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**DEVELOPMENT OF A KNOWLEDGE BASE OF Ti-ALLOYS FOR
BIOMEDICAL APPLICATIONS FROM FIRST-PRINCIPLES AND
COMPUTATIONAL THERMODYNAMICS**

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Abstract

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Acknowledgments

Dedication

Chapter 1

Introduction

1.1 Motivation

Titanium (Ti) and its alloys have been used in biomedical applications for many years because of their biocompatibility and corrosion resistance properties [38]. In recent years, there has been an increasing interest in developing better materials for load-bearing implants, due to the increase in total knee and hip replacements. Krutz et al. predicted that the total number of hip and knee replacements would increase by 174% and 673%, respectively, from 2005 to 2030, leading to 572,000 hip and 3.48 million knee procedures in 2030 [39]. Two of the driving factors for this situation are an increasing number of younger individuals requiring these replacements and the fact that the average life of total hip and knee replacements is only about 7-12 years before another replacement must be done [40]. These factors all contribute significantly to the necessity for the development of better implant materials. The primary considerations for biomedical implants, such as load-bearing knee and hip implants, are biocompatibility, corrosion resistance, fatigue strength, and Young's modulus (E) [38]. In previous years, the most common implants for these applications have been Ti-6Al-4V, stainless steels, and MoCoCr alloys [35,41]. However, there have been issues with these materials, such as, cytotoxicity that has been observed with aluminum and vanadium [42]. Another important impediment concerning the common implant materials is stress shielding, which leads to implant failure. Stress shielding occurs when the E of the implant is higher than that of bone. Due to the difference in E , load applications to the joint result in the implant material absorbing all of the stress and causing the bone surrounding the implant to

atrophy, which leads to a loss in bone density, and can result in implant loosening and failure [38]. Table 1.1 summarizes the comparison of the E of common implant materials (> 100 GPa) to bone (10-40 GPa) [38]. This data indicates the extreme elasticity mismatch between the various materials. Computational thermodynamics and development of a knowledge base of Ti and its alloys will be useful tools in overcoming these challenges.

This work will focus on investigating the thermodynamics and elastic properties of the biocompatible Ti-Mo-Nb-Sn-Ta-Zr system. The thermodynamic and elastic properties will be calculated using first-principles based on Density Functional Theory (DFT). The parametrization of the properties will be completed using an integrated first-principles based on DFT calculations and CALPHAD modeling approach. The combination of these two methodologies has been shown to eliminate the need for trial-and-error metallurgy, thus saving time, money and other resources. New computational methodology to predict the metastable phase formation will be presented and verified by neutron scattering experiments. The culmination of this work will provide a fundamental understanding of the thermodynamics and elastic properties for the Ti-Mo-Nb-Sn-Ta-Zr system.

1.2 Overview

The phase stability of Ti alloys has been seen to greatly influence the mechanical properties of the alloys and thus understanding the phase of a Ti alloy will greatly impact its effectiveness as a biomedical implant.

1.2.0.1 Equilibrium Phases

Titanium is stable in the α (hexagonal close packed, hcp) phase under the standard temperature and pressure. However, β (body centered cubic, bcc) Ti alloys have received much attention because of their low E and high specific strength and is thus targeted for the current application [43, 44]. Mo, Nb and Ta are all biocompatible elements and considered strong β -stabilizers, while Zr is a bio-compatible weak β -stabilizer individually but strong stabilizer when in combination with other elements [38]. In conjunction with their bcc phase stability, Mo, Nb, Ta and Zr, in the presence of many non-toxic elements, studies have shown excellent corrosion resistance and no allergy problems [45]. Recently, tin (Sn) has also been studied

for use in Ti-alloys, due to its biocompatibility and low cost [35]. Due to these reason, the effects of alloying Ti with Mo, Nb, Sn, Ta and Zr on the thermodynamic properties were studied. The combined DFT and CALPHAD approach was used to evaluate previous models or build new models for the binary and ternary alloys in the Ti-Mo-Nb-Sn-Ta-Zr system to build a completed database describing the thermodynamic properties of the system.

1.2.1 Elastic Properties

The mechanical properties, in combination with studies of the various stable phases of Ti-alloys, have been experimentally determined for alloys such as Ti-13Nb-13Zr, Ti-35Nb-5Ta-7Zr-0.4O, Ti-29Nb-Ta-Zr and Ti-25Nb-Ta-Zr with Young's moduli between 71 and 57 GPa which starts to approach the E of bone [32, 38, 45]. While new metallic alloys are continually being designed, being able to predict the elastic properties before trying to make alloys for biomedical implants will reduce the need for trial and error and narrow down the scope of alloys being selected. With this goal in mind, this dissertation completes an extensive systematic study of the elastic properties of the pure elements, binary and ternary alloys in the bcc phase is completed using Density Functional Theory (DFT). Using the DFT data, CALPHAD modeling is then done to build a completed database that can predict the elastic properties as a function of composition.

1.2.1.1 Metastable Phases

While the thermodynamic database will predict the formation of the equilibrium phases and alloys in the bcc phase can then be targeted and their elastic properties predicted, Ti and its alloys form two metastable phases, α'' and ω . α'' is an orthorhombic martensitic phase (space group Cmcm). The martensitic transformation is displacive and closely related to the system critical phenomenon [46, 47]. Thermodynamically the martensitic phase is a first-order transformation that is initiated due to some supercooling defined by $T_0 - M_S$ where T_0 is the temperature where bcc goes to hcp and M_S is the martensitic temperature where the martensitic transformation starts. An applied stress can also contribute to the driving force for a martensitic transformation. Kinetically the martensitic transformation propagates in an athermal manner which suggests that the velocity of the interface and the

force causing its movement contain an instability. The ω phase is a metastable hexagonal phase (space group P6/mmm) of Ti that has lattice parameters closely matching that of bcc Ti. The ω phase has been seen to form athermally when Ti is alloyed with β stabilizing elements such as Mo, Nb and Ta. The formation of ω and α'' have been observed in Ti-Mo, Ti-Ta and Ti-Nb alloys. It is seen that different cooling of certain compositions of these binary alloys from a temperature in the single-phase bcc region to room temperature causes either the α'' phase or the ω phase with the untransformed bcc phase. Quenching the samples leads to the formation of α'' while slow cooling the sample leads to the ω phase. The formation of these phases causes variations to the predicted elastic properties as seen in Figure 1.1 where the closed symbols represent the calculated E and the open symbols represent the experimentally determined E . The calculations and experiments match up well on the Ti-rich and Ta-rich sides of the graph but in the purple boxed region, the experiments show a much higher E than predicted. This is due to the formation of α'' and ω . While the formation of the metastable phases greatly effects the properties of the Ti-alloys, the properties of unstable structures cannot be efficiently predicted by DFT-based first-principles calculations. In this dissertation, the phase stability and effect on the elastic properties of the α'' and ω phases are studied for the Ti-Nb and Ti-Ta systems. First, the ground state energy and elastic properties of multiple structures in the α'' , ω , bcc and hcp are calculated, across all compositions, for the Ti-Ta and Ti-Nb systems. The partition function approach is then adapted to predict the concentrations and phases fractions where the metastable phases are likely to form. The predicted phase fractions are then used to predict the elastic modulus and phonon density of states using a rule of mixtures. The predictions are confirmed with inelastic neutron scattering experiments. By looking at the diffraction patterns obtained at 300 °K the phase fractions can be obtained and compared to the predicted phase fractions. The phonon density of states (DOS) obtained from neutron scattering experiments at 300 °K can be compared with a mixed force constant first-principles phonon density of states. The plotting of the phonon density of states obtained through neutron scattering at different temperatures will be analyzed to help further understand the transformations taking place.

This completed thesis will consist of the following main tasks:

1. Using first-principles calculations based on DFT and the CALPHAD method to investigate the thermodynamics of the Ti-Mo-Nb-Sn-Ta-Zr system.
 - (a) The previous binary models will be evaluated with the available experimental data as well as the first-principles calculated enthalpy of formation of the bcc phase
 - (b) The thermodynamic description of the Sn-Ta binary alloy will be modelled
 - (c) The thermodynamic descriptions of the Ti-containing ternary alloys will be modelled
2. Using first-principles calculations the elastic properties of the Ti-Mo-Nb-Sn-Ta-Zr system in the bcc phase will be systematically studied. The results, as well as the CALPHAD method, will be used to build a database to predict the elastic properties as a function of composition.
3. The metastable phase formation in Ti alloys will be investigated through first-principles calculations, the CALPHAD method and experiments done on the Ti-Nb and Ti-Ta systems
 - (a) The ground state energy and elastic properties of the Ti-Nb and Ti-Ta systems in the hcp, bcc, ω and α'' will be predicted using first-principles calculations
 - (b) From first-principles the:
 - i. Adapted partition function approach will predict the phase fractions
 - ii. The phase fractions will be used in a rule of mixtures to plot the phonon density of states and elastic properties
 - (c) From neutron scattering:
 - i. The phase fractions will be determined and compared to the predictions

- ii. The phonon density of states will be plotted at 300 °K to compare to the mixed force constant predicted phonon density of states
- iii. The temperature dependent phonon density of states will be plotted to study the transformation

Table 1.1. Young's modulus of common implant materials compared with the Young's modulus of bone [38].

Alloy	Young's Modulus (GPa)
Bone	10-40
cp-Ti*	105
Ti-6Al-4V	110
Stainless Steel	200
CoCrMo	200-230

*cp-commercially pure titanium

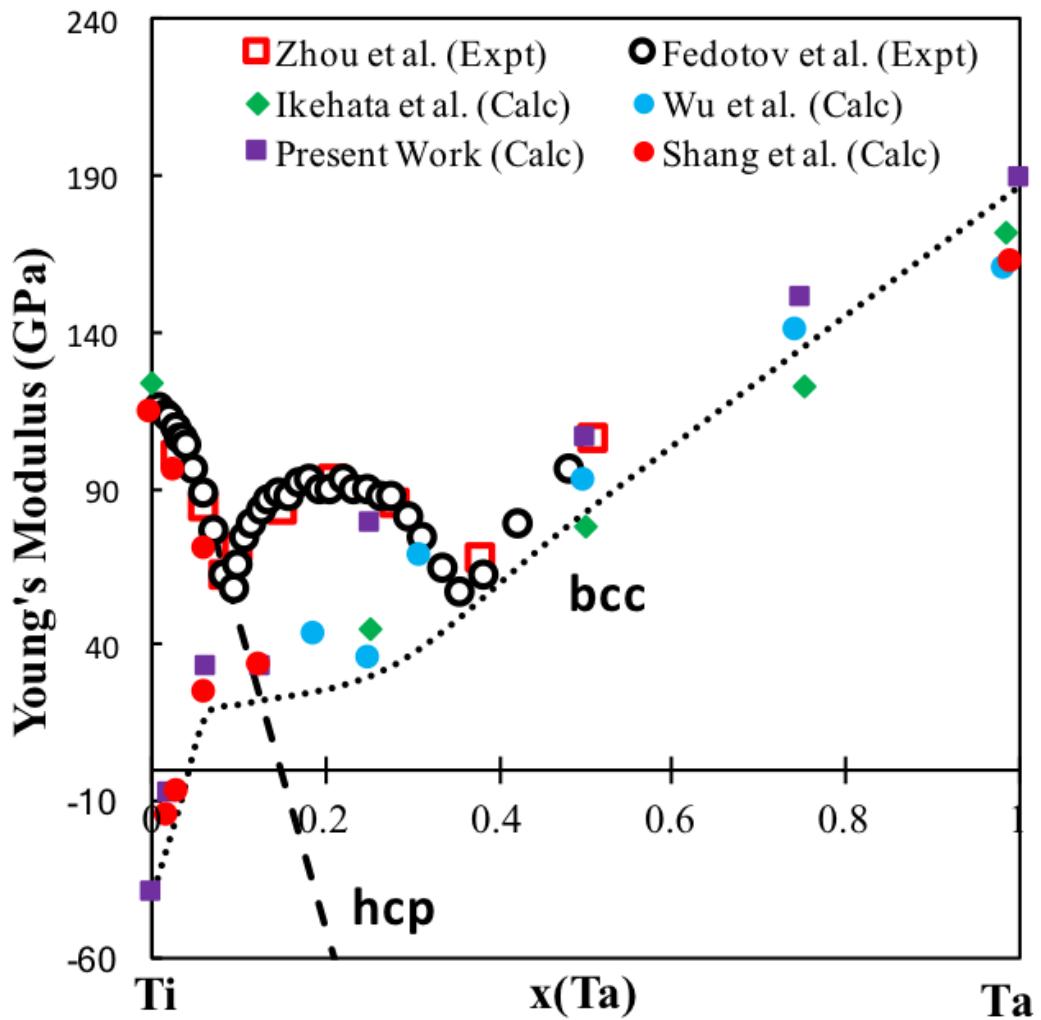


Figure 1.1. Comparison of first-principles calculations [1, 2] and experimental measurements of the Young's modulus of Ti-Ta alloys [3–5]. The purple box refers to the composition range when the calculations and experimentally determined E do not match up due to the formation of two metastable phases ω and α'' .

Chapter 2

Methodology

2.1 First-Principles Calculations

In this dissertation, the ground state energy structures, thermodynamic properties and mechanical properties are calculated using first-principles based on Density Functional Theory. The first-principles refers to the calculations originating from "first-principles", meaning that the inputs are the atomic coordinates and atomic numbers. This method computes the interactions between atoms in a periodic supercell. This is determined using quantum mechanical electronic theory that is based on the electronic charge density and does not rely on any empirical data. This section provides a description of the DFT methodology.

Schrödinger's time-independent non-relativistic equation is a solution to the many-body problem of calculating the interactions of positively charged nuclei and negatively charged electrons. The Schrödinger equation is:

$$\left[\sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla_i^2 + V_{ext}(r_i) \right) + \sum_{i < j} U(r_i, r_j) \right] \Psi = E_0 \Psi \quad (2.1)$$

where the first bracketed part represents the Hamiltonian (\hat{H}), Ψ describes the wave function of electrons, E_0 describes the system's ground state energy. The \hat{H} of the system is described by three parts, the first part represents the kinetic energy with N being the total number of electrons in the system, \hbar being Planck's constant and m the mass of an electron. The second term V_{ext} gives the external potential and U is the potential of the electron-electron repulsion.

Eq. 2.1 can be solved for Ψ with the lowest energy E_0 being the ground state

energy, assuming the nuclei-nuclei interactions are neglected due to the Born-Oppenheimer approximation. The Born-Oppenheimer approximation allows us to assume the nuclei are stationary and ignore the motion of the nuclei on the electronic timescale, due to the mass difference, with nuclei being $\sim 10^3$ to 10^5 larger than electrons. However, even with this approximation solving Eq. 2.1 is difficult to deal with due to the electron-electron Columb interactions making the electronic motion correlated and the fact that the many-body problem results in too many variables because there are $3N$ degrees of freedom.

Hohenberg-Kohn formulated two theorems to simplify this problem [48]. The first theorem is that the external potential is a unique functional of the electron density. The second theorem states that the density that minimizes the total energy is the exact ground state density and thus the ground state is obtained variationaly. With these theorems, Kohn-Sham proved that the problem can be solved as if the electrons are not interacting and still obtain the density as if they were, by [49]:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ext}(r) + V_{Hartree}(r) + V_{XC}(r) \right] \phi_1(r) = \epsilon_i \psi_i(r) \quad (2.2)$$

where $V_{ext}(r)$ describes the electron-nuclei interaction similar as in Eq. 2.1:

$$V_{ext} = -e^2 \sum_a \frac{Z_a}{|r_i - R_a|} \quad (2.3)$$

where r_i represents the position of electron i and R_a represents the position of nucleus a with a charge valance of Z_a . The electron-electron interactions are represented by $V_{Hartree}$:

$$V_{Hartree}(r) = e^2 \int \frac{\rho(r)}{|r - r_j|} d^3r \quad (2.4)$$

where r and r_j represent the electrons and $\rho(r)$ is described by :

$$\rho(r) = \sum_i^N |\psi_i(r)|^2 \quad (2.5)$$

The final term of V_{xc} is the exchange correlation potential that is described in terms of an exchange-correlation energy. While there is no exact solution to the exchange-correlation (X-C) energy available, there are multiple different approximations. Each approximation is done to account for different things. In the present

work, the generalized gradient approximation by Perdew and Wang (PW91) [50] and the generalized gradient approximation by Perdew, Burke and Ernzerhoff (PBE) [51] where used. The generalized gradient approach improves the total energies, atomization energies as opposed to other methods such as the local density approximation [52] but can over-correct for the expansion and softening of bonds. The generalized gradient approximation (GGA) is favored for densities that are inhomogeneous. Based on previous research done by Perdew et al. [51], GGA's are considered to be adequate approximations for calculating metals. The use of PW91 vs PBE was compared when looking at the elastic properties of the Ti-Ta system in Figure 2.1. The results showed little difference in calculated elastic properties. The PW91 X-C functional was designed to satisfy as many exact conditions as possible and thus has some issues. Perdew introduced the PBE X-C functional as an improvement to PW91 which satisfied less exact conditions and only looked at the ones that were energetically significant for metals. Due to this and the fact the results vary so little, the PBE X-C functional was chosen to be used for the present thesis work. By implementing the theorems and the Kohn-Sham equation, the energy of the system can thus be calculated.

2.1.1 Density Functional Theory at 0 °K

The ground state energy at 0 °K without the contribution of zero-point vibrational energy can be calculated by using the equation of states (EOS) fitting for the relationship between the energy and volume of the structure. The EOS fitting is achieved through an energy-volume ($E_0 - V$) curve of 5 or more relaxed volumes and using the four-parameter Birch-Murnaghan (BM4) EOS [53]:

$$E_0(V) = a + bV^{-\frac{2}{3}} + cV^{-4/3} + dV^{-2} \quad (2.6)$$

where a , b , c and d are fitting parameters. From this, the volume V_0 , ground state energy E_0 , bulk modulus B_{EOS} , and first derivative with respect to pressure B'_{EOS} can be calculated.

From the ground state energies, the energy of formation and enthalpy of formation at 0 °K can be calculated by finding the difference between the structures energy and a reference state, normally the standard element reference (SER) state at standard pressure and temperature. The valance configuration for each element

was selected based on the VASP recommendations. The p electrons were treated as valance for the Mo and Ta, the d electrons were treated as valance for Sn and the s electrons were treated as valance for Ti, Nb, and Zr [54, 55].

2.1.2 Finite-temperature thermodynamics

The Helmholtz energy, $F(V, T)$ can be calulated, with DFT, as a function of temperature T and volume V :

$$F(V, T) = E_0(V) + F_{vib}(V, T) + F_{T-el}(V, T) \quad (2.7)$$

where E_0 is the static contribution at 0 °K calculated from Eq. 2.6, F_{vib} is the temperature-dependent vibrational contribution, and F_{T-el} is the thermal electronic contribution. At ambient pressure, the Helmholtz energy of the system is equal to the Gibbs energy, which is used in the CALPHAD modeling. The vibrational contribution is obtained through the phonon quasiharmonic supercell (phonon approach) or the Debye-Grüneisen method (Debye). The phonon approach is a more accurate approach compared to the Debye model but it is also more computationally expensive. In the present work, both the phonon and Debye models are used in different sections. The vibrational contribution is obtained through phonon calculations of at least five different volumes [56]:

$$F_{vib}(V, T) = k_b T \int_0^\infty \ln \left[2 \sinh \frac{\hbar \omega}{2k_B T} \right] g(\varrho) d\varrho \quad (2.8)$$

where $g(\varrho)$ is the phonon density of states as a function of phonon frequency ϱ at volume V . In addition, the Debye model is used to estimate the vibrational contribution [53]:

$$F_{vib}(V, T) = \frac{9}{8} k_b \theta_D(V) + k_B T \left[3 \ln \left(1 - e^{-\frac{\theta_D}{T}} \right) - D \left(\frac{\theta_D}{T} \right) \right] \quad (2.9)$$

where θ_D is the Debye temperature, T is the temperature, and $D \left[\frac{\theta_D}{T} \right]$ is the Debye function. θ_D is calculated through:

$$\theta_D = s \frac{(6\pi^2)^{\frac{1}{3}} \hbar}{k_B} V_0^{\frac{1}{6}} \left(\frac{B}{M} \right)^{\frac{1}{2}} \left(\frac{V_0}{V} \right)^\gamma \quad (2.10)$$

where s is the Debye temperature scaling factor, γ is the Grüneisen parameter

determined by the pressure derivative of bulk modulus (B'_{EOS}), B_{EOS} is the bulk modulus, M is the atomic mass, and V_0 is the equilibrium volume. Here the equilibrium properties V_0 , B_{EOS} , and B'_{EOS} are estimated from the EOS of Eq. 2.6. The Debye temperature scaling factor was determined by Moruzzi et al. [57] to be 0.617 for nonmagnetic metals. However, this value has been shown to be less accurate for other materials. Liu et al. extensively looked at the Debye scaling factor and how to calculate the scaling factor based on the Poisson's ratio of a material [58]. The methodology by Liu et al. [58] was used for the present work to calculate the scaling factor:

$$s(\nu) = 3^{\frac{5}{6}} \left[4\sqrt{2} \left(\frac{1+\nu}{1-\nu} \right)^{\frac{3}{2}} + \left(\frac{1+\nu}{1-\nu} \right)^{\frac{-1}{3}} \right] \quad (2.11)$$

where ν is the Poisson's ratio, which can be calculated from the elastic stiffness constants.

