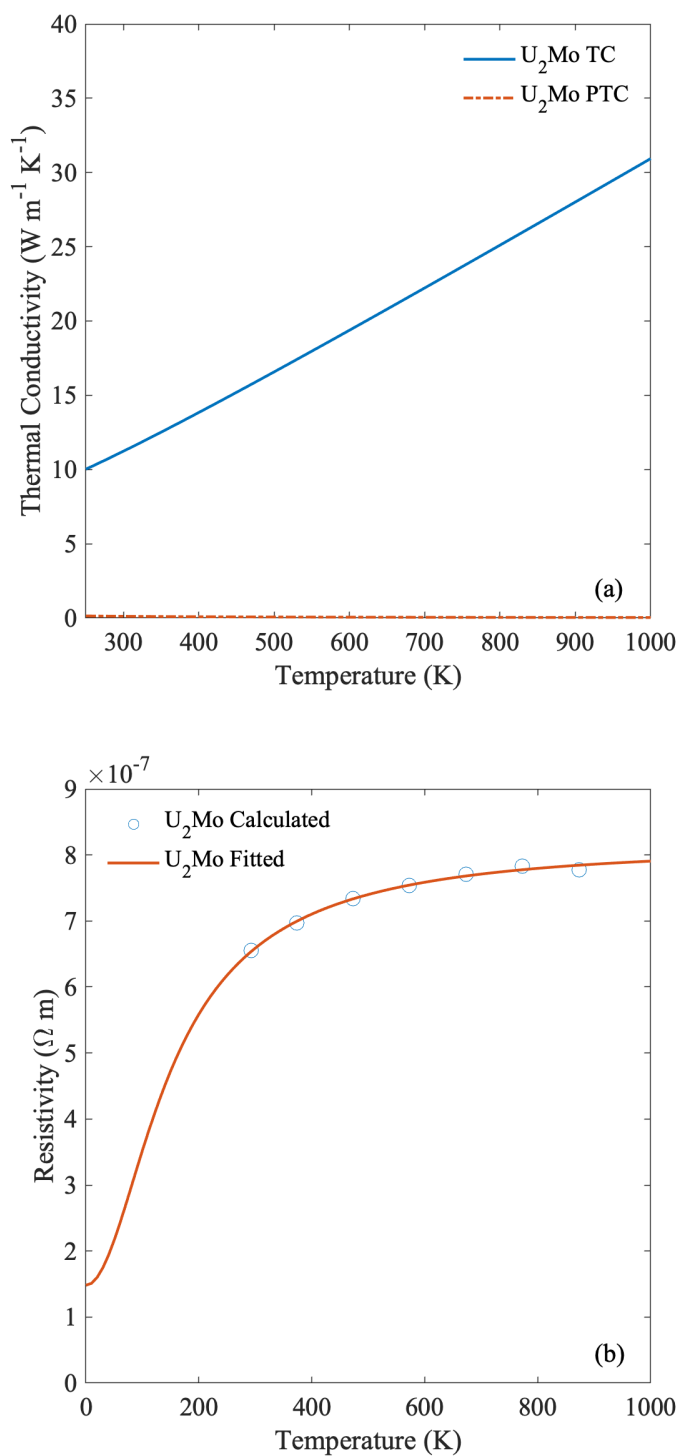


Figure 4.10. Plot of (a) the thermal conductivity (TC) and phonon thermal conductivity (PTC) of U_2Mo from 250K to 1000K, and (b) the calculated and fitted resistivity of U_2Mo from 0K to 1000K.

4.4.2.2 Stage 2: model the solid solutions with varying compositions ($\alpha(U)$)

The only solid solution in the Mo at%<33% region is $\alpha(U)$. Same as $\alpha(U)$ alloying with Zr, $\alpha(U)$ alloying with Mo is calculated by our approach for dilute alloying in Section 4.3.2. For phonon contribution, 1 at% Mo atoms gives a mass variance parameter $g = 3.6 \times 10^{-2}$, similar to that of $g = 3.8 \times 10^{-2}$ for 1 at% Zr, due to the close atomic masses of Zr and Mo. Therefore, the phonon thermal conductivity decrease due to 1 at% Mo is close to it of 1 at% Zr. The phonon thermal conductivities for $\alpha(U)$ alloying with Mo are calculated for alloying atomic concentration 0.2%, 0.4%, and 0.6%, shown in **Figure 4.11(a)**.

For resistivity, the values of the parameters V_{atom} and E_F are as same as $\alpha(U)$ with Zr alloying, listed in Table 4.2(b). For A_{cs} of Mo in $\alpha(U)$, the value of residual resistivity per atomic present alloying at dilute case is $\sim 1.6 \times 10^{-8} \Omega m/at\%$ from Hellwege et al. [153]. For 0.1 at% alloying, the value of A_{cs} is calculated to fix the residual resistivity to be $1.6 \times 10^{-9} \Omega m$. The calculated A_{cs} values are tableted in **Table 4.2(b)**. The modeled resistivity for alloying atomic concentration 0.2%, 0.4%, and 0.6% are shown in **Figure 4.11(b)**, and the modeled thermal conductivity for these concentrations are shown in **Figure 4.11(c)**. Similar to Zr in $\alpha(U)$, the effects of thermal conductivity decrease and resistivity increase due to Mo in $\alpha(U)$ is negligible.

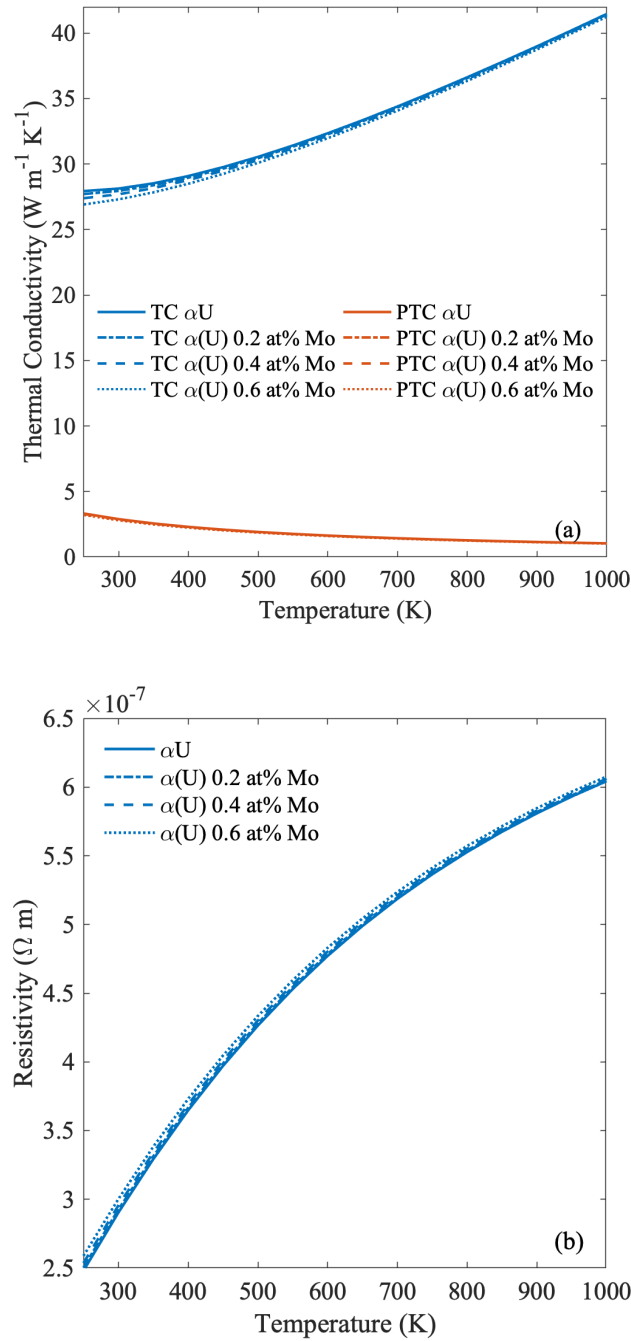


Figure 4.11. Plots of (a) the thermal conductivity (TC) and phonon thermal conductivity (PTC), and (b) resistivity as functions of temperature from 250K to 1000K for $\alpha(U)$ alloying with Mo. The curves with different styles indicate the different alloying concentration.

4.4.2.3 Stage 3: model the multi-phase mixtures ($\alpha(U)$ - U_2Mo)

As mentioned in Section 4.4.2.1, the two averaging schemes, the Series Model and EMT, are compared by applying them in our model and calculating the errors in reference to experimental U-Mo data. The results are calculated for 500K, which is presented in **Figure 4.12**. While comparing with experimental data, we first exclude the data of U-0.5at% Mo and U-4at% Mo, which are much lower than both the Series Model and EMT results. The reason why they have low thermal conductivity is discussed in Section 4.6.1. For all other experimental data, and the Series Model has the smaller RMSE value than EMT, which are $2.42W/mK$ and $2.53W/mK$, respectively. By applying the Series Model to the two-phase region $\alpha(U)$ - U_2Mo , the thermal conductivity of U-Mo alloys can be calculated as functions of temperature, as presented in **Figure 4.13**, and compared with experimental data and Kim et al.'s pure fitting model [23]. Our model is very close to Kim et al.'s model, which the difference between the two models are smaller than the difference among experiments of U-21.6at% Mo, see in **Figure 4.13(c)**. Then compared with experimental data, the ME and RMSE are $0.26W/mK$ and $2.44W/mK$ respectively for our model, and are $-0.51W/mK$ and $2.54W/mK$ respectively for Kim et al.'s model. Our model has slight better ME and RMSE values than Kim et al.'s model.

The major reason of the RMSE is that there are large discrepancies between the experimental results from different groups. Although the measurement uncertainty is about $2W/mK$ according to Burkes et al.'s experiments [157], the difference between the experimental data from different groups can be $9W/mK$ for U-21.6at%Mo (see in **Figure 4.12**). This indicates that, besides the experimental uncertainty, other reasons which causing the large discrepancy of experimental data is likely existing. The differences in the experimental samples is one possible reason, which includes the phase difference and the microstructure difference. For the phase difference, Creasy et al. [24] measured the gamma phase decomposition and the thermal

conductivity when the U-21.6at%Mo samples just quenched and heat treated at 773K for 40 hours and 96 hours. For the samples heat treated for 0 hour, 40 hours, and 96 hours, respectively, the gamma phase decomposition is 0%, 50%, and 97%. The measured thermal conductivity is shown in **Figure 4.14** as triangles with different colors (two sets of data is measured for 50% gamma phase decomposition), compared with our model, Kim et al.'s model, and other experiments. It clearly shows that, the existence of gamma phase in U-Mo samples decreases the thermal conductivity. Therefore, the difference of phase compositions can cause the difference in thermal conductivity. Besides that, the two sets of data for 50% gamma phase decomposition also show differences $\sim 2W/mK$ over the temperature range. This may be caused by the local microstructure difference, besides the uncertainty of the measurement. Again, our current model for the multi-phase region only serves as the best prediction according to current experimental data. Due to the lack of the information about phase compositions, phase separations, and microstructures from experiments, currently we find it hard to analyze these effects on thermal conductivity quantitatively.

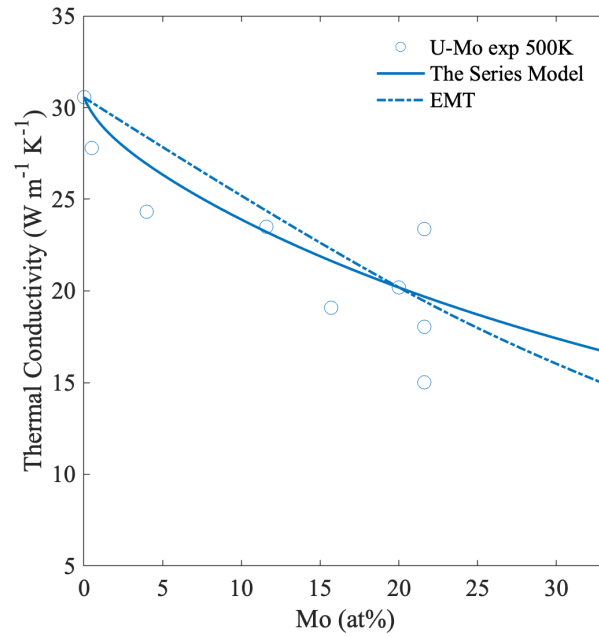
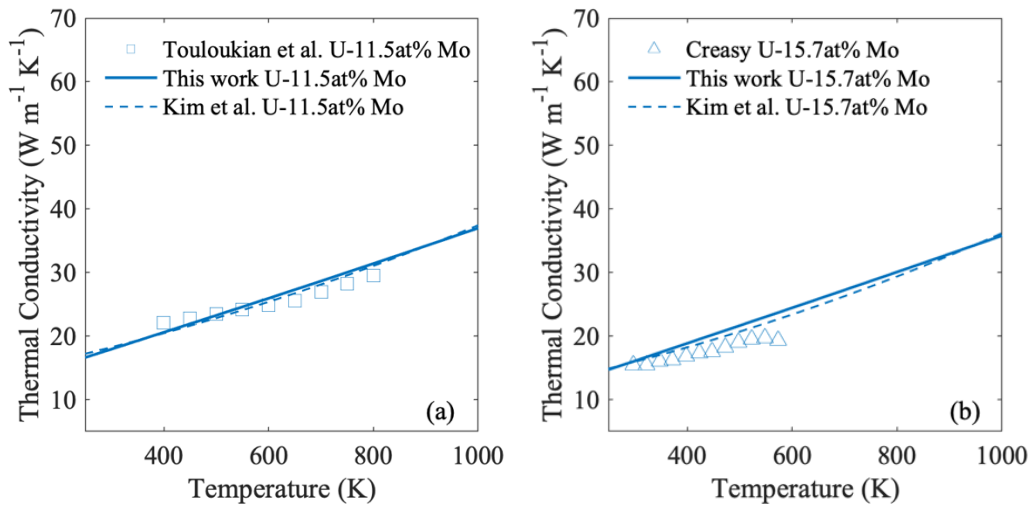


Figure 4.12. Plot of thermal conductivity of U-Mo alloys as a function of Mo at%. The curves are our modeled thermal conductivity, calculated with different averaging schemes, the Series Model and EMT. The symbols are experimental data from Ref. [17,18,23,24,156]



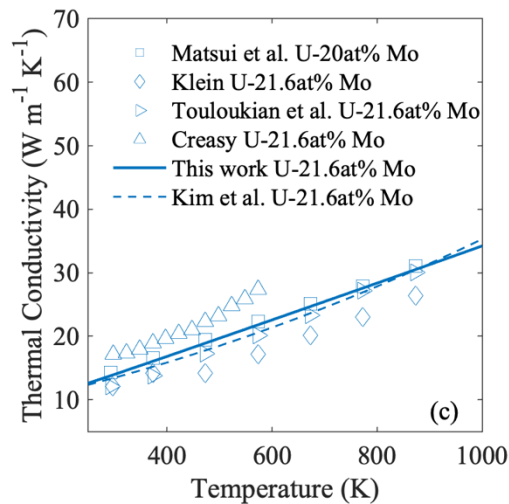


Figure 4.13. Plots of thermal conductivity of U-Mo alloys as functions of temperature for (a) U-11.5at% Mo, (b) U-15.7at% Mo, and (c) U-20at% Mo and U-21.6at% Mo. The solid curves are our modeled thermal conductivity, and the dashed curves are Kim et al.'s model [23]. The symbols are experimental data from Ref. [17,18,23,24,156]

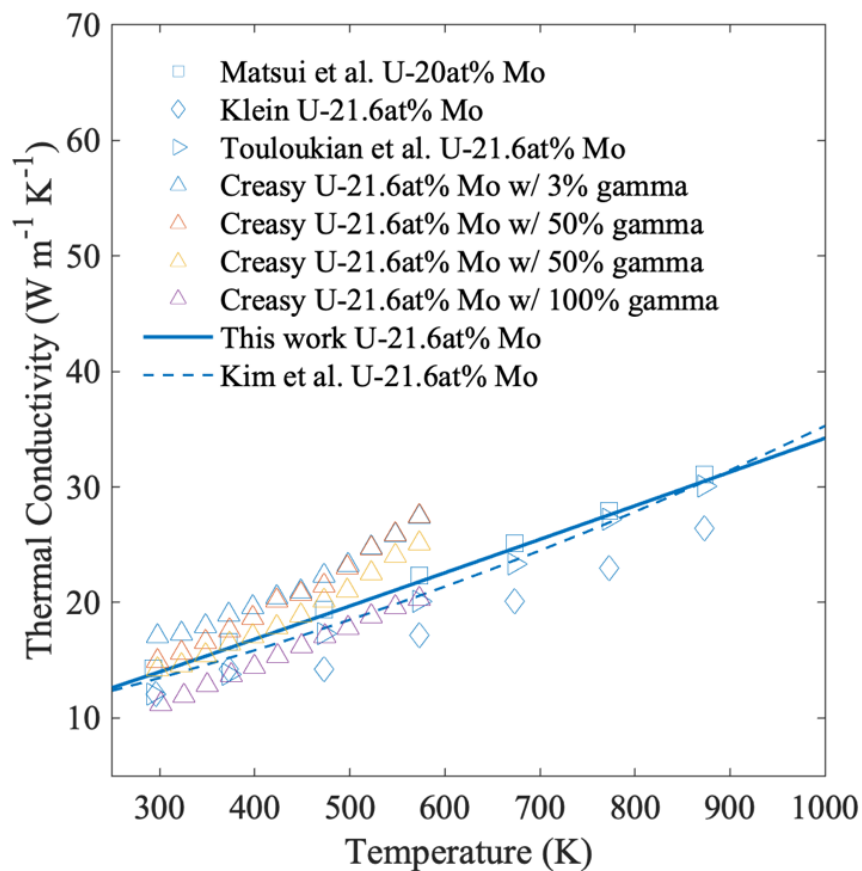


Figure 4.14. Plot of thermal conductivity of U-21.6at%Mo alloys as functions of temperature. The solid curve is our modeled thermal conductivity, and the dashed curve is Kim et al.'s model [23]. The symbols are experimental data from Ref. [17,18,23,24,156].

4.5 Conclusions

A staged physics-based computational model of thermal conductivity for different types of metal alloys has been constructed, with an emphasis on U-Zr and U-Mo alloys. Our model combines DFT calculations and DFT-BTE analysis together with experimental data to incorporate three types of metal alloy materials, including solid solutions with fixed compositions, solid solutions with varying compositions, and multi-phase mixtures. This model uses different stages to model the thermal conductivity of different types of metal alloys: the solid solution with fixed compositions and experimental data can be modeled by the Stage 1 model of anchor structures,

which incorporates the physics of different electron and phonon scattering processes to obtain the thermal conductivity; the solid solutions regions are modeled by the Stage 2 model, which for general model, the solid solution are modeled by linear interpolation or extrapolation of modeled anchor structures from the Stage 1 model, and for dilute alloying they are modeled by adding electron and phonon scattering with alloying atoms into the Stage 1 model; the multi-phase mixtures are modeled by the Stage 3 model, which uses the averaging schemes to combine the thermal conductivities on phase boundaries from the Stage 1 or 2 models. This model has been applied to U-Zr and U-Mo alloys and provides a baseline of typical thermal conductivity values for the contributions of each phonon and electron scattering process in different types of compositions, for the contributions of dilute alloying in metals, and for the effects of phase mixtures on thermal conductivity. The methodology developed here is extensible to thermal conductivity modeling of other metals and metal alloys for any application where heat management and thermal transport are key issues, thus functioning as a useful tool to guide further modeling of thermal conductivity to aid materials and device design.

4.6 Appendixes

4.6.1 Correction of Takahashi et al.'s Data

In Takahashi et al.'s paper, they measured the thermal diffusivity of U-Zr alloys, and the thermal conductivity κ is calculated by:

$$\kappa = \alpha \rho c_p, \quad (\text{A4.1})$$

where α is the thermal diffusivity, ρ is the density, and c_p is the specific heat capacity. They mentioned that the heat capacity they used in their calculations were calculated by the additivity

law, using heat capacity values from uranium [158] and zirconium [159], but their heat capacity values were not directly given. The density values they used were not mentioned.

First we re-calculate the thermal conductivity by the same formula Eq.(A4.1), with the density data from Rough [154], and the heat capacity values from Xiong et al.'s model [160]. All Takahashi et al.'s data, including thermal conductivity and thermal diffusivity are read from the plots. The re-calculated thermal conductivity, compared with Takahashi et al.'s thermal conductivity data, are presented in **Figure A4.1**. Generally our re-calculated thermal conductivity has a good agreement with Takahashi et al.'s data, except for U-52at% Zr, which Takahashi et al.'s data is approximately identical to the data of U-72at% Zr, while our re-calculated data is higher than the data of U-72at% Zr for about $1W/mK$. This is also justified by the ME and RMSE values comparing our re-calculated thermal conductivity with Takahashi et al.'s data: for U-14at%, 35at%, 52at%, 72at%, and 91at% Zr respectively, the ME is $0.45W/mK$, $-0.25W/mK$, $1.0W/mK$, $0.03W/mK$, and $0.10W/mK$, and the RMSE is $0.82W/mK$, $0.63W/mK$, $1.1W/mK$, $0.16W/mK$, and $0.23W/mK$. U-52at% has the only ME above $0.5W/mK$, while its ME is close to its RMSE, which means our re-calculation results are higher than Takahashi et al.'s original data for approximately $1W/mK$ over the temperature range.

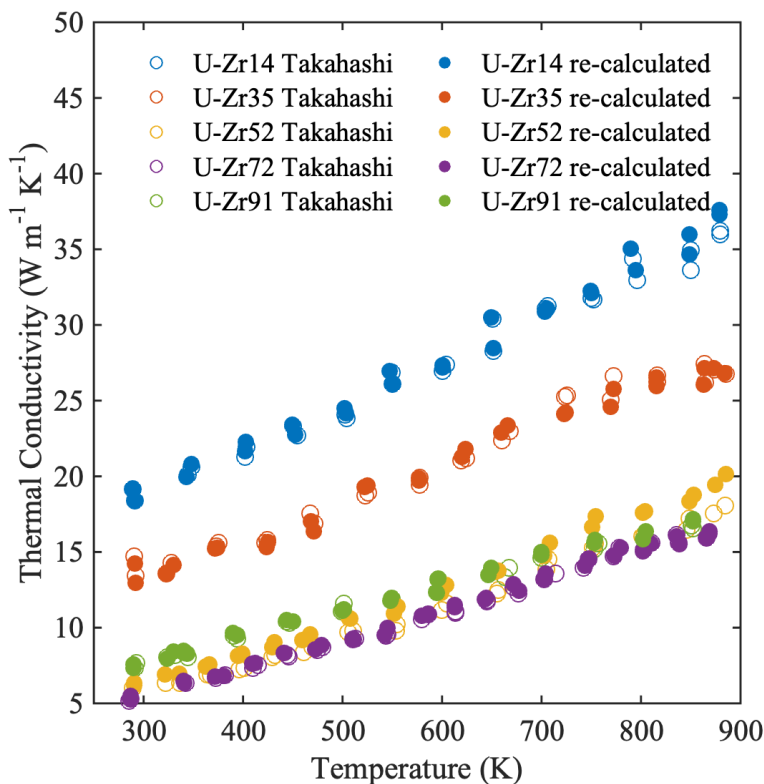


Figure A4.1. Plot of Takahashi et al.'s thermal conductivity data [19] (open symbols), compared with our re-calculation results of thermal conductivity (filled symbols) using Takahashi et al.'s thermal diffusivity data, Rough [154], and Xiong et al.'s heat capacity model [160]. The different color of symbols indicates U-Zr alloys with different Zr at%.

We also try to issue where the thermal conductivity difference of U-52at% Zr comes from. As our calculation and Takahashi et al.'s calculation uses the same values of diffusivity from Takahashi et al.'s, the thermal conductivity difference of U-52at% Zr must come from different values of heat capacity or density used in the calculations. For density, the density data from Rough are compared with the additivity law in **Figure A4.3**, and they show good agreements for <5% difference. Therefore, no matter Takahashi et al. used the density data from experiments or the density values obtained from the additivity law, the results should be approximately identical. For heat capacity, Xiong et al.'s model [160] is compared with the additivity law and the heat capacity

values used by Takahashi et al. (which is calculated by Eq.(A4.1), where the thermal conductivity and diffusivity are from Takahashi et al., and the density are from Rough). The Xiong et al.'s model has a good agreement with the additivity law, which also has a good agreement with the values used by Takahashi et al. except U-52at% Zr. For U-52at% Zr, the heat capacity values used by Takahashi et al.'s are close to the heat capacity values of U-35at% Zr used by them, which are also closed to the additivity law and Xiong et al.'s model of U-35at% Zr. Therefore, one possible reason of the lower thermal conductivity data from Takahashi et al. is the heat capacity of U-35at% Zr is used for U-52at% Zr by mistake. Therefore, throughout this work, the Takahashi et al.'s thermal conductivity of U-52at% Zr is replaced by our re-calculation results.

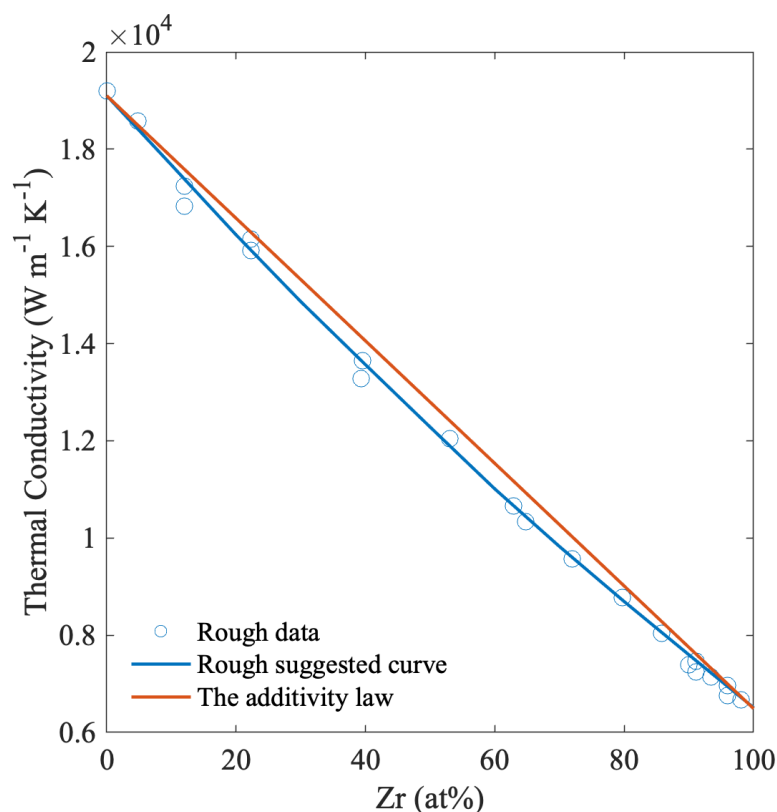


Figure A4.2. Plot of the density as a function of Zr at% in U-Zr alloys. The blue symbols and the blue curve are the data and suggested curve, respectively, from Rough [154]. And the red curve is calculated by the additivity law.

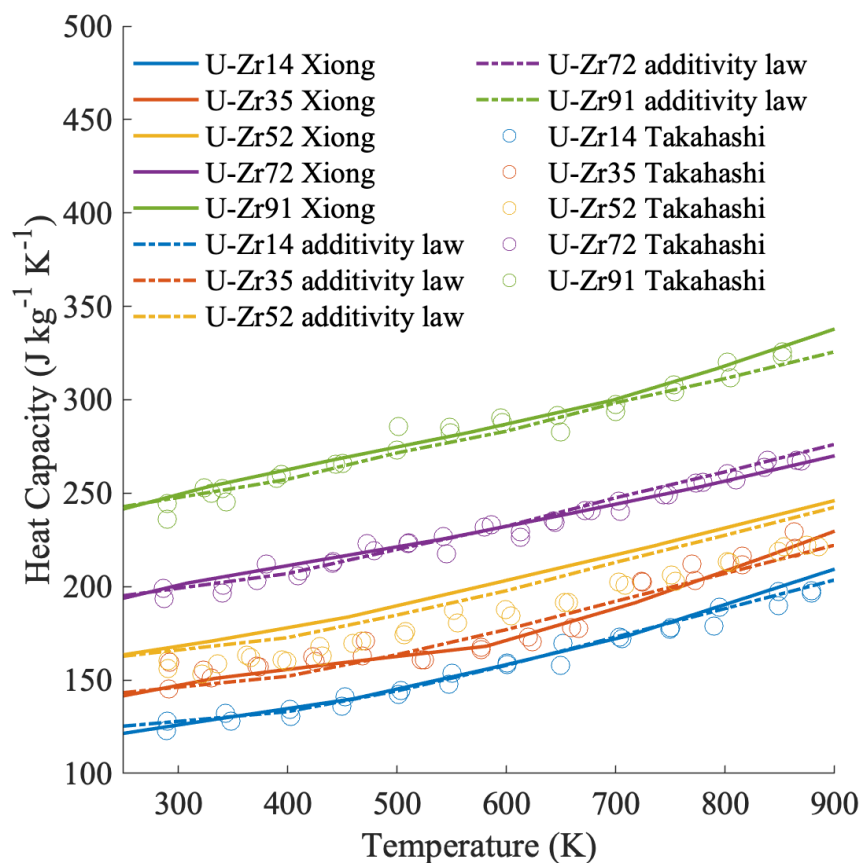


Figure A4.3. Plot of the specific heat capacity as a function of temperature for U-Zr alloys. The curves and symbols with different color indicate different Zr at% in U-Zr alloys. The solid curves are from Xiong et al.'s model [160], the dashed curves are calculated by the additivity law, and the symbols are the calculated heat capacity values used in Takahashi et al.'s thermal conductivity calculation [19].

4.6.2 The Resistivity and Thermal Conductivity of U-99at%Zr.

In Section 4.4.1.4, our modeled thermal conductivity are compared with each set of U-Zr alloy data. For U-99at% Zr, the experimental data is much lower than our modeled results of two-phase mixture. The effect of soluble U atoms in $\alpha(\text{Zr})$ on thermal conductivity are calculated in Section 3.1.2. Although the maximum solubility of U in $\alpha(\text{Zr})$ is 0.4 at% at about 900K, which is smaller than 1at% in U-99at% Zr, the thermal conductivity of oversaturated solid solution U-

99at% Zr can still be calculated using our Stage 2 model, which the results are presented in **Figure A4.4**, compared with experimental U-99at% Zr data from Touloukian et al. and our two-phase model results of U-99at% Zr. The thermal conductivity of calculated oversaturated U-99at% Zr has a better agreement with experimental U-99at% Zr data, than our two-phase model. Therefore, the low thermal conductivity values for experimental U-99at% Zr may be due to the experimental samples are oversaturated.