The thermal electronic contribution is based on the electronic density of states and calculated with the Fermi-Dirac statistics [53, 59]:

$$F_{T-el} = E_{T-el} - TS_{T-el} \quad (2.12)$$

The E_{T-el} and S_{T-el} represent the energy and entropy of the thermal electron excitations, respectively. The E_{T-el} is expressed by:

$$E_{T-el}(V, T) = \int n(\epsilon, V) f(\epsilon, T) \epsilon d\epsilon - \int^{\epsilon_f} n(\epsilon) \epsilon d\epsilon \quad (2.13)$$

and the entropy S_{T-el} is expressed by:

$$S_{T-el}(V, T) = -k_B \int n(\epsilon, V) [ln f(\epsilon, T) + (1 - f(\epsilon, T)) ln(1 - f(\epsilon, T))] d\epsilon \quad (2.14)$$

where $n(\epsilon, V)$ is the electronic density of states (DOS) at energy ϵ , $f(\epsilon, T)$ is the Fermi-Dirac distribution, ϵ_f is the Fermi energy level and k_B is Boltzmann's constant. The Fermi-Dirac distribution $f(\epsilon, T)$ is expressed by:

$$f(\epsilon, T) = \left[\exp \left(\frac{\epsilon - \mu}{k_B T} \right) + 1 \right]^{-1} \quad (2.15)$$

and μ is the chemical potential of the electrons.

2.1.3 Elastic stiffness calculations

The single crystal elastic stiffness constants ($c_{ij}'s$) were calculated from the ground state energy structure using a stress-strain method developed by Shang et al. [60]. With this method, a set of independent strains $\varepsilon = (\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6)$ are imposed on the crystal lattice, where $\varepsilon_1, \varepsilon_2$, and ε_3 are the normal strains, $\varepsilon_4, \varepsilon_5$, and ε_6 the shear strains, and a set of stresses $\sigma = (\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6)$ are generated. Hooke's law is then used to calculate the elastic stiffness constants:

$$\begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{22} & c_{23} & 0 & 0 & 0 \\ c_{13} & c_{23} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{pmatrix} = \begin{pmatrix} \varepsilon_{1,1} & \varepsilon_{1,n} \\ \varepsilon_{2,1} & \varepsilon_{2,n} \\ \varepsilon_{3,1} & \dots & \varepsilon_{3,n} \\ \varepsilon_{4,1} & \varepsilon_{4,n} \\ \varepsilon_{5,1} & \varepsilon_{5,n} \\ \varepsilon_{6,1} & \varepsilon_{6,n} \end{pmatrix}^{-1} \begin{pmatrix} \sigma_{1,1} & \sigma_{1,n} \\ \sigma_{2,1} & \sigma_{2,n} \\ \sigma_{3,1} & \dots & \sigma_{3,n} \\ \sigma_{4,1} & \sigma_{4,n} \\ \sigma_{5,1} & \sigma_{5,n} \\ \sigma_{6,1} & \sigma_{6,n} \end{pmatrix} \quad (2.16)$$

where "-1" represents the pseudo-inverse. Due to symmetry, the bcc structure only has three independent elastic stiffness constants. However, with a lack of bcc stability for some of the calculations, all of the elastic stiffness constants are calculated and the average \bar{C}_{11} , \bar{C}_{12} and \bar{C}_{44} values are calculated:

$$\bar{C}_{11} = \frac{(c_{11} + c_{12} + c_{44})}{3} \quad (2.17)$$

$$\bar{C}_{12} = \frac{(c_{12} + c_{13} + c_{23})}{3} \quad (2.18)$$

$$\bar{C}_{44} = \frac{(c_{44} + c_{55} + c_{66})}{3} \quad (2.19)$$

This case is for the unstable bcc elastic calculations to mimic the behavior of a cubic structure. The largest variance between the similar elastic stiffness constants, when calculating the average, is used to show the deviation from the bcc symmetry in the calculations, shown as error bars. The stable bcc structures shows no variance and thus no error bars. To examine the effects of different strain on the elastic

properties, three groups of non-zero strain magnitudes, ± 0.01 , ± 0.03 , and ± 0.07 , are tested in chapter 5 and it can be noted that the results have negligible changes with respect to the three groups of strains tested herein. Therefore, ± 0.01 is used for all the calculations. The calculated elastic stiffness constants are used to calculate the polycrystalline elastic properties including bulk (B), shear (G), and E modulus using the Voigt-Reuss-Hill (VRH) approach [61], and the average results from the Hill approach are reported herein.

The mechanical stability of the bcc phase can be determined based on Born's criteria $\overline{C}_{11} - \overline{C}_{12}$ [62, 63]:

$$\overline{C}_{11} - |\overline{C}_{12}| > 0 \quad (2.20)$$

$$\overline{C}_{11} + 2\overline{C}_{12} > 0 \quad (2.21)$$

$$\overline{C}_{44} > 0 \quad (2.22)$$

when $\overline{C}_{11} - \overline{C}_{12}$ becomes negative then the phase loses mechanical stability.

2.1.4 Special quasirandom structures (SQS)

To calculate the energies, enthalpies of formation and elastic properties across the entire binary and ternary composition range, varying compositions of special quasirandom structures (SQS) are used. The SQS are small supercells used to mimic randomly substituted structures in terms of correlation functions. The binary and ternary bcc SQS used in the present work were previously generated by Jiang et al. [64, 65]. The relaxation of these structures is complicated because local atomic relaxations can cause the structure to lose the bcc lattice symmetry. To preserve structural symmetry, methodology discussed by Liu et al. [66] and Zacherl et al. [67] was used and the calculations were carried out with different relaxation schemes only alloying the cell shape and cell volume to be relaxed to determine the lowest energy structure. In order to ensure the bcc symmetry was preserved the energies were plotted as a function of composition. Then the symmetry was verified. There are two ways to verify whether the SQS is still bcc or not after the relaxation. The first is to merge different elements into one element for the SQS structure, and then, use codes available to check the symmetry or space group (such as VASP and phonopy codes). The second is to visualize the structure directly

using a visualization software such as VESTA and compare the symmetry to the unrelaxed bcc structure. For the present work, the relaxed structures were plotted in the visualization software and compared to the unrelaxed structure. In some cases, even without comparing it was very obvious that the structure had lost bcc symmetry. For the cases where it wasn't obvious the comparison was done using symmetry codes (VASP, phonopy, etc). After the relaxation, at least five different volume structures are generated and the ions are allowed to relax. This yields the different volumes needed for the EOS fitting described above, which allows a better prediction of the different properties as a function of composition.

2.1.5 High-throughput partition function

ADD

2.1.6 First-principles calcualtion error

The error between the previous results and present results was calculated using:

$$\sqrt{\frac{\sum[(A_{calc} - A_{ref})]^2}{\kappa}} = Error \quad (2.23)$$

where A_{calc} is from the present calculation and A_{ref} is from the previous calculation, and κ is the total number of data points.

2.2 CALPHAD method

The CALPHAD method evaluates parameters to represent the Gibbs energy of individual phases as a function of temperature, pressure and composition. Thermochemical and phase boundary data obtained from experiments and first-principles calculations are used in the PARROT module of Thermo-Calc to evaluate the parameters [68]. The Gibbs free energy is described by enthalpy H , temperature T and entropy S as follows:

$$G = H - TS \quad (2.24)$$

The Gibbs energy is then parameterized and expressed by:

$$G - H^{SER} = a + bT + cT\ln T + dT^2 + \sum_2^n e_n T^n \quad (2.25)$$

where H^{SER} refers to the elemental enthalpy in the SER state and a, b, c, d, e are coefficients. Other thermodynamic properties such as, enthalpy, entropy and heat capacity can be derived from this equation. The parameterized equations for the pure elements have been determined and widely adopted from the SGTE to ensure global compatibility between different databases [26].

2.2.1 Solution phases

The databases are built upon the pure elements and then the effects of the binary and ternary interactions are modeled. Normally, the effects of alloying are modeled as solution phases or stoichiometric phases. The solution phases with one sublattice are described by:

$$G_m^\phi = \sum x_A^0 G_A^\phi + RT \sum x_A \ln x_A + {}^{XS}G_m^\phi \quad (2.26)$$

where x_A is the mole fractions of elements A and ${}^0G_A^\phi$ is the molar Gibbs energy of pure element A in the specific phase (ϕ) being modeled, the second term describes the ideal interaction between elements. The last term represents the excess mixing energy, representing the non-ideal interactions between species A and B . The excess mixing energy can be expressed by the Redlich-Kister polynomial as [69]:

$${}^{XS}G_m^\phi = \sum x_A x_B \sum_{k=0}^k L_{A,B}^\phi (x_A - x_B)^k \quad (2.27)$$

where ${}^kL_{A,B}^\phi$ represents the interaction parameter for elements A and B in phase ϕ described by:

$$L_{A,B}^\phi = {}^k a + {}^k bT \quad (2.28)$$

in which ${}^k a$ and ${}^k b$ are evaluated model parameters. Eq. 2.27 can be extended to multi-component systems as:

$${}^{xS}G_m^\phi = \sum x_A x_B \sum_{k=0}^k L_{A,B}^\phi (x_A - x_B)^k + \sum x_A x_B x_C \\ \left[{}^0L_{A,B,C}^\phi (x_A + \delta_{A,B,C}) + {}^1L_{A,B,C}^\phi (x_B + \delta_{A,B,C}) + {}^2L_{A,B,C}^\phi (x_C + \delta_{A,B,C}) \right] \quad (2.29)$$

where the ternary interaction parameters $L_{A,B,C}^\phi$ are described the same as the binary interaction parameters in Eq. 2.28 and $\delta_{A,B,C}$ is defined as $\delta_{A,B,C} = (1 - x_A - x_B - x_C)/3$

In the present thesis, while no order-disorder modeling is done, the order-disorder model is used in many of the previous models evaluated. At low temperatures in many of the Ti-containing binary alloys, the randomly substituted bcc-A2 phase goes through a second order transition to become the ordered simple cubic B2 phase (CsCl-type). This modeling is discussed extensively in the COST 507 by Ansara [6].

2.2.2 Stoichiometric compounds

The Gibbs energy of stoichiometric compounds is modeled in per mole unit formula. For the stoichiometric compound, A_pB_q , the Gibbs energy is expressed by [67]:

$${}^0G_m^{A_pB_q} = a + bT + p * {}^0G_A^{SER} + q * {}^0G_B^{SER} \quad (2.30)$$

where a and b are the evaluated parameters, ${}^0G_A^{SER}$ is the Gibbs energy of pure element A in the SER phase, ${}^0G_B^{SER}$ is the Gibbs energy of pure element B in the SER phase, p is the number of atoms per unit formula of element A and q is the number of atoms per unit formula of element B .

2.2.3 Elastic Properties

To obtain the elastic properties as a function of composition, the CALPHAD modeling approach was adopted and the Redlich-Kister polynomial was used to describe the elastic properties by [69, 70]:

$$E(x) = \sum x_A E_A^\phi + \sum x_A x_B^k L_{A,B}^\phi + \sum x_A x_B x_C^0 L_{A,B,C}^\phi \quad (2.31)$$

where similar to Eq. 2.27 and 2.29 the x_A , x_B , and x_C refer to the mole fraction of element A , B , and C respectively, E_A is the elastic property of element A , $k L_{A,B}^\phi$

and ${}^k L_{A,B,C}^\phi$ are the binary and ternary interaction parameters, respectively. The binary and ternary interaction parameters are described in terms of Eq. 2.28 but with solely an a coefficient.

2.3 Experimental

ADD

2.3.1 Ti-Nb sample preparation

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2.3.2 Neutron Scattering

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2.3.2.1 ARCS

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2.3.2.2 Data Analysis

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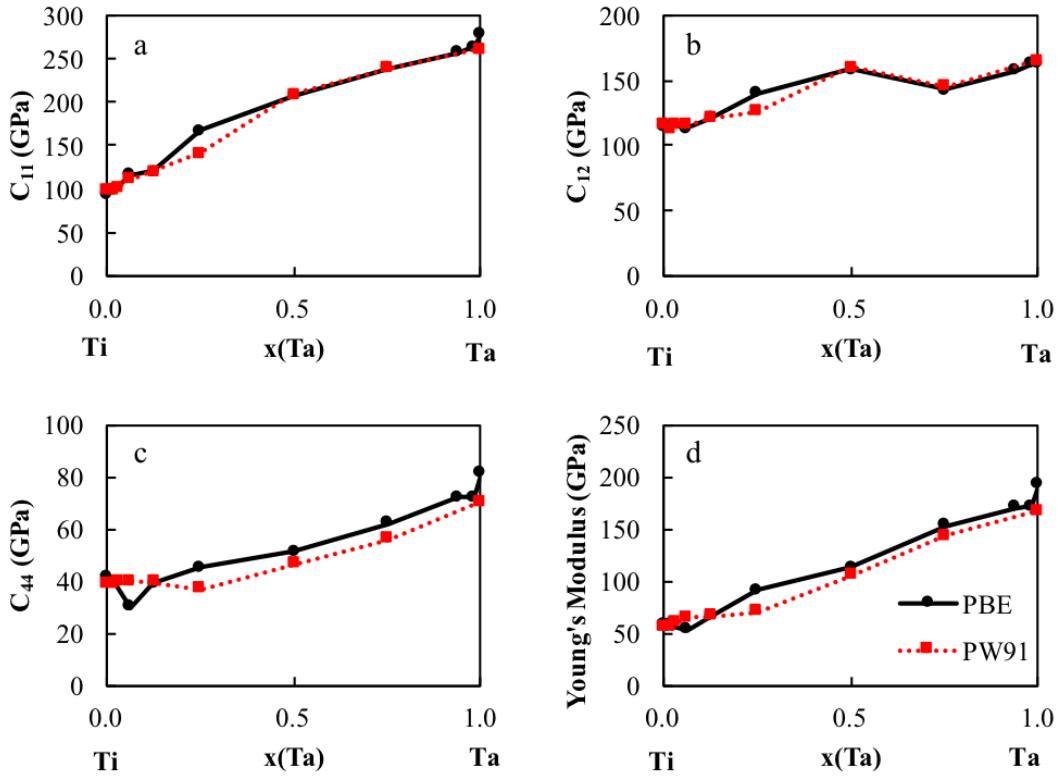


Figure 2.1. Elastic stiffness constants of the bcc Ti-Ta binary system calculated with the GGA and PBE exchange correction functions, respectively.

Chapter 3 |

Ti-Mo-Nb-Sn-Ta-Zr Thermodynamic Database

3.1 Introduction

The design of Ti-alloys for biomedical applications necessitates a completed thermodynamic database that will facilitate the prediction of phase compositions and fractions as a function of composition and temperature. However, there is no completed thermodynamic database for the Ti-Mo-Nb-Sn-Ta-Zr system and thus the present work aims at building a complete database with special focus on the Ti-rich alloys and bcc phase models. With this in mind the pure elements have been extensively studied and are widely adopted from the SGTE database [26]. The modeling of the binary systems has been widely documented with the exception of the Ta-Sn and Mo-Sn systems, while experimental phase boundary data is available for the ternary systems but little to no modeling has been completed. The Mo-Sn and Sn-Ta subsystems have high melting temperatures and little to no experimental data. In these cases, first-principles calculations based on DFT can be used to aid in modeling and supplement the lack of experimental data. The complete modeling of the Ta-Sn system is discussed in Ch3. In the present chapter, the thermodynamic descriptions of the Ti-Mo-Nb-Ta-Zr system are described.

While many of the alloys in this Ti system have been studied experimentally, yielding phase equilibrium data, only limited calorimetry data is available. With the present work focuses on bcc Ti-rich alloys, first-principles calculations based on DFT of the enthalpy of formation of the bcc phase were calculated. The thermodynamic

descriptions were built or evaluated using available experimental phase boundary data and present calculated thermochemical data. This work looks at evaluating new and previous models for the binary and Ti-containing ternary systems.

3.2 Computational details

First-principles results based on Density Functional Theory (DFT) are used to predict the enthalpy of formation of specific phases. In the present work, the enthalpy of formation of the bcc phase was calculated for the Ti-X and Ti-X-Y ($X \neq Y = Mo, Nb, Ta, Zr$) using the calculated energy of the pure elements in their SER states. For each Ti-containing binary system at least 5 composition energy structures were calculated and three compositions for the Ti-containing ternary system. For each system, three special quasirandom structures (SQS) of varying compositions were relaxed to get an accurate representation of the enthalpy of formation across the composition range. For the binary phases the compositions are each 16-atom unit cells at Ti_4X_{12} , Ti_8X_8 , and $Ti_{12}X_4$ and the ternary phase compositions of $Ti_{12}X_{12}Y_{12}$ (36-atom), $Ti_{16}X_8Y_8$ (32-atom), $Ti_{48}X_8Y_8$ (64-atom) structures are used with one X_8Y_8 (16-atom), where X and Y are the alloying elements. These SQS in the bcc phase that were implemented were developed by Jiang et al. [64, 65]. Relaxation of these structures is complicated and explained in the methodology section. The DFT calculations are completed using VASP (Vienna ab-initio Simulation Package) [54]. The ion-electron interactions were described using the projector augmented wave (PAW) [55, 71] method. Based on the work of comparing X-C functionals (Figure 2.1) the exchange-correlation functional of the generalized gradient approach depicted by Perdew, Burke, and Ernzerhof (PBE) was employed [51]. For consistency, a 310 eV energy cutoff was adopted for all calculations, which is roughly 1.3 times higher than the default value. The energy convergence criterion was 10⁻⁶ eV/atom, and the Monkhorst-Pack scheme is used for Brillouin zone sampling [54, 72].

3.3 Binary systems

In order to build the database, as discussed above, the pure elements were adapted from the SGTE database [26]. After the incorporation of the pure elements, all the

binary systems were then evaluated. When applicable, previous models of the binary systems were evaluated for accuracy and model compatibility and incorporated into the database. After incorporation of all binary systems, the Ti-containing ternary systems were evaluated, with the exception of Mo-Nb-Ta which had a previous model available by Xiong et al. [12] and was incorporated into this work. To do the binary and ternary evaluations, the enthalpy of formation of the bcc phase for the Ti-containing alloys was calculated across the composition ranges. To calculate the enthalpy of formation of the bcc phase, the enthalpy of the pure elements had to be calculated in their standard element reference states (SER). The phases and results are listed in Table 3.1. In order to ensure the accuracy of the calculations, the bulk modulus B calculated in the present work was compared with the experimental data. The experimental B varied on average by 1 GPa from the calculated B . This discrepancy is not large and is attributed with the temperature difference thus these calculations prove to be accurate.

The previous thermodynamic descriptions for the Ti-containing binaries were evaluated with experimental data as well as looking at the enthalpy of formation of the bcc phase using present first-principles calculations. The enthalpy of formation of the bcc phase calculated for each Ti-containing binary from first-principles is listed in Table 3.2.

3.3.1 Ti-Mo

The Ti-Mo binary evaluation was taken from the COST 507 database and the thermodynamic description was evaluated by Saunders [6]. This model was chosen because it is the modeled incorporated into the Ti-Mo-Zr modeling done by Kar et al. [18]. Interaction parameters were evaluated for the liquid, fcc (face centered cubic), hcp, bcc#1, bcc#2 ordered and disordered phases, AlM-D019, AlM-D022, and the AlTi-L10 phases. Figure 3.1a shows the comparison of the available phase boundary data from Murray et al. [7] with the Saunders model. The phase boundary data is reproduced in the with the Saunders model. Figure 3.1b shows the enthalpy of formation of the bcc phase predicted from the model at 300 K compared with the present first-principles results at 0 °K. The enthalpy of formation of the bcc phase predicted varies from the first-principles calculations drastically between 20 and 80 at % Mo. This discrepancy is seen due to the disagreement on the existence

of a bcc miscibility gap. Previous research has shown the need for a bcc miscibility gap which would fit what is seen in the first-principles calculations [73, 74]. Kar et al. showed that the experimental data from higher-component systems fit better with the description containing no miscibility gap. Based on this, the model by Saunders was adopted for the database with no changes.

3.3.2 Ti-Nb

The Ti-Nb binary evaluation was taken from Zhang et al. [8] and plotted in Figure 3.2a. Originally the binary evaluation was taken from Kumar et al. [9]. The figure shows solidus data (\square) and hcp and bcc solvus data (\circ) used in the Kumar et al. evaluation. The model from Kumar was used in the modeling of the Ti-Nb-Zr. The phase diagram was evaluated using phase boundary data on the Ti-rich side and liquidus data. Not only was the binary evaluation adapted due to the use in the Ti-Nb-Zr ternary but it also reproduced the experimental phase boundary data reasonably well. However, the model was changed to the new model by Zhang et al. (\triangle) due to the new phase boundary data on the Nb rich side. The present first-principles calculations of the enthalpy of formation of the bcc phase are plotted in Figure 3.2b. The present DFT results (circles) are at 0 °K while the CALPHAD prediction (solid line) is at 300 °K which explains the average variance of 0.17 kJ/mol-atom between the DFT and CALPHAD predictions. However, even with the variance the CALPHAD prediction compares well with the DFT results and the sublattice models are similar to the database being built. With the reproduction of experimental data and the first-principles results no alterations were made to the thermodynamic evaluation.

3.3.3 Ti-Ta

The Ti-Ta binary was taken from the COST 507 database and evaluated by Saunders [6]. The phase diagram is shown in Figure 3.3a. The figure is plotted with liquidus and solidus experimental data (\diamond , Y) as well as bcc and hcp solvus data (\triangle , \square , \circ). The evaluation includes interaction parameters for the fcc, hcp, liquid, AIM-D019, AIM-D022, AlTi-L10 and the bcc#1 and bcc#2 ordered and disordered phases. The thermodynamic description reproduces the phase boundary experimental data from Murray et al. [10]. The first-principles results (circles) and

the enthalpy of formation of the bcc phase predicted by the CALPHAD modeling is shown in Figure 3.3b. The CALPHAD prediction of the enthalpy of formation reproduces the results from first-principles reasonably well on the Ti-rich and Ta-rich sides. The first-principles results between 10 and 60 at % Ta vary on an average by 0.17 kJ/mol-atom. However, the CALPHAD prediction is at 300 °K and the first-principles are at 0 °K which explains the variance and the CALPHAD prediction follows the same trend that is seen in the first-principle results. The modeling and sublattices used were compatible with the database being built and thus the thermodynamic description by Saunders was not altered.

3.3.4 Ti-Zr

The thermodynamic description of the Ti-Zr alloy system evaluated by Kumar et al. [11] is used in the present work. The model by Kumar et al. was used in the ternary modeling of the Ti-Mo-Zr and Ti-Nb-Zr ternary alloys. The sublattice modeling was consistent with the previous binary systems. The evaluation introduced interaction parameters for the liquid, bcc, and hcp solution phases. Figure 3.4a plots the evaluation compared with phase boundary data for the bcc to hcp phase (\circ) transformation and solidus (\diamond). The thermodynamic description accurately reproduces the phase boundary data. The evaluation also included heat of transformation data shown in the paper by Kumar et al. [11]. Figure 3.4b plots the first-principles results (circles) versus the CALPHAD prediction (solid line) for the enthalpy of formation of the bcc phase. The DFT results and CALPHAD modeling vary on average by 1.2 kJ/mol-atom. The variance is larger than the other binary alloys due to the instability of the bcc phase at both 0 °K and 300 °K for the Ti-Zr alloy but the calculations and CALPHAD prediction follow the same trend. Based on the agreement between the experimental data, first-principles and CALPHAD prediction no alterations were made to the thermodynamic description.

3.3.5 Non Ti-containing binaries

Figure 3.5 shows the evaluation of the Mo-Nb, Mo-Ta, and Nb-Ta alloys. The Mo-Nb, Mo-Ta and Nb-Ta binary descriptions were adapted from the Mo-Nb-Ta ternary paper by Xiong et al. [12]. Xiong et al. introduced binary interaction parameters for the liquid and bcc solution phases. The Mo-Nb evaluation was

completed using differential thermal analysis experiments that measured both the liquidus and solidus temperature. Multiple authors measured experiments and Xiong et al. picked the experiments (shown in the figure as X, +) that estimated the pure elements reasonably well to build the evaluation on. Xiong et al. saw that the experiments shown by \circ , \triangle , \square agreed well with the thermodynamic description. The remaining work (\diamond , *) was too low and thus wasn't included in the evaluation of the binary alloy. The Mo-Ta alloy evaluation was done using two sets of experimental data (\triangle , *, \diamond , \square) for the evaluation that agree well with the accepted melting temperatures of Mo and Ta. The remaining experimental data (\circ) was higher than the other experimental work by 70 °C and thus was not used for the evaluation. The Nb-Ta binary evaluation was done using the melting temperature experimental data (\circ , \triangle , \square) because it predicted the melting temperatures of Nb and Ta accurately. The remaining experimental work which measured the solidus temperature (*) was not used because the melting temperatures of Nb and Ta showed discrepancy. The remaining experimental work (\diamond) was not included in the evaluation because similarly to the Mo-Ta alloy the experimental work was 70 °C higher than the other work. These three evaluations were chosen because these binaries were evaluated to make up the Mo-Nb-Ta ternary alloy and the modeling was done consistently using the same sublattices models. The evaluations fit well with available experimental data and thus they can be added to the database without any changes.

Figure 3.6 shows the Mo-Zr, Nb-Zr, and Ta-Zr alloys. For the Mo-Zr binary alloy system, there were multiple previous thermodynamic descriptions and experimental results available. In the present work, the evaluation by Perez et al. [13] was chosen. The experimental data plotted was determined for the single-phase region, two-phase region, phase boundaries and peritectic and eutectoid reactions. Perez et al. goes into more detail on the available experimental data and was included in the evaluation of the thermodynamic description. The thermodynamic description generally reproduces all experimental data and is compatible with the sublattice modeling used in the database. The Perez et al. model was also incorporated into the Ti-Mo-Zr ternary modeling. Perez et al. introduced interaction parameters for the liquid, bcc, hcp and MZr_2 (laves_c15) phases. The Nb-Zr alloy thermodynamic description evaluated by Guillermet [14] was chosen for the present work. The figure shows the solidus experimental data (\diamond , *) as well as the hcp solvus (Y , \circ) and bcc

miscibility gap (\square , $+$, \triangle)data. The description includes interaction parameters for the liquid, bcc and hcp solution phases. The thermodynamic description was chosen because it was the description that Kumar et al. [11] included in his modeling of the Ti-Nb-Zr alloy system. The experimental phase boundary and liquidus data from Abriata et al. [15] fits well with the model. The Ta-Zr binary evaluated by Guillermet [16] was chosen for the present database. As Guillermet discusses there was quite a lot of experimental data, shown in the figure. Guillermet discusses the experimental data more in his paper. The figure plots single-phase, two-phase, phase boundary, and solidus experimental data. Interaction parameters were introduced for the bcc, hcp and liquid phases. Guillermet had phase boundary results from at least 5 different authors and thermodynamic results from three different authors. The evaluation reproduced the data fairly well. The sublattice modeling fit with the database and thus this binary was selected. The interaction parameters for all the binary systems are listed in Table ??.

3.4 Ti-containing ternary sections

3.4.1 Ti-Mo-Nb

A thermodynamic description for the Ti-Mo-Nb ternary system has never been evaluated. Two experimental investigations were done on the Ti-Mo-Nb system at 873 °K and 1373 °K [19, 75]. While both investigations agree that the isothermal section at 1373 °K is solely the bcc phase, the investigations differed on the phase boundary data at 873 °K. It is suspected that at such a low temperature the samples did not reach equilibrium which accounts for the discrepancy. Based on this, the binary interpolation of the isothermal sections at 1373 °K and 873 °K were plotted. The phase diagram at 1373 °K agreed with the experimentally determined phase diagram to be solely the bcc phase. The phase diagram at 873 °K is plotted in Figure 3.7a. The discrepancy at 873 °K, is the existence of the bcc miscibility gaps as well as what compositions the phase boundary lines lie at. First-principles calculations of the enthalpy of formation of the bcc phase are plotted against the binary interpolation in Figure 3.7b. While the first-principles calculations are at 0 °K and the binary interpolation is at 300 °K the calculation results are reproduced with the CALPHAD prediction. The prediction varies by less than 1.5 kJ/mol-

atom for all the calculations except at $\text{Mo}_{0.5}\text{Nb}_{0.5}$. While the calculation varies substantially from the prediction at $\text{Mo}_{0.5}\text{Nb}_{0.5}$, in order to improve this, the Mo-Nb binary system would have to be adjusted. In the present work, no thermochemical data was used to ensure the accuracy of the non Ti-containing binary systems but the previous binary models were able to reproduce the phase boundary data as discussed above. Based on the discrepancy between the experimental data and the fact that the thermochemical first-principles calculations are reproduced well by the binary interpolation, no ternary interaction parameters were evaluated.

3.4.2 Ti-Mo-Ta

The thermodynamic description of the Ti-Mo-Ta alloys system had not been previously modeled. The binary interpolation of the Ti-Mo-Ta alloy is plotted in Figure 3.8a at 873 °K and compared with experimental data from Nikitin et al. [17]. At 873 °K, the Ti-Mo-Ta alloy has the bcc and hcp solution phases. The experimental data showed a two-phase bcc-hcp region in the Ti-rich corner, while the binary interpolation shows a bcc miscibility gap which forms a tie triangle with the hcp phase. Figure 3.8b shows the first-principles calculations (circles) of the enthalpy of formation of the bcc phase compared with the binary interpolation from the CALPHAD prediction. The first-principles calculations line up fairly well with the CALPHAD prediction. However, due to the discrepancy of the experimental data, ternary interaction parameters were evaluated using the experimental and first-principles results. Interaction parameters for the hcp and bcc phases were investigated. The evaluated interaction parameters are listed in Table 3.3. After assessing the ternary interaction parameters, the isothermal section was again plotted and compared with experimental data in Figure 3.9a and the enthalpy of formation of the newly assessed bcc phase is plotted as a dashed line in Figure 3.8b. The assessment reproduces the first-principles results. With the introduction of the interaction parameters the isothermal section fits with the experimental data. Figure 3.9b is zoomed in on the Ti-rich corner. The work by Nikitin determined hcp phase boundary data plotted as (○) and two phase experimental data as (●). The two phase experimental data is reproduced by the current model. The hcp phase boundary data is not reproduced. However, reliable solid phase boundary data is difficult to obtain at such a low temperature and if the evaluation is altered

to fit the data it then over fits and stabilizes non-equilibrium phases.

3.4.3 Ti-Mo-Zr

The thermodynamic description of the Ti-Mo-Zr alloy system was previously modeled by Kar et al. [18]. The same binary phases used in the modeling by Kar et al. were included in the database. The phases in this system are liquid, bcc, hcp and laves_c15. After interpolating the ternary system from the binary models and comparing to two sets of available experimental data, Kar et al. introduced interaction parameters for the laves_c15 phase. Using the model by Kar et al., the present work plotted the ternary isothermal section at 1273 °K comparing to phase boundary data plotted in Figure 3.10a. As discussed by Kar et al. there is phase boundary data from two authors. The sets of phase boundary data conflict on how far out the two-phase region should extend toward the Ti-rich corner and whether there is a bcc miscibility gap. After plotting the data, Kar et al. decided not to introduce any bcc, liquid or hcp interaction parameters. Only one set of phase boundary data is plotted [19]. The phase boundary data fits well on the Zr-Mo binary side. The predicted enthalpy of formation of the bcc phase is plotted with the first-principles results in Figure 3.10b. The first-principles results vary on average by 0.025 kJ/mol-atom. Based on the available experimental data, first-principles calculations and the conclusions from Kar et al. the present work agrees with the introduction of the ternary laves_c15 interaction parameters and lack of liquid, bcc and hcp ternary interaction parameters. The ternary laves_c15 interaction parameters are listed in Table 3.3.

3.4.4 Ti-Nb-Ta

A thermodynamic description of the Ti-Nb-Ta had not been evaluated but different isothermal sections had been estimated by Na et al. [20] using phase boundary data. The phase boundary data was obtained through XRD. Na et al. looked at samples at 823 °K and 673 °K. The authors discussed that it is likely that the alloys at 673 °K never reached equilibrium conditions. The experimental results were plotted on the binary interpolation in Figure 3.11a and Figure 3.11b. The bcc phase boundary data does not match with the binary interpolation. Figure 3.11c plots the enthalpy of formation of the bcc phase predicted by the CALPHAD

modeling and compared with the first-principles results. The first-principles results vary from the CALPHAD prediction. The variance of the first-principles results and the variance of the experimental data lead to the evaluation of ternary interaction parameters for the bcc and hcp phases. The evaluation was done using the 823 °K experimental data and first-principles calculations. Due to the conclusion by Na et al. that the 673 °K samples did not reach equilibrium the data was neglected during the evaluation. The evaluation led to only one bcc ternary interaction parameter needed and it is listed in Table 3.3. After evaluation, the ternary isothermal sections are plotted with the phase boundary data in Figure 3.12a and Figure 3.12b. The isothermal sections at both 673 and 823 °K reproduces the experimental data reasonably well. The prediction of the enthalpy of formation of the bcc phase also improved to accurately predict the first-principles results.

3.4.5 Ti-Nb-Zr

The Ti-Nb-Zr was previously evaluated by multiple authors. In the present work the ternary isothermal sections were compared with work by Kumar et al. [11] and Tokunaga et al. [21]. The Ti-Zr and Nb-Zr binary alloys were the same modeled binaries as chosen by Kumar et al. The Ti-Nb binary however was changed to a newer evaluation by Zhang et al. [8] which was discussed above. In the evaluation done by Kumar et al. [11], the liquidus projection and various isothermal sections were interpolated from the binary alloys but not compared with experimental data. In the present work, the binary interpolation was used to plot the isothermal sections at the same temperature as Kumar et al. The ternary isothermal sections varied due to the change in the Ti-Nb binary. The binary interpolation of the isothermal section at 843 °K is plotted in Figure 3.13a and compared with experimental data for the tie triangle (\triangle) and two-phase region (\square) shown in the paper by Tokunaga et al. [21]. The binary interpolation reproduced the hcp and bcc disordered and ordered tie triangle phase boundary data and the two-phase bcc miscibility gap region. The enthalpy of formation of the bcc phase is plotted in Figure 3.3b. The CALPHAD prediction varies on an average by 1.34 kJ/mol-atom. While it the CALPHAD prediction varies more drastically than the other enthalpies of formation from the calculated first-principles results, it follows the same trend and fits well with the experimental data. So, the conclusion was reached to not introduce ternary

interaction parameters.

3.4.6 Ti-Ta-Zr

For the Ti-Ta-Zr alloys system, Lin et al. [22] calculated the isothermal sections using binary interpolations and introduced no interaction parameters. The isothermal sections at 1273 and 1773 °K are plotted in Figure 3.14a and Figure 3.14b. Experimental phase boundary data (○) along the bcc miscibility gap at 1273 °K and single phase ● and two phase region ◉ data using x-ray diffraction at 1773 °K are plotted to compare with the binary interpolation [22,23]. The phase boundary data is reproduced excellently. The single-phase data fits well with the interpolation with the two-phase region falling on the phase boundary line. Figure 3.14c is the enthalpy of formation of the bcc predicted from first-principles calculations and the binary interpolation. On average the first-principles varies by 3.69 kJ/mol-atom. While this variance is larger than other plots it can be attributed to the temperature difference and instability of the bcc phase at 300 °K and 0 °K. Since the experimental data is reproduced, it was concluded that no overfitting to the first-principles calculations was needed and thus none were evaluated. After evaluation, the thermodynamic descriptions of all the binary systems and Ti-containing ternary systems are listed in Table 3.3 and combined into a single tdb database in the appendix.

3.5 Conclusion

The present work builds a thermodynamic database for the Ti-Mo-Nb-Ta-Zr system using descriptions of the pure elements, binary systems and Ti-containing ternary systems. The thermodynamic descriptions of the pure elements was adapted from the SGTE database [26]. The previous models for the binary systems were evaluated for compatibility and accuracy. With the present application focusing on Ti-alloys, first-principles results for the enthalpy of formation of the bcc phase was used to ensure the accuracy of the thermodynamic descriptions in predicting thermochemical data. Binary interpolations were predicted for the Ti-containing ternary systems and compared with isothermal experimental data as well as first-principles of enthalpy of formation of the bcc phase. When needed the ternary interaction, parameters were evaluated. The compatible thermodynamic descriptions were

complied into a single tdb database. The raw first-principles data as well as the tdb database are in appendix A.

Table 3.1. Bulk modulus B and enthalpy are listed for each pure element in their SER phase listed. The sv and pv refer to the electrons chosen as valance according to the VASP recommendations. The results are compared with available experimental data.

Pure Elements	Reference	Phase	Enthalpy (kJ/mol-atom)	B (GPa)
Ti_sv	Shang [76]	hcp	-7.89	113
	Expt 300 K [77]			110
Mo_pv	This work 0 K	bcc	-10.84	262
	Expt 300 K [78]			261
Nb_sv	This work	bcc	-10.22	171
	Expt 300 K [79]			172
Ta_pv	This work 0 K	bcc	-11.85	196
	Expt 300 K [79]			196
Zr_sv	Shang 0 K [76]	hcp	-8.51	94
	Calc 0 K [80–83]			94

Table 3.2: First-principles calculations of the enthalpy of formation of the bcc phase in kJ/mol-atom for different atomic percent compositions of the Ti-X binary systems at 0 K.

BCC Phase 0 K	x(Ti)	x(X)	HForm (kJ/mol-atom)
Ti	1.000	0.000	7.29
Ti15Mo	0.937	0.063	3.08
Ti7Mo	0.875	0.125	2.82
Ti75Mo25	0.750	0.250	1.12
Ti50Mo50	0.500	0.500	-3.67
Ti25Mo75	0.250	0.750	-5.18
TiMo15	0.063	0.937	1.79
TiMo53	0.019	0.981	5.82
Mo	0.000	1.000	0.00
Ti53Nb	0.981	0.019	6.92
Ti7Nb	0.875	0.125	5.88
Ti75Nb25	0.750	0.250	7.57
Ti50Nb50	0.500	0.500	8.54
Ti25Nb75	0.250	0.750	1.15
TiNb15	0.063	0.938	0.59
TiNb53	0.019	0.981	0.20
Nb	0.000	1.000	0.00
Ti53Ta	0.981	0.019	7.21
Ti15Ta	0.938	0.063	7.04
Ti7Ta	0.875	0.125	9.28
Ti75Ta25	0.750	0.250	4.89
Ti50Ta50	0.500	0.500	3.94
Ti25Ta75	0.250	0.750	3.10
TiTa15	0.063	0.938	0.94
TiTa53	0.019	0.981	0.28
Ta	0.000	1.000	0.00
Ti53Zr	0.981	0.019	5.49
Ti75Zr25	0.750	0.250	4.59

Table 3.2: First-principles calculations of the enthalpy of formation of the bcc phase in kJ/mol-atom for different atomic percent compositions of the Ti-X binary systems at 0 K.

BCC Phase 0 K	x(Ti)	x(X)	HForm (kJ/mol-atom)
Ti50Zr50	0.500	0.500	1.94
Ti25Zr75	0.250	0.750	3.50
TiZr15	0.063	0.938	5.72
Zr	0.000	1.000	8.19

Table 3.3: Thermodynamic parameters for the Ti-Mo-Nb-Ta-Zr system. The thermodynamic description of the pure elements is not included. The pure elements were adopted from the SGTE database and are listed in the supplementary tdb file [38].

Phase	Reference	Interaction Parameter
Liquid	[6]	$0_{Ti,Mo}^L = -9000.0 + 2.00 * T$
	[8]	$0_{Ti,Nb}^L = 7406.1$
	[6]	$0_{Ti,Ta}^L = 1000.0$
	[6]	$0_{Ti,Ta}^L = -7000.0$
	[11]	$0_{Ti,Zr}^L = -967.7$
	[12]	$0_{Mo,Nb}^L = 15253.7$
	[12]	$1_{Mo,Nb}^L = 10594.2$
	[12]	$0_{Mo,Ta}^L = 13978.9$
	[13]	$0_{Mo,Zr}^L = -24055.1 + 8.146 * T$
	[13]	$1_{Mo,Zr}^L = -5132.17 + 4.804 * T$
	[14]	$0_{Nb,Zr}^L = 10311.0$
	[14]	$1_{Nb,Zr}^L = 6709.0$
	[16]	$0_{Ta,Zr}^L = 13832.1$
	[16]	$1_{Ta,Zr}^L = -7150$
BCC	[6]	$0_{Ti,Mo}^L = 2000.0$
	[6]	$1_{Ti,Mo}^L = -2000.0$
	[8]	$0_{Ti,Nb}^L = 13045.3$
	[6]	$0_{Ti,Ta}^L = 12000.0$
	[6]	$1_{Ti,Ta}^L = -2500.0$
	[11]	$0_{Ti,Zr}^L = -4346.2 + 5.49 * T$
	[12]	$0_{Mo,Nb}^L = -68202.6 + 29.86 * T$
	[12]	$1_{Mo,Nb}^L = 8201.3$
	[12]	$0_{Mo,Ta}^L = -75129.2 + 30.00 * T$
	[12]	$1_{Mo,Ta}^L = 6039.2$
	[13]	$0_{Mo,Zr}^L = 17936.0 + 3.10 * T$
	[13]	$1_{Mo,Zr}^L = -991.0 + 4.30 * T$
	[12]	$0_{Nb,Ta}^L = 1298.0$

Table 3.3: Thermodynamic parameters for the Ti-Mo-Nb-Ta-Zr system. The thermodynamic description of the pure elements is not included. The pure elements were adopted from the SGTE database and are listed in the supplementary tdb file [38].

Phase	Reference	Interaction Parameter
	[14]	$0_{Nb,Zr}^L = 15911.0 + 3.35 * T$
	[14]	$1_{Nb,Zr}^L = 3919.0 - 1.09 * T$
	[16]	$0_{Ta,Zr}^L = 29499.6 + 2.67 * T$
	[16]	$1_{Ta,Zr}^L = -4396.2 + 4.43 * T$
	[16]	$2_{Ta,Zr}^L = -6353.3 + 4.91 * T$
	This work	$0_{Ti,Mo,Ta}^L = -154731.2$
	This work	$0_{Nb,Ta,Ti}^L = -136603.3$
	This work	$1_{Nb,Ta,Ti}^L = -136602.7$
HCP	[6]	$0_{Ti,Mo}^L = 22760.0 - 6.00 * T$
	[8]	$0_{Ti,Nb}^L = 11742.4$
	[6]	$0_{Ti,Ta}^L = 8500.0$
	[11]	$0_{Ti,Zr}^L = 5133.0$
	[13]	$0_{Mo,Zr}^L = 26753.8 + 4.56 * T$
	[14]	$0_{Nb,Zr}^L = 24411.0$
	[16]	$0_{Ta,Zr}^L = 30051.7$
FCC	[6]	$0_{Ti,Mo}^L = 16500.0$
	[6]	$0_{Ti,Ta}^L = 8500.0$
Al3M_D022	[6]	$0_{Ti:Ti}^L = 4 * GFCTTI$
	[6]	$0_{Mo:Mo}^L = 4 * GFCCMO$
	[6]	$0_{Ti:Mo}^L = GFCCMO + 3.0 * GFCTTI$
	[6]	$0_{Mo:Ti}^L = 3.0 * GFCCMO + GFCTTI$
	[6]	$0_{Ti:Ta}^L = GFCTTA + 3.0 * GFCTTI$
AlM_D019	[6]	$0_{Ti:Ti}^L = 4.0 + 4.0 * GHSERTI$
	[6]	$0_{Mo:Mo}^L = 4.0 * GHCPMO$
	[6]	$0_{Ta:Ta}^L = 4.0 * GHCPTA$
	[6]	$0_{Ti:Mo}^L = 17072.0 - 4.5 * T + GHCPMO + 3.0 * GHSERTI$
	[6]	$0_{Mo:Ti}^L = 17072.0 - 4.5 * T + 3.0 * GHCPMO + GHSERTI$

Table 3.3: Thermodynamic parameters for the Ti-Mo-Nb-Ta-Zr system. The thermodynamic description of the pure elements is not included. The pure elements were adopted from the SGTE database and are listed in the supplementary tdb file [38].