The similarly low thermal conductivity values exist in U-0.5at% Mo and U-4at% Mo, too (see in Section 4.4.2.3), possibly caused also by that the alloys are oversaturated. However, for U-0.5at% Mo, our calculated thermal conductivity for oversaturated solid solution is $27W/mK$ at 300K (see in Section 4.4.2.2), while the experimental value from Francis [18] is $22W/mK$. Therefore, the oversaturated U-0.5at% Mo is not the main reason to have such low thermal conductivity. It's likely due to the gamma phase U-Mo in the samples, but it's not justified as no information about the phase compositions in their samples is provided.

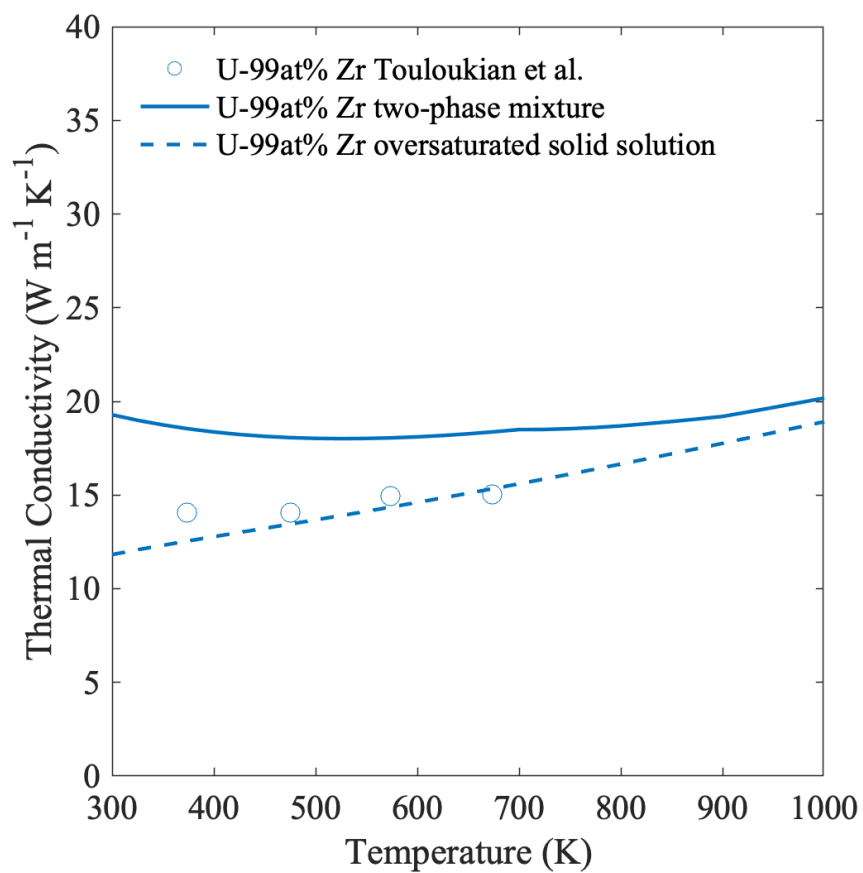


Figure A4.4. Plot of our modeled thermal conductivity for U-99at% Zr in two-phase mixture state (solid curve) and oversaturated solid solution state (dashed curve), compared with Touloukian et al.'s experimental data [17].

Chapter 5 : The Thermal Conductivity Modeling for Concentrated Binary Alloys: Demonstration on U-Zr, U-Nb, and U-Mo

5.1 Chapter Abstract

In this work, we developed a computational model of thermal conductivity based on density functional theory calculations, physics rules, and experimental data, for concentrated binary metal alloys. The model is demonstrated on body-centered cubic phase U-Zr, U-Nb, and U-Mo alloys and displays good agreement with experimental data, with a root-mean-square error of about 1.8 W/m-K (<10% error versus experiment) comparing with all alloy data. This work requires few alloy data due to the input of density functional theory calculations and physics rules, while gives accurate prediction. This model also provides insight into the semi-quantitative relationships of the thermal conductivity changes resulting from concentrated alloying as a function of composition. This model offers both a powerful tool for quantitative semi-empirical modeling of thermal conductivity in concentrated binary metal alloys and materials design insight for the control of thermal conductivity in metal alloys.

5.2 Introduction

Thermal conductivity describes how fast the heat is transferred at a given temperature gradient in a material, and the high-quality thermal conductivity data is critical to many technologies and materials, ranging from thermoelectrics to nuclear fuel materials, including traditional oxide fuels and metallic Uranium (U) fuels like U-Zr, U-Nb, and U-Mo alloys. Experimental thermal conductivity data is usually difficult to obtain over a range of temperatures and compositions due to the high cost and time required of traditional thermal conductivity measurement techniques [1,2]. Therefore, thermal conductivity modeling is widely used to

interpolate or extrapolate thermal conductivity data from experimental measurements, and to understand the impact of different factors, including temperature and composition on the thermal conductivity.

Thermal conductivity modeling includes different types of models: the traditional empirical interpolation formulae [17,25,161] directly interpolate between measured experimental data and conveniently produce thermal conductivity results at various conditions, but rely on the existence of massive experimental data at different conditions and provide little physical insight; recent thermal conductivity models use the density functional theory (DFT) calculations, combined with Boltzmann transport equations (BTE), to provide input information, which is based on the fundamental equations of quantum mechanics and the physics of heat transport, and require less experimental data. For phonon dominated materials, the DFT-BTE approach, where DFT are used to produce the interatomic force constants and phonon Boltzmann transport equations are used to calculate the transport properties including thermal conductivity, had been applied to semiconductors like Si [4], thermoelectric materials like PbSe [5], and multiple zincblende-type compounds [6]. For electron dominated materials, this approach had also been applied on multiple elemental metals [7]. Furthermore, some recent works are trying to combine the DFT-BTE approach for electrons and phonons and incorporate with defects like point defects [115,162].

Based on the DFT-BTE approach, we have developed thermal conductivity models for metallic alloy system, involving elemental metals, solid solutions, and multi-phase mixtures. Our model for elemental metals [115] was based on DFT-BTE approach, semi-classical physics rules, and experimental data, and was demonstrated on alpha-uranium (α U). This model provided the quantitative predictions of the thermal and electrical resistivity of over a wide temperature range, and the quantitative insights of the magnitudes of the physical mechanisms governing the thermal

conductivity of αU in terms of different electron and phonon scattering mechanisms. Then this model was extended to model metal alloys with different phase compositions including solid solutions and multi-phase mixtures using a staged computational model in Chapter 5], shown in the schematic diagram **Figure 5.1**.

- Stage 1: model at solid solutions at fixed composition (so called anchor structures). Stage 1 is using our physics-based model [115] to model the thermal conductivity of anchor structures. This model incorporates with different electron and phonon scattering processes by DFT-BTE approach, and is fitted to experimental thermal and electrical conductivity data.
- Stage 2: model the solid solutions with varying compositions. For general cases, Stage 2 is modeling solid solutions with linear interpolation or extrapolation of closest two anchor structures modeled by Stage 1. Besides the general case, one edge case of dilute alloying is modeled by DFT-BTE approach.
- Stage 3: model the multi-phase mixtures. Stage 3 is modeling the multi-phase region by combining the thermal conductivity at phase boundaries, modeled by Stage 1 or 2, through appropriate averaging schemes.

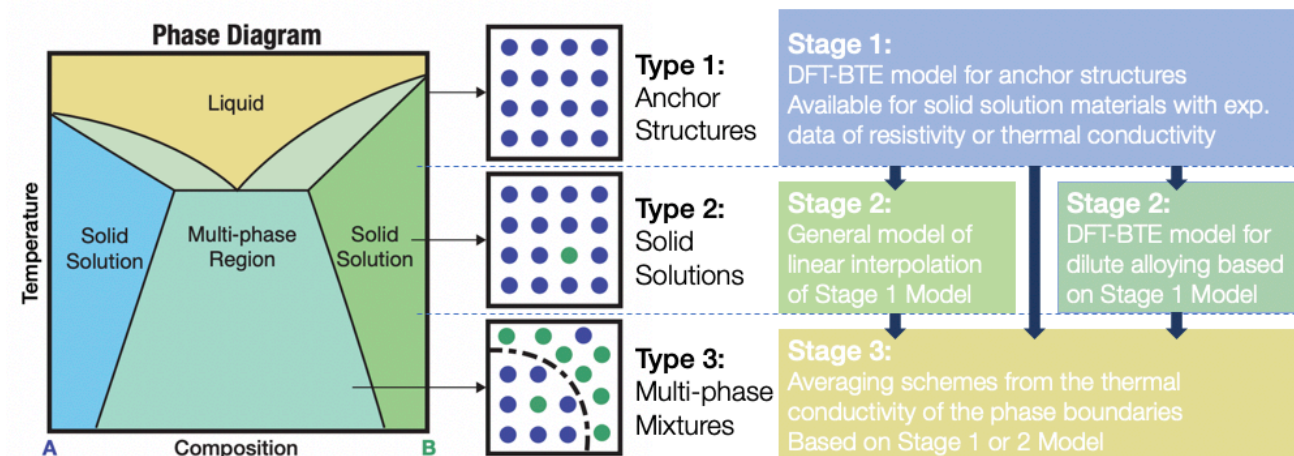


Figure 5.1. The schematic diagram of the three-stage modeling approach of thermal conductivity of metal alloys.

This approach is general and shown good agreements when demonstrated on U-Zr and U-Mo alloy systems in Chapter 5. However, this model can be improved, especially for the general approach of Stage 2. The general approach of solid solutions in Stage 2 uses linear interpolation and/or extrapolation on modeled anchor structures, therefore, the number of the modeled anchor structures may directly affect the accuracy of the model. E.g., to model concentrated alloys A_xB_{1-x} where $0 \leq x \leq 1$, one can image with only three anchor structures, A , B , and $A_{0.5}B_{0.5}$, the interpolation may cause significant errors; and with 11 anchor structures where $x = 0.0, 0.1, 0.2, \dots, 1.0$, the agreement of the interpolation will be improved. However, the Stage 1 model for anchor structures relies on their experimental data, and modeling the thermal conductivity for concentrated solid solutions with little experimental data is still a challenge. In our previous work, we focus on using the input from DFT calculations to decrease the amount of data needed in the model while keeps the high accuracy. And in this work, we follow the same path, use DFT calculation results as input for residual resistivity of concentrated alloys, and

develop a thermal conductivity model for concentrated solid solutions requires few experimental data.

As our previous staged model is demonstrated on metallic U alloys, this concentrated alloy model is also demonstrated on metallic U alloy systems. More specifically, the thermal conductivities of body-centered cubic (BCC) U alloys of U-Zr, U-Nb, and U-Mo, or represented as (γ U, β Zr), (γ U,Nb), and (γ U,Mo), are modeled. Metallic U alloys possess multiple advantages compared to the UO_2 -based fuels that are widely used in current thermal reactors, including: higher thermal conductivity, high burn-up capability, ease of recycling, and lower radiotoxicity of nuclear waste [9,10]. These advantages make metallic U alloys promising materials for use as nuclear fuels in thermal reactors and especially in the future deployment of fast reactors as Generation IV nuclear reactor designs [11]. Although metallic U alloys have higher thermal conductivities than UO_2 -based fuels, the melting temperature of metallic U alloys are lower than U oxides, which leads to lower operating temperature and more critical temperature control of metallic U alloys. Consequently, understanding the magnitude of change in thermal conductivity due to temperature changes and compositions becomes a critically important issue for heat management and temperature control of fuel reactors using metallic U alloys. Although the phase transition temperature, which for BCC U-rich alloys is about 900K-1000K, is higher than the operating temperature for $\sim$ 600K, BCC U alloys still attract research interests. This is mainly due to the stable swelling and fission gas nucleation under low-burnup, high temperature irradiation conditions of isotropic BCC phase [163,164], while α U shows cavitation swelling under irradiation [165]. BCC phase U alloys are also known for their corrosion resistance in water and water steam environments [166].

Among metallic BCC U alloys, U-Zr, U-Nb, and U-Mo are of most interest to research and have most electrical and/or thermal conductivity measurements existed, but their experimental data are still rare, mainly due to the high temperature. For U-Zr, the experimental data available before 1970 has been summarized by Touloukian et al. [17], and only several points are within the stable temperature range of BCC U-Zr. Since 1970 the main experimental data includes the BCC phase is by Argonne National Laboratory [22]. For U-Mo, the experimental data available before 1991 has been summarized by Madelung et al. [18], where we find one set of metastable BCC U-Mo data and several points in the stable temperature range of BCC U-Mo from another set of data. After that the main experimental data is from Creasy et al. [24] for metastable U-Mo. For U-Nb, only two sets of Nb-rich data were found from Madelung et al. [18]. Therefore, the experimental thermal conductivity data of these BCC U alloys are very limited in amount, due to the difficulties and high cost in measurements.

Due to the rarity of the experimental data of these BCC U alloys, the current empirical models, Kim et al.'s pure fitting model for U-Zr [25] and for U-Mo [26], does not cover the temperature range of BCC phase. Therefore, in this work, we develop a physics-based computational model of thermal conductivity in concentrated metal alloys, and demonstrated on BCC U-Zr, U-Nb, and U-Mo alloys. This model incorporates physics rules of scattering processes, DFT calculations, and empirical fitting, where the DFT calculations are used to provide input information and decrease the number of fitting parameters, and the physics rules ensure our model have a reasonable physics basic. The demonstration of this model on U-Zr, U-Nb and U-Mo alloys serves as the first predictive model of the thermal conductivity as a function of temperature and composition for these alloys. They also serve as a foundation for understanding the physical insights of the thermal conductivity in these alloys, to help further understanding of more complex

thermal conductivity of realistic U alloy fuels. This model is also a useful tool to guide further modeling of thermal conductivity to aid materials and device design.

5.3 Modeling Methods

In metal alloys, the thermal conductivity κ is the sum of electron thermal conductivity κ_e and phonon thermal conductivity κ_{ph} [29]:

$$\kappa = \kappa_e + \kappa_{ph}. \quad (5.1)$$

Because the electron dominates the heat transportation in metals, the phonon thermal conductivity κ_{ph} is neglected in this work. As examples of metals, in α U our previous work [115] shows the phonon thermal conductivity contribute $\sim 9\%$ of total thermal conductivity at 300K, and contribute $< 5\%$ above 600K, and in Al, Ag, and Au respectively, Jain et al.'s calculation [167] shows the phonon thermal conductivities contribute 2.5%, 1.0%, and 0.7% at 300K. Therefore, this approximation $\kappa \approx \kappa_e$ works with 10% error criteria for temperature above room temperature, and will be more accurate while temperature increases.

The electronic thermal conductivity κ_e is related to the electrical resistivity by the Wiedemann-Franz law [29]:

$$\kappa \approx \kappa_e = \frac{LT}{\rho}, \quad (5.2)$$

where L is the Lorenz number. The Lorenz numbers for various metals are approximately constants over temperature, and are closed to the theoretical value $L_0 = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.44 \times 10^{-8} W \Omega K^{-2}$, but may vary for different metals [30]. In the following sections 5.3.1 and 5.3.2, we will present how we model the resistivity ρ of unalloyed elemental metals and

concentrated binary metal alloys, respectively, and their thermal conductivities are modeled by Eq.(5.2) with fitted L values for different metals.

5.3.1 Approach for unalloyed elemental metals

In this work, the materials we focus on are concentrated binary metal alloys, represented as A_xB_{1-x} , in a solid solution phase. We first model the unalloyed elemental metals in the same phase, pure A and B , as the basic to model the concentrated alloys A_xB_{1-x} . The model for elemental metals follow the DFT-BTE approaches for electrical and thermal conductivity we developed both in our previous α U model [115] and as the Stage 1 in our staged model for multi-phase metal alloys in Chapter 5. In this DFT-BTE approach, DFT calculations are used to calculate the structural, and electronic properties of materials, and BTE calculations are used to calculate transport properties like electronic and thermal conductivity from the DFT calculated results. The only missing term in this process is the relaxation time, which is separated into the relaxation times of different electron scatterings and modeled by either semi-classical physics formulae or empirical fitting. The separation of the relaxation times also separates the contributions of different scattering processes in thermal conductivity, which will be presented as below.

The resistivity ρ is separated into three terms, the intrinsic resistivity ρ_{int} (which is the sum of the electron-phonon contribution ρ_{e-ph} and the electron-electron contribution ρ_{e-e}), the residual resistivity ρ_{res} due to point defects, and the saturation resistivity ρ_{sat} due to the resistivity saturation effect in metals [119], using Cote et al.'s formula [120]:

$$\rho = \left(1 - \frac{\rho}{\rho_{sat}}\right) \rho_{int} + \rho_{res} e^{-2W(T)}, \quad (5.3)$$

where the $e^{-2W(T)}$ term is the Debye-Waller factor, which is generally close to 1 [121–123]. For example, it was previously verified by Gomi et al. [121] using a Debye model that for Fe, $1 >$

$e^{-2W(T)} > 0.99$ below 1000K, and $1 > e^{-2W(T)} > 0.95$ below 5000K. Rearranging Eq. (5.3) and assuming $e^{-2W(T)} = 1$, the total resistivity ρ can be given by the equation

$$\rho = \frac{\rho_{int} + \rho_{res}}{1 + \rho_{int}/\rho_{sat}} = \frac{\rho_{e-ph} + \rho_{e-e} + \rho_{res}}{1 + (\rho_{e-ph} + \rho_{e-e})/\rho_{sat}}. \quad (5.4)$$

Note that for unalloyed elemental metals for which $\rho_{res} \approx 0$, this equation reduces to $\rho^{-1} = \rho_{int}^{-1} + \rho_{sat}^{-1}$, which is Wiesmann *et al.*'s parallel resistor formula [119,124]. This approximation, $\rho_{res} \approx 0$, is applicable for elemental metals as the residual resistivity ratio (RRR) is larger than 100 for multiple metals [168,169] with state-of-the-art fabrication techniques, which means the residual resistivity contribute <1% of total resistivity at 300K. The saturation resistivity ρ_{sat} is a constant for one metal, obtained by fitting to experimental data in this approach.

For these resistivity contributions ρ_{e-ph} and ρ_{e-e} , the DFT-BTE approach is applied. The resistivity can be readily calculated using the BTE method with the relaxation time approximation (RTA) approach with DFT-calculated electronic band structures [125]:

$$\rho_{e-ph,e-e} = \frac{1}{\sigma_{e-ph,e-e}} = \frac{1}{\left(\frac{\sigma}{\tau}\right) \tau_{e-ph,e-e}} = \frac{1}{s \tau_{e-ph,e-e}}, \quad (5.5)$$

where σ is the electrical conductivity and τ is the electronic relaxation time. ρ_{e-ph} and ρ_{e-e} can be calculated when τ take the values of the relaxation times of electron-phonon scattering τ_{e-ph} and electron-electron scattering τ_{e-e} , respectively. $s \equiv \frac{\sigma}{\tau}$ is calculated using the BTE-RTA and the rigid band approximation following the work of Madsen and Singh [125]. $\sigma(T)$ is calculated as the trace of the full electronic conductivity tensor, which can be calculated from the conductivity distributions:

$$\sigma_{\alpha\beta}(T) = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\varepsilon) \left[-\frac{\partial f_{\mu}(T, \varepsilon)}{\partial \varepsilon} \right] d\varepsilon, \quad (5.6)$$

where $f_\mu(T, \varepsilon)$ is the Fermi-Dirac distribution function, $\frac{\partial f_\mu(T, \varepsilon)}{\partial \varepsilon}$ is the temperature smearing, which is determined using the electronic density of states and the Fermi-Dirac distribution evaluated at the appropriate temperature, Ω is the system volume (taken as the DFT-calculated unit cell volume), T is the temperature, ε is the band energy, μ is the Fermi level, and $\sigma_{\alpha\beta}(\varepsilon)$ is the transport distribution given by:

$$\sigma_{\alpha\beta}(\varepsilon) = \frac{e^2}{N} \sum_{i,k} \tau_{i,k} v_\alpha(i, k) v_\beta(i, k) \frac{\delta(\varepsilon - \varepsilon_{i,k})}{d\varepsilon}, \quad (5.7)$$

where k represents elements of a set of k -points spanning reciprocal space in the Brillouin zone, N is the number of k -points sampled, i is the band index, v_α is the electron group velocity, e is the elementary charge, and $\tau_{i,k}$ are the relaxation times for each electron band i and k -point.

The input parameters for calculating the electrical conductivity tensor $\sigma_{\alpha\beta}(T)$ are the relaxation times $\tau_{i,k}$ and the electronic band structure information calculated from DFT. Here, we simplify the input of $\tau_{i,k}$ by assuming it is a constant which neither depends on band index i nor direction k , which has been shown to be a satisfactory assumption for many metals [126,127]. With this approximation, $s = \frac{\sigma}{\tau}$ depends on only the electronic band structure through Eqs. (5.6)-(5.7), which values can be obtained from DFT-BTE calculations. This approach of assuming a constant, single τ value to obtain $\rho(T)$ from DFT-BTE calculated $s(T)$ has been successfully applied to Ag-Cu alloys [128] and W with vacancies [129].

The relaxation times of electron-phonon scattering τ_{e-ph} and electron-electron scattering τ_{e-e} can be approximated by the semi-classical formula:

$$\tau_{e-ph}^{-1} = BT, \quad (5.8)$$

$$\tau_{e-e}^{-1} = CT^2, \quad (5.9)$$

where B and C are typically assumed to be constants [63–65,130] and obtained from fitting to experimental resistivity data. Note Eq. (5.8) works only for $T > \sim \theta_D$, where θ_D is the Debye temperature which is about 100K for metals.

To summarize, for unalloyed elemental metals, calculating ρ requires calculation of $s = \frac{\sigma}{\tau}$, which are calculated by the DFT-BTE approach:

$$\rho = \frac{(BT+CT^2)/s}{1+(BT+CT^2)/(s\rho_{sat})}, \quad (5.10)$$

where it has three fitting parameters in total, B in electron-phonon scattering time, C in electron-electron scattering time, and ρ_{sat} as the saturation resistivity. These three parameters are obtained from fitting ρ to experimental data. and the total thermal conductivity can be calculated by applying Eq. (5.2) with modeled ρ . The Lorenz number for different elemental metals are obtained by fitting to thermal conductivity data.

5.3.2 Approach for concentrated binary metal alloys

For concentrated binary metal alloys A_xB_{1-x} , their resistivities are still modeled by Eq.(5.4), $\rho = \frac{\rho_{int} + \rho_{res}}{1 + \rho_{int}/\rho_{sat}}$. However, the intrinsic resistivity ρ_{int} , the residual resistivity ρ_{res} , and the saturation resistivity ρ_{sat} are functions of atomic concentration x . For ρ_{int} and ρ_{sat} , some formulae are applied to interpolation them from their values of elemental metals A and B , and for ρ_{res} , Wei et al.'s residual resistivity model [112] is applied. These formulae and models will be introduced below.

An empirical formula for the intrinsic resistivity ρ_{int} of binary alloys are given by Ho et al. [170] as:

$$\rho_{int}(x) = x\rho_{int}^A + (1 - x)\rho_{int}^B, \quad (5.11)$$

where ρ_{int}^A and ρ_{int}^B are the intrinsic resistivity of elemental metals A and B , respectively, and x is the atomic concentration of A (which is equivalent to the alloy composition A_xB_{1-x}). This formula is validated by Ho et al. [170] on Ag-Au alloy system, which is in FCC phase for all alloying concentration.

The saturation resistivity ρ_{sat} can be related to some structural and electronic properties by semi-classical formula, assuming a spherical Fermi surface [119]:

$$\rho_{sat} = \frac{3\pi^2\hbar^3}{2m_e e^2 E_F l_{min}} = \frac{3\pi^2\hbar^3}{2m_e e^2 E_F n a}, \quad (5.12)$$

where E_F is the Fermi energy and l_{min} is the minimum value of electron mean free path l . The electron mean free path in metal has a minimum value, due to the Ioffe-Rogel criterion, which states $l < a$ (a is the interatomic distance) is generally impossible [119,171,172]. Therefore, the saturation resistivity roughly corresponds to $l_{min} \sim a$ [119,172]. The parameter n is defined as $l_{min} = na$, as a multiplier based on the interatomic distance a for minimum electron mean free path on l_{min} . Also we approximate a with $a = \sqrt[3]{\frac{6V_{atom}}{\pi}}$, which represents the diameter of a sphere having its volume equals to the volume per atom V_{atom} . As for elemental metals, the ρ_{sat} is obtained by fitting to experimental data as mentioned in Section 5.3.1, V_{atom} and E_F can be obtained by DFT calculations, the value of n can be obtained from Eq.(5.12). To obtain the saturation resistivity values ρ_{sat} for binary alloys, n as a function of atomic concentration x is needed. We use a linear combination as an approximation here:

$$n(x) = xn_A + (1 - x)n_B, \quad (5.13)$$

where n_A and n_B are the n values of elemental metals A and B , respectively, and x is the atomic concentration of A (which is equivalent to the alloy composition A_xB_{1-x}). Then ρ_{sat} as a function

of atomic concentration x can be calculated by Eqs.(5.12)-(5.13) with DFT calculated V_{atom} and E_F for binary alloys. The modeled results for BCC U-Nb alloys using this approximation, Eq.(5.13), have generally good agreements with experimental resistivity data (see in Section 5.4.2). Therefore, this approximation is applied to estimate the saturation resistivity for binary alloys. Note that, our general model Eq.(5.4) can incorporate with saturation resistivity obtained by other methods if applicable, like some advanced computational methods, replacing the semi-classical saturation resistivity formula Eq.(5.12). However, no such method is available yet, as far as we know, so we model the saturation resistivity by semi-classical model.

For residual resistivity ρ_{res} , the model we applied is Wei et al.'s residual resistivity model for binary alloys [112]. The electron scattering probability in A atom site from s orbital to i orbital (i can be s, p, d , or f) is:

$$p_{A,s-i} = x_A x_B^2 \langle \psi_{i,k'}^A | \Delta V | \psi_{s,k}^A \rangle^2 g_i^A(E_F), \quad (5.14)$$

where x_A and x_B are the concentrations of atom A and B , respectively, $\psi_{s,k}^A$ and $\psi_{i,k'}^A$ are the wave function of s - and i -electrons of an A atom, respectively, ΔV is the potential difference between atom A and B , and $g_i^A(E_F)$ is the density-of-states (DOS) of i -electrons at the Fermi level. An approximation is applied to estimate the value of the integrals, which the scattering potential ΔV is assumed to be constant for a given species at a given composition. With this approximation, the integrals is given by:

$$\langle \psi_{i,k'}^A | \Delta V | \psi_{s,k}^A \rangle^2 = C_{A,s-i} V_A^2 g_i^A(E_F) g_s^A(E_F), \quad (5.15)$$

where V_A represents the (constant) scattering potential of an A atom, and the fitting parameters C are introduced here to account for the differences between the exact value of the scattering interaction integral and the approximated constant scattering potential, and can be viewed as the

“scattering efficiency” for the given s - i scattering process. V_A here are estimated by the local average potential calculated from DFT.

Combining Eqs.(5.14)-(5.15), the total scattering probability of s - i scattering at A atom is given by:

$$p_{A,s-i} = C_{A,s-i} x_A x_B^2 V_A^2 g_i^A(E_F)^2 g_s^{total}(E_F). \quad (5.16)$$

And the residual resistivity is given by:

$$\rho_{res} = \frac{1}{g_s^{total}(E_F)} \sum_{j=A,B} \sum_{i=s,p,d,f} p_{j,s-i} = \sum_{j=A,B} \sum_{i=s,p,d,f} C_{j,s-i} x_j x_{j'}^2 V_j^2 g_i^j(E_F)^2, \quad (5.17)$$

where j' represents the atom other than j , e.g., j' is B when j is A , vice versa. The average local potentials V and DOS are calculated by DFT with given alloying concentration, and the parameters C are obtained by fitting to experimental data. This formula represents that, the total residual resistivity is the sum of the residual resistivity produced by each s - i scattering process at each atom site. Therefore, if all four scattering, s - s , s - p , s - d , and s - f , are considered for a binary alloy $A_x B_{1-x}$, the total residual resistivity contains eight residual resistivity terms generally. However, this can be simplified according to the actual DOS of the given atoms. E.g., Wei et al. [112] applied their model on binary alloys constructed by some group IB and VIIIB transition metal elements (Cu, Ag, Au, Pd, Pt, and Rh). These atoms have no f -electron, and their DOS of p -electrons are negligible compared with the DOS of s - and d -electrons at Fermi level. Therefore, the number of residual resistivity terms is decreased from 8 to 4: $\rho_{res} = x_A x_B^2 V_A^2 [C_{A,s-s} g_s^A(E_F)^2 + C_{A,s-d} g_d^A(E_F)^2] + x_A^2 x_B V_B^2 [C_{B,s-s} g_s^B(E_F)^2 + C_{B,s-d} g_d^B(E_F)^2]$. And in our case, for U-X alloys when X =Zr, Nb, or Mo, the major DOS at Fermi level is the d - and f -electrons of U and the d -electrons of X, which will be presented later in Section 5.4.2. Therefore, Eq.(5.17) is simplified to:

$$\rho_{res} = x_U x_X^2 V_U^2 [C_{U,s-d} g_d^U(E_F)^2 + C_{U,s-f} g_f^U(E_F)^2] + x_U^2 x_X V_X^2 C_{X,s-d} g_d^X(E_F)^2. \quad (5.18)$$

To summarize, the resistivities of concentrated binary metal alloys are modeled by Eq.(4.10), where the intrinsic resistivity ρ_{int} , the residual resistivity ρ_{res} , and the saturation resistivity ρ_{sat} are modeled by Eq.(5.11), Eqs.(5.12)-(5.13), and Eq.(5.17), respectively. Eqs. (5.11)-(5.13) need the inputs of ρ_{int} and ρ_{sat} of elemental metals and DFT calculated V_{atom} and E_F . Eq. (5.17) needs DFT calculated average local potentials V and DOS at Fermi level $g(E_F)$, and the parameters C are obtained from fitting to experiments. These properties calculated by DFT apply the special quansirandom structure (SQS) [117] as an approximation for their crystal structures. Then the thermal conductivity can be calculated by Eq. (5.2), while the only unknown value is the Lorenz number as a function of alloying concentration. A linear combination is applied as an approximation, for $A_x B_{1-x}$:

$$L(x) = xL_A + (1 - x)L_B. \quad (5.19)$$

where L_A and L_B are the Lorenz number of elemental metals A and B , respectively.

5.3.3 Approximations in the approach and the demonstration on BCC U-Zr, U-Nb, and U-Mo

The general approach is presented in Section 5.3.1 and 5.3.2, and will be demonstrated on BCC U-Zr, U-Nb, and U-Mo alloys in Section 5.4. Later in this paper, the metals and alloys refer to their BCC phase, except the phase are specifically mentioned. Besides the approximations applied in the general approach, some further approximations are applied for these U alloys. All these approximations are summarized in this section, together with the processes of the demonstration.

First, we list here the approximations applied in the general approach:

- For unalloyed elemental metal model:
 - The phonon thermal conductivity is neglected.
 - The Lorenz number is constant for a metal, fitted from experimental data.
 - The resistivity model with electronic calculations: the BTE method for electron with the relaxation time approximation (RTA); the electron relaxation times of electron-phonon and electron-electron scattering are approximated by semi-classical formulae; the Cote et al.'s formula for the resistivity saturation effect; the residual resistivity is neglected for elemental metals.
- For concentrated binary metal alloy model:
 - The phonon thermal conductivity is neglected.
 - The Lorenz number is constant for an alloy with fixed composition; the Lorenz number is approximated by linear combination of the elemental metals.
 - The resistivity model: the intrinsic resistivity is approximated by linear combination of the elemental metals; the saturation resistivity is modeled by semi-classical formula, while the parameter n is approximated by linear combination of the elemental metals.
 - The residual resistivity model from Wei et al. [112]: the scattering potential is constant, estimated by the local average potential.

For U-Zr, U-Nb, and U-Mo alloys, there are still some challenge while applying this approach, due to the lack of experimental data. The major one is to obtain the saturation resistivity values for U, Zr, Nb, and Mo from fitting. For U and Zr, as the transition temperature for BCC

phase is above 1000K, the experimental resistivity data have very limited temperature range for several hundred Kelvin. While fitting three parameters, B , C , and ρ_{sat} with such limited data, the uncertainty of each parameter is significant. For Nb and Mo, as BCC is their only stable solid phase, their resistivity data do have large temperature range, however, do not show significant resistivity saturation (see in **Figure 5.2**). While fitting the parameters to such data, although the uncertainties of B and C are small, the uncertainties of ρ_{sat} is still large. As in Eq.(5.4) if ρ_{sat} takes any value which is much larger than the intrinsic resistivity, we always have $\rho = \frac{\rho_{int} + \rho_{res}}{1 + \rho_{int}/\rho_{sat}} \approx \rho_{int} + \rho_{res}$, which shows no significant resistivity saturation. Therefore, for all four elemental metals here, accurately predicting their saturation resistivity is a challenge.

The idea is (1) to fit γ U with extra constraint, then (2) to calculate the saturation resistivity of Zr, Nb, and Mo by the saturation resistivity value of a given alloy. For (1), the ratio of resistivity contribution of electron-phonon scattering and of electron-electron scattering is assumed to be unchanged for α U and γ U at 1000K. This assumption represents the relative strength of electron-phonon and electron-electron scattering is approximately equivalent in α U and γ U. This assumption is unjustified, however, the fitted resistivities of elemental metals and alloys have good agreements with experiments, see in Section 5.4.1 and 5.4.2. For (2), as Eq.(5.13) shows n is a linear function which can be fixed by two fixed points. Therefore, if the n values at two different compositions are known, the n values at any concentration can be calculated. One n value known is n_U for γ U, or say at concentration $x = 1$ for binary alloy U_xX_{1-x} , which the saturation resistivity and n_U of γ U is fitted in (1). The another n value needed can be fitted from alloys with available data which shows significant resistivity saturation. The most ideal case is, for one alloy, the resistivity is approximately constant with temperature. This corresponds to the case, $\rho_{res} = \rho_{sat}$ in Eq.(5.4), which leads to $\rho = \rho_{sat}$ directly. The constant resistivity is exactly equals to the value

of the saturation resistivity of the alloy. This situation is observed on U-70at% Zr, U-60at% Nb, and U-30at% Mo. Therefore, with the help of the saturation resistivity values from these alloys, the n values, as well as the ρ_{sat} of Zr, Nb, and Mo can be calculated. Then the parameters B and C for these elemental metals can be obtained by fitting to experimental resistivity data with fixed saturation resistivity.

The approximation applied in the demonstration of concentration binary alloy approach is, as mentioned in Section 5.3.2, only considering the scattering due to the d - and f -electrons of U and the d -electrons of X (X=Zr, Nb, and Mo) in the residual resistivity model.

5.3.4 DFT details

All DFT calculations were performed with periodic boundary conditions with a plane-wave basis set using VASP. Initial crystal structures for U, Zr, Nb, and Mo (all in BCC structure, Space group: $Im\bar{3}m$, No. 229) were obtained based on the work in Refs. [173,174]. The electron-ion interaction of U and Zr used the projector augmented wave (PAW) method [142] as implemented by Kresse and Joubert [82]. The valence electron configuration for the U, Zr, Nb, and Mo pseudopotential was $6s^2 6p^6 5f^3 6d^1 7s^2$, $4s^2 4p^6 4d^2 5s^2$, $4s^2 4p^6 4d^4 5s^1$, and $4s^2 4p^6 4d^5 5s^1$ respectively. The exchange correlation functional parameterized in the generalized gradient approximation (GGA) [83] by Perdew, Burke, and Ernzerhof (PBE) [84] was used. The plane wave cutoff energy was set to 450 eV, and the stopping criteria for self-consistent loops were 1 meV per cell for electronic and ionic relaxation. The Monkhorst-Pack [143] k -point grid was used in all DFT calculations. For the four elemental metals, BCC conventional cells with 2 atoms were used. The electronic band calculations are performed by a selfconsistent calculation with a smaller k -points to obtain charge density, and a non-selfconsistent calculation with a larger k -points using the

charge density from selfconsistent calculations as input. The k -points for crystal relaxations, selfconsistent electron calculations, and non-selfconsistent electron calculations are $17 \times 17 \times 17$, $24 \times 24 \times 24$, and $36 \times 36 \times 36$, respectively. With calculated electron bands, the electron and phonon BTE calculations are performed respectively with the BoltzTraP [125] software with the RTA. The number of q -points used in the electronic BTE calculations was set to be 7 times that of the k -points used in the DFT band structure calculation.

For binary alloys, the crystal structures were generated by SQS using Alloy Theoretic Automated Toolkit (ATAT) [144], and fifteen different alloying concentrations $\frac{1}{16}, \frac{2}{16}, \frac{3}{16}, \dots, \frac{15}{16}$ were calculated for each U-X alloys where X=Zr, Nb, and Mo. In the crystal relaxation, only the cell volumes were relaxed, the cell shape and atom coordinates were fixed, as Wei et al. suggested for BCC U-Zr [175]. The k -points for crystal relaxation, selfconsistent electron calculation, and non-selfconsistent electron calculation is $11 \times 11 \times 11$, $11 \times 11 \times 11$, and $17 \times 17 \times 17$, respectively. The cell volume, Fermi energy, and DOS are obtained in the results of non-selfconsistent calculation.

5.4 Results and Discussions

5.4.1 Models for elemental metals: U, Zr, Nb, and Mo

As mentioned in Section 5.3.1 and 5.3.3, the resistivity and thermal conductivity models for elemental metals are used as bases for concentrated binary alloy models, as many terms, e.g. intrinsic resistivity ρ_{int} and saturation resistivity ρ_{sat} , are calculated by interpolation from elemental metals. Therefore, to apply our concentrated alloy model for U-Zr, U-Nb, and U-Mo, we first apply our elemental metal model for U, Zr, Nb, and Mo, which the model processes are mentioned in Section 5.3.3. The ab-initio calculation inputs for this elemental metal model are $s(T)$ of U, Zr, Nb, and Mo, calculated from DFT-BTE approach by Eqs.(5.6)-(5.7). The modeled

resistivity and thermal conductivity are presented in **Figure 5.2** and **Figure 5.3**, respectively, compared with experimental data. The fitting parameter values used in the elemental metal model are tableted in **Table 5.1**. For U, as mentioned in Section 5.3.3, when fitting our resistivity model (Eq. (5.10) with experimental resistivity data, one more approximation is applied, which the ratio of resistivity contribution of electron-phonon scattering and of electron-electron scattering is assumed to be unchanged for α U and γ U at 1000K. For α U, the value of ρ_{e-ph}/ρ_{e-e} is 1.4 at 1000K for α U, according to our previous modeling work in Chapter 5. Therefore, the value of ρ_{e-ph}/ρ_{e-e} at 1000K is set to 1.4 for γ U in the fitting. With the modeled resistivity, the Lorenz number of γ U is fitted by Eq.(5.2) and experimental thermal conductivity data, and all the fitting parameters for U are tableted in **Table 5.1**. For Zr, Nb, and Mo, also as mentioned in Section 5.3.3, the saturation resistivity values of U-70at% Zr, U-60at% Nb, and U-30at% Mo are used to estimate the saturation resistivity of Zr, Nb, and Mo, respectively. The experimental resistivities of U-70at% Zr, U-60at% Nb, and U-30at% are approximately independent with temperature, so their saturation resistivities approximately equal to their resistivity values, which are $11.3 \times 10^{-7} \Omega m$, $9.5 \times 10^{-7} \Omega m$, and $9.5 \times 10^{-7} \Omega m$ respectively. With these saturation resistivity values of alloys and the fitted saturation resistivity of U, the saturation resistivities of Zr, Nb, and Mo are $1.38 \times 10^{-6} \Omega m$, $1.72 \times 10^{-6} \Omega m$, and $1.26 \times 10^{-6} \Omega m$, respectively, calculated by Eqs.(5.12)-(5.13) (The other parameters used in Eq.(5.12), including E_F and a , are calculated by DFT and will be presented later in Section 5.4.2). Using these fixed saturation resistivity values for Zr, Nb, and Mo, other parameters in our resistivity model are fitted with experimental data, and their Lorenz number are all fitted by Eq.(5.2) with their modeled resistivity and experimental thermal conductivity data. All the fitting parameters for Zr, Nb, and Mo are also tableted in **Table 5.1**.

Comparing our resistivity model of U, Zr, Nb, and Mo with experimental data, the Mean Errors (ME) are $-6.1 \times 10^{-13} \Omega m$, $-3.6 \times 10^{-10} \Omega m$, $-7.4 \times 10^{-10} \Omega m$, and $-3.6 \times 10^{-9} \Omega m$, respectively, and Mean Residual Square Error (RMSE) are $1.9 \times 10^{-9} \Omega m$, $1.6 \times 10^{-8} \Omega m$, $1.1 \times 10^{-8} \Omega m$, and $2.4 \times 10^{-8} \Omega m$, respectively. Comparing with the resistivity at 1500K, the RMSE values of the four metals are equal to 0.3%, 1.4%, 1.9%, and 6.0% of their resistivity at 1500K. If a criteria of 5% error is applied, our models of U, Zr, and Nb show great agreement with experimental data, and our model of Mo shows a slightly higher error than the 5% error criteria. The reason of this error is mainly due to the low saturation resistivity of Mo, as if the saturation resistivity of Mo is increased from $1.26 \times 10^{-6} \Omega m$ to $1.90 \times 10^{-6} \Omega m$, the RMSE will decrease from $2.4 \times 10^{-8} \Omega m$ to $1.2 \times 10^{-8} \Omega m$. The lower value of the saturation resistivity of Mo may due to our saturation resistivity approximation, Eq.(5.13), is not applicable for U-Mo system. However, while we apply this approximation for U-Mo alloys later in Section 5.4.2, the modeled resistivity and thermal conductivity for alloys have great agreements with experimental data. The another possible reason is due to the alloy data used in the estimation of the saturation of resistivity. Note that, for Zr and Nb, respectively, the saturation resistivities of U-70at% Zr and U-60at% Nb are used in the estimation of the saturation resistivities of Zr and Nb. And for Mo, U-30at% Mo is used, which is the only alloy in the U-rich side. Its composition is far from pure Mo, therefore the errors in its resistivity data can lead to a significant error in the saturation resistivity of Mo. E.g. if the resistivity data of U-30at% Mo has 10% errors, our estimated saturation resistivity of Mo will have an error of 30%. In the phase diagram of U-Mo, the stable regions of concentrated BCC U-Mo alloy contains two parts, a small region near pure Mo, where the U at% is $<5\%$, and a U-rich regions where the Mo at% vary from 0% to about 40%. As we mainly consider the U-rich part, as

well as the 6% error of our Mo model is still acceptable, this Mo model is still used to produce further resistivity and thermal conductivity modeling results.

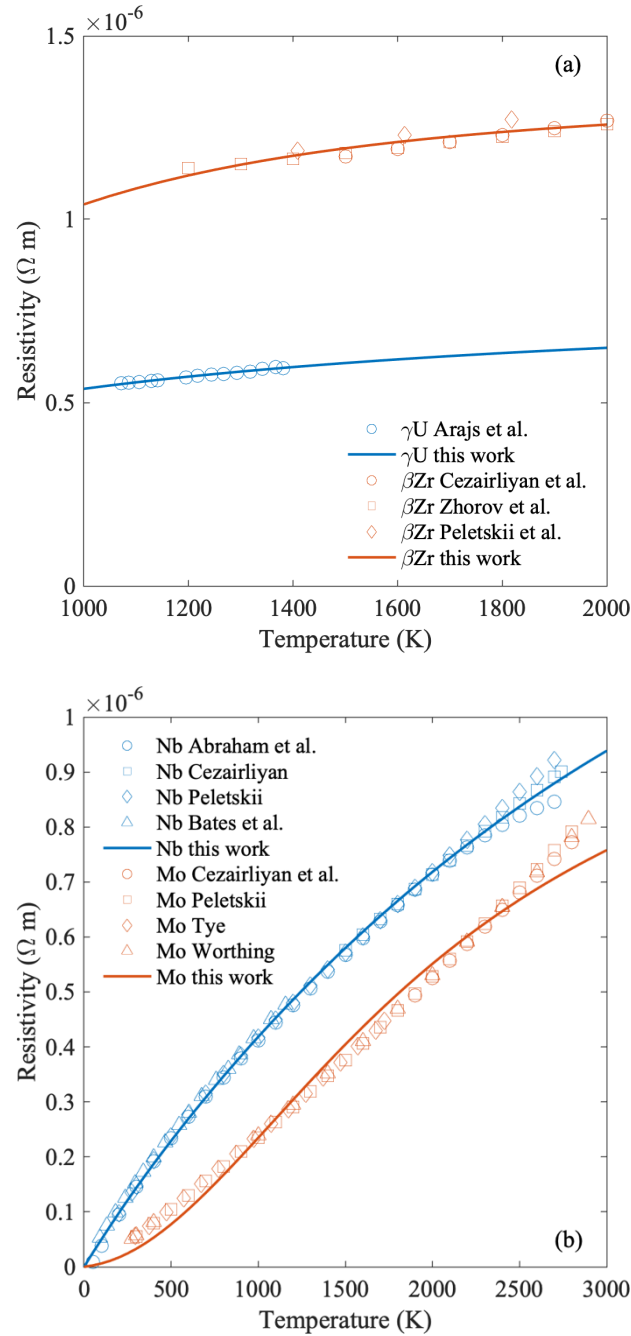


Figure 5.2. Plots of resistivity of (a) U and Zr over the temperature range of 1000K to 2000K, and (b) Nb and Mo over the temperature range of 0K to 3000K. The curves with different colors indicate the modeled resistivity for different metals. The symbols indicate the experimental resistivity from Refs. [147,150].

Then the errors in our thermal conductivity models for these metals are analyzed. While fitting with our modeled resistivity with experimental thermal conductivity data for these metals, the approximation of constant Lorenz number shows great agreement with experimental data of U, Zr, and Nb. For Mo, if we use the experimental resistivity of Mo from Peletskii [150], instead of our modeled resistivity, in the Wiedemann-Franz law, as showed by the dashed red curve in **Figure 5.3(b)**, the calculated thermal conductivity of Mo will also have great agreements with experiments. Therefore, the error between our modeled thermal conductivity and experiments of Mo are due to the errors in our resistivity model, not caused by the constant Lorenz number. While the constant Lorenz number approximation works for these metals, the fitted Lorenz numbers for these metals do not equal to the theoretical value $2.44 \times 10^{-8} W \Omega K^{-2}$, and have $\sim 5\%$ - 10% differences with the theoretical value. Comparing our thermal conductivity model for the other three metals, U, Zr, and Nb, with experimental data, the Mean Errors (ME) are $0.20 W m^{-1} K^{-1}$, $0.38 W m^{-1} K^{-1}$, and $1.46 W m^{-1} K^{-1}$, respectively, and Mean Residual Square Error (RMSE) are $0.21 W m^{-1} K^{-1}$, $0.41 W m^{-1} K^{-1}$, and $2.56 W m^{-1} K^{-1}$, respectively. Comparing with the thermal conductivity at 1500K, the RMSE values of the four metals are equal to 0.8%, 0.7%, and 3.6% of their thermal conductivity at 1500K, which are all within the 5% criteria. This shows that, the approximations of constant Lorenz number and negligible phonon thermal conductivity are applicable for these metals. For Mo, as we mentioned in the last paragraph, we mainly consider the U-rich region, so the errors in pure Mo model is acceptable.

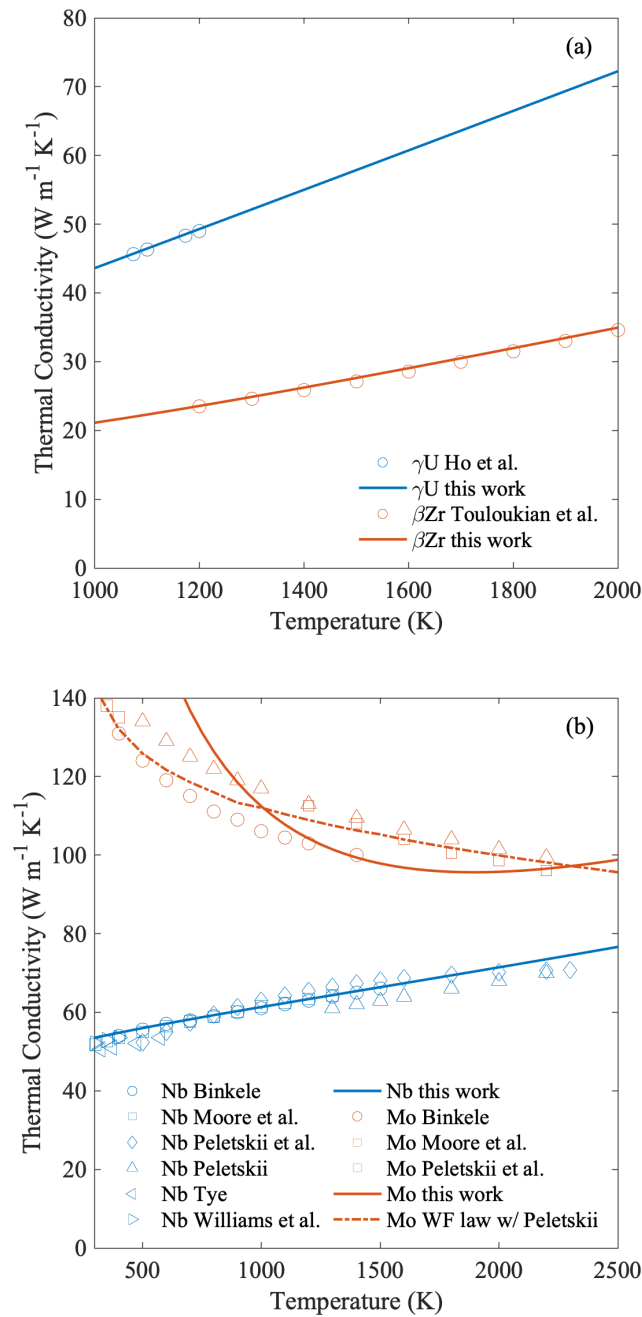


Figure 5.3. Plots of thermal conductivity of (a) U and Zr over the temperature range of 1000K to 2000K, and (b) Nb and Mo over the temperature range of 300K to 2500K. The solid curves with different colors indicate the modeled thermal conductivity for different metals. The dashed red curves in plot (b) indicates the thermal conductivity calculated by Wiedemann-Franz law (WF law) with the resistivity data from Peletskii [150]. The symbols indicate the experimental thermal conductivity from Refs. [18,151,176].

Table 5.1. The values of fitting parameters of elemental metals used in this work.

Parameters	U	Zr	Nb	Mo	Note
L/L_0	0.96	0.90	1.05	1.08	The Lorenz number used in Eq.(5.2), where the theoretical value $L_0 = 2.44 \times 10^{-8} W \Omega K^{-2}$.
$B (s^{-1} K^{-1})$	7.13×10^{11}	7.13×10^{11}	3.09×10^{11}	1.47×10^{10}	The parameter in electron-phonon scattering, used in Eq.(5.8).
$C (s^{-1} K^{-2})$	5.10×10^8	1.08×10^9	1.70×10^7	7.48×10^7	The parameter in electron-electron scattering, used in Eq.(5.9).
$\rho_{sat} (\Omega m)$	7.29×10^{-7}	1.38×10^{-6}	1.72×10^{-6}	1.26×10^{-6}	The saturation resistivity, used in Eq.(5.10).

5.4.2 Models for concentrated binary alloys: U-Zr, U-Nb, U-Mo

For concentrated binary alloys, our resistivity model is Eq.(5.4), $\rho = \frac{\rho_{int} + \rho_{res}}{1 + \rho_{int}/\rho_{sat}}$, while the intrinsic resistivity ρ_{int} is calculated by Eq.(5.11), the saturation resistivity ρ_{sat} is calculated by Eq.(5.12)-(5.13), which both are interpolations between elemental metals. ρ_{int} and ρ_{sat} are already available when our model for elemental metals are built. ρ_{res} for U alloys are modeled by Eq.(5.18), which includes three parameters, $C_{U,s-d}$, $C_{U,s-f}$, and $C_{X,s-d}$, and they are obtained by fitting with experimental resistivity data for these U alloys. Some inputs from DFT is needed in the fitting, includes E_F and a in Eq.(5.12), and DOS at Fermi level in Eq.(5.18), as functions of compositions. They are all calculated in DFT with SQS. The fitted values for the parameters $C_{U,s-d}$, $C_{U,s-f}$, and $C_{X,s-d}$ in U-Zr, U-Nb, and U-Mo alloys are tableted in **Table 5.2**. And the fitted results of the resistivity of these alloys are presented in **Figure 5.4**.

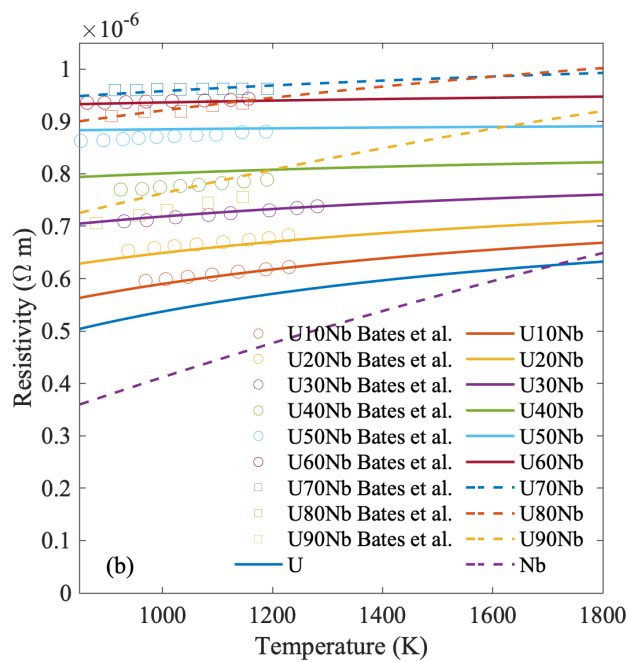
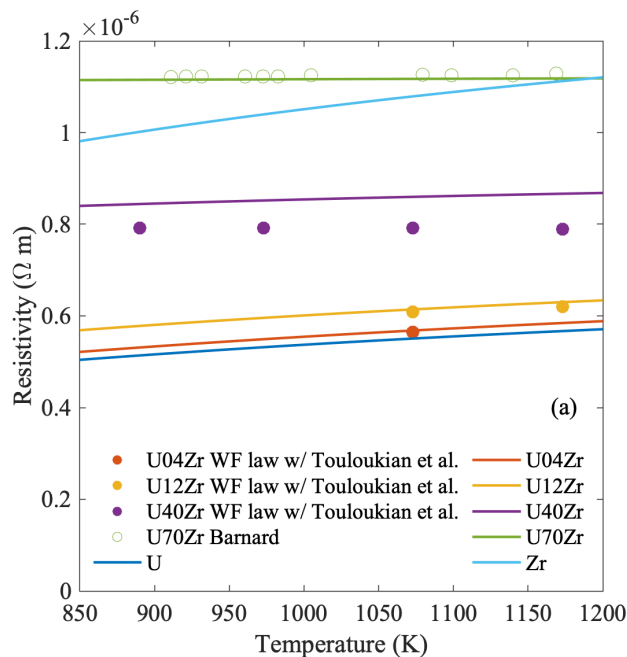
Our modeled resistivity for U-Zr, U-Nb, and U-Mo are presented in **Figure 5.4(a)**, **(b)**, and **(c)**, respectively, as the curves. The different colors of the curves indicate the different alloy compositions, in atomic percentage (at%). Our modeled resistivity is comparing with experimental resistivity data of these alloys [152,177,178], shown as open circles in **Figure 5.4**, and the calculated resistivity data, which is obtained by the Wiedemann Franz law with experimental

thermal conductivity data of U-Zr from Touloukian et al. [17], shown as the filled circles in **Figure 5.4(a)**. The calculated resistivity data for U-Zr is needed due to the lack of resistivity data, as we only found one set of U-Zr resistivity data, U-70at% Zr data from Barnard [152], from literature. Therefore, these calculated resistivity data are used in the fitting of residual resistivity of U-Zr, to help us develop a more accurate model with different compositions.

When comparing our modeled resistivity with all experimental data in **Figure 5.4**, we also plot our predicted resistivity vs. experimental resistivity in **Figure 5.5**. The values of the coefficient of determination (R^2) of U-Zr, U-Nb, and U-Mo are 0.86, 0.99, and 0.998, respectively. The R^2 values of U-Nb and U-Mo are very close to 1, which represents that our predicted resistivity is highly correlated with experimental resistivity. For U-Zr, as we only have one set of experimental data, and this set of data for U-70at% Zr are approximately constant with temperature (see the green open circles in **Figure 5.4(a)**), all the data points in **Figure 5.5(a)** are very close to each other, which leads to the low value of R^2 . For U-Zr, U-Nb, and U-Mo, the ME values are $-7.6 \times 10^{-9} \Omega m$, $6.2 \times 10^{-9} \Omega m$, and $-5.9 \times 10^{-10} \Omega m$, respectively, and the RMSE values are $7.7 \times 10^{-9} \Omega m$, $1.5 \times 10^{-8} \Omega m$, and $2.3 \times 10^{-9} \Omega m$, respectively. As the mean resistivity values of the alloys at 1200K, estimated from the data of different compositions, are about $1.1 \times 10^{-6} \Omega m$, $0.8 \times 10^{-6} \Omega m$, and $0.7 \times 10^{-6} \Omega m$, for U-Zr, U-Nb, and U-Mo respectively, the RMSE values equal to 0.7%, 1.8%, and 0.3% of the mean resistivity values at 1200K. Therefore, the RMSEs are all within the 5% criteria range, and our model have great agreements with experimental data. This suggest that our Mo model which has slightly high errors is still applicable, if we only consider the U-rich U-Mo alloys as shown in **Figure 5.4**.

Table 5.2. The fitting parameter values in the residual resistivity model (Eq.(5.18)) of binary concentrated alloy U-X (X = Zr, Nb, Mo) used in this work.

Parameters	U-Zr	Nb	Mo
$C_{U,s-d} (\Omega m)$	1.22×10^{-6}	1.30×10^{-9}	9.50×10^{-15}
$C_{U,s-f} (\Omega m)$	1.81×10^{-6}	1.95×10^{-11}	1.57×10^{-11}
$C_{X,s-d} (\Omega m)$	6.68×10^{-14}	1.14×10^{-8}	1.35×10^{-8}



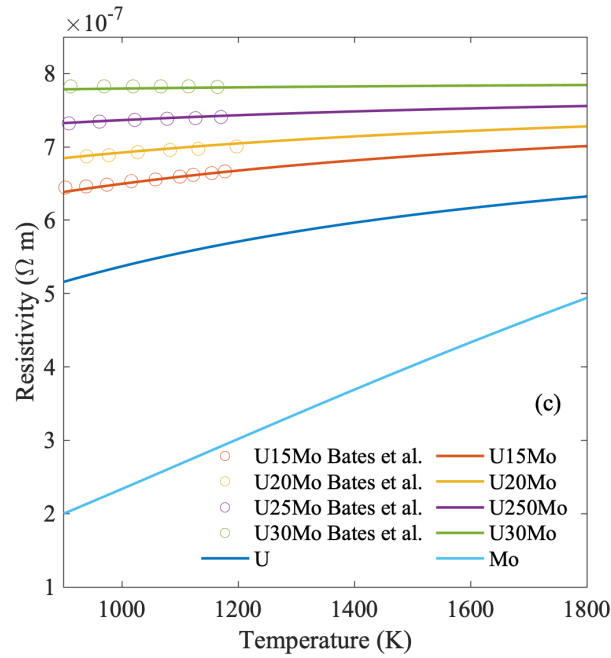


Figure 5.4. Plots of resistivity of (a) U-Zr over the temperature range of 850K to 1200K, (b) U-Nb over the temperature range of 850K to 1800K, and (c) U-Mo over the temperature range of 850K to 1800K. The curves with different colors indicate the different alloy compositions, in atomic percentage (at%). The open circles indicate the experimental resistivity from Refs. [152,177,178], and the filled circles in plot (a) are the resistivity calculated by Wiedemann-Franz law (WF law) with Touloukian et al.'s thermal conductivity data [17].