Phase	Reference	Interaction Parameter
AlTi	[6]	$0_{Ti:Ta}^L = 6376.0 + GHCPA + 3.0 * GHSERTI$
	[6]	$0_{Ta:Ti}^L = 6376.0 + 3.0 * GHCPA + GHSERTI$
	[6]	$0_{Ti:Mo}^L = 51212.0 - 13.5 * T$
	[6]	$0_{Mo,Ti:Ti}^L = 51212.0 - 13.5 * T$
	[6]	$0_{Mo:Mo,Ti}^L = 5692.0 - 1.5 * T$
	[6]	$0_{Ti:Ti,Mo}^L = 5692.0 - 1.5 * T$
	[6]	$0_{Ta,Ti:Ta}^L = 19128.0$
	[6]	$0_{Ta,Ti:Ti}^L = 19128.0$
	[6]	$0_{Ta:Ta,Ti}^L = 2128.0$
	[6]	$0_{Ti:Ta,Ti}^L = 2128.0$
BCC_B2	[6]	$0_{Ti:Ti}^L = 2.0 * GFCTI$
	[6]	$0_{Mo:Mo}^L = 2.0 * GFCCMO$
	[6]	$0_{Ta:Ta}^L = 2.0 * GFCTA$
	[6]	$0_{Ti:Mo}^L = 8250.0 + GFCCMO + GFCTI$
	[6]	$0_{Mo:Ti}^L = 8250.0 + GFCCMO + GFCTI$
	[6]	$0_{Ti:Ta}^L = 4250.0 + GFCTA + GFCTI$
	[6]	$0_{Ta:Ti}^L = 4250.0 + GFCTA + GFCTI$
	[6]	$0_{Mo,Ti:Mo}^L = 8250.0$
	[6]	$0_{Mo,Ti:Ti}^L = 8250.0$
	[6]	$0_{Mo:Mo,Ti}^L = 8250.0$
disordered phase	[6]	$0_{Ti:Mo}^L = 10000.0$
	[6]	$0_{Mo:Ti}^L = 10000.0$

Table 3.3: Thermodynamic parameters for the Ti-Mo-Nb-Ta-Zr system. The thermodynamic description of the pure elements is not included. The pure elements were adopted from the SGTE database and are listed in the supplementary tdb file [38].

Phase	Reference	Interaction Parameter
LAVES_C15	[6]	$0_{Ti:Ta}^L = 5000.0$
	[6]	$0_{Ta:Ti}^L = 5000.0$
	[18]	$0_{Ti:Ti}^L = 15000.0 + 3.0 * GHSERTI$
	[13]	$0_{Mo:Mo}^L = 15000.0 + 3.0 * GHSERMO$
	[13]	$0_{Zr:Zr}^L = 15000.0 + 3.0 * GHSERZR$
	[18]	$0_{Ti:Mo}^L = 15000.0 + GHSERMO$ + $2.0 * GHSERTI$
	[18]	$0_{Mo:Ti}^L = 15000.0$ + $2.0 * GHSERMO + GHSERTI$
	[18]	$0_{Ti:Zr}^L = 9000.0$ + $GHSERZR + 2.0 * GHSERTI$
	[18]	$0_{Zr:Ti}^L = 15000.0 + 2.0 * GHSERZR + GHSERTI$
	[13]	$0_{Mo:Zr}^L = -21734.8 + 0.14 * T$ + $GHSERZR + 2.0 * GHSERMO$
OMEGA	[13]	$0_{Zr:Mo}^L = 21734.8 - 0.14 * T$ + $2.0 * GHSERZR + GHSERMO$
	[13]	$0_{Mo:Mo,Zr}^L = 60000.0$
	[13]	$0_{Zr:Mo,Zr}^L = 60000.0$
	[13]	$0_{Mo,Zr:Mo}^L = 100000.0$
	[13]	$0_{Mo,Zr:Zr}^L = 100000.0$
	[18]	$0_{Ti:Mo,Zr}^L = 60000.0$
	[18]	$0_{Mo,Zr:Ti}^L = 100000.0$
	[8]	$0_{Ti}^L = 1886.7 - 0.15 * T + GHSERTI$
	[8]	$0_{Nb}^L = 15000.0 + 2.4 * T + GHSERNB$
	[26]	$0_{Zr}^L = -8878.082 + 144.432234 * T$ - $26.8556 * T * LN(T) - .002799446 * T2 + 38376 * T - 1$
		$298.15 < T < 2128$

Table 3.3: Thermodynamic parameters for the Ti-Mo-Nb-Ta-Zr system. The thermodynamic description of the pure elements is not included. The pure elements were adopted from the SGTE database and are listed in the supplementary tdb file [38].

Phase	Reference	Interaction Parameter
	[8]	$-29500.524 + 265.290858 * T - 42.144 * T * LN(T)$ $+ 7.17445E + 31 * T - 9$ $2128 < T < 6000$ $0LTi, Nb = -3775.9$

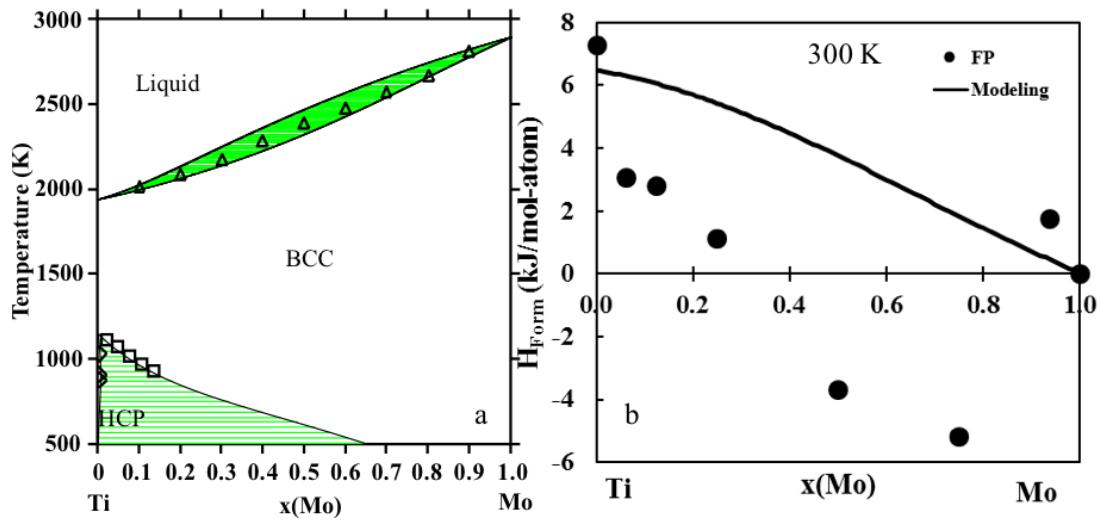


Figure 3.1. Figure a on the left plots the previously modeled thermodynamic description of the Ti-Mo system versus available experimental data to ensure accuracy [6, 7]. Figure b on the right plots the enthalpy of formation of the bcc phase predicted by the previous thermodynamic modeling (solid line) at 300 K versus the present first-principles calculations (circles) at 0 K.

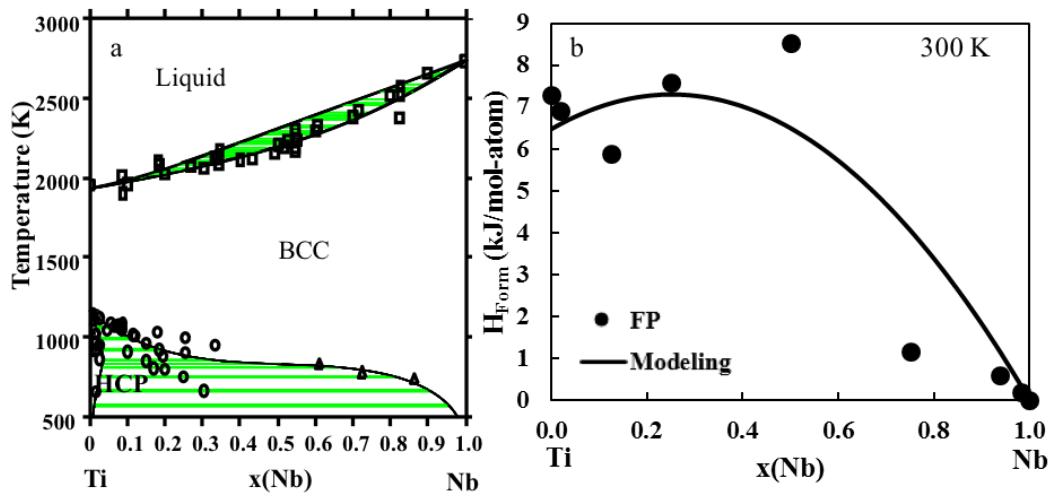


Figure 3.2. Figure a on the left plots the previously modeled thermodynamic description of the Ti-Nb system versus available experimental data to ensure accuracy [8, 9]. Figure b on the right plots the enthalpy of formation of the bcc phase predicted by the previous thermodynamic modeling (solid line) at 300 K versus the present first-principles calculations (circles) at 0 K.

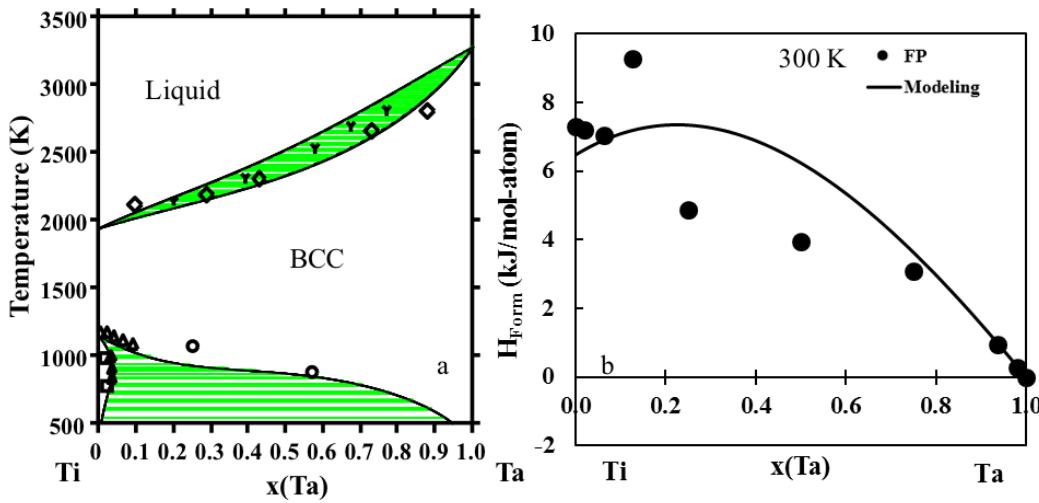


Figure 3.3. Figure a on the left plots the previously modeled thermodynamic description of the Ti-Ta system versus available experimental data to ensure accuracy [6, 10]. Figure b on the right plots the enthalpy of formation of the bcc phase predicted by the previous thermodynamic modeling (solid line) at 300 K versus the present first-principles calculations (circles) at 0 K.

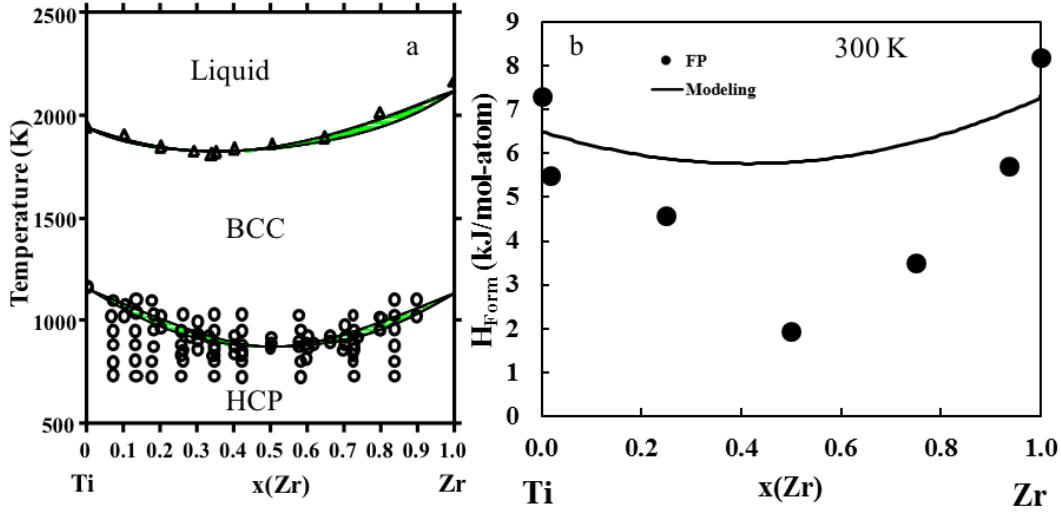


Figure 3.4. Figure a on the left plots the previously modeled thermodynamic description of the Ti-Zr system versus available experimental data to ensure accuracy [11]. Figure b on the right plots the enthalpy of formation of the bcc phase predicted by the previous thermodynamic modeling (solid line) at 300 K versus the present first-principles calculations (circles) at 0 K.

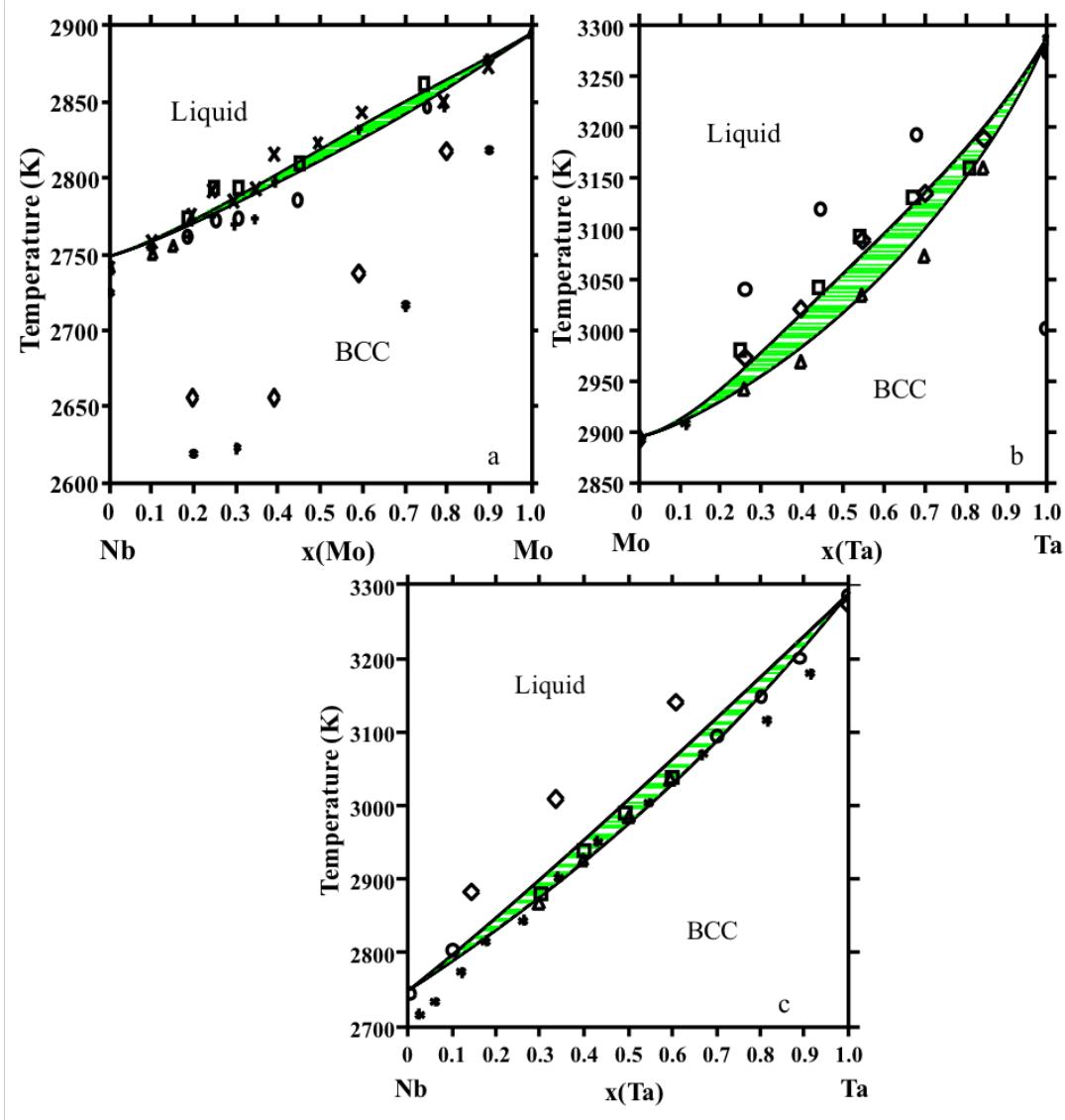


Figure 3.5. The previously modeled thermodynamic descriptions of the Mo-Nb (a) [12], Mo-Ta (b) [12] and Nb-Ta (c) [12] binary systems are evaluated by comparing with available phase boundary experimental data.

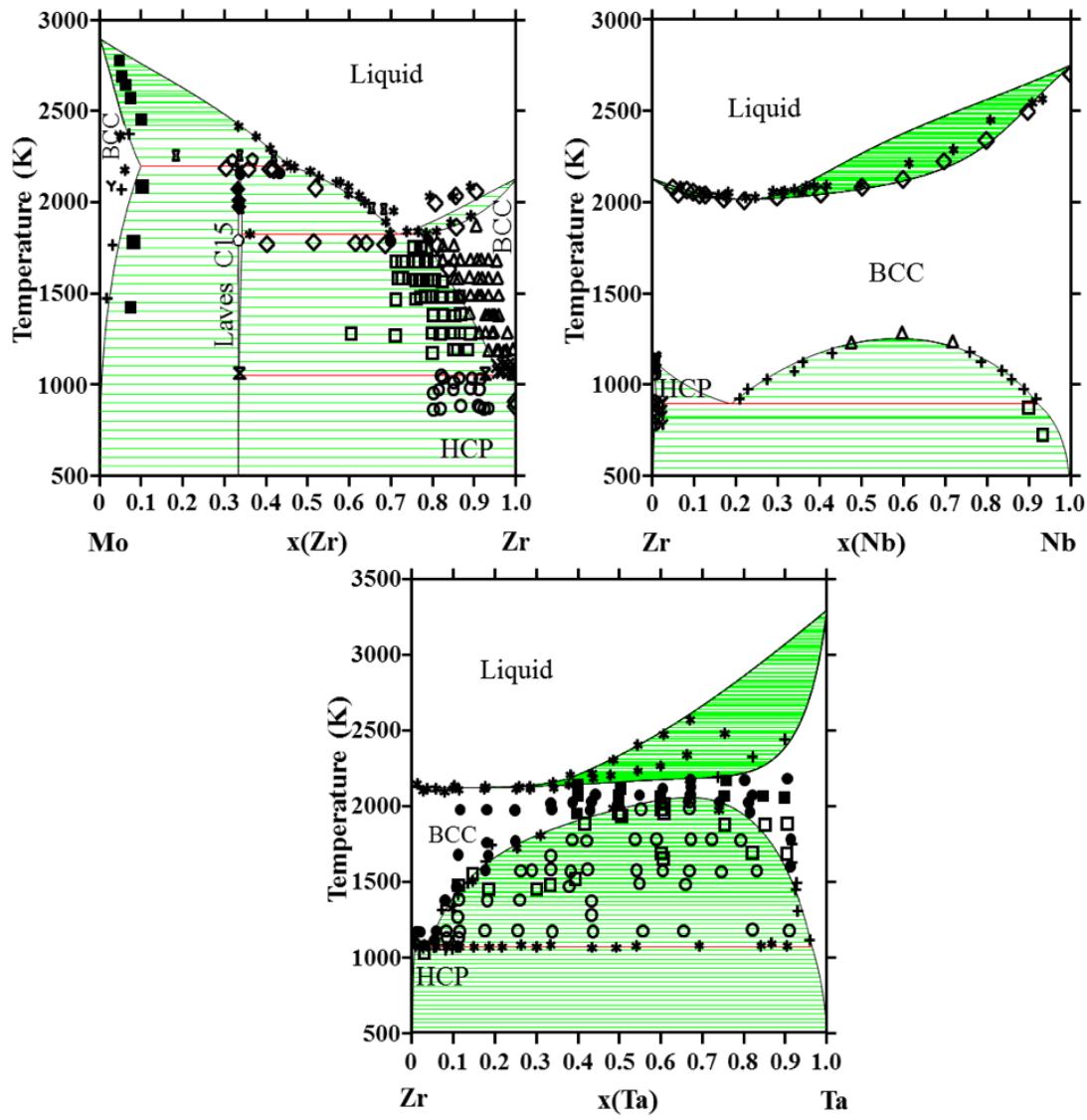


Figure 3.6. The previously modeled thermodynamic descriptions of the Mo-Zr [13], Nb-Zr [14, 15] and Ta-Zr [16] binary systems are evaluated for accuracy by comparing the available experimental phase boundary data.