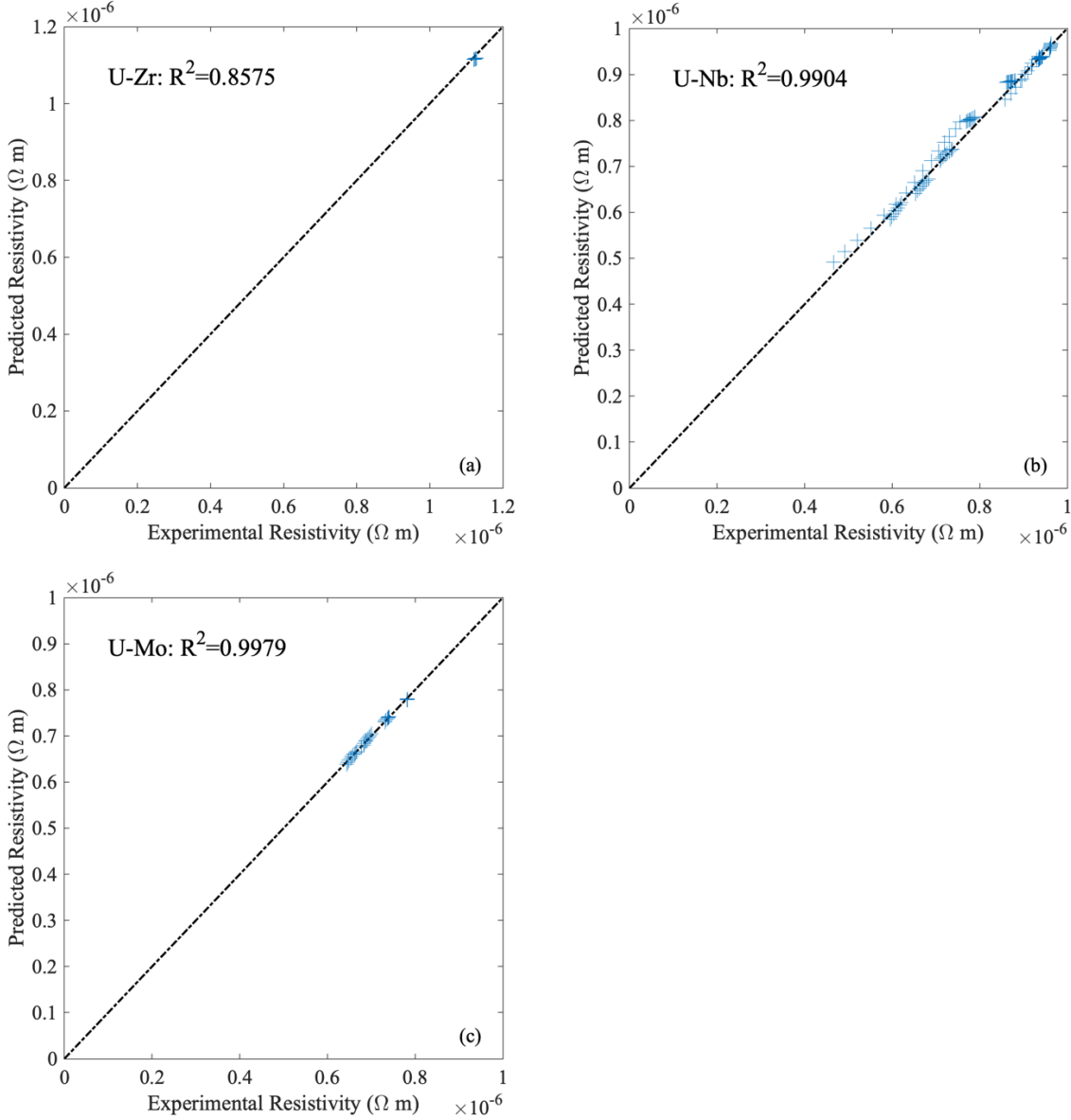
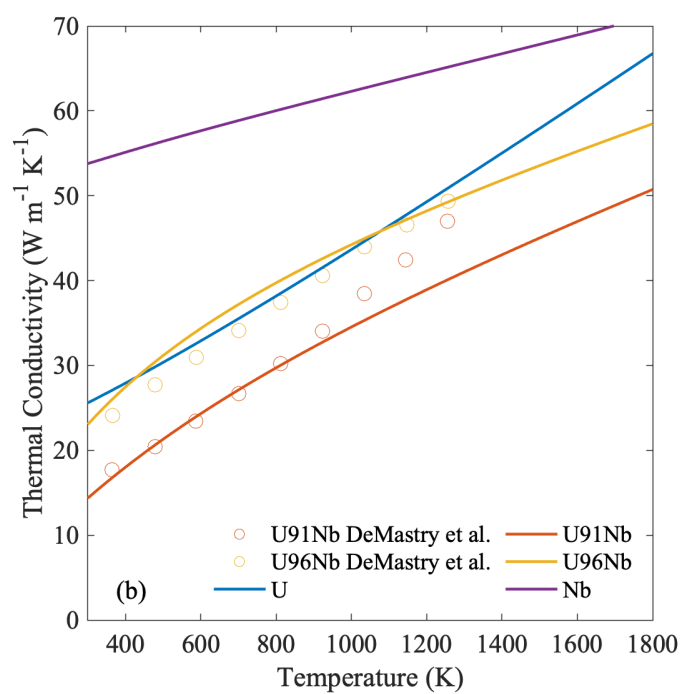
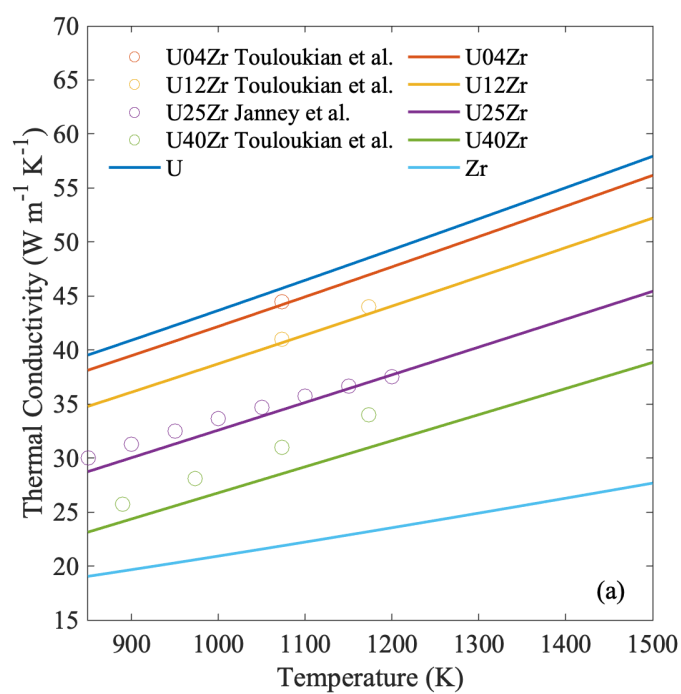


Figure 5.5. Plots of predicted resistivity by our model vs. experimental resistivity of (a) U-Zr, (b) U-Nb, and (c) U-Mo. The black dashed curves indicate that the predicted resistivity is equal to experimental resistivity. The values of the coefficient of determination (R^2) are also shown on the plots.

Then the thermal conductivity in our model can be calculated by the Wiedemann Franz law, Eq.(5.2), where the Lorenz numbers of alloys are interpolated from the elemental alloys by Eq.(5.19). The calculated thermal conductivity are presented in **Figure 5.6**, compared with experimental data. We also plot our predicted thermal conductivity vs. experimental thermal

conductivity in **Figure 5.7**. The values of the coefficient of determination (R^2) of U-Zr, U-Nb, and U-Mo are 0.99, 0.92, and 0.93, respectively. All R^2 values are higher than 0.9, which represents that our predicted thermal conductivity is highly correlated with experimental data. For U-Zr, U-Nb, and U-Mo, the ME values are $-1.12Wm^{-1}K^{-1}$, $0.05Wm^{-1}K^{-1}$, and $0.39Wm^{-1}K^{-1}$, respectively, and the RMSE values are $1.40Wm^{-1}K^{-1}$, $2.62Wm^{-1}K^{-1}$, and $1.52Wm^{-1}K^{-1}$, respectively. As the mean thermal conductivity values of the alloys at 1000K, estimated from the data of different compositions, are about $30Wm^{-1}K^{-1}$, $40Wm^{-1}K^{-1}$, and $35Wm^{-1}K^{-1}$, for U-Zr, U-Nb, and U-Mo respectively, the RMSE values equal to 4.7%, 6.5%, and 4.3% of the mean resistivity values at 1200K. Therefore, the RMSEs of U-Zr and U-Mo are both within the 5% criteria range, while the RMSE of U-Nb is slightly higher than the 5% criteria. Our modeled thermal conductivity have great agreements with experimental data.



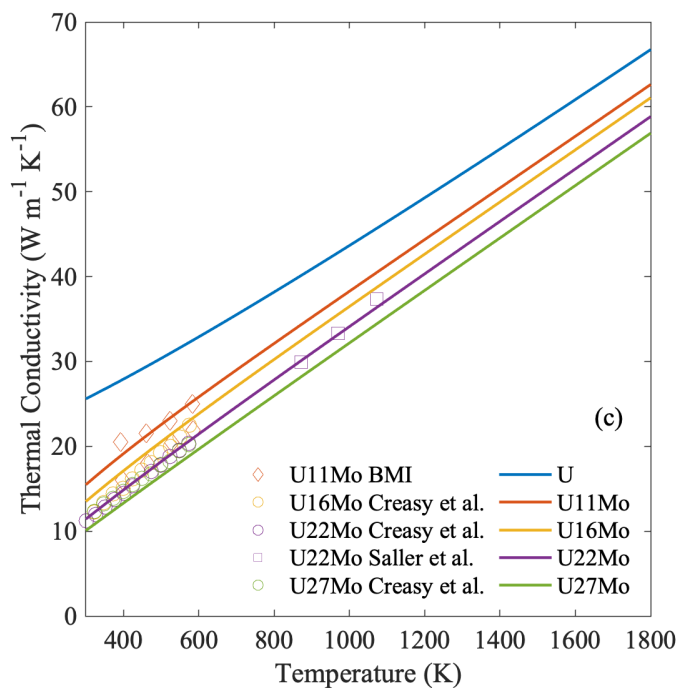


Figure 5.6. Plots of thermal conductivity of (a) U-Zr over the temperature range of 850K to 1200K, (b) U-Nb over the temperature range of 300K to 1800K, and (c) U-Mo over the temperature range of 300K to 1800K. The curves with different colors indicate the different alloy compositions, in atomic percentage (at%). The symbols indicate the experimental thermal conductivity from Refs. [17,18,22,24].

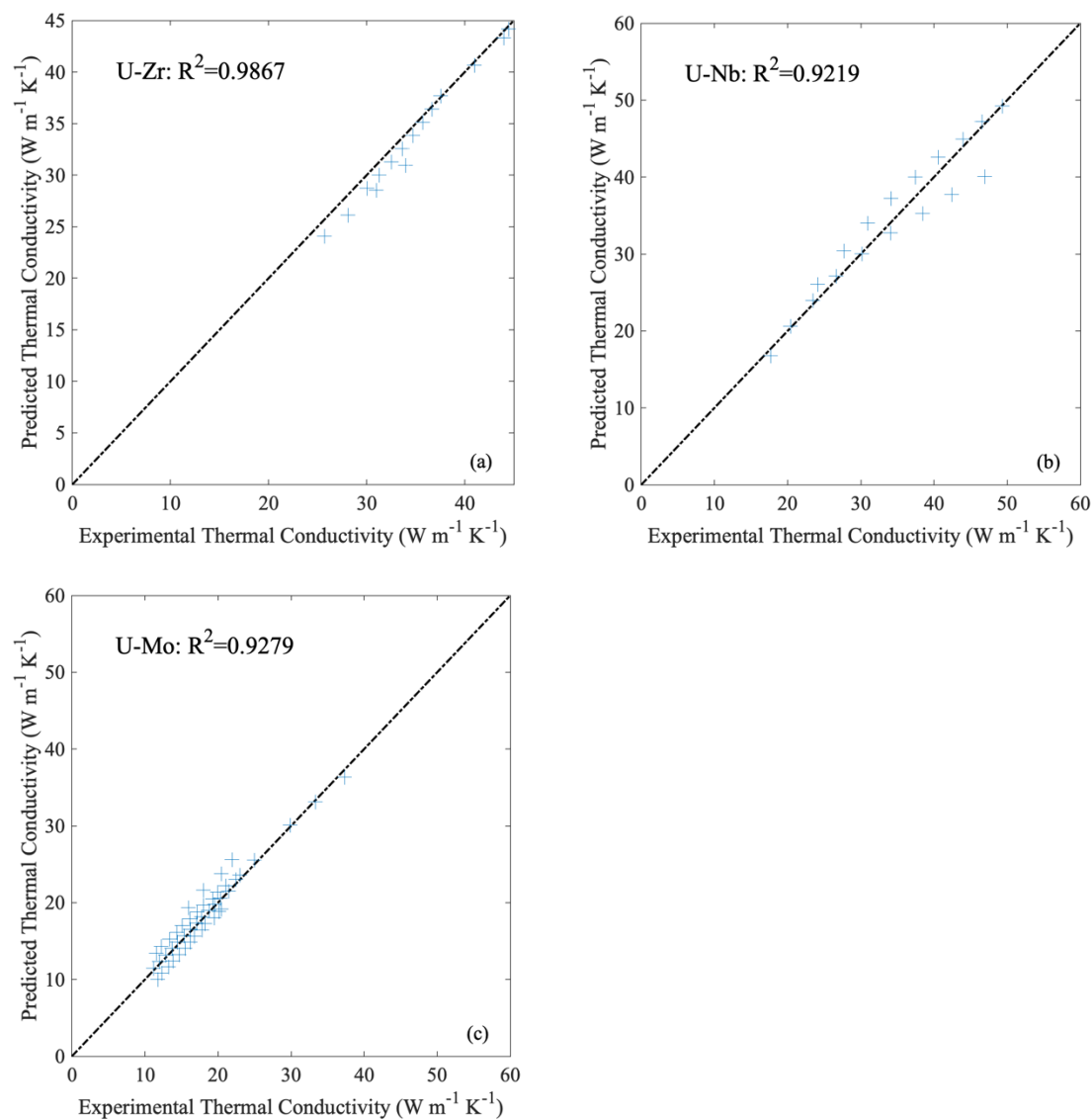


Figure 5.7. Plots of predicted thermal conductivity by our model vs. experimental thermal conductivity of (a) U-Zr, (b) U-Nb, and (c) U-Mo. The black dashed curves indicate that the predicted thermal conductivity is equal to experimental thermal conductivity. The values of the coefficient of determination (R^2) are also shown on the plots.

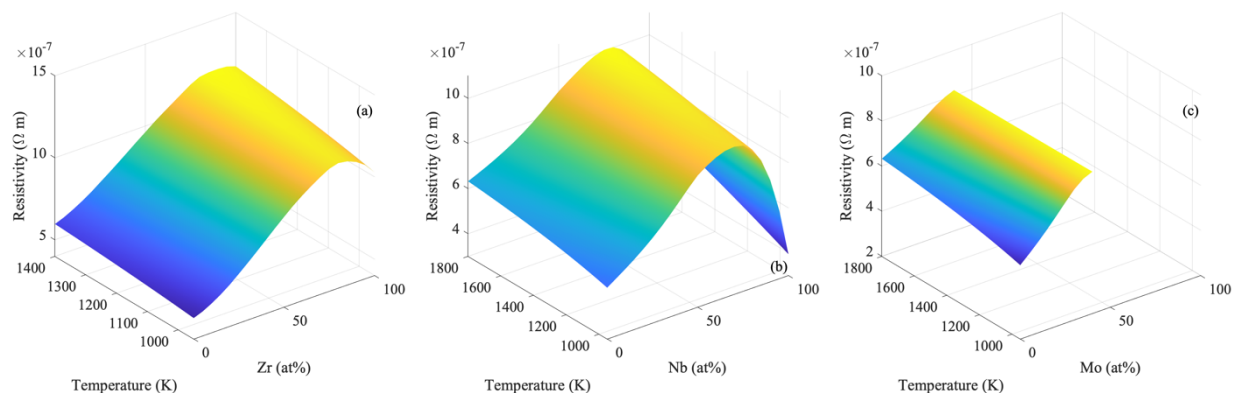
While we obtained good agreements with experimental data, we review here the input data requirement and fitting process here. In our model for a binary concentrated alloy, the data needed are the resistivity and/or thermal conductivity of the two elemental metals, and few data points of resistivity and/or thermal conductivity of the alloy. The data for elemental metals are used to fit the elemental metal model, which have 4 fitting parameters for each metal. The data for alloys are

used to fit the alloy residual resistivity model, which have 3 fitting parameters for each U alloy. Therefore, for each alloy, 11 fitting parameters in total are used in our model. However, as the existed data for alloys are more rare than them of elemental metals by the quantity and quality of the data, our model which requires only few alloy data are useful to predict the conductivity at wide temperature and composition range. E.g., the only two sets of U-Nb thermal conductivity data we found are for U-91at% Nb and U-96at% Nb. No experimental data is found for U-Nb when Nb at% < 90%, so it's impossible to use the traditional interpolation model to predict the thermal conductivity of U-Nb at that composition range. Another example is the U-Zr alloy which we only used four sets of alloy data in the fitting of residual resistivity, and there are only 7 data points in total for three sets of data among them. By our model we still get good agreement with U-Zr thermal conductivity data. As we mentioned in Section 5.2, due to the lack of experimental data, there is no established model for BCC U-Zr, U-Nb, and U-Mo as far as we know. They are the inputs from DFT calculations and the physical base of this model which help us to develop this model, which requires much less experimental data and produces accurate results.

To get a more direct look at the resistivity and thermal conductivity as functions of temperature and compositions, they are plotted as 3D plots in **Figure 5.8**. Again, for 95% > Mo at% > 40% in U-Mo, there is a two phase region, so only Mo at% < 40% is presented here. For these alloys in the plotted composition range, the resistivities are all slightly increasing with temperature. At the same temperature, the maximum resistivity and the minimum thermal conductivity occur at about U-80at% Zr and U-70at% Nb. For BCC phase U-Mo, as no data is available for Mo at% > 40%, the composition of the maximum resistivity and the minimum thermal conductivity is still uncertain. However, for U-Mo at temperature from 950K to 1400K, it has two single phase, (Mo) and (γ U). (Mo) has higher thermal conductivity than (γ U), so the

minimum thermal conductivity of U-Mo, as well as the maximum resistivity, occurs at about U-40at% Mo, which has the lowest thermal conductivity in (γ U) phase as shown in **Figure 5.8(f)**.

For U-Zr, the (α U)- δ (U,Zr)-(α Zr) region and the (γ U, β Zr) phase cover the most area of the solid phase in U-Zr phase diagram. The left regions in the phase diagram include a solid solution phase (β U), and three two phase regions, (γ U, β Zr)-(α Zr), (γ U, β Zr)-(α U), and (γ U, β Zr)-(β U). As the thermal conductivity model of (γ U, β Zr) is obtained by this work, and the thermal conductivity models of (α Zr) and (α U) are obtained by our previous work in Chapter 5, they can be combined to obtain the thermal conductivity of the two phase regions (γ U, β Zr)-(α Zr) and (γ U, β Zr)-(α U), using our multi-phase model in Chapter 5. For (β U), it can be modeled following our previous model of dilute solid solution. However, as β U has a temperature range of about only 100K near 1000K, the mean thermal conductivity value of (α U) and (γ U, β Zr) is taken as a quick estimation of the thermal conductivity of (β U). Therefore, we have developed thermal conductivity models for all solid phase of U-Zr above 300K, and the results from 300K to melting point are plotted in **Figure 5.9** as a function of temperature and composition.



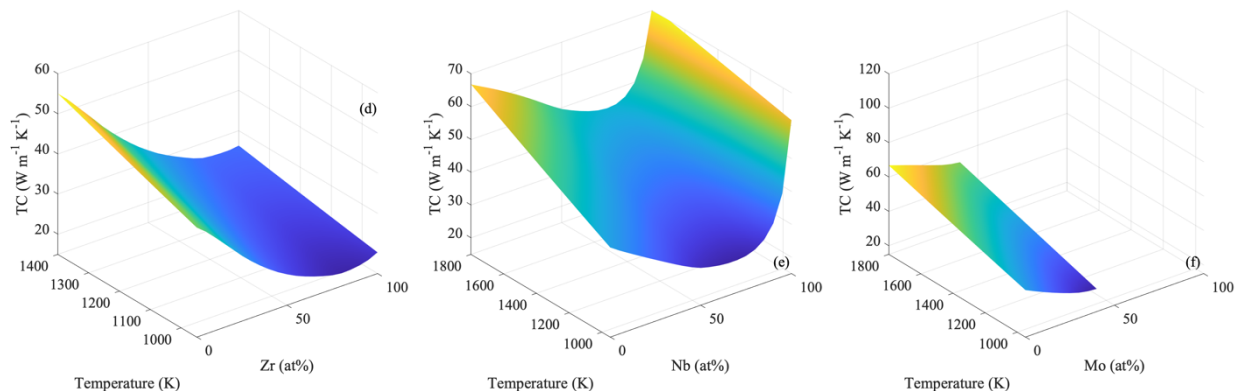


Figure 5.8. 3D Plots of our modeled resistivity of (a) U-Zr, (b) U-Nb, and (c) U-Mo, and our modeled thermal conductivity (TC) of (d) U-Zr, (e) U-Nb, and (f) U-Mo, as functions of temperature and composition.

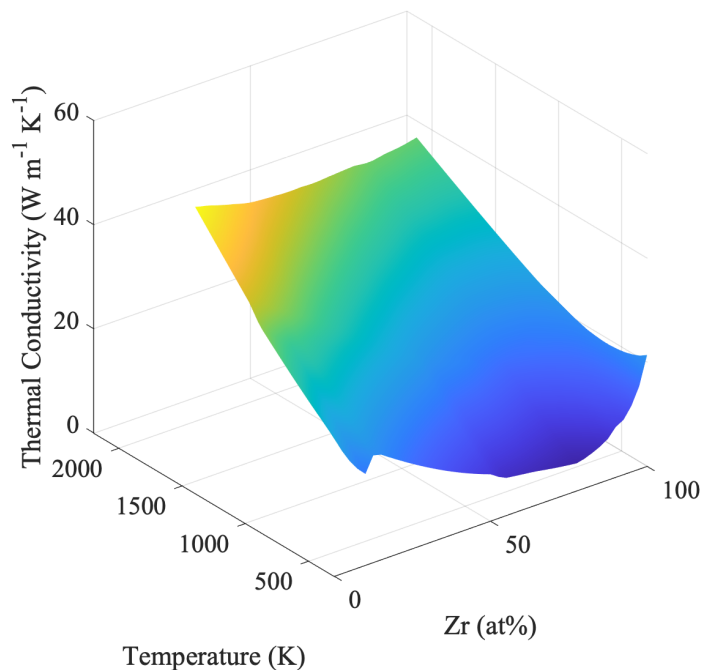


Figure 5.9. 3D Plots of our modeled thermal conductivity for U-Zr above 300K.

5.5 Conclusions

A physics-based computational model of thermal conductivity for binary concentrated alloys has been constructed, with an emphasis on BCC phase U-Zr, U-Nb, and U-Mo alloys. Our

model combines DFT calculations and DFT-BTE analysis together with experimental data to model the resistivity and thermal conductivity of elemental metals. The thermal conductivity model for elemental metals are reused to model the thermal conductivity of concentrated alloys, with extra DFT calculation inputs with SQS of alloys. With the reuse of elemental metal model and the extra inputs from DFT, this model requires few experimental data from alloy and can predict the thermal conductivity for a wide temperature and composition range. This model has been applied to BCC phase U-Zr, U-Nb, and U-Mo alloys and provides a baseline of typical thermal conductivity values for the contributions of concentrated alloying as a function of composition. The methodology developed here is extensible to thermal conductivity modeling of other metals and metal alloys for any application where heat management and thermal transport are key issues, thus functioning as a useful tool to guide further modeling of thermal conductivity to aid materials and device design.

Chapter 6 : Thermal Conductivity Modeling for Irradiation Effects in Metals: Demonstration on U-Mo

6.1 Chapter Abstract

In this work, we developed a computational model of thermal conductivity of irradiated metal and metal alloys based on density functional theory calculations and experimental data. The model incorporates the contributions of point defects (vacancies and transmutation products), grain boundaries, and noble gas bubbles (inter- and intra-granular) resulting from irradiation into the overall thermal conductivity. The model is demonstrated on α -U and U-Mo alloys and displays semi-quantitative agreement with experimental data, with a root-mean-square error of about 0.8 W/m-K ($\approx 7\%$ error versus experiment) over the typical operating temperature and burn-up range for U-Mo alloys. This work provides insight into the semi-quantitative relationships of the thermal conductivity changes resulting from the different irradiation-induced changes in atomic structure and microstructure over a wide range of temperatures, and shows that scattering of electrons from point defects produces the majority of the thermal conductivity reduction of U-Mo alloys under irradiation. Specifically, the effect of point defects decreases the thermal conductivity by about 20% when burn-up $>20\%$ (e.g. 50% burn-up), while grain boundary and gas bubble formation contribute only about another 10% reduction at 50% burn-up. The ability of our model to individually quantify the effect of different irradiation-related defects on the thermal conductivity as a function of temperature, composition, and irradiation conditions offers both a powerful tool for quantitative semi-empirical modeling of thermal conductivity in irradiated metals and materials design insight for the control of thermal conductivity in metal alloys in applications experiencing irradiation, such as next-generation nuclear reactors.

6.2 Introduction

Thermal conductivity is an important physical property which describes the heat transfer rate of a material, and high-quality thermal conductivity data is critical to many technologies, ranging from thermoelectrics to nuclear reactors. Experimental thermal conductivity data is often difficult to obtain over a range of temperature, composition and sample microstructure (e.g. single versus polycrystalline thermal conductivity data), due to the high cost and time required for traditional thermal conductivity measurement techniques [1,2]. Therefore, thermal conductivity modeling is widely used to understand the impact of temperature, composition and microstructure on the thermal conductivity. Different methods to construct models of the thermal conductivity exist, and each method has its own strengths and weaknesses. Simple empirical interpolation formulae [17,25,161] are effective for interpolating between measured experimental data, but provide little physical insight and, to be accurate, require significant amounts of experimental data adequately close to the conditions targeted by the prediction. Thermal conductivity has also been modeled using density functional theory (DFT) calculations [6,7], which are based on the fundamental equations of quantum mechanics and heat transport and require little or no experimental data. These DFT-based models provide detailed information of the electronic and vibrational materials properties (such as electronic and phonon band structures and densities of states), but are often technically challenging to implement, limited to a specific mechanism and/or composition or temperature range (thus limiting their ability to extrapolate to new regimes of temperature or composition), and are of limited quantitative accuracy. Therefore, there is a need for the development of fast, practical thermal conductivity models which integrate theory and experiment to provide both understanding and quantitative prediction. Such techniques are particularly valuable in fields with limited data for materials design guidance, such as is often the case for nuclear reactor materials.

Many metals and metal alloys are used in applications experiencing irradiation and the irradiation can significantly influence their thermal conductivity. Such radiation effects can be critical to materials performance, e.g., as in the case of cladding and fuels used in nuclear reactors. The challenges of using either purely empirical or *ab initio*-based models are only increased when incorporating irradiation effects, which often have limited data and complex changes in structure from the atomic to micron length scales. Therefore, an integrated experimental and computational approach is potentially particularly valuable for modeling the thermal conductivity of irradiated metals and metal alloys.

Our previous work [115] developed an integrated experimental and computational model of the thermal conductivity for α -U, U-Mo and U-Zr alloys over a wide temperature and composition range. This model provided fundamental understanding of the physical mechanisms governing the thermal conductivity of α -U, U-Mo and U-Zr alloys in terms of different electron and phonon scattering mechanisms. However, this model did not include the effects of irradiation on the thermal conductivity, and the extension of our previous work to include radiation effects is the goal of the present work.

Metals and metal alloys are widely used in commercial nuclear reactors, such as the use of zirconium (Zr) alloys as fuel rod cladding in light water reactors [179]. In addition, metals and metal alloys are being considered for use in future nuclear reactor designs, such as metallic uranium (U) alloys as the nuclear fuel in fast reactors [9]. Irradiation influences the microstructure of metal alloys via multiple mechanisms, including the creation of point defects (vacancies and interstitials [180], and transmutation products like xenon (Xe) atoms [181]), formation of noble gas bubbles [181–183], changes in grain size [184,185], and precipitate formation [184,186]. These irradiation effects can significantly decrease the thermal conductivity of metal alloys, with

reductions of up to 45% as shown in the work of Burkes *et al.* [183] for U-Mo alloy. The thermal conductivity reduction will lead to larger temperature gradients from the center to the edge of the fuel and potentially higher than desired temperatures in the center of the fuel. Severe overheating can lead to reactor malfunction or meltdown. Therefore, for metal alloys used in applications involving irradiation, where understanding and controlling heat transfer processes is critical, knowledge of the thermal conductivity and its evolution under different irradiation conditions is of central concern.

For irradiated metals and metal alloys, the length scales of different irradiation effects vary from the atomistic scale (i.e. the diameter of point defects is $\sim 1\text{\AA}$) to the microscale (i.e. the grain diameter in irradiated metal fuel alloys is typically $\sim 1\mu\text{m}$ [185]). For these different irradiation effects comprising different length scales, different methods have been applied to model their contributions to transport properties such as electrical resistivity and thermal conductivity. For the effects of point defects on resistivity, theoretical calculation methods were developed in the 1970s with the pseudopotential approach [187,188]. Recently, by combining the Boltzmann transport equation (BTE) with *ab initio* electronic structure calculations, an *ab initio* approach for calculating transport properties was developed and has been applied to the effect of dopants on the resistivity in diamond [189], the Heusler compound CoTiSb [190] and Ag-Cu alloy [128], and to vacancies in metals like W [129]. For the effects of gas bubbles on transport properties, a number of analytical and empirical models have been built [191–195]. In addition, direct numerical solutions, e.g., with finite element methods, are quite practical. For example, the phase field method was recently applied to simulate the bubble distribution and grain evolution in U oxide fuels [196,197] and in metallic U fuels [198], and was combined with the finite element method to calculate the thermal conductivity of U alloys [196,199,200].

Since the 1950s, many experiments have been conducted to measure the behavior of metallic fuels under irradiation [186,201,202,9]. More recently, due to increased interest in applying metallic U alloy fuels for next generation nuclear reactors, more detailed experiments have characterized the irradiation effects under different burn-up (the burn-up is the fraction of fuel atoms that have undergone fission) for multiple metal alloy fuels [183,203–207]. Among them, some experiments measured the thermal conductivity under irradiation [183,195], but experiments comparing the thermal conductivity over a wide range of irradiation conditions, temperature and compositions are rare, and the only example to our knowledge is Burkes *et al.*'s experiments on U-Mo alloys [183]. Therefore, Burkes *et al.*'s data will be used in the present work to assess our approach.

Despite these modeling and experimental advances characterizing the transport properties for a variety of materials, including under irradiation, a model of thermal conductivity which integrates the effect of dopants, gas bubbles, and grain evolution occurring as a result of irradiation, and the relative contributions of these microstructural factors on the thermal conductivity, has not been formulated. To address this problem, in this work we developed a thermal conductivity model for irradiated α -U and U-Mo alloys that combines *ab initio* methods for modeling the effect of point defects and analytical equations to model the effect of noble gas bubbles and grain boundaries on the thermal conductivity. Our model enables the straightforward prediction of thermal conductivity values under different irradiation conditions and quantifies the relative contribution of point defects, grain boundaries, and gas bubbles to the thermal conductivity. In this work, we build from our previous model, which was developed for modeling the thermal conductivity of non-irradiated α -U as a function of temperature [115].

Metallic U alloys possess multiple advantages compared to the UO_2 -based fuels that are widely used in both current thermal and fast nuclear reactors, including: higher thermal conductivity, high burn-up capability, ease of recycling, and lower radiotoxicity of nuclear waste [9,10]. These advantages make metallic U alloys promising materials for use as nuclear fuels in thermal reactors and especially in the future deployment of fast reactors as Generation IV nuclear reactor designs [11]. The model formulated in this work is demonstrated on irradiated α -U and irradiated U-Mo alloys to understand the magnitude of change in thermal conductivity due to different irradiation effects, which will help improve temperature control and guide the use of metallic U alloys in reactor environments. More specifically, this model is able to predict the thermal conductivity under different irradiation conditions, and, importantly, is extensible to more realistic metallic alloy fuels that include other irradiation effects such as impurities, transmutation product precipitates, and dislocations.

6.3 Methods

As mentioned in Section 6.2, the thermal conductivity of irradiated metallic U alloy fuels is affected by multiple physical effects produced by irradiation. Following the approach proposed by Lucuta *et al.* [208], our model combines these different irradiation-induced effects by a multiplicative decomposition:

$$\kappa_{eff} = f_{pd} f_{intra} f_{inter+gb} \kappa_0, \quad (6.1)$$

where κ_{eff} and κ_0 are the effective thermal conductivity under irradiation and the thermal conductivity for the pure metal or metal alloy, respectively. The f factors are the thermal conductivity degradation factors for each irradiation effect and $0 < f < 1$. More specifically, the f factors include f_{pd} for the effect of point defects, f_{intra} for the effect of intragranular noble gas

bubbles, and $f_{inter+gb}$ for the effect of intergranular noble gas bubbles and grain boundaries. The details of modeling the degradation factors of point defects, intragranular noble gas bubbles, and intergranular noble gas bubbles and grain boundaries is presented in Section 6.3.1, 6.3.2 and 6.3.3, respectively, in the order of length scale from smallest (point defects) to largest (grain boundaries).

6.3.1 Computational model of degradation factor of point defects

6.3.1.1 Summary of approach

We first summarize the overall approach, which involves the following steps:

1. Express the total thermal conductivity as the sum of the electron and phonon thermal conductivity contributions (Eq. (6.2)).
2. Assume the effects of point defects on the phonon contribution to the thermal conductivity are negligible and therefore focus only on point defect effects on the electronic contribution to the thermal conductivity.
3. Use the Wiedemann-Franz law to determine point defect effects on the thermal conductivity from point defect effects on electronic conductivity/resistivity (Eqs (6.3)-(6.4)).
4. Calculate the electronic resistivity contributions due to phonon, electron and point defect scattering mechanisms without the resistivity saturation effect (Eqs. (6.5)-(6.6)) through the DFT-BTE approach (Appendix I), where the computational details for α -U are presented in Section 6.3.4.
5. Combine the electronic resistivity contributions with the resistivity saturation effect using Cote *et al.*'s formula (Eq. (6.10)) to get the electronic resistivity change due to a single type of point defect.

6. Add the resistivity change due to every type of point defect to obtain the total resistivity change due to all point defect types (Eq. (6.14)).

In the rest of this section, we discuss each of the above steps in more detail, referencing each step to allow easy connection between the summary above and the detailed discussion below.

6.3.1.2 f_{pd} of single type of point defect

In metals like α -U, the thermal conductivity κ is the sum of electron and phonon thermal conductivities [62] (Step 1 Section 6.3.1.1):

$$\kappa = \kappa_e + \kappa_{ph}. \quad (6.2)$$

For α -U, the phonon contribution to the thermal conductivity is only 2%-9% for 400-933K [115]. Therefore, we can approximate the irradiation-induced changes in thermal conductivity of pure U by considering irradiation effects on just the electronic contribution (Step 2 Section 6.3.1.1), and we will make this approximation in developing the present model. The much smaller contribution of phonons to the overall thermal conductivity compared to the contribution from electrons is expected to hold for U alloys and many other metals and metal alloys under a wide-range of conditions, so this approximation is expected to be widely applicable. However, it will certainly break down under some conditions (e.g., low temperature), in which cases the approximation and the model developed in this work will not be accurate. The electronic thermal conductivity κ_e is related to the electrical resistivity by the Wiedemann-Franz law [29] (Step 3 Section 6.3.1.1):

$$\kappa_e(T) = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 \frac{T}{\rho(T)}. \quad (6.3)$$

Therefore, for f_{pd} , we have:

$$f_{pd}(c, T) = \frac{\kappa(c, T)}{\kappa(0, T)} \approx \frac{\rho(0, T)}{\rho(c, T)}, \quad (6.4)$$

where c is the concentration of a single type of point defect, $\kappa(0, T)$ and $\rho(0, T)$ are the thermal conductivity and resistivity for the undefected metal or metal alloy as a function of temperature (they may also be denoted as κ_0 and ρ_0 for convenience), and $\kappa(c, T)$ and $\rho(c, T)$ are the thermal conductivity and resistivity for the metal containing point defects with concentration c . For α -U, the value of ρ_0 is known from experiments [25], which is also true for most metals [150] and many metal alloys, while the values of $f_{pd}(c, T)$ and $\rho(c, T)$ depend on the concentration of point defects as well as temperature.

For ideal metals, by which we mean metals where the resistivity saturation effect can be neglected because their resistivity values are much lower than their saturation resistivities, the point defects increase the resistivity by two mechanisms: (1) through changes to the electronic band structure and (2) through the decrease of electron-electron scattering time. For metals like U alloys, where the resistivity saturation effect plays an important role, it is useful to treat the resistivity as having an ideal contribution, which is modeled with the semiclassical BTE approach, and then modify this ideal contribution with a saturation effect, which was how we treated the resistivity of α -U in our previous work [115]. Therefore, we first calculate the point defect effects in the ideal contribution, then add the resistivity saturation effect. Throughout this work, we will use ρ_{id} to represent the ideal resistivity contribution without saturation effects due to electron-electron and electron-phonon scattering, and ρ_{pd} to represent the resistivity contribution of electron-(point defect) scattering without saturation effects, similar to the notation used in Gomi *et al.*'s work for Fe alloys [121].

For these resistivity contributions ρ_{id} and ρ_{pd} , the DFT-BTE approach (see Appendix I) is applied with correlated electron relaxation times τ (Step 4 Section 6.3.1.1):

$$\rho_{id}(c, T) = \frac{1}{s(c, T)\tau_{id}(T)}, \quad (6.5)$$

$$\rho_{pd}(c, T) = \frac{1}{s(c, T)\tau_{pd}(c)}, \quad (6.6)$$

where $s(c, T) \equiv \frac{\sigma(c, T)}{\tau(c, T)}$ (the electrical conductivity divided by the electronic relaxation time) is calculated using DFT-BTE for the metal containing point defects with concentration c (note that $s(0, T)$ is for the undefected metal and may also be written as s_0). $\tau_{id}(T)$ is the electronic relaxation time for the undefected metal without the resistivity saturation effect, which contains information on the electron scattering such as electron-electron and electron-phonon scattering. For α -U, $\tau_{id}(T)$ can be calculated by Eq. (6.5) with the $\rho_{id}(0, T)$ values obtained in our previous work [115] and the calculated s_0 as $\tau_{id}(T) = 1/(s_0\rho_{id}(0, T))$. $\tau_{pd}(c)$ is the electronic relaxation time of electron-(point defect) scattering without the saturation effect, which is calculated using the semi-classical formula [29]:

$$\tau_{pd}(c) = \frac{V_{atom}}{cA_{cs}v_F} = \frac{V_{atom}}{cA_{cs}} \sqrt{\frac{m_e}{2E_F}}, \quad (6.7)$$

where V_{atom} is the volume per atom, c is the concentration of point defects, A_{cs} is the area of electron-(point defect) scattering cross section (for an atomic sized point defect this should be on the scale of πr_{atom}^2 , where r_{atom} is the radius of the atom [29] (for example, in for α -U the scattering cross section is about $9\text{\AA}^2$, determined from the atomic volume in **Table 6.1**), m_e is the electron mass, and E_F and v_F are the Fermi energy and Fermi velocity, respectively. V_{atom} , v_F and E_F can be calculated by DFT and their values for α -U are presented in **Table 6.1**. The value of A_{cs} for α -U is also presented in **Table 6.1**, and the rationale for the choice of its value is discussed in Section 6.4.1.

$s(c, T)$ can be calculated by the DFT-BTE approach (Appendix I) for concentrated alloys. However, experimentally observed point defect concentrations for metals are much lower than typical concentrations used in DFT calculations, due to limitations in the system size that can be simulated with DFT. As the point defect concentration discussed in this work is dilute, at the dilute limit $c \ll 1$, $s(c, T)$ is approximately equal to $s_0(T)$, which means the perturbation of electron band structure due to dilute point defects can be neglected in this work:

$$s(c, T) \approx s_0(T), \text{ for } c \ll 1. \quad (6.8)$$

From Eq.(6.5), $\rho_{id}(c, T)$ only depends on the defect concentration c from $s(c, T)$. Based on the assumption of dilute defect concentration and Eq. (6.8), the ideal resistivity contribution ρ_{id} is also unchanged at the dilute limit: $\rho_{id}(c, T) \approx \rho_{id}(0, T)$, for $c \ll 1$.

For ideal materials without the resistivity saturation effect, ρ_{id} (the resistivity contributions of electron-electron and electron-phonon scattering) and ρ_{pd} (the electron-(point defect) scattering contribution) can be combined into a total resistivity using Matthiessen's rule [29]: $\rho = \rho_{id} + \rho_{pd}$. For materials with the resistivity saturation effect, there is some uncertainty on how the saturation effect should be combined with other scattering mechanisms, and the answer depends on the physics giving rise to the resistivity saturation. Various theories explaining the sources of the resistivity saturation effect have been proposed since the 1970s, which are summarized in Gunnarsson *et al.*'s review [119]. However, there is still no single accepted theory to explain, or generally accepted formula to express, the resistivity saturation effect of a complex alloy. Here, we follow Cote *et al.*'s formula [120] which was developed to add the resistivity saturation effect in disordered alloys (Step 5 Section 6.3.1.1). Cote *et al.*'s formula [120] was recently successfully applied to model the resistivity of Fe alloys and can be written [121]:

$$\rho(c, T) = \left(1 - \frac{\rho(c, T)}{\rho_{sat}}\right) \rho_{id}(c, T) + \rho_{pd}(c, T) e^{-2W(T)}, \quad (6.9)$$

where ρ_{sat} is the saturation resistivity, and the $e^{-2W(T)}$ term is the Debye-Waller factor which is generally negligible [121–123]. For example, it was previously verified by Gomi et al. [121] using a Debye model that for Fe, $1 > e^{-2W(T)} > 0.99$ below 1000K, and $1 > e^{-2W(T)} > 0.95$ below 5000K. Rearranging Eq. (6.9) and assuming $e^{-2W(T)} = 1$ the total resistivity ρ can be related to ρ_{id} , ρ_{pd} , and ρ_{sat} by the equation:

$$\rho(c, T) = \frac{\rho_{id}(c, T) + \rho_{pd}(c, T)}{1 + \rho_{id}(c, T)/\rho_{sat}}. \quad (6.10)$$

Note that for pure metals for which $\rho_{pd}(c, T) \approx 0$, this equation reduces to $\rho^{-1} = \rho_{id}^{-1} + \rho_{sat}^{-1}$, which is Wiesmann *et al.*'s parallel resistor formula [119,124] used in our previous work for pure α -U [115].

To summarize, the resistivity of metals containing a single type of point defect with concentration c in our model is given by

$$\rho(c, T) = \frac{\rho_{id}(0, T) + \frac{c A_{cs}}{s_0(T) V_{atom}} \sqrt{\frac{2E_F}{m_e}}}{1 + \frac{\rho_{id}(0, T)}{\rho_{sat}}}, \quad (6.11)$$

where $\rho_{id}(0, T)$ and ρ_{sat} are obtained from our previous approach for undefected metals with the resistivity saturation effect and applied to α -U [8], s_0 , E_F , and V_{atom} are calculated by electronic DFT-BTE calculations, and A_{cs} is the electron-(point defect) scattering cross section given in **Table 6.1**.

6.3.1.3 f_{pd} of multiple types of point defects

Eq. (6.11) provides the contribution from just a single point defect, so to determine the total resistivity of the metal containing multiple types of point defects we need to develop a way

to extend Eq. (6.4). To do this extension we first consider the value of residual resistivity of a single type of point defect by

$$\rho_{res}(c, T) = \rho(c, T) - \rho_0(T). \quad (6.12)$$

Our results show that for the case of dilute point defects, $\rho_{res}(c, T)$ is approximately constant vs. temperature, and that Matthiessen's rule [29] $\rho_{res}(c, T) \propto c$ approximately holds, which will be presented in Section 6.4.1 in detail. Assuming the effects arising from different types of point defects are independent of each other, the total resistivity of metals containing multiple types of point defects is given by [131]:

$$\rho(c_1, c_2, \dots, c_n, T) = \rho_0(T) + \sum_{X=1}^n \rho_{res,X}(c_X, T), \quad (6.13)$$

where X denotes the different types of point defects, e.g. vacancy, interstitial, soluble transmutation product atoms, etc. As an example, in Section 6.4.1, we consider X = single vacancy, and substitutional helium (He), krypton (Kr), and Xe atoms in the U alloy matrix. However, this framework is general and is expected to work for many kinds of point defect and point defect complexes at low concentration, so long as the effects arising from different types of point defects are independent of each other [131].

From the above analysis, the f factor for the effect of point defects f_{pd} is given by (Step 6 Section 6.3.1.1):

$$f_{pd}(T) = \frac{\rho_0(T)}{\rho(c_1, c_2, \dots, c_n, T)} = \frac{\rho_0(T)}{\rho_0(T) + \sum_{X=1}^n \rho_{res,X}(c_X, T)}, \quad (6.14)$$

where $\rho_{res,X}(c_X, T)$ is calculated by Eqs. (6.11)-(6.12).

In summary, throughout this analysis in Section 6.3.1 to obtain Eq.(6.14), the approximations we made were: (1) the electronic thermal conductivity dominates the total thermal conductivity and the modification of the phonon thermal conductivity can thus be neglected (e.g.

$T > 400\text{K}$ on $\alpha\text{-U}$ for which electronic thermal conductivity is $> 90\%$ of total thermal conductivity); (2) the relaxation time approximation (RTA) is accurate (it is used in the DFT-BTE approach); (3) the resistivity saturation effect is described using Cote *et al.*'s formula (Eqs. (6.9)-(6.10)); (4) the point defect concentrations are dilute, and the effects arising from different types of point defects are independent of each other.

6.3.2 Computational model of degradation factor of intragranular bubbles

Irradiation produces transmutation products like Xe atoms, and these atoms form fission gas bubbles at high burn-up, including intragranular bubbles within the grains and intergranular bubbles at grain boundaries. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) results have shown that typical intragranular bubbles have a diameter of $\approx 2\text{nm}$ and a bubble spacing of $\approx 6\text{nm}$ in U-Mo alloy for about 35% burn-up [182,209]. As the thermal conductivity of a gas is much smaller than the thermal conductivity of metals, these intragranular and intergranular bubbles may significantly decrease the thermal conductivity. As mentioned in Section 6.2, analytical and empirical models have already been formulated to treat the effect of these bubbles on the thermal conductivity, particularly for relatively uniformly distributed intragranular bubbles, including: Maxwell-Eucken [116,191] (Eq. (6.15)), effective mean field (EMT, or so-called Bruggeman model) [26,116] (Eq. (6.16)), Cunningham and Peddicord [210] (Eq. (6.17)), and Bauer's model [194] (Eq. (6.18)):

$$f_{intra} = \frac{2k_m + k_p - 2p_{intra}(k_m - k_p)}{2k_m + k_p + p_{intra}(k_m - k_p)}, \quad (6.15)$$

$$f_{intra} = 1/4 \left\{ (3p_{intra} - 1) \frac{k_p}{k_m} + (2 - 3p_{intra}) + \sqrt{\left[(3p_{intra} - 1) \frac{k_p}{k_m} + (2 - 3p_{intra}) \right]^2 + 8 \frac{k_p}{k_m}} \right\}, \quad (6.16)$$

$$f_{intra} = e^{-2.14p_{intra}}, \quad (6.17)$$

$$f_{intra} = (1 - p_{intra})^{2.58}, \quad (6.18)$$

where p_{intra} is the porosity (volume fraction) of intragranular bubbles, and k_p and k_m are the thermal conductivity in the porous noble gas bubbles and of the metal matrix, respectively. For bubbles the limit of $k_p \ll k_m \Rightarrow \frac{k_p}{k_m} \approx 0$, which holds in this work, Eqs. (6.15)-(6.16) approximately give the same results. p_{intra} can be related to the production of transmutation product gasses by the number of transmutation product atoms per unit volume of material in the grain, n_{intra} , and the volume per atom in intragranular bubbles v_{intra} : $p_{intra} = n_{intra}v_{intra}$.

In experiments, it is difficult to separate the contributions of intragranular and intergranular bubbles on the thermal conductivity. In particular, to our knowledge, no experimental study showing the decrease of thermal conductivity of metallic U alloys due to just intragranular bubbles is available. Therefore, modeling the contribution of intragranular bubbles on the thermal conductivity must be done without direct experimental data for validation. To evaluate which of the known empirical models of incorporating intragranular bubbles is most accurate, we use the recent calculation results of Hu *et al.*'s 3D phase-field simulations [198] and Lasir *et al.*'s 2D finite element calculations [200] for U-Mo alloy to compare with known empirical models. The results of these comparisons will be presented in Section 6.4.2. As a summary, we found that Bauer's model (Eq. (6.18)) has the best agreement with the simulation results of Hu *et al.* [26] and Lasir *et al.* [28] for U-Mo alloy, and is therefore best suited to describe the degradation factor of intragranular bubbles f_{intra} for U alloys in this work.

6.3.3 Computational model of degradation factor of grain boundaries and intergranular bubbles

In polycrystalline materials, grain boundaries reduce the thermal conductivity due to the discontinuities in the crystal lattice acting as scattering sites. In irradiated U alloys, large noble gas bubbles, which for U-Mo alloy with about 35% burn-up have a diameter of $\approx 0.15\mu\text{m}$ and a typical separation of $\approx 0.4\mu\text{m}$, have been shown to appear at grain boundaries [203]. These intergranular bubbles couple with the grain boundary, and collectively decrease the thermal conductivity in irradiated U alloys with reductions in the thermal conductivity due to both the presence of the grain boundary and the presence of the intergranular bubbles.

We first consider the degradation factor of only the grain boundary f_{gb} . We use the DFT-BTE approach for modeling the effect of the grain boundary, which is similar to Eq. (6.4), and f_{gb} is given by:

$$f_{gb} = \frac{\rho_0}{\rho}, \quad (6.19)$$

where ρ_0 is the resistivity for a single-crystal undefected metal, and ρ is the total resistivity in a polycrystalline metal containing grain boundaries with no other defects. Similar to Eq. (6.10), $\rho_0 = \frac{\rho_{id}}{1+\rho_{id}/\rho_{sat}}$, and $\rho = \frac{\rho_{id}+\rho_{gb}}{1+\rho_{id}/\rho_{sat}}$, where ρ_{gb} is the resistivity contribution of electron-(grain boundary) scattering. Similar to Eqs. (6.5)-(6.6), $\rho_{id} = \frac{1}{s_0\tau_{id}}$, and $\rho_{gb} = \frac{1}{s_0\tau_{gb}}$. We assume the grain boundary functions as a purely short-range interfacial effect, which only changes the electronic relaxation time and doesn't change the bulk electronic structure. Therefore, $s = \left(\frac{\sigma}{\tau}\right)$ is identical whether grain boundaries are present or not, and s takes the value of the single-crystal undefected metal s_0 . τ_{gb} is the relaxation time for electron-grain boundary scattering, which is calculated using the semi-classical formula [211]:

$$\tau_{gb} = \frac{2D}{3Pv_F} = \frac{2D}{3P} \sqrt{\frac{m_e}{2E_F}}, \quad (6.20)$$

where D is the grain size, $\frac{2}{3}D$ is the average distance between two spherical grain boundaries [211], and P is the probability of an electron scattering with the grain boundary when passing through it, which has values $0 < P < 1$. Therefore, by combining Eqs. (6.20)-(6.21), f_{gb} is given by:

$$f_{gb} = \frac{1}{1 + \frac{\tau_{id}}{\tau_{gb}}} = \frac{1}{1 + \frac{3P}{2Ds_0\rho_{id}\sqrt{\frac{2E_F}{m_e}}}}. \quad (6.21)$$

The calculation results will be presented in detail in Section 6.4.3, and the main result is communicated here. We found that for most cases, f_{gb} is >0.99 , which means the contribution of the grain boundary itself to the thermal conductivity decrease is $<1\%$. Therefore, the effect of grain boundaries is almost negligible, which has also been shown by the theoretical calculation of Brailsford and Major [212]. Therefore, the total effect of the grain boundary interface is dominated by the contribution of intergranular bubbles. Although the effect of grain boundaries and the effect of intergranular bubbles are coupled, since the effect of grain boundaries is $<1\%$, the contributions of grain boundaries and intergranular bubbles are approximately identical to the contribution of only the intergranular bubbles:

$$f_{gb-inter} \approx f_{inter}. \quad (6.22)$$

Note in Eq. (6.22), $f_{gb} = \frac{1}{1 + \frac{\tau_{id}}{\tau_{gb}}}$, τ_{gb} can be replaced by the scattering relaxation time of other scattering processes, e.g. scattering of electrons off dislocations, to calculate the effect of other defect types on the thermal conductivity.

For the effect of intergranular bubbles, we combine Bauer's empirical model (Eq. (6.18)) and an analytical model of electronic resistors following the work of Tonks *et al.* for UO_2 [213], to give f_{inter} as a function of intergranular bubble porosity p_{inter} :

$$f_{inter} = \frac{1}{1 + 3.20p_{inter}}. \quad (6.23)$$

To connect Eq. (6.24) with experiments, p_{inter} can be derived using measurable parameters like bubble size d , bubble density per grain area ρ_s , and grain size D . With these parameters f_{inter} is also given:

$$f_{inter} = \frac{1}{1+5.03\frac{\rho_s d^3}{D}}. \quad (6.24)$$

The derivation of f_{inter} is shown in Appendix II, and the results of the effect of intergranular bubbles on the thermal conductivity by applying Eq. To connect Eq. (6.24) with experiments, p_{inter} can be derived using measurable parameters like bubble size d , bubble density per grain area ρ_s , and grain size D . With these parameters f_{inter} is also given: is detailed in Section 6.4.3. Similarly with p_{intra} , p_{inter} can be related to the production of transmutation products by the number of transmutation product atoms per unit volume at the grain boundary, n_{inter} , and the volume per atom of the intergranular bubbles v_{inter} : $p_{inter} = n_{inter}v_{inter}$.

6.3.4 Computational details of DFT calculations

All DFT calculations were performed with periodic boundary conditions with a plane-wave basis set using the Vienna Ab initio Simulation Package (VASP) [214,215]. Initial atomic coordinates for α -U were obtained from the orthorhombic structure (Space group: $Cmcm$, No. 63) based on the work in Refs. [136,137]. The electron-ion interaction of U uses the projector augmented wave (PAW) method [142] as implemented by Kresse and Joubert [82]. The valence electron configuration for the U pseudopotential was $6s^2 6p^6 7s^2 5f^3 6d^1$. The exchange correlation functional parameterized in the generalized gradient approximation (GGA) [83] by Perdew, Burke, and Ernzerhof (PBE) [84] was used. The plane wave cutoff energy was set to 450 eV, and the stopping criterion for self-consistent loops were 1 meV per cell for electronic and ionic relaxation.

For α -U, the relaxed crystal structure used in this work is the same as in our previous model [115], and band structure calculations for α -U were performed with a single unit cell (2 atoms) of α -U. A self-consistent calculation with a $24 \times 24 \times 24$ Monkhorst-Pack k -point grid is performed to calculate the charge density, which is used in a non self-consistent calculation with a $36 \times 36 \times 36$ Monkhorst-Pack k -point grid to obtain high-accuracy results of electron band structures. A set of calculations with different k -point grids is also performed to check the convergence of our calculation setups, which shows the convergence error of $s(T)$ is $<5\%$ for α -U. The electronic BTE calculations were performed with the BoltzTraP [125] software using the relaxation time approximation (RTA). The number of q -points used in the electronic BTE calculations was set to be 7 times that of the k -points used in the DFT band structure calculation.

6.4 Results and Discussions

Throughout Section 6.4, the temperature range of all figures and results presented is 43-933K, because α -U is stable in the temperature range of 43-933K [216]. This temperature range covers the expected operating temperature range of metallic fuels for nuclear reactors, which is 320-600K [183].

6.4.1 Degradation factor of point defects

A general model to calculate the degradation factor of point defects f_{gb} for metals containing multiple types of point defects was presented in Section 6.3.1. In this section, we use this model to assess the impact of point defects on the thermal conductivity, using α -U as an

example. The impact of point defects can be obtained by using Eq.(6.11) and Eq.(6.14), as discussed in Section 6.3.1.

The DFT-BTE calculation results of $s(T)$ for pure α -U are plotted in **Figure 6.1** and given in **Table A6.2** of Appendix III. The black solid curve in **Figure 6.1** shows $s(T)$ for pure α -U, which is approximately constant over the examined temperature range. Based on the calculated $s(T)$, for each type of point defect, all parameters needed in Eq.(6.11) to model the resistivity change are known, except the cross section. The cross section can be obtained by using Eq.(6.11) if we have the theoretical or experimental value of residual resistivity due to one type of point defect. For example, Brailsford's theoretical calculation [217] yielded $\rho_{res} = 2.7 \times 10^{-7} \Omega\text{m}$ per 1% vacancy in α -U, and the cross section is $A_{cs} = 13.9 \text{ \AA}^2$ calculated by Eq. (6.11) at 0K. This method indicates that if the theoretical or experimental residual resistivity results at some temperatures and concentrations already exist, one can use Eq. (6.11) to produce the residual resistivity as a function of temperature and concentration via DFT calculations. However, for soluble He, Kr, and Xe atoms, there are no theoretical or experimental residual resistivity results to the best of our knowledge. Therefore, here we use the total cross section of He, Kr, and Xe from elastic electron scattering experiments as an estimation of their respective cross sections in bulk α -U. Near Fermi energy in α -U, which is 15eV from **Table 6.1**, the total electron scattering cross sections are $4.2 \text{ \AA}^2$ for He [218], $25.2 \text{ \AA}^2$ for Kr [219], and $39.3 \text{ \AA}^2$ for Xe [219]. We note here that the theories and approximations of the cross section values from total electron scattering and the cross section values used in our model are different. However, due to the lack of experimental results of scattering cross sections of He, Kr, and Xe, the values used here from elastic electron scattering experiments are our current best approximation. In addition, as we will predict the

residual resistivity due to He, Kr, and Xe later in this section, our calculated residual resistivity can be compared with experiments in the future.

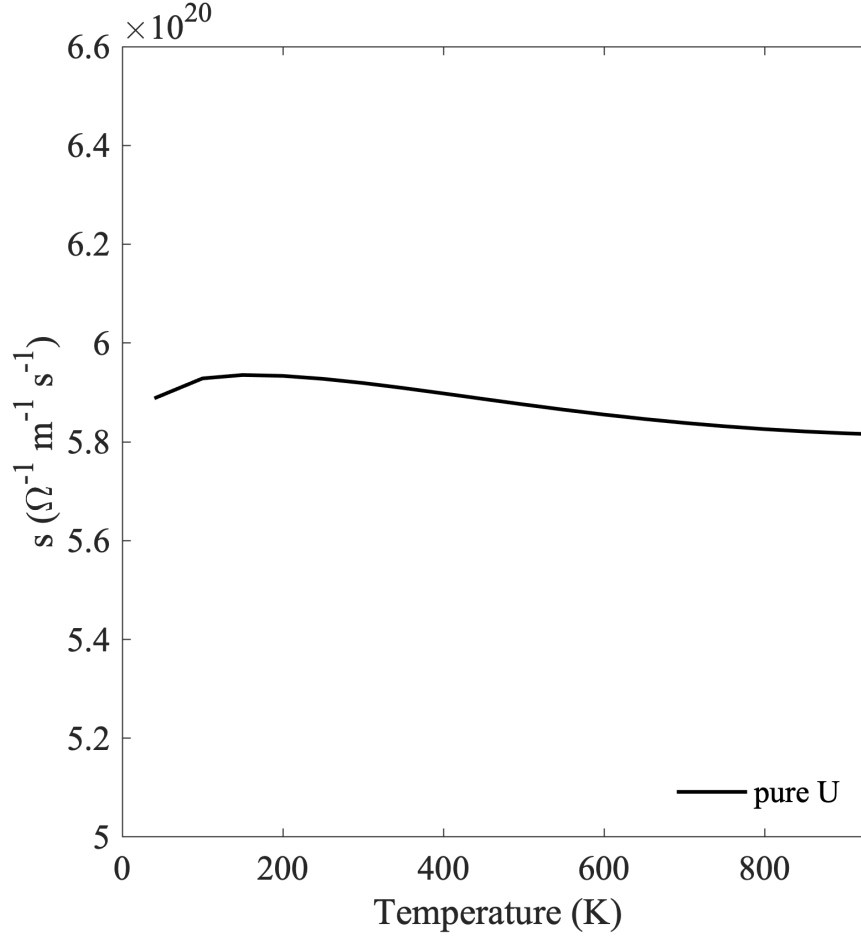


Figure 6.1. Plot of $s(T)$ (which is defined as electrical conductivity divided by relaxation time) in α -U crystal.