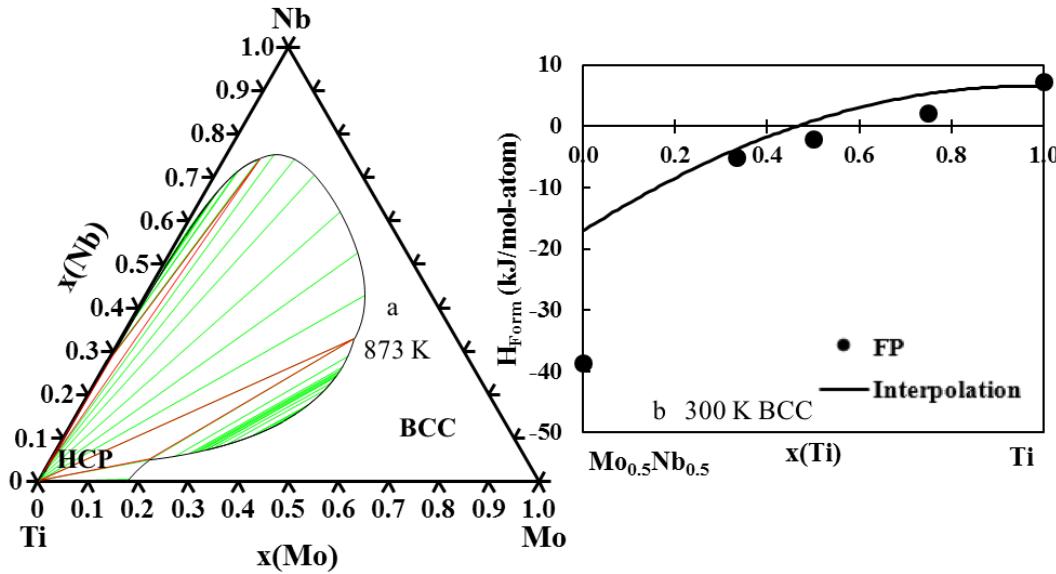


Figure 3.7. Figure a) on the left is a binary interpolation of the isothermal section of Ti-Mo-Nb plotted at 873 K. Figure b) plots the present calculations (circles) and binary interpolation (solid black line) of the enthalpy of formation of the bcc phase.

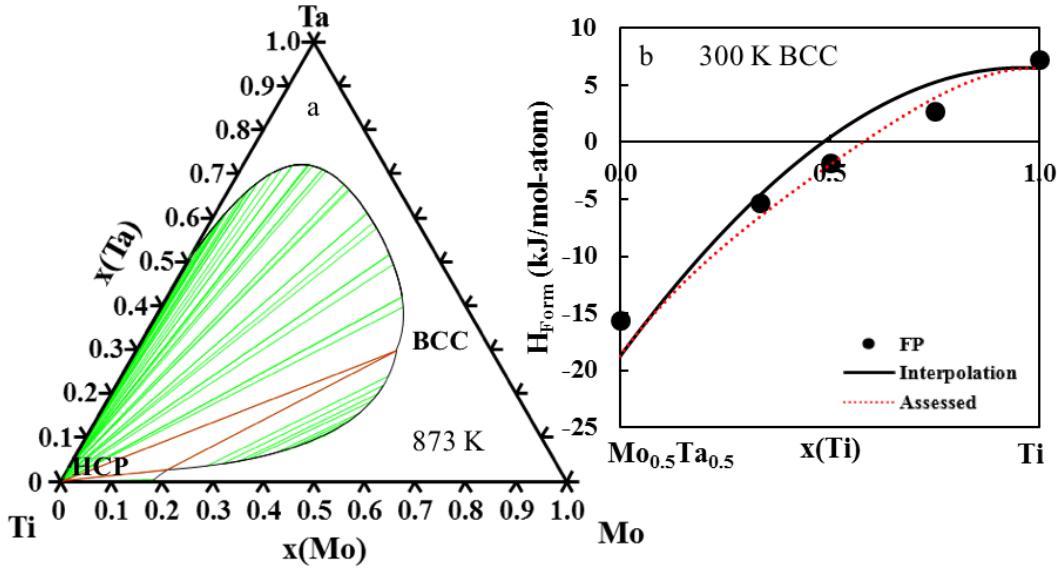


Figure 3.8. Figure a) on the left is a binary interpolation of the isothermal section of Ti-Mo-Ta plotted at 873 K. Figure b) plots the present calculations (circles), binary interpolation (solid black line) and ternary assessed (red dotted line) enthalpy of formation of the bcc phase.

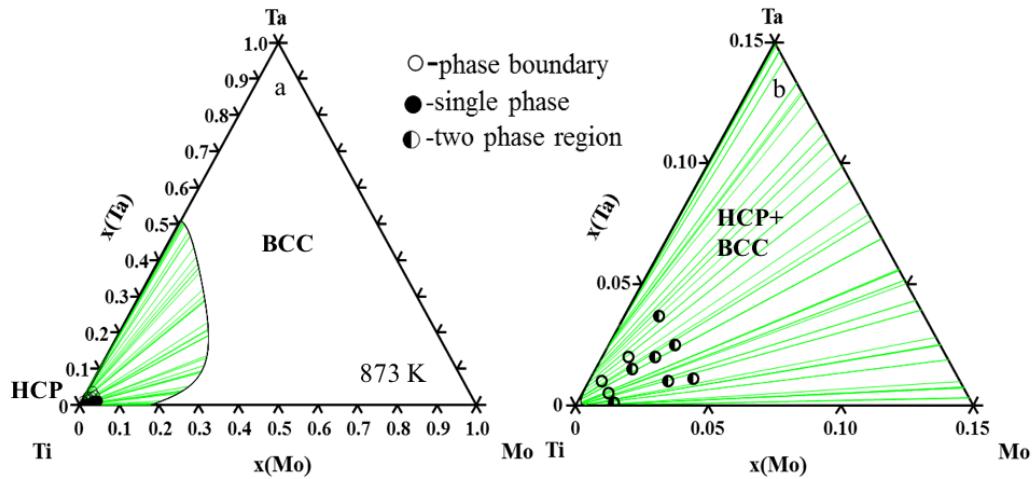


Figure 3.9. Figure a) on the left is the isothermal plot of Ti-Mo-Ta at 873 K after evaluation of the ternary interaction parameters. Figure b) on the right is zoomed in to show the comparison with the experimental data [17].

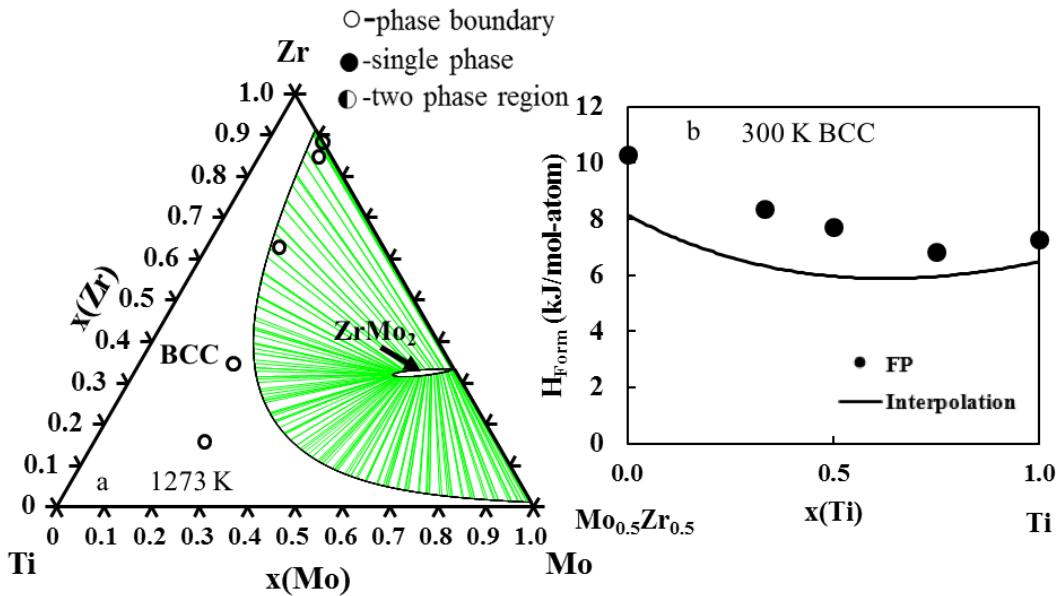


Figure 3.10. Figure a) on the left is a binary interpolation of the isothermal section of Ti-Mo-Zr plotted at 1273 K with experimental phase data obtained at the same temperature [18,19]. Figure b) plots the present calculations (circles) and binary interpolation (solid black line) of the enthalpy of formation of the bcc phase.

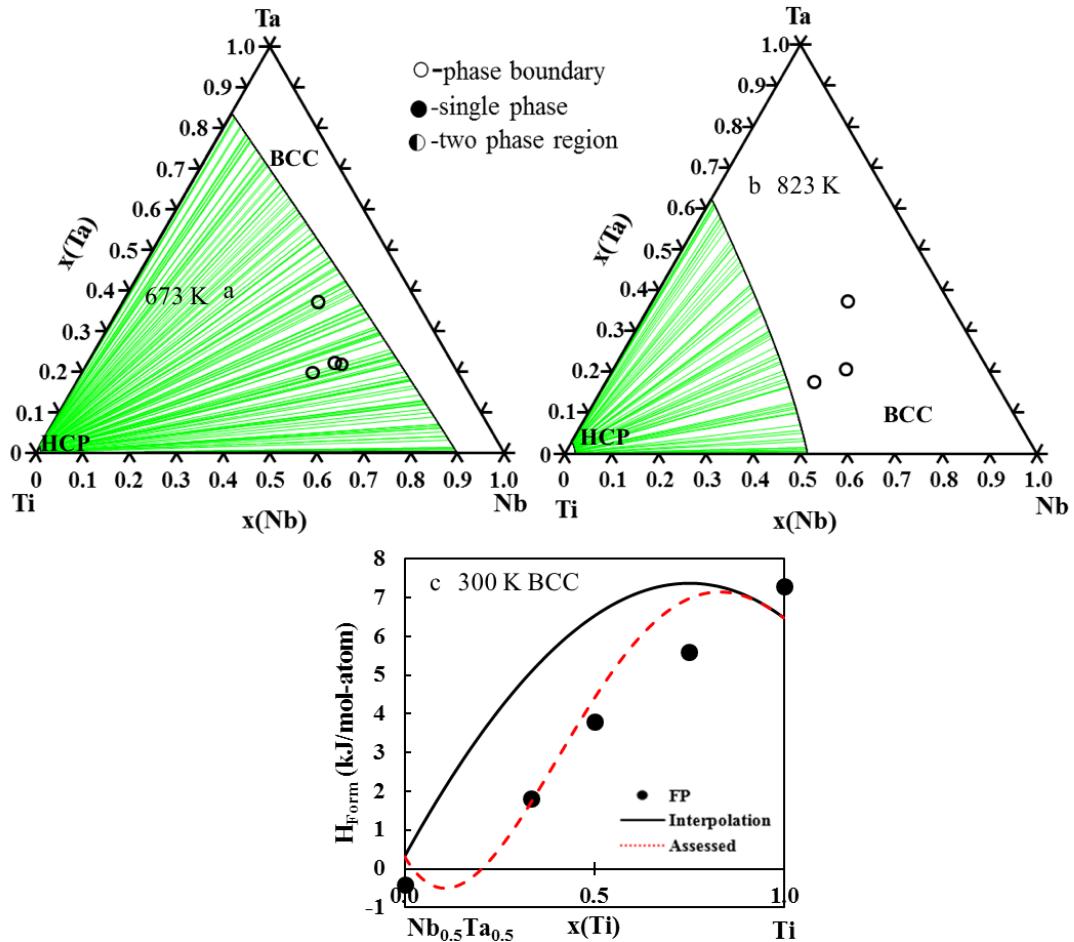


Figure 3.11. Figure a) on the top left is a binary interpolation of the isothermal section of Ti-Nb-Ta plotted at 673 K. Figure b) is a binary interpolation of the isothermal section of Ti-Nb-Ta at 823 K. Both binary interpolations are compared with experimental phase boundary data [20]. Figure c) plots the present calculations (circles), binary interpolation (solid black line) and ternary assessed (red dotted line) enthalpy of formation of the bcc phase.

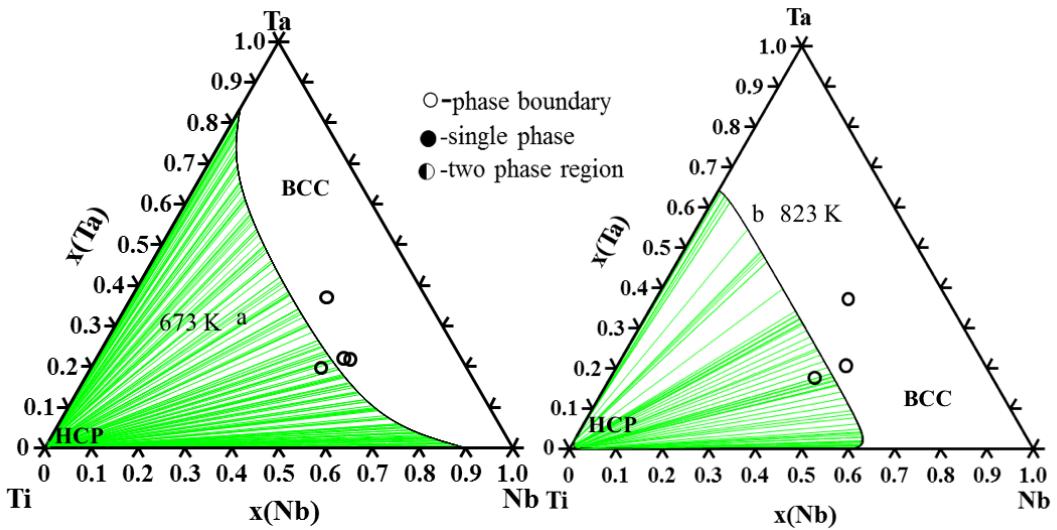


Figure 3.12. Figure a) on the left is the isothermal plot of Ti-Nb-Ta at 673 K after evaluation of the ternary interaction parameters. Figure b) is the evaluated isothermal plot of Ti-Nb-Ta at 823 K. Both plots have experimental phase boundary data [20].

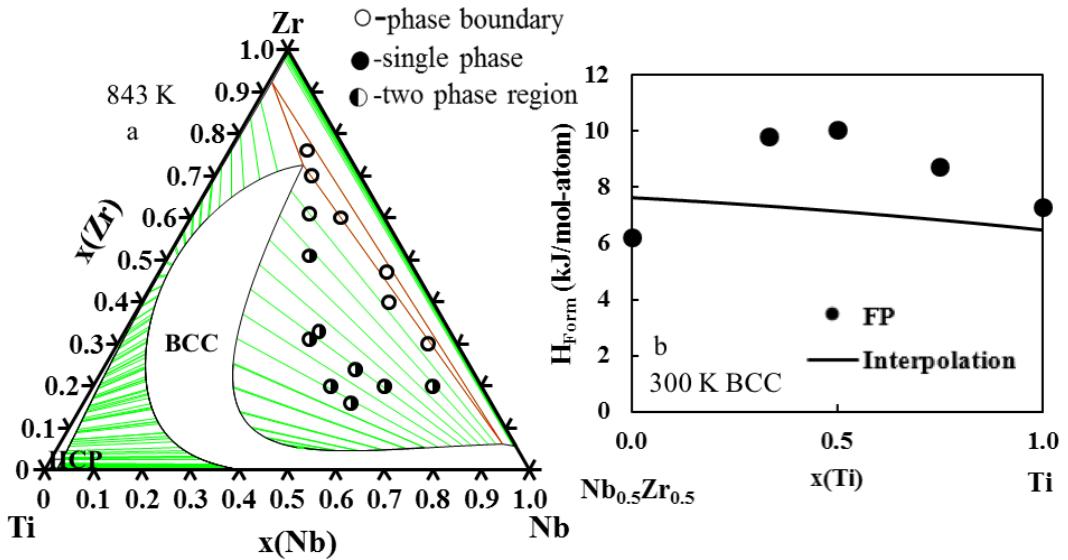


Figure 3.13. Figure a) on the left is a binary interpolation of the isothermal section of Ti-Nb-Zr plotted at 843 K with experimental phase data [21]. Figure b) plots the present calculations (circles) and binary interpolation (solid black line) of the enthalpy of formation of the bcc phase.

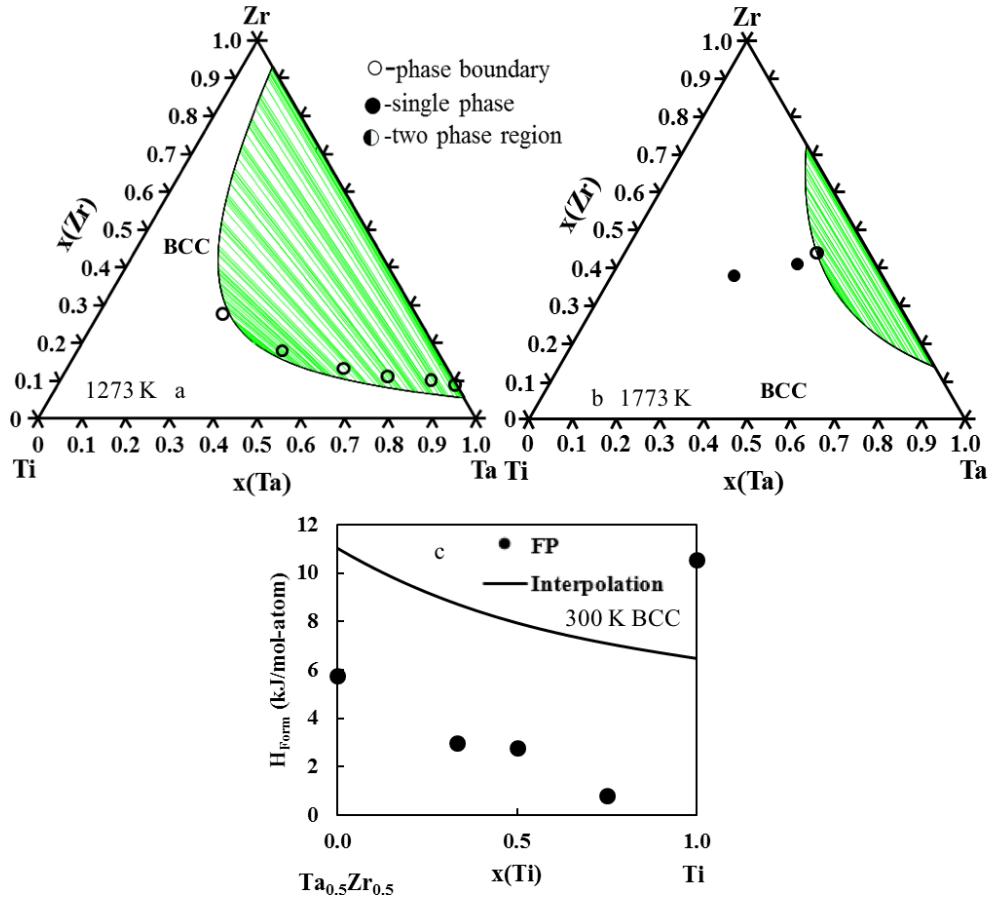


Figure 3.14. Figure a) on the top left is a binary interpolation of the isothermal section of Ti-Ta-Zr plotted at 1273 K. Figure b) is a binary interpolation of the isothermal section of Ti-Ta-Zr at 1773 K. Both binary interpolations are compared with experimental data [22, 23]. Figure c) plots the present calculations (circles) and binary interpolation (solid black line) for the enthalpy of formation of the bcc phase.

Chapter 4

First-principles aided thermodynamic modeling of the Sn-Ta system

4.1 Introduction

Currently, the biomaterial implant research of Ti alloys is focused on biocompatible elements that stabilize the body centered cubic (bcc, β) phase of Ti and help to lower its elastic modulus. Tantalum (Ta) is a biocompatible element and is considered to be a strong α -stabilizers [44]. Recently, tin (Sn) has also been researched for use in Ti-alloys due to its biocompatibility and low cost [35]. Kuroba et al. [84] studied various Ti-alloys such as Ti-29-Nb-13Ta-2Sn (weight percentage, and similarly hereinafter unless specified otherwise), Ti-29Nb-13Ta-4Mo, and Ti-29Nb-13Ta-6Sn for use as biocompatible implant materials. Kuroba and Hagiwara [85] also studied new Ti-Cu-Ni-Sn-Ta alloys for the artificial materials used in orthopedic surgeries. The Sn-Ta system is thus an important sub-system for this purpose [86]. A complete knowledge base of the thermodynamic description of Sn-Ta can be used to examine the effects of temperature and composition on phase stability for higher order systems and help to tailor experimental alloy selections to viable options. The CALPHAD technique, in combination with first-principles and phonon calculations based on the DFT, has been proven to provide valuable data to model the thermodynamic properties of binary such as Ta-Sn that lack sufficient experimental data [87]. The Sn-Ta system has three solid solution phases and two intermetallic compounds,

i.e. the bcc, body centered tetragonal (bct), and diamond solution phases, and the intermetallic compounds Ta_3Sn with space group $Pm\bar{3}n$ and $TaSn_2$ ($Ta_{1.2}Sn_{1.8}$) with space group $Fddd$ [88].

In the present work, thermodynamic data was predicted using first-principles calculations for the two intermetallics and for the bcc, bct and diamond solution phases. The finite temperature properties of the phases were obtained using the Debye-Grüneisen model [53] and phonon calculations based on the supercell approach [56]. The DFT data was used to model the parameters of the Gibbs energy of each phase using the CALPHAD technique.

4.2 Literature Review

The Sn-Ta binary system was studied by Okamoto [88], Studnitzky and Schmid-Fetzer [89], and Basile [90]. Both of the intermetallic phases, Ta_3Sn and $TaSn_2$, were shown to have a very narrow homogeneity range. Basile [90] observed that $TaSn_2$ is located around $Ta_{1.2}Sn_{1.8}$ which was then designated as Ta_2Sn_3 by Okamoto [88]. It seems that $TaSn_2$ is a more compatible description of the stoichiometric compound based on the descriptions of similar systems (V-Sn, and Nb-Sn) [91–93], and thus will be used in the present work. Basile [90] determined $TaSn_2$ has a peritectic reaction at 595 °C and used X-ray diffraction (XRD) to elucidate the lattice parameters of $TaSn_2$.