Given these values of the electron scattering cross section for different types of point defects, as listed in **Table 6.1**, the influence of point defects on $\tau(T)$ can be calculated. Note that the change in total relaxation time $\tau(T)$ is correlated to the saturation effect, which is not caused by point defects. Therefore, we compare the change in $\tau(T)$ with and without point defects, assuming the saturation effect does not exist ($\rho_{sat} \rightarrow \infty$). Under this assumption, the total relaxation time is given from Eqs.(6.5)-(6.7): $\frac{1}{\tau(c,T)} = \frac{1}{\tau_{id}(T)} + \frac{1}{\tau_{pd}(c)}$, where $\tau_{id}(T)$ is calculated

from Eq.(6.5) with $c = 0$, and $\tau_{pd}(c)$ is calculated from Eq.(6.7). The calculation results are presented in **Figure 6.2** for two point defect concentrations, 0.1% and 1%, and for two types of point defects, He and Xe, as He and Xe have the smallest and largest cross sections, respectively, among the four types of point defects we have considered. In **Figure 6.2**, the total relaxation time decreases with increasing temperature, which is mainly due to the increased magnitude of electron-phonon scattering with increasing temperature. For a particular defect concentration, the relaxation time decreases with increasing defect cross section, which is shown in **Figure 6.2** as Xe resulting in a lower relaxation time than He for a particular concentration. With a defect concentration $c = 0.1\%$, the total relaxation time due to He is approximately unchanged relative to the relaxation time for the undefected α -U, and the relaxation time decrease due to Xe is about 4-10% above 500K. For $c = 1\%$, which is an estimation of the upper bound of defect concentration, the relaxation time decrease due to He is about 4-10% above 500K, and the decrease due to Xe is about 31-49% above 500K. Therefore, even when the point defect concentration is as high as 1% (which is at least a factor of two larger than typical experimental defect concentrations resulting from irradiation), and the cross section is as large as about $40 \text{ \AA}^2$, the major contribution of total relaxation time of irradiated α -U is still τ_{id} rather than τ_{pd} at the temperature above 500K. The major contribution of total relaxation time is the smallest component relaxation time, and the conclusion that the major contribution of total relaxation time is τ_{id} still holds. Therefore, for realistic scenarios where we have multiple types of point defects, their average cross section $A_{cs} < 40 \text{ \AA}^2$ and total concentration $c < 1\%$, the conclusion that the major contribution of the total relaxation time is electron scattering with phonons and other electrons, rather than scattering with point defects, is always valid.

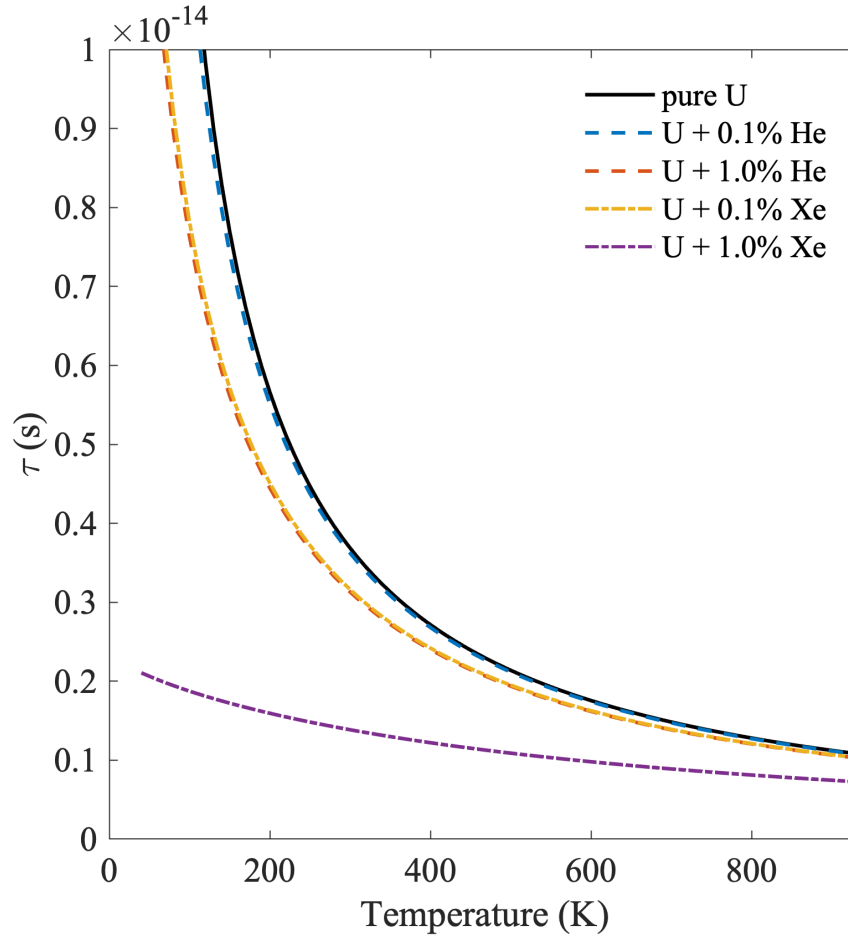


Figure 6.2. Plot of total electronic relaxation time in α -U crystal and α -U containing point defects over the temperature range of 43K to 933K, assuming the resistivity saturation effect does not exist. The black solid curve presents the relaxation time of pure α -U, while the dashed curves are for α -U crystal containing soluble He or Xe atoms at different concentrations.

Table 6.1. The values and sources of parameters used in our model.

Parameters	Values (unit)	Used in	Definitions and notes
A_{cs}	Vacancy: 13.9 ($\text{\AA}^2$) He:4.2 ($\text{\AA}^2$) Kr:25.2 ($\text{\AA}^2$) Xe:39.3 ($\text{\AA}^2$)	f_{pd}	The area of electron-(point defect) scattering cross section. Obtained by fitting calculated residual resistivity with theoretical calculation for single vacancy or using the experimental total cross section of elastic electron scattering for He, Kr, and Xe (in Section 6.4.1).
V_{atom}	20.06 ($\text{\AA}^3$)	f_{pd}	The volume per atom of α -U. Obtained by DFT.

C_{eff}	Eq. (A6.13) in Appendix IV	f_{pd}	The effective total point defect concentration. Obtained by fitting C_{max} in Eq. (A6.13) with experimental data (in Section 6.4.5).
E_F	15.03 (eV)	f_{pd}, f_{gb}	The Fermi level of α -U. Obtained by DFT.
P	0.3	f_{gb}	The probability an electron scatters off a grain boundary. Obtained by calculations for Cu and Al (in Section 6.4.3).
D	Eq. (A6.10) in Appendix IV	f_{gb}, f_{inter}	The grain size (diameter). Obtained by fitting microstructure measurement results (in Appendix IV).
d	Eq. (A6.8) in Appendix IV	f_{inter}	The intergranular bubble size (diameter). Obtained by fitting microstructure measurement results (in Appendix IV).
ρ_s	Eq. (A6.9) in Appendix IV	f_{inter}	The intergranular bubble density per grain area. Obtained by fitting microstructure measurement results (in Appendix IV).
p_{intra}	Eq. (A6.11) in Appendix IV	f_{intra}	The porosity due to intragranular bubbles. Obtained by fitting microstructure measurement results (in Appendix IV).

Now that $s(T)$ and electronic relaxation time with point defects have been determined, the resistivity and residual resistivity for α -U containing point defects can be calculated by Eq. (6.11) and Eq.(6.12), respectively. The calculated resistivity and residual resistivity at a point defect concentration of 0.1% is shown in **Figure 6.3**. In addition, residual resistivity data at the same defect concentration of 0.1% is tabulated in **Table A6.1** of Appendix III, which enables straightforward application of this model to other defect concentrations with Eq. (6.13). The curves in **Figure 6.3** with different colors indicate the resistivity for different point defect types: α -U containing 0.1% vacancies, He, Kr, or Xe atoms. As mentioned before, a value of $A_{cs} = 13.9\text{\AA}^2$ for vacancies makes the residual resistivity equal to Brailsford's theoretical calculation [217], which yields $\rho_{res} = 2.7 \times 10^{-8} \Omega\text{m}$ for 0.1% vacancy in α -U near 0K. The point defects with larger

cross section lead to larger residual resistivity, which can be justified by Eq.(6.11). The residual resistivities decrease with temperature, where the decrease is due to the saturation effect. Near 600K, the resistivity increases produced by 0.1% vacancies, He, Kr, and Xe are 2.5%, 0.7%, 4.5%, and 6.9%, respectively.

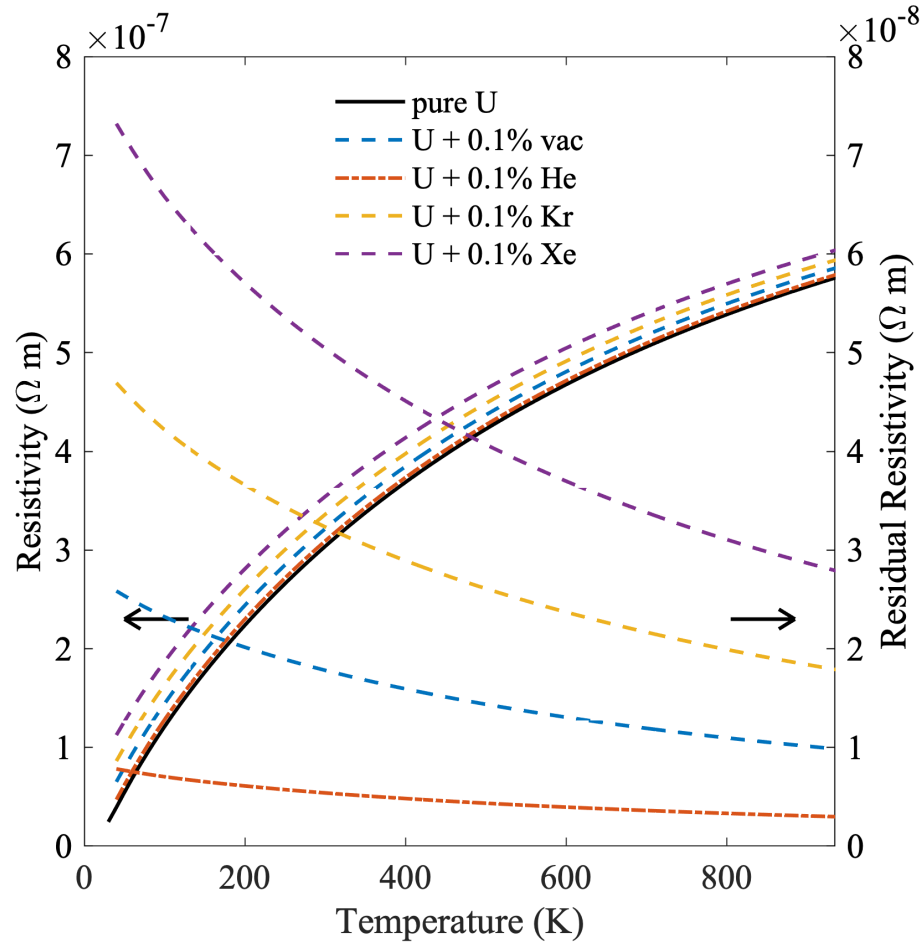


Figure 6.3. Plot of resistivity and residual resistivity in pure α -U and α -U crystal containing point defects over the temperature range of 43K to 933K. The curves with different colors indicate the resistivity and residual resistivity of α -U with different types of point defects.

The simplified model for the total resistivity of a material containing multiple types of point defects given in Eq. (6.13) is simple to apply, so it is valuable to assess if the key assumption in its derivation from Eq. (6.12), which is the validity of Mathiessen's rule, is accurate. Using α -

U crystal containing vacancies as an example, we can check the resistivity calculated by Eq.(6.11) as a function of point defect concentration to assess if Matthiessen's rule can be used. The calculation results of resistivity and residual resistivity at vacancy concentrations of 0.1%, 0.2%, 0.3%, 0.4%, and 0.5% are shown in **Figure 6.4(a)** and **Figure 6.4(b)**, respectively. In **Figure 6.4(b)**, the symbols and their error bars represent the mean values and standard deviations, respectively, for different vacancy concentrations over the temperature range of 43K to 933K. **Figure 6.4(a)** shows that the increasing vacancy concentrations increase the resistivity, and by comparing to the linear fitting in **Figure 6.4(b)** we see that, for the dilute case, the residual resistivity is approximately proportional to the vacancy concentration. Therefore, Matthiessen's rule [29] $\rho_{res}(c, T) \propto c$ approximately holds for vacancies. We have done similar checks for other point defects including He, Kr, and Xe atoms, and also found that Matthiessen's rule holds. Actually, $\rho_{res}(c, T) \propto c$ can be easily justified from Eq.(6.11) and Eq.(6.12), for each type of point defect. Therefore, we can use Eq.(6.13) to estimate the total resistivity while containing multiple types of point defects.

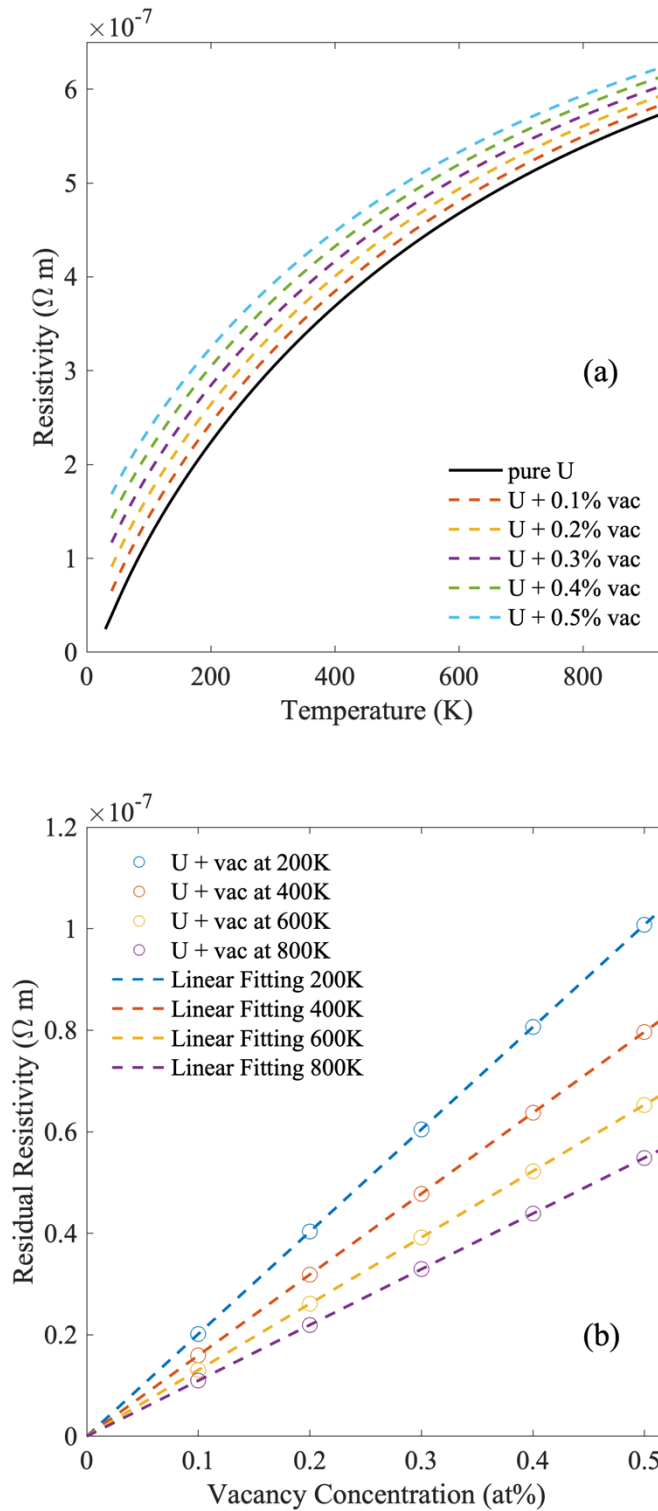


Figure 6.4. (a) Plot of resistivity in pure α -U and α -U crystal containing vacancies in various concentrations over the temperature range of 43K to 933K. The curves with different colors indicate the resistivity with different vacancy concentrations. (b) Plot of residual resistivity in α -U

crystal containing vacancy as a function of vacancy concentration at the temperatures of 200K, 400 K, 600 K, and 800K. The symbols present the residual resistivity at different temperatures over the vacancy concentration range of 0 to 0.5at%, and the dashed lines are linear fittings for each temperature.

Finally, the degradation factor of point defects can be calculated by Eq.(6.14). In Eq. (6.14), the total residual resistivity is $\rho_{res} = \sum_X \rho_{res,X}(c_X, T)$, where X=vacancy, He, Kr, and Xe, and $\rho_{res,X}(c_X, T)$ is the residual resistivity produced by point defect X with defect concentration c_X . Therefore, the concentrations of vacancies, He, Kr, and Xe (represented as c_{vac} , c_{He} , c_{Kr} , c_{Xe} , respectively) are all needed, and, to our knowledge, there is no such defect concentration data of irradiated metallic fuel systems available. Therefore, for the following discussions, one assumption is made, which is the concentrations of vacancies, He, Kr, and Xe are all equal, $c_{vac} = c_{He} = c_{Kr} = c_{Xe} = \frac{1}{4} c_{total}$, where c_{total} is the total concentration of point defects. This assumption is equivalent to having the average cross section of all point defects as $\overline{A_{cs}} = \frac{1}{4} (A_{cs,vac} + A_{cs,He} + A_{cs,Kr} + A_{cs,Xe}) = 20.7 \text{Å}^2$. However, the actual average cross section of all four types of point defects depends on the ratio of the concentrations of all point defects, and can vary from $A_{cs,He}$ to $A_{cs,Xe}$. With this assumption, the total residual resistivity $\rho_{res}(c_{total}, T) = \frac{1}{4} [\rho_{res,vac}(c_{total}, T) + \rho_{res,He}(c_{total}, T) + \rho_{res,Kr}(c_{total}, T) + \rho_{res,Xe}(c_{total}, T)]$, and by using $f_{pd} = \frac{\rho_0}{\rho_0 + \rho_{res}(c_{total}, T)}$ (Eq.(6.14)), we plot the degradation factor f_{pd} as a function of temperature, as shown in **Figure 6.11**, with five different c_{total} values $c_{total} = 0.1\%$, 0.2% , 0.3% , 0.4% , and 0.5% . From **Figure 6.11**, f_{pd} increases with increasing temperature, and higher defect concentrations lead to lower f_{pd} values. In realistic alloys, rather than single vacancy, soluble He, Kr, and Xe atoms, more types of point defects may exist. We still use $\overline{A_{cs}} = 20.7 \text{Å}^2$ to estimate the effects of all types of point defects, and use another term, total effective point defect concentration c_{eff} , to describe the

concentration while using this $\overline{A_{cs}}$ value. For future comparisons with U-Mo alloys, c_{total} is fitted with experimental data, the details of which are presented in Section 6.4.4 and Appendix IV.

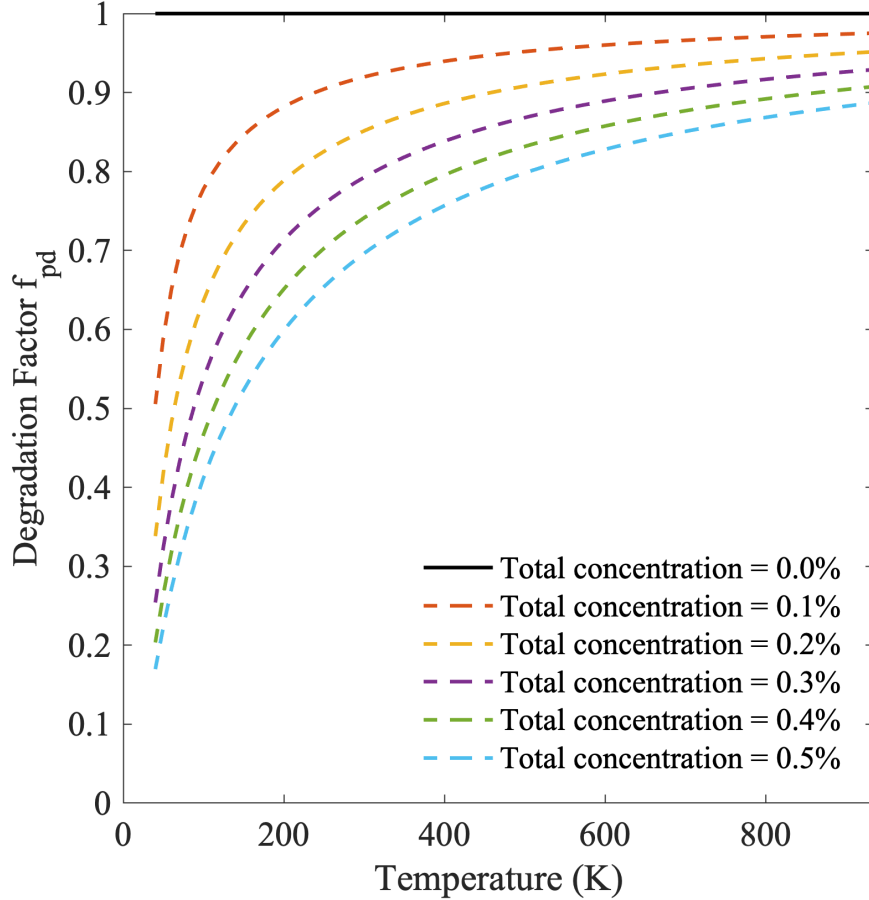


Figure 6.5. Plot of degradation factor of point defects f_{pd} over the temperature range of 43K to 933K. The curves with different colors indicate the f_{pd} for different total concentrations of point defects.

6.4.2 Degradation factor of intragranular bubbles

In this section, we will compare previously developed empirical and analytical models (Eqs.(6.15)-(6.18)) for the effect of intragranular bubbles on the thermal conductivity with recent simulation results of Hu *et al.*'s 3D phase-field simulations [198] and Lasir *et al.*'s 2D finite

element calculations [200]. These empirical and analytical models consist of the Maxwell-Eucken [116,191] model, Effective mean field (EMT) [116] model, model of Cunningham and Peddicord [53], and Bauer's model [194] (see Section 6.3.2). **Figure 6.6** contains the comparison of these empirical and analytical models with the simulated results from Hu *et al.* and Lasir *et al.* The degradation factors f_{intra} from all models decrease with increasing porosity, which indicates the thermal conductivity decreases with increasing porosity (i.e. total intragranular bubble volume). At 0.1 porosity, the value of f_{intra} from different models varies from 0.76-0.86, resulting in a thermal conductivity decrease of $\approx 10\%$. Hu *et al.*'s simulations [198] used phase-field calculations to produce the 3D structures of different porosities for U-Mo and calculated their thermal conductivities at 423K, and their data is shown as the circle symbols in **Figure 6.6**. Lasir *et al.*'s calculations [200] used simplified 2D porosity structures of U-Mo and calculated their thermal conductivity as a function of temperature at 0.1 porosity. We used Lasir *et al.*'s calculated thermal conductivities at 423K and divided by the thermal conductivity of U-Mo to obtain f_{intra} at 0.1 porosity, as presented in **Figure 6.6**. From the empirical and analytical models examined here, Bauer's model (Eq.(6.18)) resulted in the best agreement with the simulation results of Hu *et al.* and Lasir *et al.* at 423K for U-Mo alloys and we therefore use Bauer's model to calculate f_{intra} in our model.

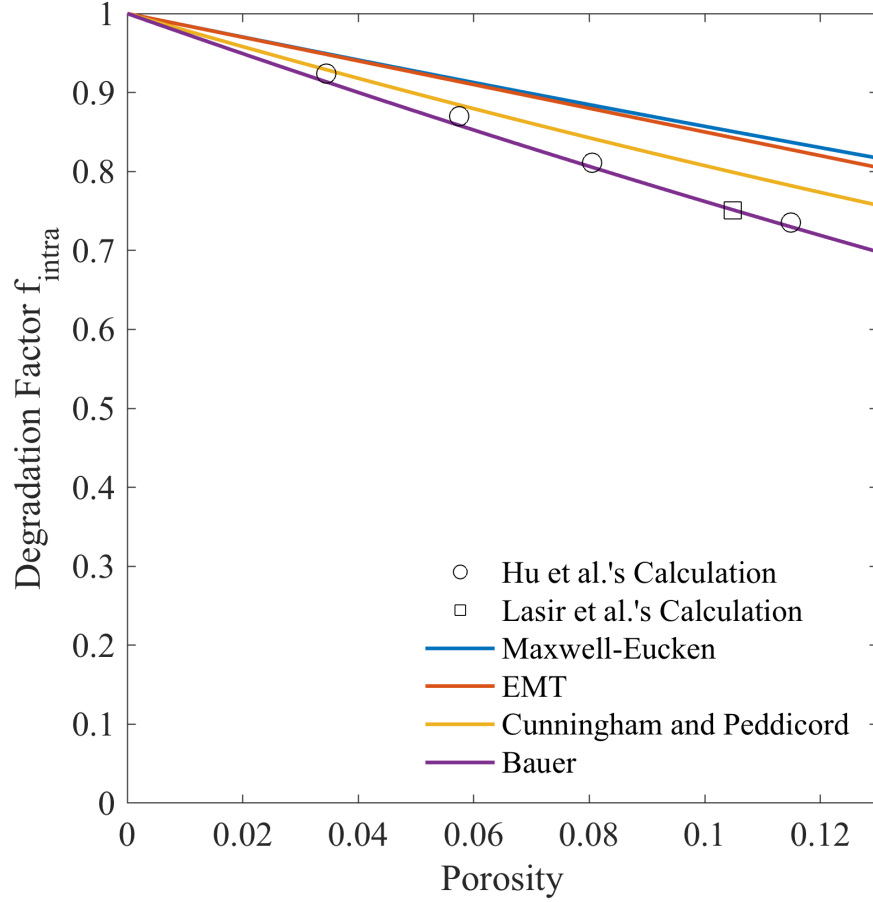


Figure 6.6. Plot of degradation factor of intragranular bubbles f_{intra} over the porosity range of 0 to 13% (curves), compared with calculation results from Hu *et al.* [198] (circle symbols) and Lasir *et al.* [200] (square symbol) at 423K. The curves with different colors indicate different empirical or analytical models for intragranular bubbles, and the symbols indicate different simulation results.

6.4.3 Degradation factor of grain boundaries

In this section, we will first incorporate our model for f_{gb} in Section 6.3.3, with experimental data of grain boundary resistivity to estimate the value of P (the probability an electron scatters off a grain boundary) in Eq.(6.22). The grain boundary resistivities of copper (Cu) and aluminum (Al) were measured by Andrews *et al.* [211] at 4.2K, resulting in measured values

of $\rho_{gb} = 3.12 \times 10^{-16} \Omega m^2$ for Cu and $\rho_{gb} = 2.45 \times 10^{-16} \Omega m^2$ for Al. The total resistivity is a function of grain boundary resistivity and grain size is $\rho_{total} = \rho_0 + \frac{\rho_{gb}}{D}$, therefore, the degradation factor is also a function of grain boundary resistivity: $f_{gb} = \frac{\rho_0}{\rho_{total}} = \frac{1}{1 + \frac{\rho_{gb}}{D\rho_0}}$. By comparing this formula with Eq.(6.22), we obtain $P = \frac{2\rho_{gb}}{3v_F} s_0$ (recall that P is the probability an electron will scatter off a grain boundary). For Cu, $v_F = 1.57 \times 10^6 m/s$ [130], $s_0 = 2.09 \times 10^{21} (\Omega ms)^{-1}$ (calculated from σ and τ values from [128]), therefore, $P = 0.28$. For Al, $v_F = 2.03 \times 10^6 m/s$ [130], $s_0 = 3.17 \times 10^{21} (\Omega ms)^{-1}$ (obtained from test calculation results of BoltzTrap [125]), therefore, $P = 0.26$. While this value of P is approximate, using our model Eq.(6.22) with $P \approx 0.3$ results in good agreement with the measured grain boundary resistivities for Cu and Al. Therefore, we use $P = 0.3$ for our calculations of α -U (see values listed in **Table 6.1**), and use $P = 1.0$ to demonstrate the lower theoretical limit (largest possible effect) of f_{gb} for the case where an electron always scatters from a grain boundary it encounters.

For α -U, to calculate the degradation factor f_{gb} resulting only from grain boundaries, we use Eq.(6.22) with the resistivity data of α -U from **Table A6.1** in Appendix III, E_F from **Table 6.1**, and s_0 from **Table A6.2**. The calculated value of f_{gb} as a function of temperature is shown in **Figure 6.7**. To estimate the lower limit (strongest effect) of f_{gb} , $D = 2\mu m$ (which is smaller than the typical smallest grain size for all burn-up $< 70\%$ [203], see Appendix IV for more details) and the theoretical upper limit of electron scattering probability $P = 1.0$ are used, and f_{gb} is still found to be > 0.98 for temperatures over 400K. For all other conditions we explored of $T > 400K$, $D > 2\mu m$ and $P < 1.0$, we find f_{gb} is always > 0.99 , which indicates the thermal conductivity decrease produced by grain boundaries is likely $< 1\%$. Therefore, as mentioned in Section 6.3.3, the effect

of grain boundaries, based on Eq.(6.22), is found to have a negligible impact on the thermal conductivity.