Studnitzky and Schmid-Fetzer [89] used powder samples to study the Ta_3Sn intermetallic phase and verified the results previously reported by Basile [90]. They cold pressed the pure element powders at 600 MPa and then heated the pellets at 1000 °C for up to 48 hours. The resulting pellet was then cold pressed at 600 MPa again. Under these conditions $TaSn_{4.2}$ was observed at 400 °C, but was not present as the temperature increased to 600 °C. In the work by Courtney et al. [94], Ta_3Sn was studied to see how the temperature affects the long-range ordering parameter. In Courtney et al.’s work, Ta_3Sn powder samples were sintered at 600, 700, 950, 1200, and 1450 °C for 2, 4, 7, and 16 days, respectively. Each sample was then studied using XRD at room temperature to examine the phases present and the long-range ordering. They concluded that the transition temperature of superconductivity for Ta_3Sn varied by a maximum of 4 °K based on heat treatment and sintering times due to long-range ordering that occurred. Courtney et al. also

measured the lattice parameter of each sample and reported the average value of this cubic phase being 5.285 Å.

4.3 Modeling and Calculations

4.3.1 First-principles details

In the present work, the Vienna ab-initio Simulation Package (VASP) was used to perform the first-principles calculations [54]. The projector augmented-wave (PAW) [55, 71] method was used to describe the electron-ion interactions. Based on the work of comparing X-C functionals (Figure 2.1) the exchange-correlation functional of the generalized gradient approach depicted by Perdew, Burke, and Ernzerhof (PBE) was employed [51]. A sigma value of 0.2 eV and a plane wave energy cutoff of 1.3 times higher than the highest default cutoff was adopted. The Brillouin zone sampling was done with Blöchl corrections [71] using a gamma centered Monkhorst-Pack (MP) scheme [72]. The k-points grid for diamondSn, bcc-Ta, TaSn₂, and bcc-Sn were 4x4x4, 6x6x6, 10x10x5, and 6x6x6 respectively. The k-point grids for the bct-Sn, Ta₃Sn and bcc SQS calculations used an automated k-point mesh generator in VASP with the length of the subdivisions specified as 80. The energy convergence criterion of the electronic self-consistency is set as 10⁻⁴ eV/atom and 10⁻⁴ eV/A was set as the stopping criteria for the ionic relaxation loop for all of the calculations.

To calculate the enthalpy of formation of the bcc phase across the entire composition range, the enthalpy of formation of Ta and Sn in the bcc phase were calculated with five different compositions of Ta_{1-x}Sn_x, where x=0.0185 (Ta₅₃Sn, 54 atoms), 0.25, 0.5, 0.75, and 0.9815 (TaSn₅₃, 54 atoms). For x=0.0185 and 0.9815, calculations were performed on a diluted 54 atom cell where all atoms but one was Sn or Ta (Ta₅₃Sn and TaSn₅₃). For x=0.25, 0.5, and 0.75, 16-atom special quasirandom structures (SQS) in the bcc phase developed by Jiang et al. [64] were used to mimic the behavior of random structures. The relaxation of these structures is complicated and discussed in the methodology section. The enthalpy of formation was plotted as a function of composition and then used for the modeling.

4.3.2 CALPHAD

The Gibbs energy functions of pure elements were adopted from the SGTE (SSUB) database [26]. In the present work, the bcc and liquid phases were modeled in conjunction with the two intermetallics Ta_3Sn and $TaSn_2$. Dilute first-principles calculations of Ta in Sn were done for the diamond and bct phases. However, there is little solubility of Ta in these phases and there is no description of pure Ta in these phases available in SGTE. So, no binary interaction parameters were introduced in the modeling similar to other Sn systems such as Nb-Sn and V-Sn [91, 93]. The energy of the liquid and bcc solution phases were modeled using Eq. 2.26 and 2.27, while Ta_3Sn and $TaSn_2$ were modeled according to Eq. 2.30.

4.4 Results and discussion

4.4.1 First-principles

To evaluate the accuracy of phonon calculations for the present system, both the dispersion curves and the phonon DOS are plotted for bcc-Ta, bct-Sn, $TaSn_2$, and Ta_3Sn in Figure 4.1, Figure 4.2, Figure 4.3, and Figure 4.4, respectively. The bcc-Ta phonon dispersion curve in Figure 4.1 is compared with values obtained by Taioli et al. [24] using neutron scattering, showing good agreement. The longitudinal modes (LO) and the transverse modes (TO) measured by Raman spectroscopy [25] (open square) along with the previous theoretical predictions at the M point (filled square) for bct-Sn are compared with the calculated phonon dispersion curve in Figure 4.2. The substantial difference for the LO mode may be due to the temperature and pressure differences as pointed out by Olijnyk [25]. No imaginary phonon frequencies are obtained in the phonon DOS plots for bcc-Ta, bct-Sn, $TaSn_2$, Ta_3Sn , indicating that they are all mechanically and dynamically stable at 0 °K.

The calculated lattice parameters at 0 °K from the EOS fitting and with the Debye and phonon models at 298 °K are compared to available experimental and previous DFT results in Table 4.1. The lattice parameters of Ta are compared with the experimental lattice parameters by Predmore and Arsenault [95] at room temperature and the previous 0 °K DFT results by Shang et al. [76] who used the GGA-PW91 exchange correlation functional. The Sn lattice parameters are

compared to experimental work by Allen et al. [96] at 298 °K and calculations by Arróyave et al. [97]. The properties of the TaSn₂ and Ta₃Sn intermetallics have not been calculated previously and are compared to experimental values by Calvert et al. [98] and Courtney et al. [94], respectively. The results show a less than 0.5% difference when compared with other DFT results at 0 °K. There is a less than 2% difference between the DFT 0 °K results and the experiments, which are listed in Table 4.1. The variance is due to the fact that the calculations are at 0 °K and the experiments are at a higher temperature. When comparing the calculated lattice parameters at 298 °K to the experiments, all of the predictions improve to show a less than 1% difference with the exception of Sn, which shows a less than 2% difference.

Table 4.2 shows the equilibrium volume, V_0 , bulk modulus, B_{EOS} , and the derivative of bulk modulus B'_{EOS} obtained by the EOS E-V fitting of the first-principles data at 0 °K. The Sn and Ta calculations are compared with previous first-principles calculations and available experiments. The volume shows a less than 0.5% difference between the previous DFT results and current DFT results for both Sn and Ta [95, 99]. The comparison of the DFT results at 0 °K and the experimental results at 298 K for volume show a slightly higher variance of less than 5 % due to the different in temperature [76, 99]. The B_{EOS} comparison of previous 0 °K DFT results and the present 0 °K DFT results show a less than 7 GPa difference and the DFT results at 0 °K vary by less than 11 GPa from the experimental results at 298 °K [76, 95, 99]. The difference between the current calculations and the previous values may be due to many reasons; e.g. the different choices in input parameters used by Peltzer et al. [99] and different exchange correlation functionals. Another reason is due to the temperature difference 0 °K (calculations) versus 298 °K (experiments). Figure 4.5 shows the enthalpy and entropy of Ta from the Debye and phonon approaches in comparison with the data from the SGTE pure element database [26]. Figure 4.6 shows the comparison of the enthalpy and entropy calculated for Sn from the phonon and Debye model to the SGTE pure element database [26]. Both show excellent agreement.

The elastic stiffness constants and polycrystalline elastic properties calculated by the Hill approach and the scaling factors for the Debye model are shown in Table 4.3. To ensure the accuracy of the scaling factor, the elastic stiffness constants and moduli are compared with previous first-principles results [81–83, 100, 101]. The

previous calculation results and present calculation results only vary slightly for the TaSn₂ structure. The present work calculated the elastic stiffness constants for the Ta₃Sn structure at 2 different atom sizes and compared the results with previous calculations by the Materials Project [81–83, 100, 101]. The present elastic stiffness results are quite similar. There is a larger variance between the present results and the Materials Project results. This can be attributed to the different input parameters and exchange correlation functional used (PBE in the present work and GGA-PW91 in Materials Project). B calculated from the c_{ij} methodology is compared with the $B)_{EOS}$ obtained from the EOS fitting, showing a difference of less than 3%. Since the B_{EOS} from the EOS fitting is already compared to experiments, the elastic calculations and the scaling factor for the Debye model are thus deemed accurate.

4.4.2 CALPHAD

The PARROT module in the Thermo-Calc software [68] is used to optimize the parameters of the Gibbs energy function of the TaSn₂ and Ta₃Sn intermetallics as well as the binary interaction parameters for the bcc and liquid phases. The Gibbs energy parameters of the intermetallics are first estimated from the thermodynamic properties obtained by the phonon supercell method because the phonon calculations are regarded as more accurate than the Debye model. While the decomposition temperature of the TaSn₂ intermetallic is known to be 868 °K from experiments, the decomposition of the Ta₃Sn intermetallic has not been reported in the literature. It is noted that both the Nb-Sn and V-Sn systems, which are quite similar to the Ta-Sn system, have the X₃Sn phase forming through a peritectic reaction of bcc+Liquid→X₃Sn [91–93]. Based on the assumption from similar works that Ta₃Sn is also formed through a peritectic reaction, the Ta₃Sn parameters are adjusted and the parameters for the liquid phase are evaluated. The evaluation of the Gibbs parameters along with the results from the Debye model and the phonon quasiharmonic approach for TaSn₂ and Ta₃Sn are plotted in Figure 4.7 and Figure 4.8, respectively. As seen in both figures, the data from the phonon method correlates well with the current CALPHAD modeling. This is to be expected since this data was used to evaluate the parameters. It is noted in Figure 4.7, that the heat capacity and entropy of TaSn₂ from the current CALPHAD modeling is higher

than those from the first-principles calculations. This is due to the fact that the enthalpy and entropy values from DFT were adjusted with the experimental data of the peritectic temperature.

The bct and diamond phases are treated as ideal due to the little solubility. As previously stated, the enthalpies of formation of the bcc phase for five different Sn-Ta compositions are calculated and plotted in Figure 4.9, showing asymmetrical behavior. There is a discrepancy between the first-principles value and the CALPHAD modeling for the lattice stability of bcc-Sn. The first-principles predicts a value of 15.48 kJ/mol-atom and the CALPHAD model gives 4.42 kJ/mol-atom. This difference is expected to be due to the instability of Sn in the bcc phase. Wang et al. [102] concluded and discussed the same discrepancy when comparing first-principles DFT results to SGTE data for Os and Ru. Wang et al. calculated the lattice stability of bcc and fcc (face centered cubic) structure for Os and Ru, both stable in the hexagonal close packed phase at standard temperature and pressure, and concluded a difference of approximately 40 and 60 kJ/mol for Ru and Os, respectively. Wang et al. attributed this difference to the fact that when using first-principles calculations of unstable structures, frequencies of some of the phonon modes would become imaginary and thus the results would be less accurate. On the other hand, the CALPHAD technique can extrapolate lattice stabilities from binary solutions for which an alloying element has stabilized the otherwise unstable structure. These enthalpies of formation calculated from the SQS first-principles calculations are used to evaluate the bcc binary interaction parameters in the present CALPHAD modeling. The enthalpy of formation of the bcc phase is negative at the Ta rich side and becomes positive at the Sn rich side. This is common for X-Sn systems [91,93], such as the Nb-Sn system [93] shown in Figure 4.9. It should be noted that Toffolon et al. [92,93] used experimental data on the Sn-rich bcc phase to evaluate the Nb-Sn system's bcc interaction parameters. Due to the asymmetry of enthalpy of formation for the bcc phase, a subregular ^1L interaction parameters is introduced.

The interaction parameters obtained in the present work are listed in Table 4.4. Based on these model parameters, the phase diagram is calculated and shown in Figure 4.10. The melting temperature of Ta_3Sn is predicted to be 2884 °K. Both the intermetallics decompose incongruently similar to those in the Nb-Sn and V-Sn systems. As seen in Table 4.4, both intermetallic phases have a negative enthalpy

of formation and a negative entropy of formation. This goes along with previous predictions by Arroyave and Liu [103] where they showed that the enthalpy and entropy of formation have the same sign. The calculated enthalpy of mixing of the liquid phase is plotted in Figure 4.11. The interaction parameter for the liquid phase allows for an accurate representation of the phase stability in Figure 4.10 but may need to be slightly adjusted if experimental data would come available.

4.5 Conclusion

The present work incorporates the thermodynamic data from DFT-based first-principles calculations and the available experimental data in the literature to model the Gibbs energies for the bcc and liquid solution phases and the stoichiometric Ta_3Sn and TaSn_2 phases of the Sn-Ta system. First-principles calculations are used to predict the enthalpy of formation of the bcc phase for the evaluation of interaction parameters in the phase. The decomposition temperature of Ta_3Sn is predicted to be 2884 °K. The completed thermodynamic description is complied into a tdb file. The tdb file and raw data from the first-principles calculations are in appendix b.

Table 4.1. Lattice parameters from first-principles calculations compared with experimental values.

Phase	Space Group	a (Å)	b (Å)	c (Å)	Reference
bcc-Ta	Im $\bar{3}$ m	3.316			This work (0 °K)
		3.328			This work phonon (298 °K)
		3.330			This work Debye (298 °K)
		3.30			Expt. [95]
		3.32			DFT (0 °K) [76]
bct-Sn	I4 ₁ /amd	5.939	3.214		This work (0 °K)
		5.959	3.236		This work phonon (298 °K)
		5.954	3.222		This work Debye (298 °K)
		5.83	3.18		Expt. [96]
		5.93	3.23		DFT (0 °K) [97]
TaSn ₂	Fd $\ddot{\text{d}}$ d	5.641	9.766	19.200	This work (0 °K)
		5.652	9.786	19.238	This work phonon (298 °K)
		5.652	9.785	19.238	This work Debye (298 °K)
		5.63	9.80	19.18	Expt. [98]
Ta ₃ Sn	Pm $\bar{3}$ n	5.304			This work (0 °K)
		5.319			This work phonon (298 °K)
		5.319			This work Debye (298 °K)
		5.29			Expt. [94]

Table 4.2. Equilibrium volume V_0 , bulk modulus B_{EOS} , and the first derivative of bulk modulus with respect to pressure B'_{EOS} , from fitted equilibrium properties from the EOS at 0 °K compared to experimental work and previous DFT studies.

Phase	V_0 ($\text{\AA}^3/\text{atom}$)	B_{EOS} (GPa)	B'_{EOS}	Reference
bcc-Ta	18.241	193.7	3.84	This work
	17.9685	200		Expt. [95]
	18.313	195.3	3.82	DFT [76]
bct-Sn	28.431	47.7	4.61	This work
	27.055	58.0		Expt. [99]
	28.396	54.0		DFT [99]
TaSn ₂	22.631	104.3	4.80	This work
Ta ₃ Sn	18.668	182.4	4.27	This work

Table 4.3. Elastic stiffness constants and elastic properties predicted using the Hill approach and the scaling factors used in the Debye model, calculated from the Poisson ratio, see Eq. 2.11. To ensure the accuracy of the calculated scaling factor, the bulk modulus (B) calculated from the elastic constants was compared to the B_{EOS} calculated from the EOS fitting Eq. 2.6.

	TaSn ₂		Ta ₃ Sn		
	Present Work	FP	Present Work	Present Work	FP
	[81–83, 100]		8 atoms	32 atoms	[81–83, 101]
C ₁₁ (GPa)	166	161	297	310	226
C ₁₂ (GPa)	79	78	127	131	155
C ₁₃ (GPa)	62	57			
C ₂₂ (GPa)	189	182			
C ₂₃ (GPa)	68	68			
C ₃₃ (GPa)	187	183			
C ₄₄ (GPa)	37	35	65	68	22
C ₅₅ (GPa)	59	55			
C ₆₆ (GPa)	61	60			
E (GPa)	135		210	202	
G (GPa)	53	51	80	76	27
Poisson Ratio	0.288	0.29	0.32	0.32	0.43
Scaling factor	0.789		0.71	0.71	
B (GPa)	107	107	184	190	179
B_{EOS} (GPa)	104		182		

Table 4.4. Modeled parameters in SI units in the present work for the phases in the Sn-Ta binary system. These parameters were incorporated with the SGTE data for the pure elements [26].

Phase (model)	Modeled Paramters
bcc-A2(Sn,Ta)	${}^0L_{Ta,Sn}^b cc = + 70451$ ${}^1L_{Ta,Sn}^b cc = + 112237$
Liquid (Sn,Ta)	${}^0L_{Ta,Sn}^L iq = 17118$
TaSn ₂	$G^{TaSn_2} = {}^0G_{Sn}^{bct} + {}^0G_{Ta}^{bcc} = -29678 - 4.202T$
Ta ₃ Sn	$G^{Ta_3Sn} = {}^0G_{Sn}^{bct} + 3{}^0G_{Ta}^{bcc} = -68844 - 6.000T$

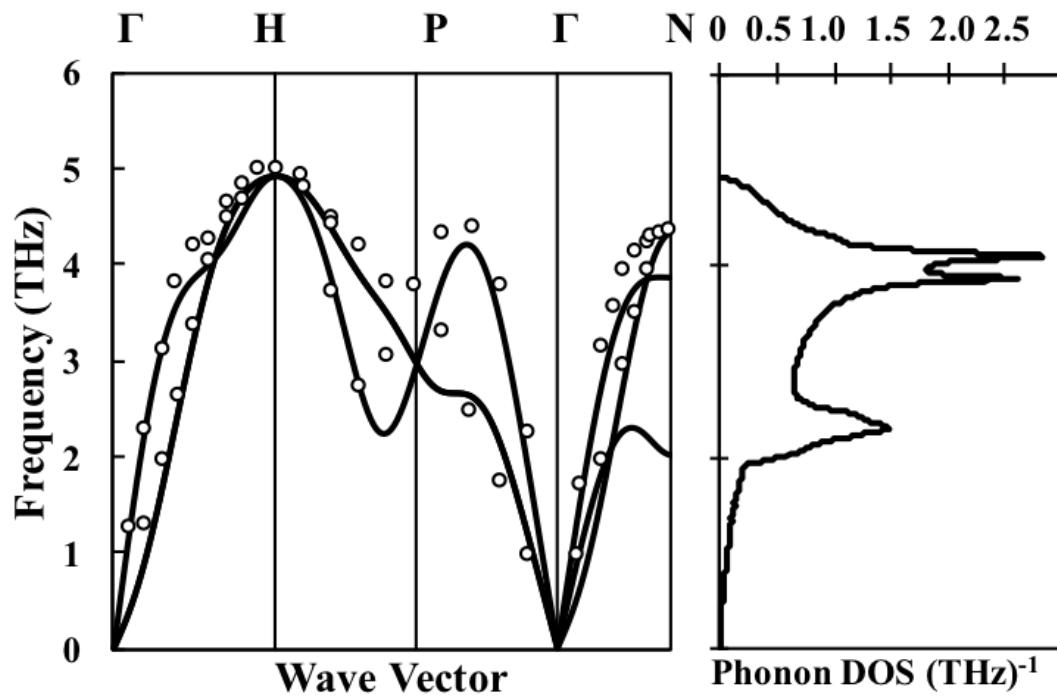


Figure 4.1. Calculated phonon dispersion curve of bcc-Ta, compared with neutron diffraction experiments (\circ) [24] along with the phonon DOS.

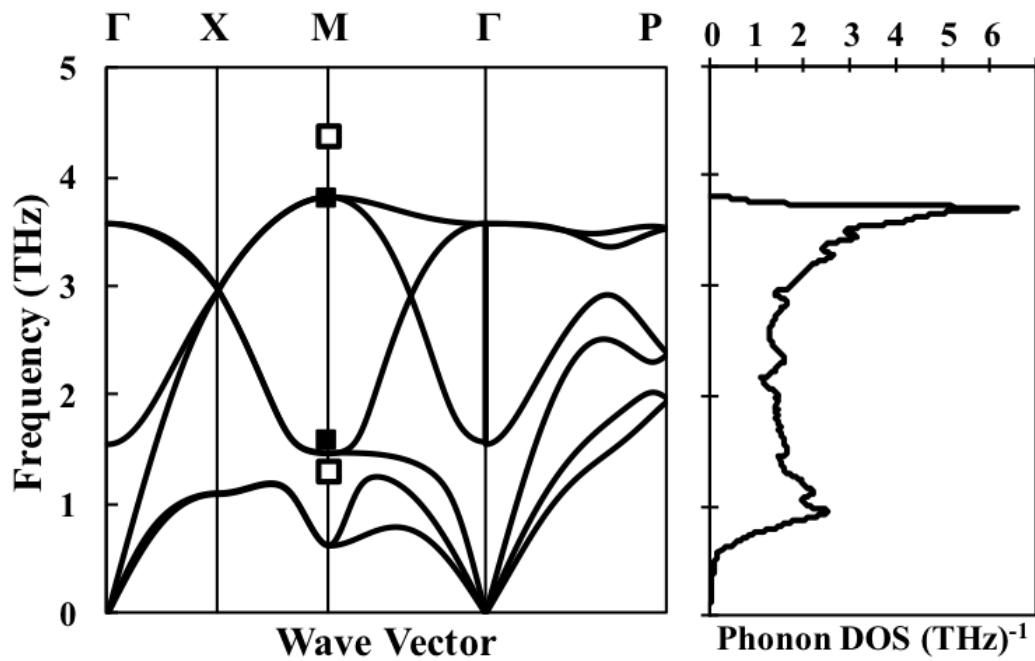


Figure 4.2. Calculated phonon dispersion curve of bct-Sn on the left and phonon DOS on the right. The open squares (\square) are the LO and TO modes from Raman [25] and the filled squares the theoretical prediction of the LO and TO modes at the M point [25].

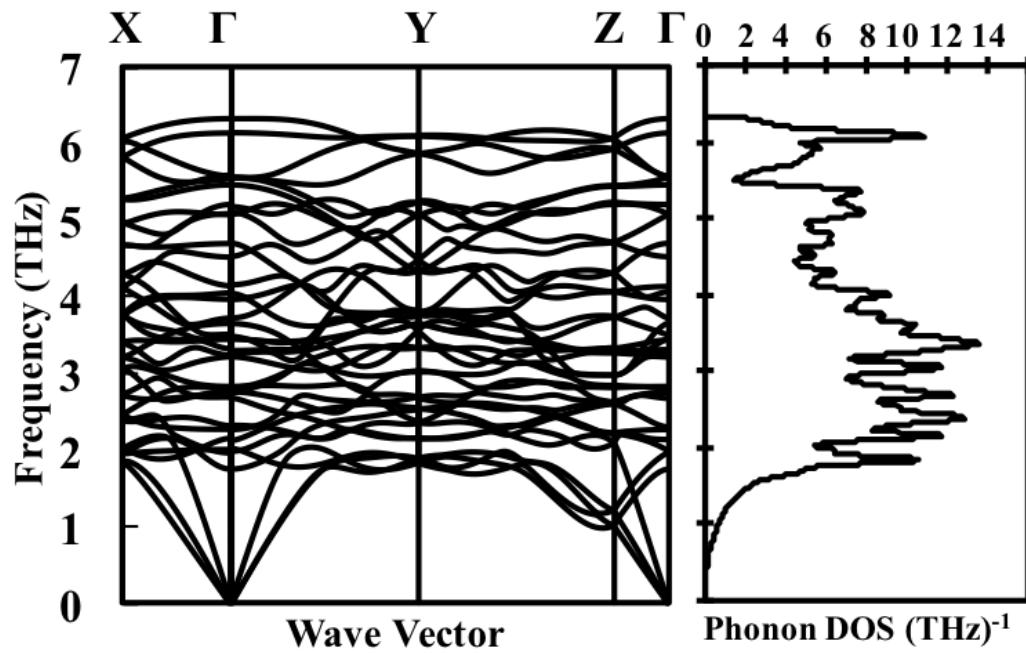


Figure 4.3. Calculated phonon dispersion curve for TaSn_2 at 0 $^{\circ}\text{K}$ and the phonon DOS.

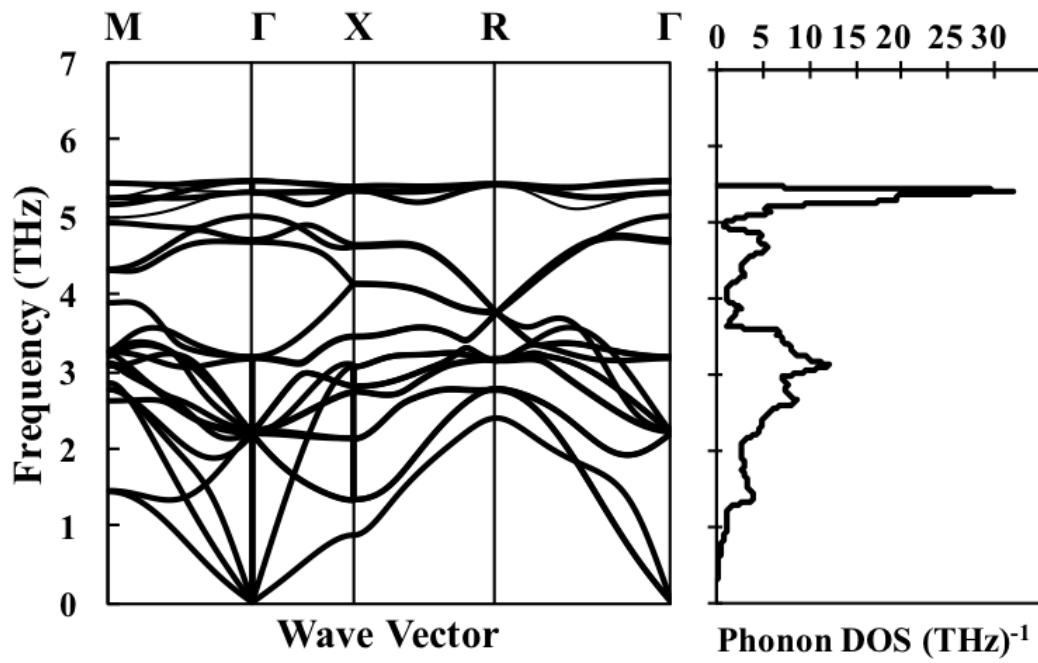


Figure 4.4. Calculated phonon dispersion curve of Ta_3Sn at 0 °K on the left and the phonon DOS on the right.

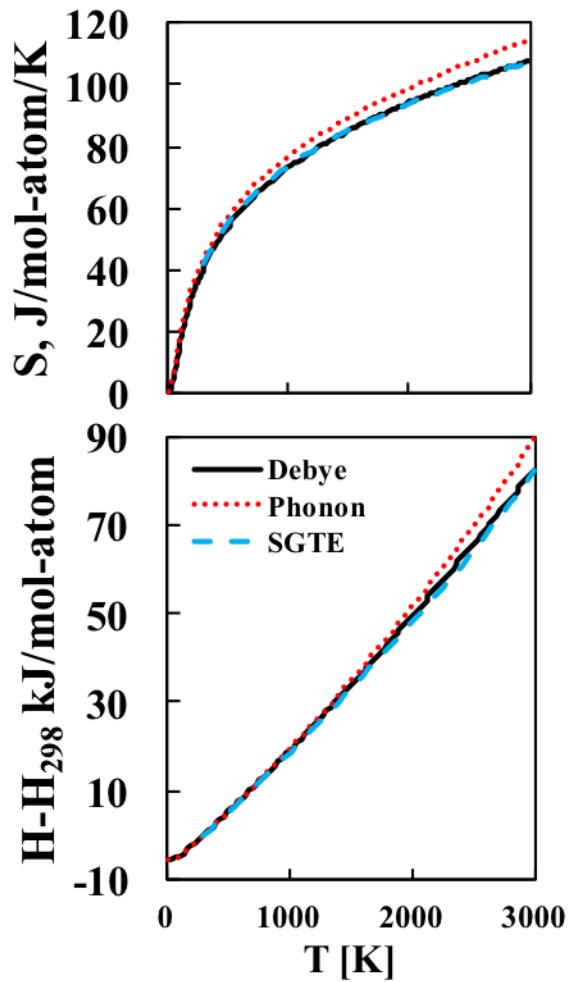


Figure 4.5. Comparison of the enthalpy and entropy of bcc-Ta from the Debye model (solid line) and the quasiharmonic phonon calculations (red dotted line) to the SGTE data (blue dashed line) [26].

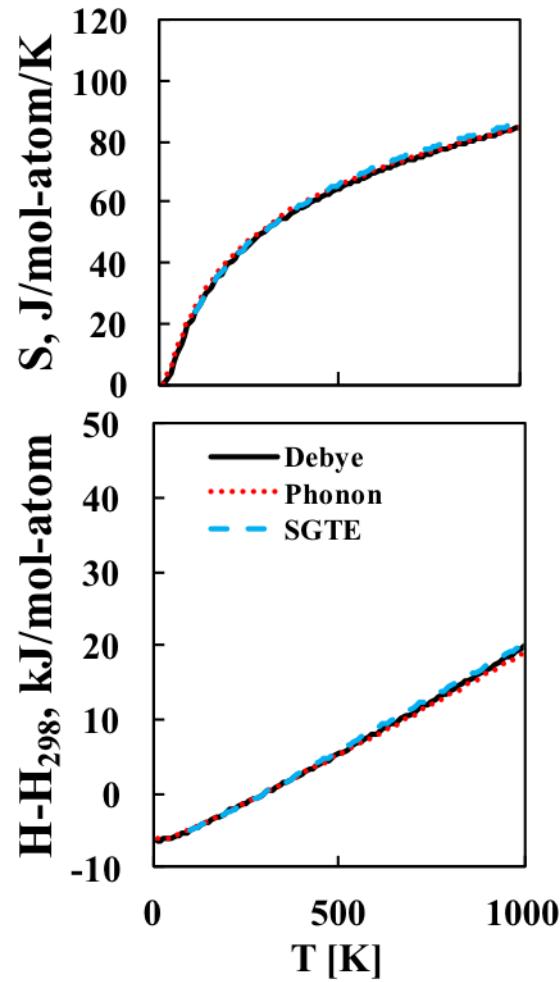


Figure 4.6. Comparison of the Gibbs energy of bct-Sn from the Debye model (solid line) and the quasiharmonic phonon calculations (red dotted line) to the SGTE data (blue dashed line) [26].

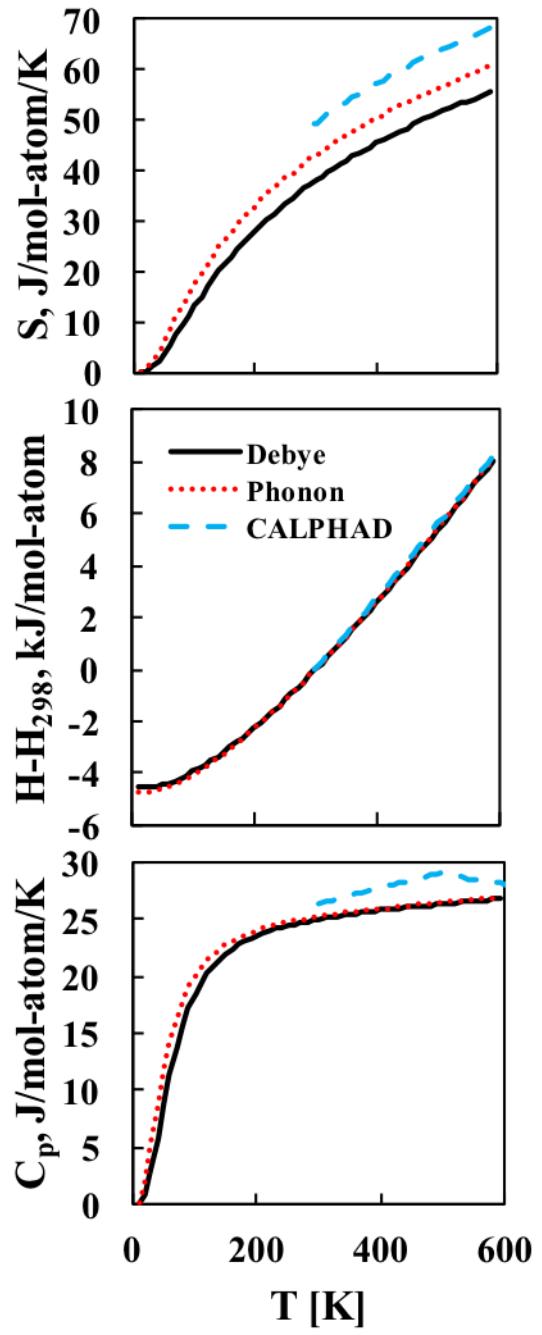


Figure 4.7. Heat capacity, enthalpy and entropy of TaSn_2 using the Debye model (solid line) and the quasiharmonic phonon calculation (red dotted line) from first-principles calculations, compared with those from the current CALPHAD modeling (blue dashed line).

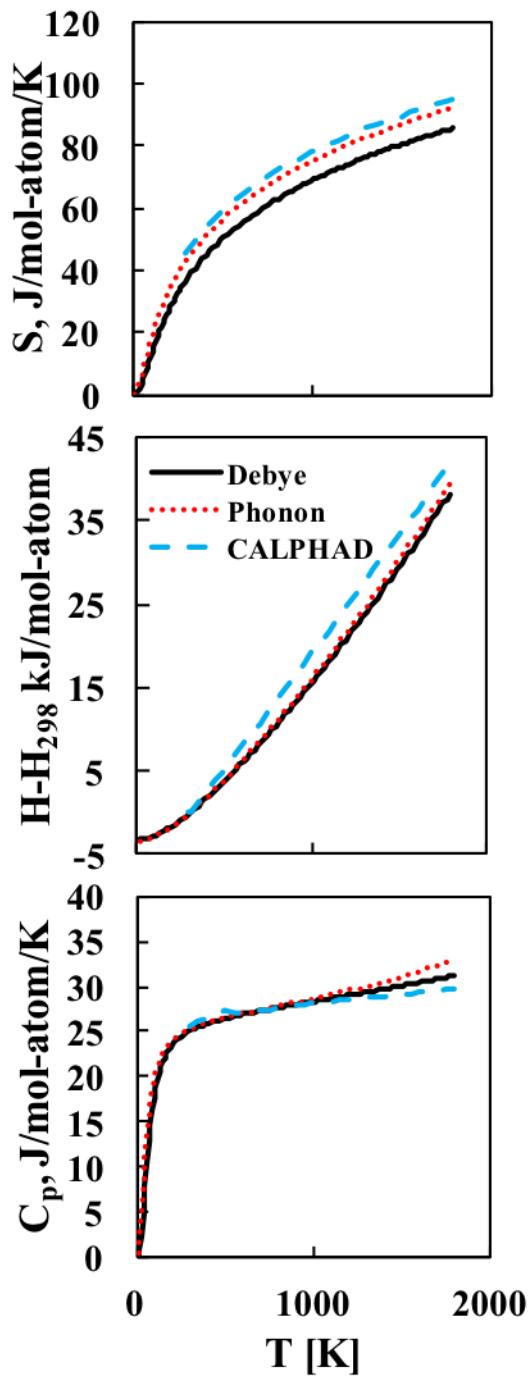


Figure 4.8. Heat capacity, enthalpy and entropy of Ta₃Sn using the Debye model (solid line) and the quasiharmonic phonon calculation (red dotted line) compared with those from the current CALPHAD modeling (blue dashed line).

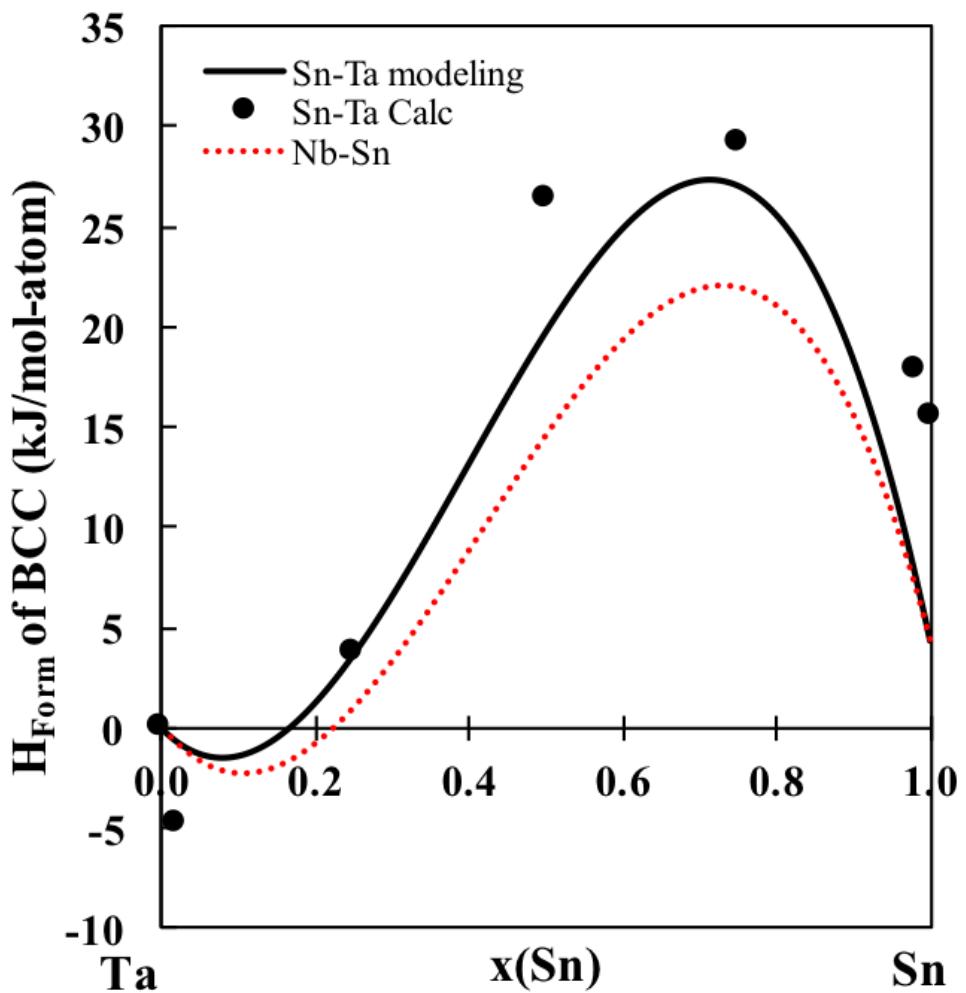


Figure 4.9. Heat capacity, enthalpy and entropy of Ta_3Sn using the Debye model (solid line) and the quasiharmonic phonon calculation (red dotted line) compared with those from the current CALPHAD modeling (blue dashed line).

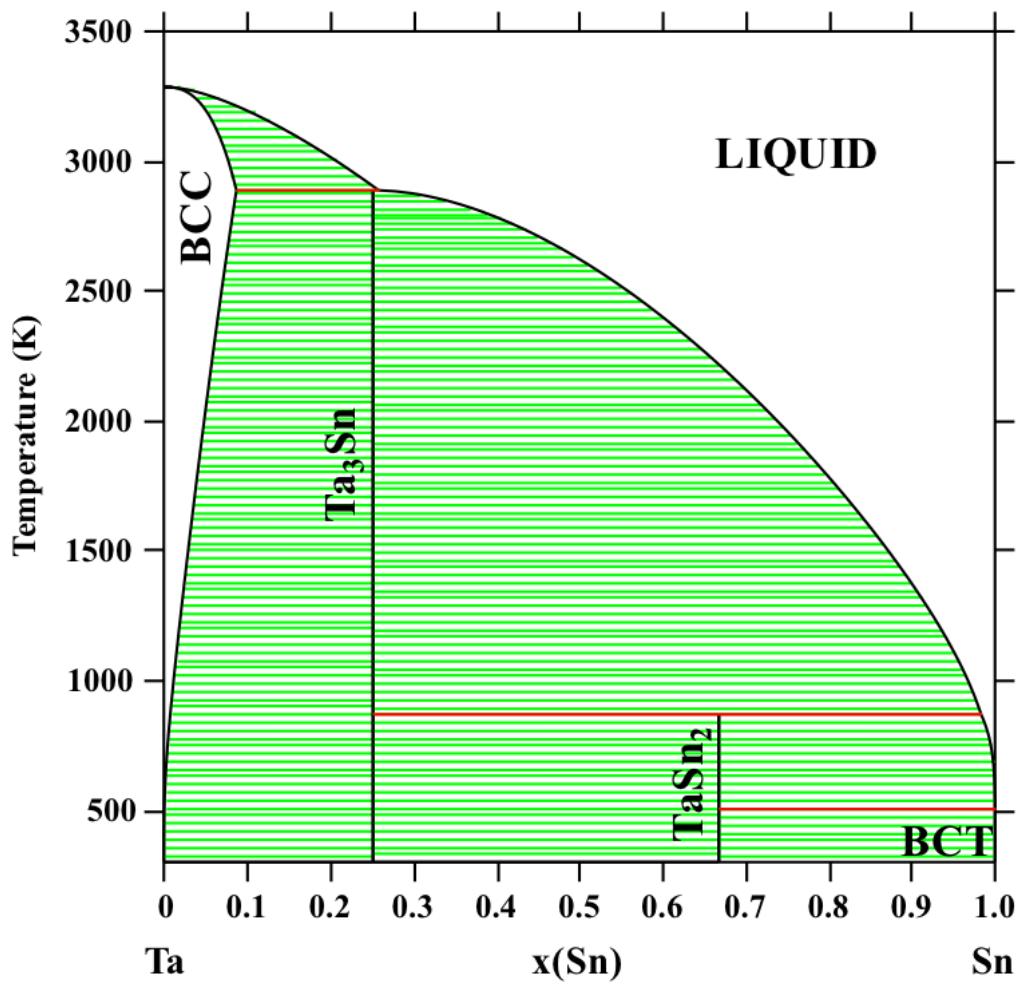


Figure 4.10. Calculated Sn-Ta phase diagram using the present thermodynamic description.