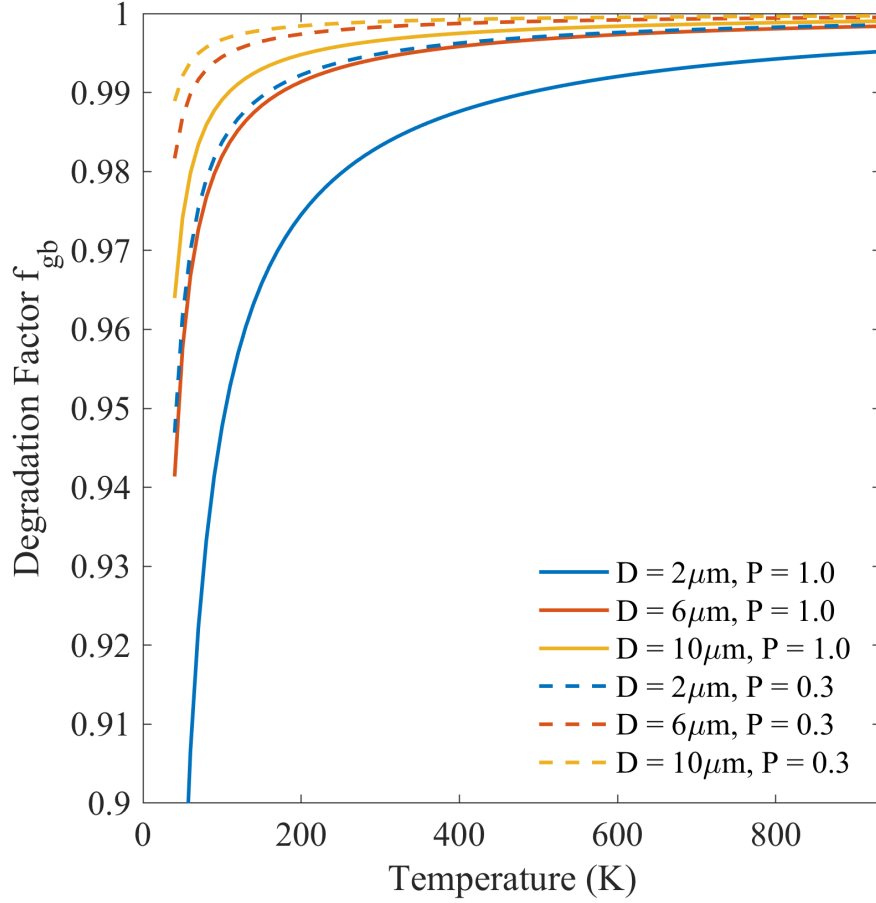
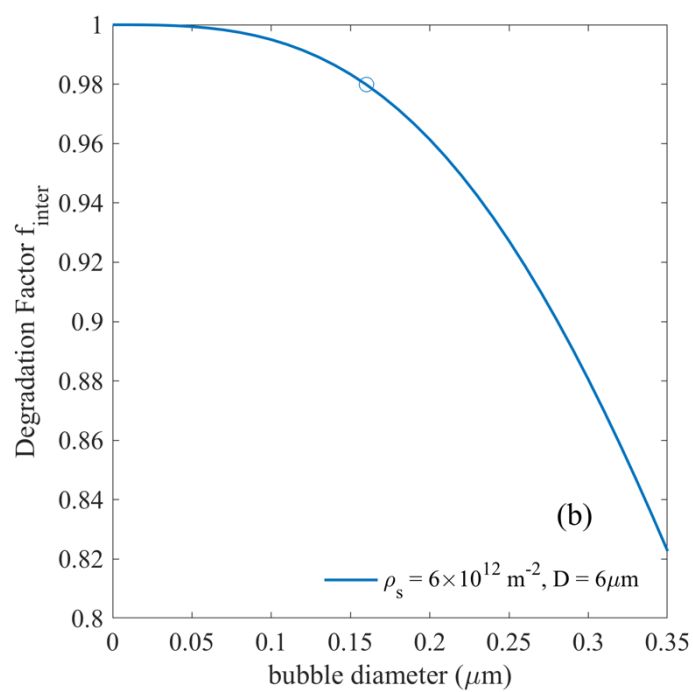
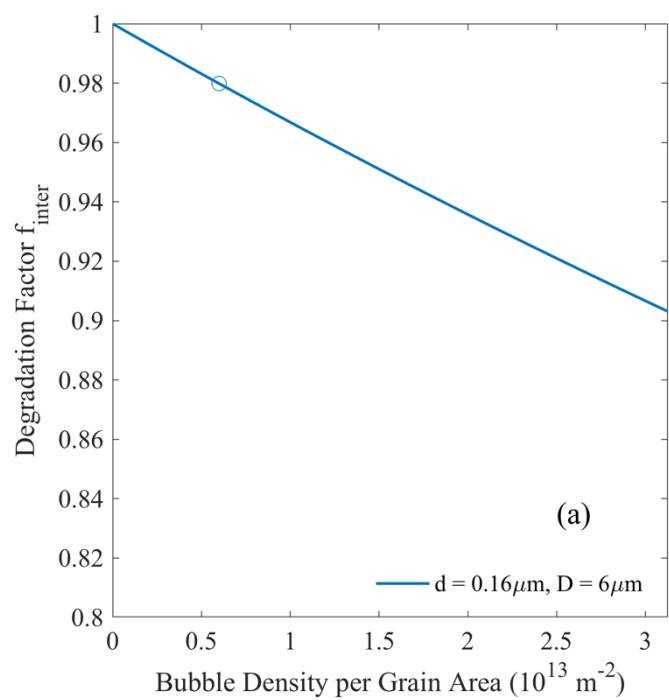


Figure 6.7. Plot of degradation factor of grain boundaries f_{gb} over the temperature range of 43K to 933K. The curves with different colors indicate the value of f_{gb} for different grain sizes D and electron scattering probability with single grain boundary P .

6.4.4 Degradation factor of intergranular bubbles

The derivation of the degradation factor of intergranular bubbles f_{inter} (see Appendix II for more details) demonstrates that f_{inter} is a function of three parameters: bubble diameter d ,

bubble density per grain area ρ_s , and grain size D . From Eq.(6.24), it is straightforward to evaluate the effect of intergranular bubbles on the thermal conductivity with different irradiation conditions assuming one can obtain the corresponding values of d , ρ_s , and D . We explore how these variables impact typical values of f_{inter} by fixing the values of two of these parameters and changing the value of the third parameter in Eq. (6.24), as shown in **Figure 6.8**. In **Figure 6.8**, the values of the fixed parameters are given in the legends, and the symbols in **Figure 6.8** (a), (b) and (c) show the common point at $\rho_s = 6 \times 10^{12} m^{-2}$, $d = 0.16 \mu m$ and $D = 6 \mu m$ (these values were chosen to match conditions for 40% U235 burn-up in U-Mo alloy, see Appendix IV). The value of f_{inter} is generally fairly close to 1 (=0.98 for the common point) although smaller for higher bubble density, larger bubble diameter and smaller grains, as expected.



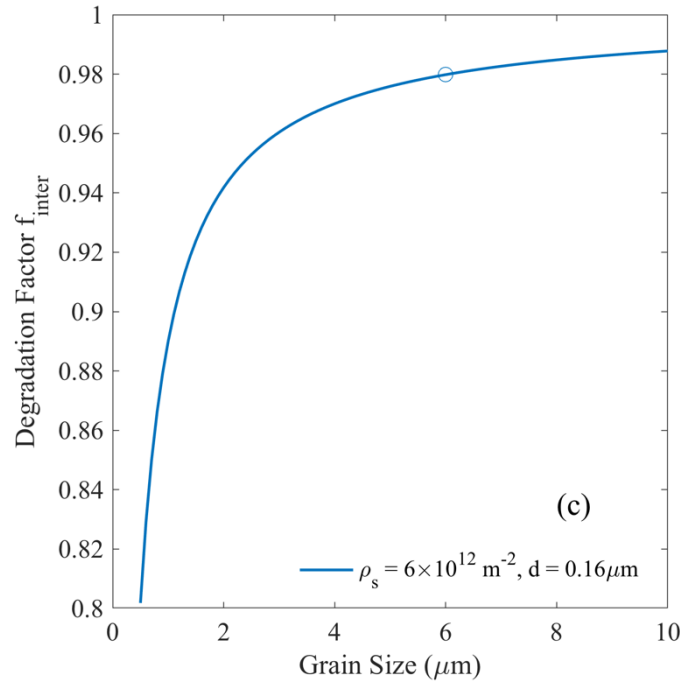


Figure 6.8. Plot of degradation factor of intergranular bubbles f_{inter} as a function of (a) bubble density per grain area ρ_s , (b) bubble diameter d , and (c) grain size D . The symbols in (a), (b) and (c) show the value of f_{inter} at $\rho_s = 6 \times 10^{12} \text{ m}^{-2}$, $d = 0.16 \mu\text{m}$ and $D = 6 \mu\text{m}$. The f_{inter} degradation factor depends only the bubble density per grain area, bubble diameter and grain size and thus functions as a general model.

To validate the accuracy of Eq. (6.24), we compare our model with phase field simulation results from Hu *et al.* [198]. The work of Hu *et al.* calculated the thermal conductivity of structures with different grain boundary coverage by gas bubbles. We can obtain the values of f_{inter} as a function of grain boundary coverage from Hu *et al.*'s phase field simulation results, and compare these results with our model in Eq. (A6.6) (which is another form of Eq. (6.24)). However, the values of the other two parameters, d and D , for each point in Hu *et al.*'s calculation results were not given. Thus, we have used some typical values of $d = 0.21 \mu\text{m}$ and $D = 6 \mu\text{m}$ to compare our model with Hu *et al.*'s calculation results, as shown in **Figure 6.9**. Comparing with Hu *et al.*'s calculation results, the three sets of parameters all display good agreement when the grain

boundary bubble coverage is smaller than 0.5, and our model results in slightly higher values of f_{inter} compared to Hu *et al.*'s calculation results for grain boundary bubble coverages ranging from 0.5 to 0.8. As shown in Appendix III, Eq.(6.24) only keeps the lowest order term of bubble coverage of grain boundaries, and when the grain boundary coverage is high, the higher order terms are not negligible. Therefore, at higher coverage, Eq. (A6.2) or (A6.3) can be used to calculate f_{inter} , the results of which are shown in **Figure 6.9** as dashed curves. Including the higher order terms results in calculated f_{inter} values that are smaller compared to the results obtained used Eq. (6.24), and now somewhat lower than the results of Hu *et al.* Eq. (6.24) and Eqs.(A6.2-3) all give similar and correct (when compared to Hu *et al.*) predictions of f_{inter} when the grain boundary coverage is <0.5 . Experimentally, it has been found that the grain boundary coverage is <0.2 for U-Mo alloys (see Appendix IV for more details), so Eq.(6.24) is sufficient to use for the irradiation conditions considered in this work.

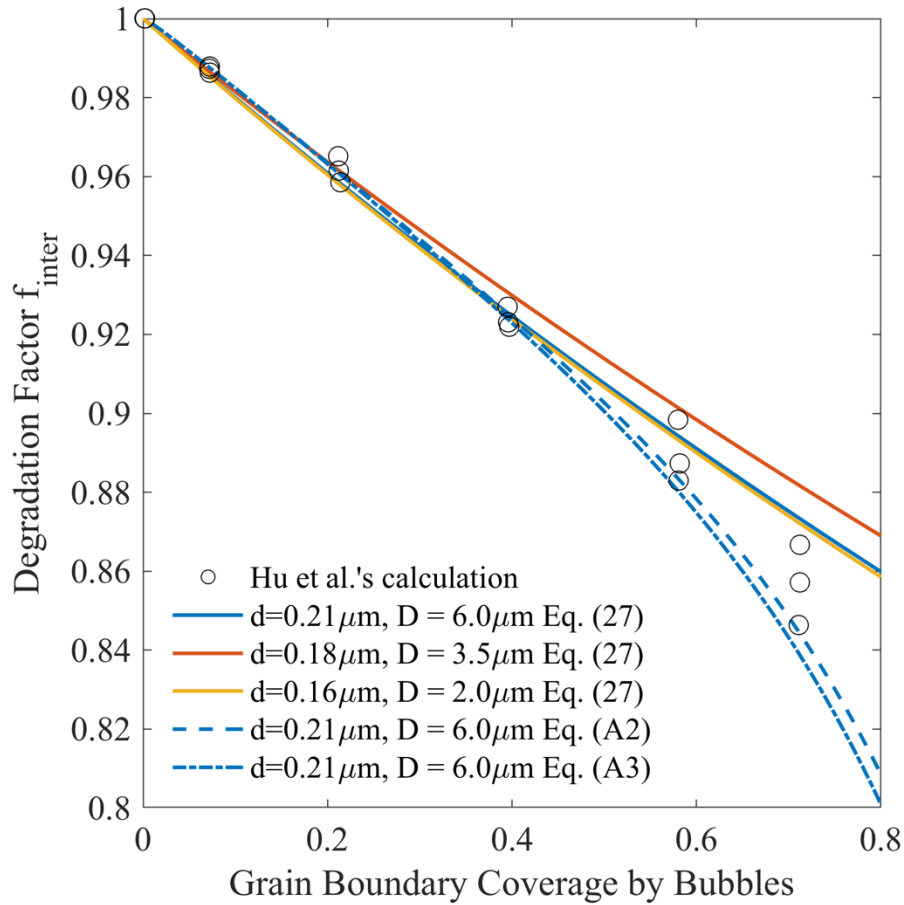


Figure 6.9. Plot of degradation factor of intergranular bubbles f_{inter} as a function of grain boundary coverage by bubbles (curves), compared with Hu *et al.*'s calculation results [198] (symbols). The solid curves with different colors indicate the value of f_{inter} for different d and D values using Eq.(6.24). The dashed curves present the calculation results with Eq. (A6.2) and Eq. (A6.3) at $d = 0.21 \mu m$ and $D = 6 \mu m$.

6.4.5 Effective thermal conductivity for U-Mo alloy after irradiation

Now that the calculated values of the degradation factors f_{pd} , f_{intra} , and $f_{gb-inter}$ in our model have been detailed in Sections 6.4, they can be combined using Eq.(6.1) to calculate the effective thermal conductivity under irradiation. To our knowledge, no thermal conductivity data of irradiated α -U is available. Because of this lack of experimental irradiated thermal conductivity data in pure α -U, we will compare our model with data of irradiated U-22at%Mo. The degradation

factor due to point defects f_{pd} in U-22at%Mo are assumed to approximately hold for it in α -U, and we perform the analysis by replacing the resistivity of unirradiated α -U with the resistivity of unirradiated U-22at%Mo as the initial state of the system in Eq.(6.14).

Here, we have used the irradiated U-22at%Mo thermal conductivity data from the work of Burkes *et al.* [183] and Huber *et al.* [220]. Burkes *et al.* measured the thermal conductivity of U-22at%Mo under irradiation as a function of fission density (equivalently, burn-up) at 323K, 473K, and 573K, and compared with Huber *et al.*'s results of 323K. For unirradiated U-22at%Mo thermal conductivity data, measurements from different experiments show large discrepancies of up to 6 W/m-K (about 30% of the thermal conductivity of U-22at%Mo at 600K) [23]. We use the suggested values for unirradiated U-22at%Mo from Kim *et al.*'s work [23,221]. As our model depends on five microstructural parameters (total effective point defect concentration c_{eff} , intragranular bubble porosity p_{intra} , intergranular bubble diameter d and density per grain boundary area ρ_s , and grain size D , see **Table 6.1**), knowledge of these five parameters as a function of burn-up is required in order to model the thermal conductivity as a function of burn-up for different irradiation conditions. For the last four parameters (intragranular bubble porosity p_{intra} , intergranular bubble diameter d and density per grain boundary area ρ_s , and grain size D), their values have been reported under different burn-up in U-Mo systems [198,203,222] and the results are summarized in **Table A6.2** and **Table A6.3** of Appendix IV. We fit these four parameters as functions of burn-up with polynomial functions in Appendix IV. For the point defect concentration, we use an empirical formula [223,224] with one fitting parameter, the point defect saturation concentration c_{eff} , as discussed in Appendix IV. The point defect saturation concentration c_{eff} was obtained by fitting to Huber *et al.*'s and Burkes *et al.*'s results.

To summarize, our final model for adding irradiation effects has 9 parameters, as listed in **Table 6.1**. Among them, E_F and V_{atom} are calculated by DFT, A_{cs} are determined with theoretical calculations or experiments as discussed in Section 6.4.1, P is determined using experiments for other metals as discussed in Section 6.4.3, and D , d , ρ_s , and p_{intra} are determined by microstructure measurement results as given in Appendix IV. The only parameter here fitted to U-Mo alloy data is c_{eff} . To obtain the modification in thermal conductivity for a new set of irradiation conditions in the same alloy one might need to update the four microstructure values of D , d , ρ_s , and p_{intra} and the point defect density c_{eff} . To obtain the modification in thermal conductivity for a specific irradiation condition in an entirely new metal alloy one would have to obtain D , d , ρ_s , p_{intra} , and c_{eff} , likely from experiments, modeling, or a combination of the two. One would also have to determine the E_F and V_{atom} of the unirradiated material, which is straightforward with DFT. Finally, A_{cs} could be quickly determined with simple size arguments and P taken as a typical metal value, as in this U-Mo study.

Using the parameters in **Table 6.1**, we can calculate the values of all degradation factors resulting from different irradiation effects as functions of burn-up (discussed more in Section 6.4.6), and their combined effect on the thermal conductivity of U-22at%Mo. The thermal conductivity as a function of burn-up is shown in **Figure 6.10**, where the calculated results of our model (curves) are compared with Huber *et al.*'s and Burkes *et al.*'s experiments (symbols). For all irradiated data, the root-mean-square error (RMSE) between experiments and our model is 0.72 W/m-K. In addition, in **Figure 6.11** we have calculated the thermal conductivity of U-22at%Mo as a function of temperature under different burn-up conditions. In **Figure 6.11**, the calculated results from our model (curves) are compared with experiments from Burkes *et al.* (symbols with colors), and the RMSE between experiments and our model is 0.84 W/m-K. The typical

experimental uncertainties in thermal conductivity measurements were ≈ 2 W/m-K in Burkes *et al.*'s experiments, and the measurement error of thermal conductivity between different sets of experiments is ~ 3 W/m-K, which can be verified from the unirradiated experimental data in **Figure 6.11**. Therefore, our calculated results in **Figure 6.10** and **Figure 6.11** are within the uncertainty range of experiments and the error range of different sets of experiments. Overall, our model shows good agreement with experiments, and demonstrates semi-quantitative predictions of thermal conductivity as a function of temperature and burn-up.

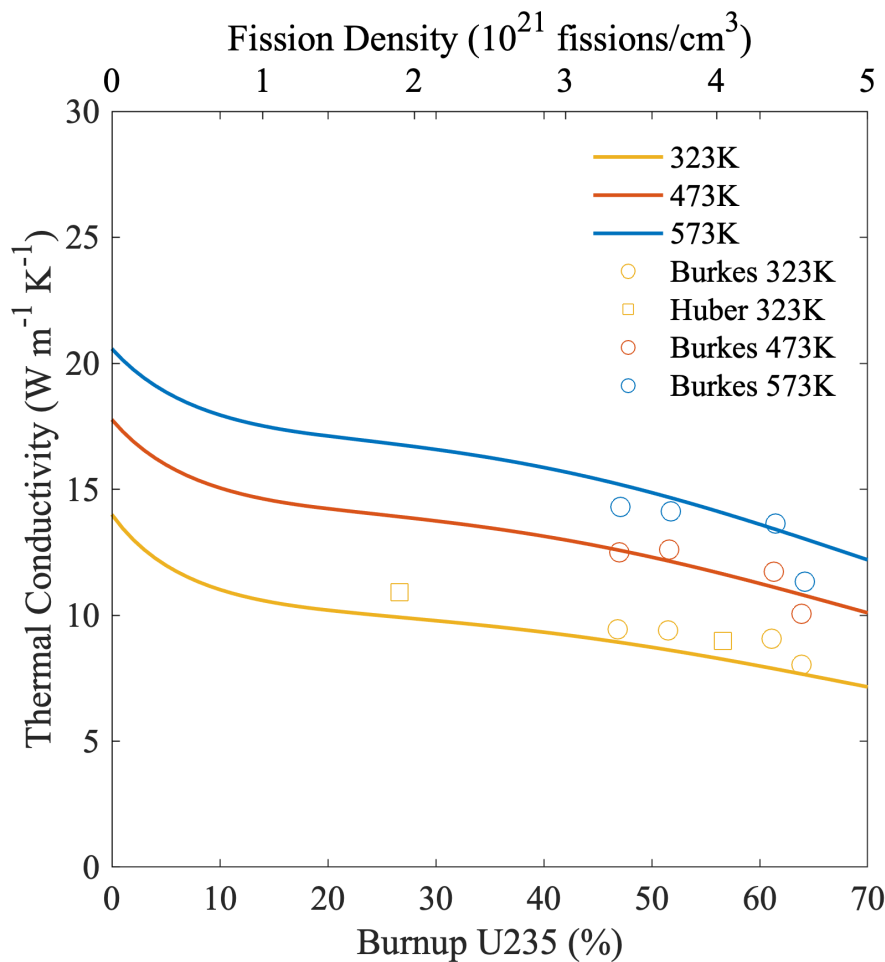


Figure 6.10. Plot of thermal conductivity of U-22at%Mo as a function of burn-up (equivalently, fission density) (curves), compared with Huber *et al.*'s [220] and Burkes *et al.*'s [183] experiments

(symbols). The curves with different colors indicate the thermal conductivity for different temperatures, with curves moving generally higher on the plot with increasing temperature.

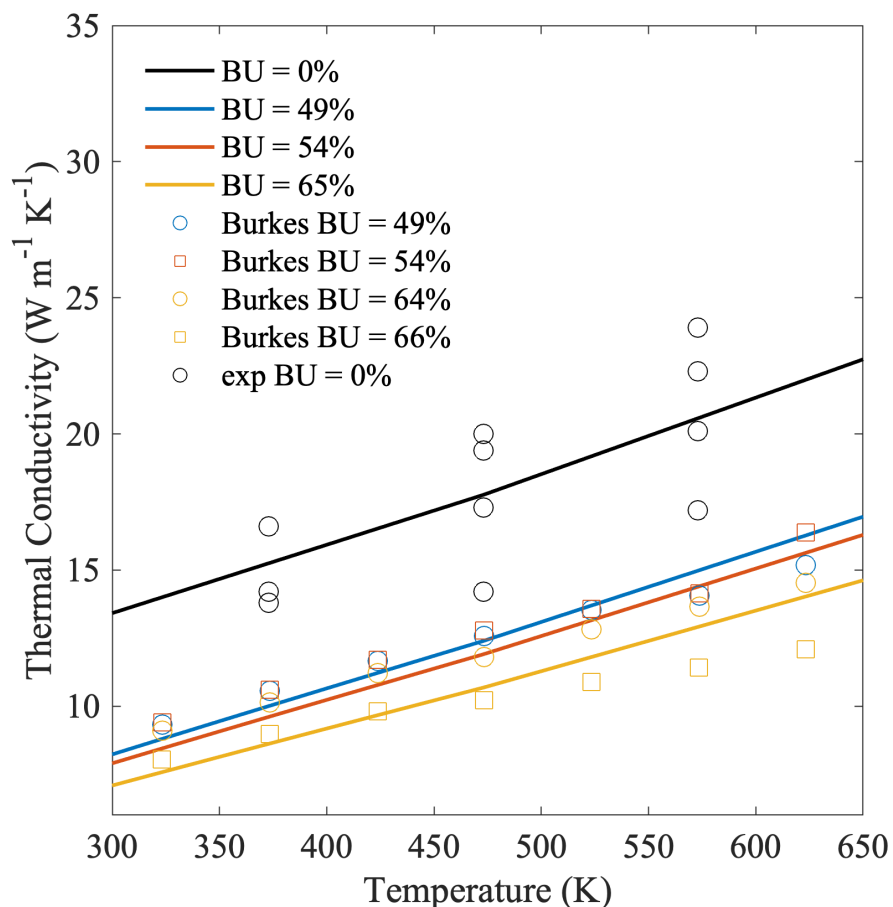


Figure 6.11. Plot of thermal conductivity of U-22at%Mo as a function of temperature (curves), compared with unirradiated thermal conductivity measurements of U-22at%Mo [17,23,183] and of U-20at%Mo [156], and Burke's *et al.*'s [183] irradiation experiments (symbols). The curves with different colors indicate the thermal conductivity under different burn-up conditions. The curves with different colors indicate the thermal conductivity for different burn-up conditions, with curves moving generally lower on the plot with increasing burnup.

6.4.6 Relative contributions of irradiation effects on thermal conductivity

We calculate the degradation factors of different irradiation effects as functions of burn-up (see **Figure 6.12**), with the irradiation effects parameters given in Appendix IV. This calculation is performed for burn-up from 0 to 80%, which includes the highest experimental burn-up realized in metallic fuels of which we are aware, which is 78% for a U-Mo alloy [222]. By comparing the degradation factors resulting from different irradiation effects, the thermal conductivity decrease produced by point defects is always the largest and dominant factor, except for extremely high burn-up of $> 75\%$, where the contribution of intragranular bubbles is the largest. The thermal conductivity decrease produced by point defects is approximately equal to the total thermal conductivity decrease when burn-up $< 25\%$. This result indicates that, when burn-up $< 25\%$, the effects of intragranular and intergranular bubbles and grain boundaries are all negligible. For burn-up $> 25\%$, the thermal conductivity decrease for intragranular bubbles is ≈ 2 times the thermal conductivity decrease resulting from intergranular bubbles. This dominance of intragranular vs. intergranular bubbles is due to the total porosity of intragranular bubbles being larger than the porosity of intergranular bubbles (see Appendix IV). These results further indicate that the thermal conductivity decrease due to grain boundaries is negligible for the full range of burn-up considered here. Our model thus provides insight into the magnitudes of the contributions of different irradiation effects on the reduction of thermal conductivity.

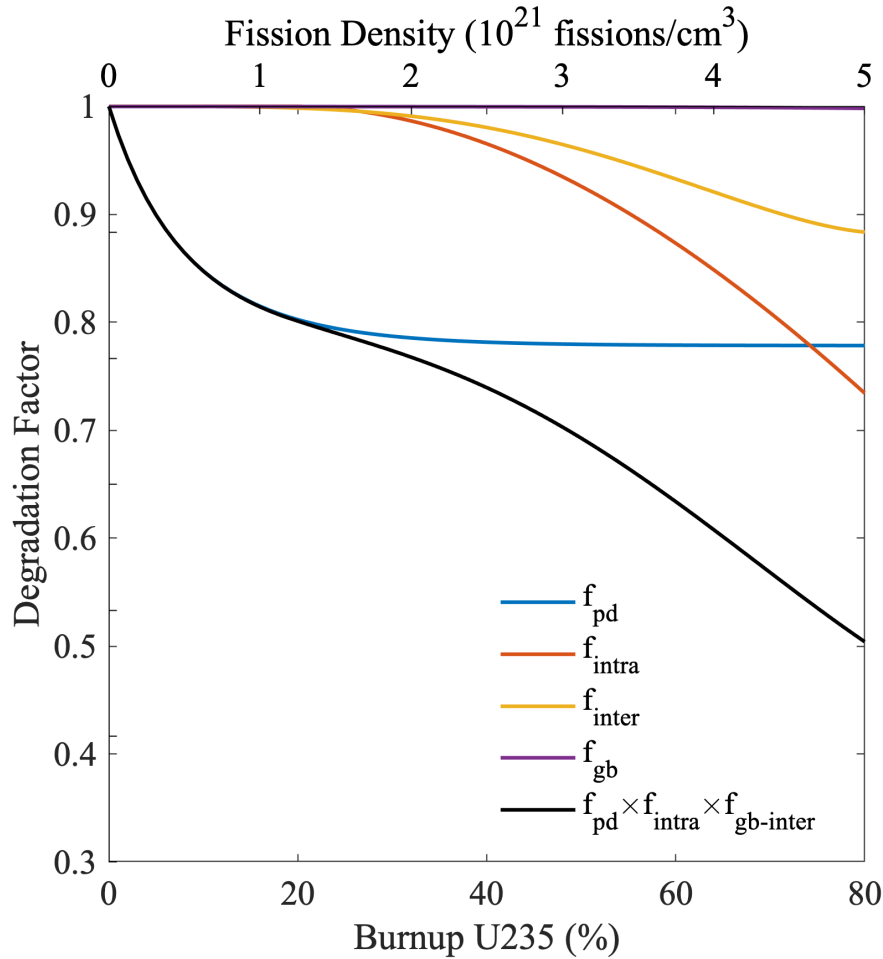


Figure 6.12. Plot of degradation factors as functions of burn-up or, equivalently, fission density of U235 (curves) at 473K. The curves with different colors indicate the degradation factors for different irradiation effects, and the black curve denotes the combined degradation factors of all irradiation effects.

6.5 Conclusions

A physics-based computational model of thermal conductivity for irradiated metals and metal alloys has been constructed, with an emphasis on α -U and U-Mo alloys. Our model combines DFT calculations and DFT-BTE analysis together with experimental data to incorporate multiple irradiation effects, including the effect of point defects (assumed to be vacancies, noble gas atoms, and potentially other transmutation products), noble gas bubbles (intra- and inter-

granular) and grain boundaries. The model is based on the relation $\kappa_{eff} = f_{pd}f_{intra}f_{inter+gb}\kappa_0 \approx f_{pd}f_{intra}f_{inter}\kappa_0$, which clearly separates out the contributions from different irradiation effects in each f_x term and provides semi-quantitative predictions of the relative contributions of point defects, intragranular bubbles, intergranular bubbles, and grain boundaries to the decrease of thermal conductivity.

Within our modeling framework the four f_x terms can be determined for any metal alloy from a set of nine variables (see **Table 6.1**). Of these, four are either determined here in a way likely applicable to many metal alloys (probability an electron scatters off a grain boundary, P), readily calculable from simple theory (area of electron-(point defect) scattering cross section, A_{CS}), or readily obtained from straightforward *ab initio* calculations or from experiments (Fermi level of unirradiated material, E_F , atomic volume of unirradiated material, V_{atom}). The five additional parameters are atomic and microstructural parameters associated with irradiation effects that, at least currently, must be obtained from experiments or significant additional modeling: total effective point defect concentration c_{eff} , intragranular bubble porosity p_{intra} , grain size D , intergranular bubble diameter d , and intergranular bubble density per grain boundary area ρ_s . These parameters must be known as a function of the irradiation conditions being modeled (e.g., as a function of burnup) to apply the model to a given alloy. As this model is for the modification of thermal conductivity due to irradiation, to obtain the final irradiated thermal conductivity it is also necessary to know the initial thermal conductivity of the unirradiated material, κ_0 .

The current work provides a full model of U-22at%Mo thermal conductivity values as a function of temperature and burn-up, as well as the impact of different irradiation effects on this thermal conductivity. We found that for a burn-up range from 0-75%, the majority of thermal conductivity decrease of U-Mo alloy is due to the effect of point defects, with intragranular and

intergranular bubbles becoming significant at about 40% burn-up and the former being about twice as important as the latter. Therefore, if one considers the thermal conductivity decrease within 30% burn-up, one only needs to consider the effect of point defects while the effects from bubbles and grains can be ignored, to obtain an approximately accurate model as pointed out by our results in **Figure 6.12**. Furthermore, if the thermal conductivity decrease near 30% burn-up already exists, then the further thermal conductivity decrease at higher than 30% burn-up can be obtained approximately by only considering effects due to intragranular and intergranular bubbles. The model we have constructed in this study may be straightforwardly applied to different irradiation conditions and different metals and metal alloys by changing the model parameters. Parameter values for new alloys and irradiation conditions are straightforward to obtain, except for the five parameters associated with quantifying the point defect and microstructural evolution under irradiation, which require significant characterization or modeling efforts. The requirement of having these point defect and microstructural properties creates significant data requirements for application of this model, but is likely a necessary characteristic of any model that seeks to capture radiation effects on thermal conductivity. The methodology developed here is useful for modeling metal thermal conductivity under irradiation conditions to aid materials and device design.

6.6 Appendices

6.6.1 Appendix I: The resistivity approach of DFT-BTE

The resistivity can be readily calculated using the BTE method with the relaxation time approximation (RTA) approach with DFT-calculated electronic band structures [125]:

$$\rho(T) = \frac{1}{\sigma(T)} = \frac{1}{\left(\frac{\sigma(T)}{\tau(T)}\right)\tau(T)} = \frac{1}{s(T)\tau(T)}, \quad (\text{A6.1})$$

where $\sigma(T)$ is the electrical conductivity and τ is the electronic relaxation time. $s(T) \equiv \frac{\sigma(T)}{\tau(T)}$ is calculated using the BTE-RTA and the rigid band approximation following the work of Madsen and Singh [125]. $\sigma(T)$ is calculated as the trace of the full electronic conductivity tensor, which can be calculated from the conductivity distributions:

$$\sigma_{\alpha\beta}(T) = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\varepsilon) \left[-\frac{\partial f_{\mu}(T, \varepsilon)}{\partial \varepsilon} \right] d\varepsilon, \quad (\text{A6.2})$$

where $f_{\mu}(T, \varepsilon)$ is the Fermi-Dirac distribution function, $\frac{\partial f_{\mu}(T, \varepsilon)}{\partial \varepsilon}$ is the temperature smearing, which is determined using the electronic density of states and the Fermi-Dirac distribution evaluated at the appropriate temperature, Ω is the system volume (taken as the DFT-calculated unit cell volume), T is the temperature, ε is the band energy, μ is the Fermi level, and $\sigma_{\alpha\beta}(\varepsilon)$ is the transport distribution given by:

$$\sigma_{\alpha\beta}(\varepsilon) = \frac{e^2}{N} \sum_{i,k} \tau_{i,k} v_{\alpha}(i, k) v_{\beta}(i, k) \frac{\delta(\varepsilon - \varepsilon_{i,k})}{d\varepsilon}, \quad (\text{A6.3})$$

where k represents elements of a set of k -points spanning reciprocal space in the Brillouin zone, N is the number of k -points sampled, i is the band index, v_{α} is the electron group velocity, e is the elementary charge, and $\tau_{i,k}$ are the relaxation times for each electron band i and k -point.

The input parameters for calculating the electrical conductivity tensor $\sigma_{\alpha\beta}(T)$ are the relaxation times $\tau_{i,k}$ and the electronic band structure information calculated from DFT. Here, we simplify the input of $\tau_{i,k}$ by assuming it is a constant which neither depends on band index i nor direction k , which has been shown to be a satisfactory assumption for many metals [126,127]. With this approximation, $s(T) = \frac{\sigma(T)}{\tau(T)}$ depends on only the electronic band structure through Eqs. (6.5)-(6.6), which values can be obtained from DFT-BTE calculations. This approach of assuming a constant, single τ value to obtain $\rho(T)$ from DFT-BTE calculated $s(T)$ has been successfully

applied to Ag-Cu alloys [128] and W with vacancies [129]. For our DFT band structure calculations we use the Vienna Ab initio Simulation Package (VASP) [214,215] (see Section 6.3.4 for additional information on the DFT calculations) and for the BTE solutions we use the BoltzTrap code [125]. $\tau(T)$ can be further replaced by the electron relaxation time due to a specific electron scattering, to calculate its resistivity contribution, e.g. using the relaxation time of electron-phonon scattering τ_{e-ph} in Eq. (A6.1) to calculate the resistivity contribution of electron-phonon scattering ρ_{e-ph} . Therefore, Eq. (A6.1) is used to calculate the resistivity contributions with different contributions of electron relaxation time in Section 6.3.1.2 (Eqs. (6.5)-(6.6)).

6.6.2 Appendix II: The analytical derivative for the effect of intergranular bubbles at grain boundaries

To simplify the structure of intergranular bubbles, we assume (1) the grains are cubes with side length A , (2) the intergranular bubble are spheres with a diameter d , forming a 2D cubic lattice with spacing a on the grain boundaries. If we assume the system can be approximated as infinite (i.e., we do not include any surface effects) then it can be treated as a periodic system with a unit cell that contains a grain and grain boundary region. An intuitive unit cell is a grain and half of the surrounding grain boundary regions, in which we can consider the unit cell to be a grain with 6 surfaces covered by half grain boundary layer each (two adjacent grains share one full grain boundary layer region). However, this intuitive cell is not the most convenient for modeling the resistivity due to it having half grain boundary regions. Therefore, we instead slightly shift the center of the unit cell so that it contains one grain with 3 surfaces covered by one full grain boundary region, and three surfaces not covered by grain boundary. A sketch of the grain and grain boundary region in the unit cell is shown in Figure A1. The grain boundary region (note that this

is the region of the grain boundary used in the model, not the width of a true grain boundary) is defined as the region which contains the bubbles and has a width of a . Because the width of the grain boundary region is taken as a , each bubble can be viewed as in the middle of a cube with side length a .

Multiple grain boundary region layers stacked together can form a cube with uniformly distributed bubbles. The resistivity of this cube can be obtained by applying Bauer's model (Eq. (6.18)). Due to the translation invariance, the resistivity of the grain boundary region (the dark blue layer of grain boundary in Figure A1) is equal to the resistivity of the cube with uniformly distributed bubbles:

$$\rho_{gbr} = \rho_0(1 - p)^{-2.58} = \rho_0 \left(1 - \frac{\pi d^3}{6a^3}\right)^{-2.58}. \quad (\text{A6.1})$$

Assuming the direction of electric current is from left to right, the resistivity of the grain is calculated by separating the grain into four portions (shown in Figure A1): (1) the bulk portion, which is a cube with side length $(A-a)$, and resistance of $R_0 = \frac{\rho_0}{A-a}$; (2) the two grain boundary region surfaces, which are parallel to the current and are directly contacting the bulk. The resistance of this portion is $R_{gb1} = \frac{\rho_{gbr}(A-a)}{2Aa-a^2}$; (3) the grain boundary region surfaces, which are perpendicular to the current and are directly contacting the bulk. The resistance of this portion is $R_{gb2} = \frac{\rho_{gbr}a}{(A-a)^2}$; (4) the remaining L-shaped grain boundary region, which is not contacting the bulk. The resistance of this portion is $R_{gb3} = \frac{\rho_{gbr}a}{2Aa-a^2}$. The resistance network is shown in Figure A2. R_{cr} is used to account for the current cross between uncontacted regions, e.g. R_0 and R_{gb3} , where $R_{cr} = 0$ and $R_{cr} = \infty$ give the lower and upper bound of the total resistance, respectively [213].

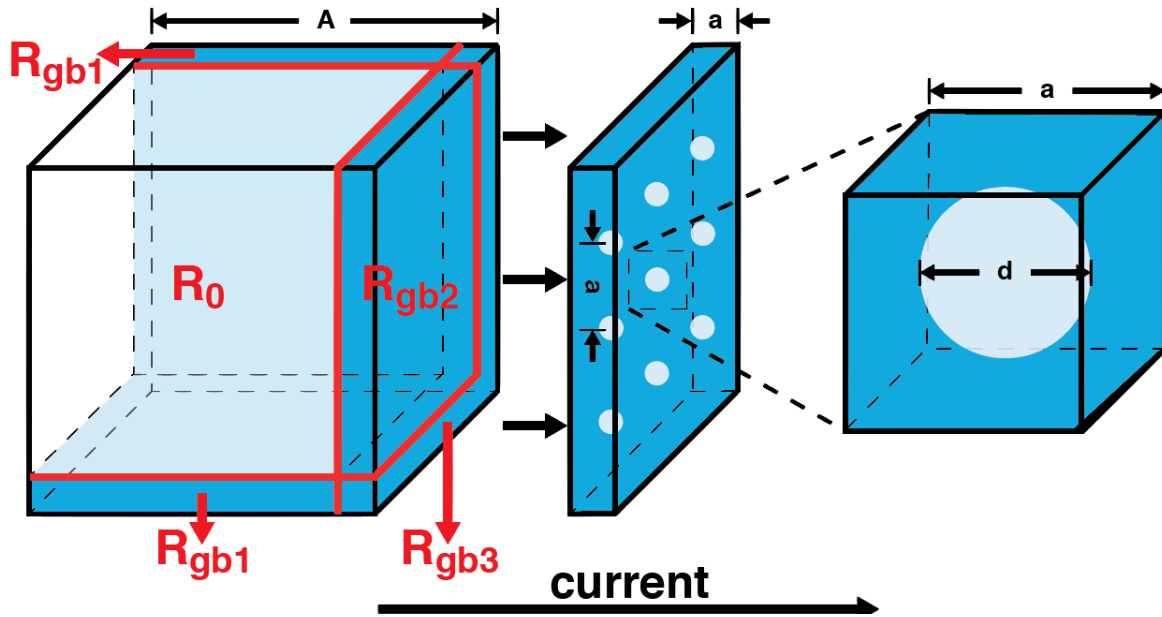


Figure A1. A sketch of a cubic grain with 3 surfaces covered by grain boundary region which contains the noble gas bubbles.

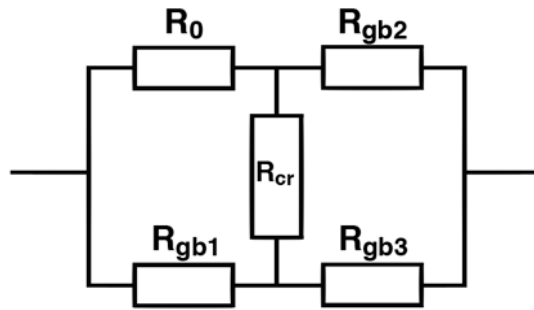


Figure A2. The resistance network used to evaluate the effective resistance of the grain.

Therefore, the lower and upper bound of the total resistance are:

$$R_{lower} = (R_0^{-1} + R_{gb1}^{-1})^{-1} + (R_{gb2}^{-1} + R_{gb3}^{-1})^{-1}, \quad (\text{A6.2})$$

$$R_{upper} = \left[(R_0 + R_{gb2})^{-1} + (R_{gb1} + R_{gb3})^{-1} \right]^{-1}. \quad (A6.3)$$

If we assume d^3/a^3 and a/A are small and Taylor expand the total resistance to first order in $\frac{d^3}{a^2A}$

we get:

$$R_{lower} = R_{upper} = \frac{\rho_0}{A} \left[1 + 4.05 \frac{a}{A} \frac{d^3}{a^3} + \dots \right]. \quad (A6.4)$$

Taking the experimental values of ρ_s , d , and D at about 40% burn-up (details in Appendix IV),

$\frac{d^3}{a^2A} = 1.24 \frac{\rho_s d^3}{D} = 1 \times 10^{-3} \ll 1$, so this equation expansion is valid. Therefore, the degradation

factor of the effect of intergranular bubbles is approximately given by:

$$f_{inter} = \frac{1}{1 + 4.05 \frac{d^3}{a^2A}}. \quad (A6.4)$$

While the bubble spacing and bubble density per grain area are related by $a^2 \rho_s = 1$, and the grain

size D of an approximate sphere-shaped grain and cube grain length A is related by $\frac{\pi}{6} D^3 = A^3$, by

replacing a and A by ρ_s and D , respectively, we have:

$$f_{inter} = \frac{1}{1 + 5.03 \frac{\rho_s d^3}{D}}, \quad (A6.5)$$

which is identical to Eq.(6.24) in the main text. Some studies have also used a parameter

F_{cov} [198,203], which is the grain boundary coverage by intergranular bubbles. By the relationship

$F_{cov} = \frac{\pi}{4} d^2 \rho_s$, f_{inter} can also be given by:

$$f_{inter} = \frac{1}{1 + 6.40 \frac{F_{cov} d}{D}}, \quad (A6.6)$$

Futhermore, one can use only one variable to present f_{inter} with p_{inter} , which is defined as the

porosity (volume fraction) of intergranular bubbles. Considering an approximate sphere-shaped

grain with grain size D , the area of its grain boundary is πD^2 , and the intergranular bubbles on its

grain boundary have a total number given by $\pi D^2 \rho_s$, and a total volume of $0.5 \times \pi D^2 \rho_s \times \frac{\pi}{6} d^3 =$

$\frac{\pi^2}{12} D^2 \rho_s d^3$ (note the factor 0.5 as each intergranular bubbles is split between two grains).

Therefore, $p_{inter} = \frac{\frac{\pi^2}{12} D^2 \rho_s d^3}{\frac{\pi}{6} D^3} = \frac{\pi \rho_s d^3}{2D}$, and f_{inter} is given by:

$$f_{inter} = \frac{1}{1+3.20p_{inter}}, \quad (\text{A6.7})$$

Comparing f_{inter} (Eq. (A6.7)) with f_{intra} (Eq. (6.18)) we have expressions for the reduction in thermal conductivity from intergranular and intragranular bubbles both in terms of a relevant porosity, which allows a more direct comparison of their influence. Specifically, for $p_{inter} = p_{intra} = p_{bubble}$ the ratio of the intergranular and intragranular degradation factors is given by

$$r = \frac{f_{inter}}{f_{intra}} = \frac{(1 + 3.20p_{bubble})^{-1}}{(1 - p_{bubble})^{2.58}} \approx \frac{1 - 3.20p_{bubble}}{1 - 2.58p_{bubble}} \approx 1 - 0.62p_{bubble}$$

Where the approximate equalities are derived by a first order Taylor expansion in p_{bubble} . Therefore, for same porosity (provided it is small), $r < 1$ and the bubbles on the grain boundary will decrease thermal conductivity more than it in the grain.

6.6.3 Appendix III: The resistivity and $s(T)$ of α -U and α -U containing 0.1% point defects (single vacancy, or soluble He, Kr, or Xe atoms).

Table A6.1. Calculation results of the residual resistivity of α -U contains 0.1% vacancies, He, Kr, or Xe atoms from 43K to 933K, compared with the resistivity of α -U.

T (K)	α -U Resistivity ($\times 10^{-7} \Omega \text{m}$) ¹	Residual resistivity of α -U + 0.1% X ($\times 10^{-7} \Omega \text{m}$)			
		vacancy	He	Kr	Xe
43	0.45	0.25	0.08	0.46	0.72
100	1.23	0.23	0.07	0.42	0.66
150	1.78	0.22	0.07	0.39	0.61
200	2.26	0.20	0.06	0.37	0.57
250	2.68	0.19	0.06	0.34	0.54
300	3.06	0.18	0.05	0.32	0.50
350	3.40	0.17	0.05	0.31	0.48

400	3.71	0.16	0.05	0.29	0.45
450	3.99	0.15	0.05	0.27	0.43
500	4.24	0.14	0.04	0.26	0.41
550	4.48	0.14	0.04	0.25	0.39
600	4.69	0.13	0.04	0.24	0.37
650	4.89	0.12	0.04	0.23	0.35
700	5.08	0.12	0.04	0.22	0.34
750	5.25	0.11	0.03	0.21	0.32
800	5.40	0.11	0.03	0.20	0.31
850	5.55	0.11	0.03	0.19	0.30
900	5.69	0.10	0.03	0.18	0.29
933	5.77	0.10	0.03	0.18	0.28

1 Values read from Ref. [115]

Table A6.2. Calculation results of $s(T)$ of α -U from 43K to 933K

T (K)	$s(T) (\times 10^{20} (\Omega\text{ms})^{-1})$
43	5.89
100	5.93
150	5.94
200	5.93
250	5.93
300	5.92
350	5.91
400	5.90
450	5.89
500	5.88
550	5.86
600	5.86
650	5.85
700	5.84
750	5.83
800	5.83
850	5.82
900	5.82
933	5.81

6.6.4 Appendix IV: The parameters of irradiation effects as functions of burn-up.

Our model is based on five point defect and microstructural parameters that can change due to irradiation effects: total effective point defect concentration, intragranular bubble porosity, grain size, intergranular bubble diameter, and intergranular bubble density per grain boundary area. We need these five parameters as functions of burn-up in order to calculate the thermal conductivity as a function of burn-up. Three parameters: grain size, intergranular bubble diameter, and intergranular bubble density at different burn-up have been measured by experiments from Kim *et al.* [203] and Rest *et al.* [222], and the results are summarized in **Table A6.3**. To interpolate and extrapolate these experimental results, we use second order polynomial functions to fit them, as shown in Figure A3(a), (b) and (c), and the fitted functions are:

$$d = -0.471x^2 + 0.595x \text{ } (\mu\text{m}), \quad (\text{A6.8})$$

$$\rho_s = -9.68x^2 + 19.82x \text{ } (\mu\text{m}^{-2}), \quad (\text{A6.9})$$

$$D = 14.54x^2 - 29.67x + 15.36 \text{ } (\mu\text{m}), \quad (\text{A6.10})$$

where x is the burn-up. When $x = 0$ there should be no intergranular bubbles, so d and ρ_s are defined to be 0, and D is estimated by annealed U-Mo grain size which is $\sim 16 \mu\text{m}$ [203].

For intragranular bubble porosity, the bubble diameters and volume densities have been summarized by Hu *et al.* [198] for burn-up from 39% to 64%. Therefore, the porosity can be calculated from the bubble diameters and volume densities data for this burn-up range, as given in **Table A6.4**. For low burn-up, Kim *et al.* 's experiments [203] show there are no bubbles observed in the interior of the grains. Therefore, we assume the intragranular bubbles appear at 20% burn-up as an approximation. Thus, for burn-up range 0-20%, the intragranular bubble porosity is 0, and for burn-up above 20%, we use second order polynomial functions to fit the experimental data, as shown in Figure A3(d). The intragranular bubble porosity as a function of burn-up is given as:

$$p = \begin{cases} 0, & \text{when } x < 20\% \\ 0.285(x - 0.2)^2 + 0.008(x - 0.2), & \text{when } x > 20\% \end{cases}, \quad (\text{A6.11})$$

where x is the burn-up.

Table A6.3. The experimental results of the intergranular bubble diameter, intergranular bubble density per grain area and grain size of U-Mo at different burn-up.

Fuel property	Burn-up U-235 (%)	fission density (10^{27} fissions/ m^3)	bubble diameter (μm)	bubble density per grain area (μm^{-2})	Grain size (μm)
U-10Mo ¹	39	3.1	0.15	6.00	6.3
U-10Mo ¹	40	3.1	0.18	7.00	3.2
U-10Mo ¹	30	2.1	0.13	6.40	6.5
U-10Mo ¹	38	2.6	0.16	6.50	7.3
U-6Mo ¹	39	2.9	0.18	5.00	4.4
U-10Mo ¹	49	3.1	0.17	7.30	5.3
U-7Mo ¹	37	2.4	0.16	6.10	6.2
U-10Mo ¹	49	3.0	0.16	6.50	8.5
U-10Mo ¹	35	2.3	0.14	6.10	4.9
U-10Mo ¹	37	2.4	0.16	6.60	8.1
U-10Mo ¹	48	3.0	0.18	6.40	3.9
U-10Mo ²	78	5.0	0.18	10.0	0.2

1 Values read from Ref. [203]

2 Values read from Ref. [222]

Table A6.4. The experimental results of the intragranular bubble diameter, volume density and porosity of U-Mo at different burn-up.

Fuel property	Burn-up U-235 (%)	fission density (10^{27} fissions/ m^3)	bubble diameter (nm)	bubble volume density (10^{24}m^{-3})	Porosity (%)
U-10Mo ¹	39	2.5	2.00	3.00	1.26
U-10Mo ¹	58	3.7	3.10	2.72	4.24
U-10Mo ¹	64	4.1	3.14	3.68	5.97

1 Values read from Ref. [198]

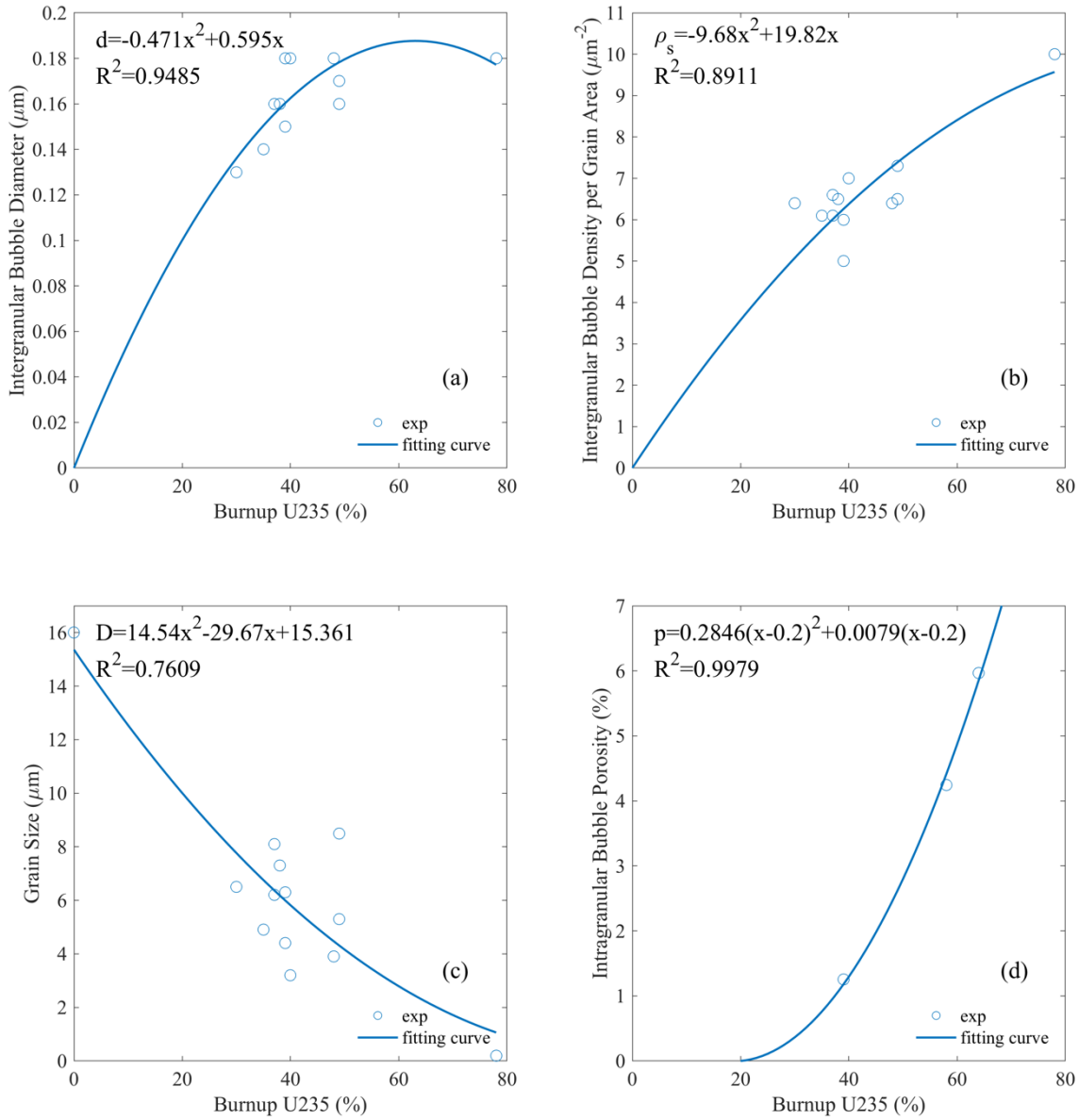


Figure A3. Fitted curves of (a) intergranular bubble diameter, (b) intergranular bubble density per grain area, (c) grain size, and (d) intragranular bubble porosity as functions of burn-up, compared with experimental data [26,33,61].

For the point defect concentration, to our knowledge there is no available data for U and U alloy system as a function of burn-up. As suggested by Horak and Blewitt [224], the residual resistivity of metals under fast neutron irradiation is a function of time:

$$\rho_{res} = \rho_{max}(1 - e^{-\beta t}), \quad (\text{A6.12})$$

where ρ_{max} is the saturation value of residual resistivity, and β is a constant. If we assume the burn-up rate is a constant, the burn-up is proportional to irradiation time. As ρ_{res} is proportional to point defect concentration, the effective total defect concentration is given as:

$$c_{eff} = c_{max}(1 - e^{-x/x_0}), \quad (\text{A6.13})$$

where c_{max} is the effective total defect concentration at saturation, x is burnup, and x_0 is a constant. It is assumed that after point defects reach their saturation, the additional point defects start to form noble gas bubbles, which are characterized as intragranular bubbles (as opposed to point defects), and start to form at about 20% burn-up (see in Figure A3(d)). Therefore, the evaluated x_0 value is set to 10%, to make c approximately saturate at 20% burn-up. c_{max} is fitted to irradiated U-Mo experimental data as mentioned in Section 6.4.4, which gives $c_{max} = 0.53\%$, a value quite similar to that obtained for other metals (0.1-0.7%) under fast neutron irradiation [224].

Here, we note that it is not our intention to propose these fitting curves are a quantitatively accurate model of irradiation parameters as functions of burn-up. These values are quick estimations to help us compare our model of thermal conductivity for irradiated U and U alloys with experimental data. These irradiation parameters may be quite different with different irradiation history. However, with different irradiation conditions, either from experiments or irradiation evolution simulations, our model can still match the irradiation conditions and predict the thermal conductivity decrease by incorporating the new values of the five defect and microstructure dependent irradiation parameters discussed in this Appendix for the new irradiation conditions.

Chapter 7 : Concluding Remarks

7.1 Summary

The research contained in Chapter 3 through Chapter 6 regarding the thermal conductivity models on metal alloys with different components, compositions, phases, and microstructures is summarized in this section.

In this work, we have developed thermal conductivity models for metal alloys based on DFT calculations, semiclassical physics rules, and limited experimental data. The models in this work contain different types of systems with increasing complexity, including elemental metals, solid solutions (both dilute and concentrated), and multiphase mixtures. These models show excellent agreement with the experimental thermal conductivity data in their demonstration on U-Zr, U-Nb, and U-Mo alloys in different phases. Compared to empirical models developed purely by fitting, the present models require less experimental data because they are based on physical insights on the scattering mechanisms of energy carriers. For the same reason, they can be applied to systems with different microstructures and even other material systems, provided inputs regarding the scattering mechanisms can be obtained. One example is the application to irradiated U-Mo alloys, which show agreement with the experiments, owing to the incorporation of the effects of lattice defects, including point defects, bubbles, and grain boundaries. The physical insights on the scattering mechanisms of energy carriers responsible for heat transport, and the quantitative models that are based on them, can help the development of metallic fuels for nuclear energy applications.

7.2 Suggestions for Future Work

As showed here, the DFT calculations are powerful resources to study the heat transport mechanisms mediated by electrons and phonons. The fundamental understanding of these mechanisms can significantly facilitate the development of quantitative, physics-based models for thermal conductivity in alloys by combining physics rules. While this work demonstrated the prominent potential of such an approach, some future developments are needed to fully capitalize this powerful approach. Three possible directions are given here:

1. Complete a comprehensive, mechanistic, and high-throughput transport property modeling approach, which is fully based on ab-initio calculations and requires no experimental data. With this tool, it would be possible to predict the thermal conductivity without any experimental measurements, which would benefit the discovery, development, and deployment for new materials. As our models show, the DFT-BTE approach may serve as a possible path to solve this problem. The major gap is to calculate the electron and phonon relaxation times fully using ab-initio calculations, as some of them are captured in this work by fitting to experimental data. There are more mechanisms we have to figure out to realize a fully ab-initio model, including high-order phonon scatterings (e.g. three-phonon scattering, four phonon scattering, etc) and the anharmonic effects in electron-phonon scattering.
2. Implement an integrated tool to solve the DFT-BTE approach. As mentioned, compared with previous empirical fitting models, the shortcoming of our model is the time required for model developments. As one can see from our models, many parameters and several computational tools are involved in our model development, which makes it hard for new, and even experienced users, to repeat this process and demonstrate it on other materials of interest. One possible solution is to develop an

integrated tool to solve the DFT-BTE approach for both electrons and phonons. Ideally, with a given DFT calculation of phonon and electron spectra as inputs, this BTE solver can solve the electron and phonon BTE and provide transport properties directly with provided relaxation times.

3. Extend our models for more systems. Although in this work, the model for solid solutions and multiphase mixtures are done, more metallic systems, like intermetallic compound systems of USi_x , UC_x , UN_x , and UAl_x , are not modeled. It's always beneficial to have more systems modeled to demonstrate the utility of the approach and refine the most efficient ways to integrate the modeling and limited experimental data.

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