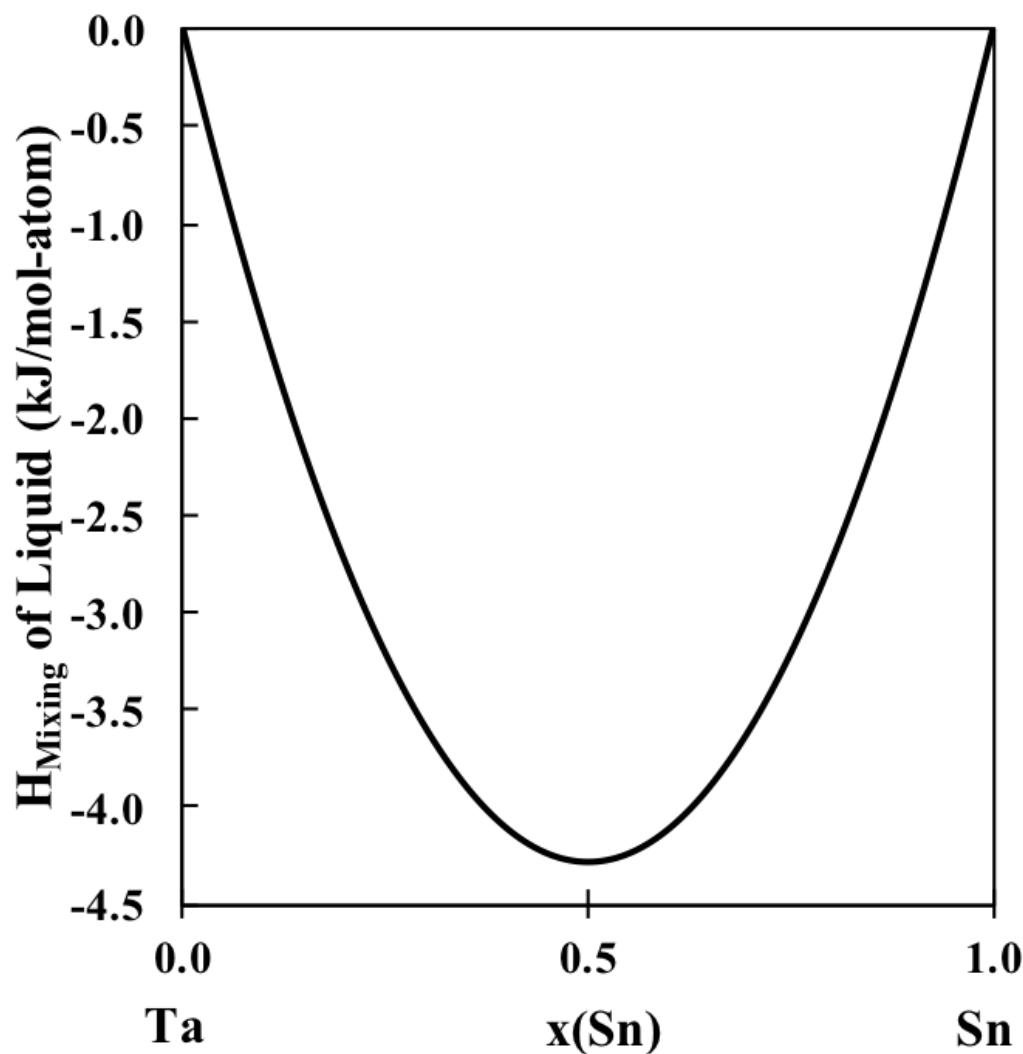


Figure 4.11. Enthalpy of mixing of the liquid phase as a function of composition at 298 °K and ambient pressure in the Sn-Ta system.

Chapter 5 |

Effects of alloying elements on the elastic properties of bcc Ti- X alloys

5.1 Introduction

The present chapter is aimed at studying the effects of alloying elements on the mechanical properties of Ti-alloys as well as completing a database to calculate the elastic properties as a function of composition. This is accomplished by systematically studying the single crystal elastic stiffness constants (c_{ij} 's) and polycrystalline aggregate properties of bcc Ti-X (X = Mo, Nb, Ta, Sn, Zr) alloys. The elastic properties are calculated using first-principles calculations based on density functional theory (DFT). The composition dependence of elastic properties of Ti-X alloys is explored through the dilute solutions and special quasirandom structures (SQS) [64] for concentrated solutions using the methodologies outlined in the methodology chapter. The obtained elastic properties are then fit using the CALPHAD method and extrapolated to higher order Ti-alloys.

5.2 Modeling and Calculations

5.2.1 Calculation details

In the present work the Vienna ab-initio Simulation Package (VASP) [54] was employed to calculate the elastic properties of pure elements and Ti-containing binary systems in the bcc phase. The ion-electron interactions were described using the projector augmented wave (PAW) [55, 71] method and based on the previous work of comparing X-C functionals (Figure 2.1) the exchange-correlation functional of the generalized gradient approach depicted by Perdew, Burke, and Ernzerhof (PBE-GGA) was employed [51]. Three magnitudes of strain were compared by doing the same calculations on the Ti-Mo system using the ± 0.01 , ± 0.013 and ± 0.007 magnitudes of strain. The three magnitudes of strain showed little variance in results, thus the calculations were done with PBE and ± 0.01 strains. For consistency, a 310 eV energy cutoff was adopted for all calculations, which is roughly 1.3 times higher than the default value. The energy convergence criterion was 10^{-6} eV/atom, and the Monkhorst-Pack scheme is used for Brillouin zone sampling [54, 72].

For the Ti-X binary systems, calculations for both dilute and SQS solutions were carried out. Three SQS cells with mole fractions of X atoms at 0.25, 0.5, and 0.75 were employed. Five dilute solutions were calculated for each Ti-X binary alloy using supercell sizes, i.e., $Ti_{53}X$ (54-atom), $Ti_{15}X$ (16-atom), Ti_7X (8-atom), $X_{15}Ti$ (16-atom), and $X_{53}Ti$ (54-atom). The interaction paramters for the elastic stiffness constants were then determined according to the methodology laid out in chapter 2.

5.2.2 Modeling details

The first-principles results are then used to model the elastic stiffness constants. The modeling was completed by calculating the difference between the first-principles calculations and a linear extrapolation between pure elements. The differences were then used to fit to the interaction parameters. Due to the limitations within the PARROT module, a mathematica script was used to fit the interaction parameters. The mathematica script is appended in appendix C. With the focus being Ti-rich alloys, the first-principles results with 70 at. % Ti or higher were weighted heavier

(x6, according to the authors' practices) than the other points for the fittings. The best fit was found by comparing the fittings obtained with one interaction parameter or with two interaction parameters. The moduli values were then calculated from the elastic stiffness constants according to Eq. Y in the methodology chapter.

5.3 Results and discussion

5.3.1 Evaluation of calculation settings

The X-C functionals of PW91 and PBE were tested on the Ti-Ta binary system. The results are plotted in Figure ???. It is shown that the c_{44} values of Ti-Ta alloys consistently differ around 10 GPa or less between the PW91 and PBE calculations. The c_{11} and c_{12} calculations differ less than 5 GPa. The c_{11} and c_{12} values with 25 at.% Ta from SQS calculations vary by 26 GPa and 13 GPa, respectively. Since overall the values vary by an error of less than 0.2 (calculated with Eq. Y), it is concluded that the X-C functional choice does not make a significant difference in the results. The PBE functional was created after PW91 and meant to be an improvement on the PW91 and was chosen for the present work.

Three magnitudes of strain were tested on the Ti-Mo binary system and plotted in 5.1. The results show that the different strain magnitudes do not affect the results. For example, the data calculated using ± 0.01 , ± 0.013 , and ± 0.007 strains at Mo_{15}Ti for c_{11} was 451 GPa, 450 GPa, and 450 GPa, respectively, varying within 1 GPa ($< 1\%$), similar to the variance in the c_{12} and c_{44} results. Overall, the variance in the c_{11} and c_{12} is less than 0.02 (Eq. Y). The largest variance is seen in the $\text{Ti}_{50}\text{Mo}_{50}$, the c_{44} values are 42 GPa, 42 GPa, and 65 GPa calculated with ± 0.01 , ± 0.013 , and ± 0.007 strains, respectively. Overall, the strain magnitude does not seem to affect the calculated results, and the ± 0.01 strain magnitude is thus used for all the calculations.

5.3.2 Calculations of the Ti-X elastic properties

The elastic stiffness constants and bulk modulus B are calculated from c_{ij} of pure elements in the bcc structure and reported in 5.1. The results in the present work were all obtained at 0 °K without considering the effect of zero-point vibrational

energy as discussed in the section of methodology. The results for Mo, Nb and Ta, which are stable in the bcc structure at low temperatures, are compared with experimental data at temperatures specified in the table [78, 79]. The error (Eq. Y) between the present results and previous results for Mo, Nb and Ta are 2.61, 7.5, and 4.25 %, respectively [61, 78, 79]. This discrepancy is partially due to the experimental values being obtained at higher temperatures than the calculations at 0 °K.

Ti and Zr are stable in the hcp structure at low temperatures, and Sn is stable in the body centered tetragonal and diamond structures at low temperatures. Due to the instability of Ti, Sn and Zr in the bcc structure at low temperatures, their elastic stiffness coefficients are compared with previous first-principles calculations at 0 °K [76] used the PW91 functional, and the errors are 2.4, 52.8 and 5.1 %, respectively. The differences are related to the instability of the bcc structure, the different exchange correlation functionals and the different input parameters chosen. Due to the bcc instability, multiple relaxation schemes were run in the present work to find the lowest energy structure retaining the bcc symmetry, making the results the most accurate representation of the bcc pure elements.

Figure 5.2 summarizes the present Young's modulus results for each Ti-X binary system (circles). The solid lines are from the Voigt-Reuss-Hill approach with the elastic coefficients from the current modeling using Eq. Y and the model parameters shown in Table 5.2. The Hill average is plotted as a solid black line while the Voigt (high bound) and Reuss (low bound) are plotted as dotted lines and dashed lines, respectively. When the structures are stable the Voigt and Reuss do not vary drastically but when the structures are unstable the Voigt and Reuss show the high and low bounds of the modulus calculations with the Hill average being what the database will predict. The results calculated for the Ti-Mo, Ti-Nb, and Ti-Ta systems are compared with previous calculated results from Ikehata et al. [2], and the difference is due to the different input parameters and structures used at each composition. Ikehata et al. used the s electrons as the valance electrons for Ti and used the B2 structure for their $Ti_{0.5}X_{0.5}$ with Ti at the body centered site and X at the corner site. For the $Ti_{0.25}X_{0.75}$ and $Ti_{0.75}X_{0.25}$ structures they used the DO_3 structure with space group $Fm\bar{3}m$, as opposed to the BCC space group of $Im\bar{3}m$. While the present work used the p electrons as valance for Ti based on updated work and new recommendations by VASP and 16-atom SQS structures from Jiang

et al. [64]. The SQS structures mimic the random substitution of elements that represent the atomic structures of solution phases better. The Ti-Mo, Ti-Nb and Ti-Ta alloy results are also compared with available experimental results [3–5, 27–30] in Table 5.3.

Figure 5.2a compares the present results for the Ti-Mo alloy system with experimental data from Zhang et al. [27], Collings et al. [28], and Sung et al. [29]. It can be seen that the Young's modulus increases from pure Ti to pure Mo. The results from Sung et al. [29] differ by about 60 GPa from the present work. However, during the XRD and TEM investigations by Sung et al, one of the metastable phases, α'' and ω , in addition to the bcc phase was observed in the samples. The ω phase is a hexagonal phase (space group P6/mmm) with lattice parameters closely matching those of the bcc phase, and the α'' phase is a martensitic orthorhombic phase (space group Cmcm). The formation of the α'' and ω phases causes variations in the mechanical properties and thus the mechanical properties are expected to vary from the elastic properties of the single bcc phase. Zhang et al. [27] and Collings et al. [28] did not observe the formation of either metastable phase. The Young's modulus determined by Zhang et al. and Collings et al. are predicted with the present Voigt-Reuss bounds but have an error of 0.39 (Eq. Y) from the Hill average Young's modulus.

The present Young's moduli of the Ti-Nb alloy system are compared with data from Ozaki et al. [30] and Collings et al. [28] in Figure 5.2b, showing an increase in Young's modulus with an increase in Nb concentration. The analyses of the samples from the work by Ozaki et al. and Collings et al. showed that the alloys all contained the single bcc phase. The Young's modulus from the present first-principles calculations show an error of 0.09 (Eq. Y) from the Young's modulus determined by Ozaki et al. and Collings et al.

The Young's modulus calculation results for the Ti-Ta alloy system are plotted in Figure 5.2d. Figure 5.2d also plots the Young's modulus values that were experimentally determined from Fedotov et al. [5] and Zhou et al. [3,4]. The present Young's moduli calculated have an error of 0.19 (Eq. Y) from the experimental Young's moduli determined by Fedotov et al and Zhou et al. The Young's modulus in the Ti-Ta alloy system increases from pure Ti to pure Ta.

The error between the Young's moduli determined experimentally and the Young's moduli calculated using DFT is expected due to the temperature difference

(calculations at 0 °K and experiments at 298 °K). The Young's modulus results determined experimentally fit well within the Voigt and Reuss bounds and the present calculations provide good prediction of the elastic properties of the Ti-Mo, Ti-Nb and Ti-Ta alloys as a function of composition.

For the Young's modulus of the Ti-Sn (Figure 5.2c) and Ti-Zr (Figure 5.2e) systems there is no experimental data to compare with due to the instability in the bcc phase. For the Ti-Sn alloy system the Young's modulus increases until around 35 at % Sn when the Young's modulus than decreases to pure Sn. The Young's modulus data, for the Ti-Zr alloy system, increases up to 40 at.% Zr, and then the Young's modulus decreases to pure Zr. Figure 5.3 plots the Young's modulus as a function of composition from pure Ti in the bcc structure to the alloying element (X = Mo, Nb, Sn, Ta, Zr) to be able to compare the effects of each alloying element on the Young's modulus.

Figure 5.4 to Figure 5.6 plots the calculated elastic stiffness constants, \bar{C}_{11} , \bar{C}_{12} , \bar{C}_{44} (circles) and compares it with the elastic stiffness constants fitting (solid line) and linear extrapolation between the pure elements for each binary alloy, Ti-Mo, Ti-Nb, Ti-Sn, Ti-Ta, and Ti-Zr. The previous results from Ikehata et al. [2] are plotted for comparison for the Ti-Mo, Ti-Nb, and Ti-Ta alloys. The trend seen in the elastic stiffness constants data depict that Mo, Nb and Ta affect the elastic stiffness constants in a similar fashion. As shown in Figure 5.4a, b and d the $i\bar{C}_{11}$ increases from Ti to X (Mo, Nb, Ta) and in Figure 5.6a, b and d the \bar{C}_{44} values first decrease and then increase with the addition of the alloying element Mo, Nb and Ta respectively. The calculated \bar{C}_{12} increases by the addition of Mo and Ta (Figure 5.5a and Figure 5.5d, respectively), and the \bar{C}_{44} first decreases and then increases by the addition of Nb (Figure 5.5b). A similar trend is shown in the \bar{C}_{11} and \bar{C}_{12} data for the Ti-Sn system (Figure 5.4c and Figure 5.5c). The \bar{C}_{11} and \bar{C}_{11} values increase and then decrease from pure Ti to pure Sn. The trend of the \bar{C}_{44} seen in Figure 5.6c increases, decreases, and then increases from pure Ti to pure Sn. In the Ti-Zr system, the \bar{C}_{11} and \bar{C}_{44} values increase and then decrease with increasing Zr concentration (Figure 5.4e and Figure 5.6e). The calculated \bar{C}_{12} values for the Ti-Zr system decrease and then increase shown in Figure 5.5e.

The instability in the bcc phase can be seen from Figure 5.7, which shows the \bar{C}_{11} - \bar{C}_{12} values from first-principles calculations and the present modeling. The bcc phase is mechanical unstable at concentrations less than 5.5, 11.5, 51.5, 9.5

and 4.0 at. % for Mo, Nb, Sn, Ta and Zr, respectively. Figure 5.8 and Figure 5.9 show the bulk and shear moduli plotted similarly to the Young's modulus in Figure 5.2 with the present results (circles), the Hill average (solid black line), and Voigt (purple dashed line) and Reuss (yellow dashed line) bounds. Similar trends in the B and G data are seen for the Ti-Mo, Ti-Nb and Ti-Ta systems. The B and G increase with increasing Mo, Nb and Ta concentration, as shown in Figure 5.8 and Figure 5.9, respectively. The bulk and shear moduli values increase and then decrease from pure Ti to pure Sn in the Ti-Sn system (Figure 5.8c and Figure 5.9c). In the Ti-Zr system, the B decreases from pure Ti to pure Zr (Figure 5.8e) and the G first increases and then decreases from pure Ti to pure Zr (Figure 5.9e).

5.3.3 Extrapolation to ternary and higher ordered systems

The interaction parameters in Table 5.2 can be used to predict the elastic stiffness constants of higher order Ti-alloys by summing the interaction parameters of each binary alloy contained in the multi-component alloy from Eq. Y. The predicted elastic stiffness constants of the multi-component alloys can be used to calculate Young's modulus as a function of composition as shown in Figure 5.3. The Hill average is plotted as solid lines while the Voigt and Reuss bounds are plotted as dotted and dashed lines, respectively. The accuracy of prediction of the elastic properties of higher ordered Ti alloys can be evaluated by comparing the predicted results with previous experimental results [32–35] as shown in Figure 5.10 and Table 5.4. The black diagonal line represents a perfect correlation between the predicted and experimental Young's modulus. The grey region is the error (3 GPa) in the first-principles calculations. The error in the first-principles is the average variance in \overline{C}_{11} , \overline{C}_{12} , and \overline{C}_{44} from Eq. Y-Eq. Y.

As it can be seen, the difference between experimental Young's modulus at the same composition from Niinomi et al. [35], Geetha et al. [33], Tane et al. [32] and Mohammad et al. [34] varies from 2 GPa to 46 GPa based on the heat treatments and measuring techniques. The scattering in the Young's modulus among experimental measurements is denoted by the vertical error bars in Figure 5.10. The horizontal error bars show the Reuss and Voigt Young's modulus ranges with the Hill average marked by the circle. The experimental Young's moduli vary from the present predictions anywhere from 0.69 to 14 GPa. This difference is partially due to

the temperature difference between the first-principles data and the experimental results. Considering the fact that the experimental results at the same composition vary drastically, the first-principles calculations give a good representation of the elastic properties of higher order Ti-alloys. Introducing the binary interaction parameters of non-Ti containing alloys in the system and the ternary interaction parameters can further improve the database predictions.

5.4 Conclusion

The effects of five alloying elements on the elastic properties of bcc Ti-X (X = Mo, Nb, Sn, Ta, Zr) alloys, including the elastic stiffness constants, bulk modulus, shear modulus, and Young's modulus, were systematically studied using first-principles calculations. The CALPAHD methodology was used to evaluate interaction parameters so that the elastic properties can be predicted as a function of composition. The present calculations showed that 5.5 at.%, 11.5 at.%, 51.5 at.%, 9.5 at.% and 4.0 at.% of Mo, Nb, Sn, Ta and Zr, respectively, were needed to stabilize the bcc phase according to the Born criteria. The trends observed were summarized for each Ti-X (X= Mo, Nb, Sn, Ta, Zr) binary system. Alloying with Mo, Nb and Ta showed to produce similar trends which is presumably due to Mo, Nb, and Ta being stable in the bcc structure at room temperature and being strong bcc stabilizers. The interaction parameters determined in the current work were used to predict the elastic properties of higher order alloys. The accuracy of database predictions of the Young's modulus was determined by comparing with the calculated and experimental Young's moduli. Overall, the database provides good predictions of the elastic properties of Ti-alloys in the bcc phase as a function of composition. To improve the database predictions, the non-Ti containing binary interaction parameters and the ternary interactions parameters should be determined.

Table 5.1. Calculated pure element elastic stiffness constants and the bulk modulus B (in GPa) by X-C functional of PBE are compared with the previous first-principles calculations (FP) by X-C functional PW91 and experiments (Expt). Sv, pv and d refereeing to the s, p, and d states being treated as valance, respectively.

Pure Elements		\bar{C}_{11}	\bar{C}_{11}	\bar{C}_{11}	B
Ti_sv	This work 0 K	93	115	41	108
	Calc 0 K [76]	96	116	40	107
Mo_pv	This work 0 K	475	164	108	268
	Expt 73 K [61]	473	156	111	
	Expt 300 K [78]	473	160	109	261
Nb_sv	This work 0 K	245	144	27	178
	Expt 4 K [61]	253	133	31	
	Expt 300 K [79]	247	135	29	172
Sn_d	This work 0 K	50	52	29	51
	Calc 0 K [76]	30	60	18	48
Ta_pv	This work 0 K	278	164	81	202
	Expt 0 K [61]	266	158	87	
	Expt 300 K [79]	267	161	83	196
Zr_sv	This work 0 K	86	91	32	89
	Calc 0 K [76]	82	94	30	90

Table 5.2. Evaluated interaction parameters L_0 and L_1 using the R-K polynomial Eq. Y for the elastic stiffness constants for the Ti-X binary systems.

Alloy	Interaction Parameter	Ti-Mo	Ti-Nb	Ti-Sn	Ti-Ta	Ti-Zr
\bar{C}_{11}	L_0	-22.16	40.46	119.46	83.65	246.97
	L_1	0	0	0	-67.76	-135.95
\bar{C}_{12}	L_0	-36.40	-32.39	15.90	38.05	-110.53
	L_1	0	0	-146.80	0	78.00
\bar{C}_{44}	L_0	-142.9	-41.54	59.79	-51.96	70.06
	L_1	0	-41.95	-94.38	0	0

Table 5.3: First-principles calculations of the elastic stiffness constants, bulk modulus B , shear modulus G , and Young's modulus E in GPa for different atomic percent compositions of the bcc Ti-X binary systems at 0 °K. As well as experimental data for the Young's modulus obtained at 300 °K by the reference stated.

Reference	$Ti_{1-b}X_b$	\overline{C}_{11}	\overline{C}_{11}	\overline{C}_{11}	B	G	E
This work	Ti	93	115	41	108	-12.91	-40.34
This work	TiMo _{6.3}	124	111	38	115	20	54
This work	TiMo _{12.5}	146	113	29	124	23	65
This work	TiMo ₂₅	178 ±3	123 ±15	32 ±11	141 ±15	30 ±15	84 ±15
This work	TiMo ₅₀	268 ±9	136 ±19	42 ±9	180 ±19	51 ±19	138 ±19
This work	TiMo ₇₅	385 ±9	146 ±6	66 ±6	226 ±9	84 ±9	224 ±9
This work	TiMo _{93.8}	451	158	96	256	114	397
This work	TiMo _{98.1}	464	163	100	263	118	308
This work	Mo	475	164	108	268	125	325
Expt 300 K [27]	TiMo ₈						83
Expt 300 K [27]	TiMo ₁₂						90
Expt 300 K [28]	TiMo ₈						84
Expt 300 K [28]	TiMo ₁₁						89
Expt 300 K [28]	TiMo ₁₈						101
This work	TiNb _{1.9}	93	115	35	108	-18	-56
This work	TiNb _{12.5}	116	116	37	116	11	31
This work	TiNb ₂₅	140 ±11	116 ±13	34 ±10	124 ±13	22 ±13	63 ±13
This work	TiNb ₅₀	181 ±9	121 ±2	31 ±10	141 ±9	31 ±10	86 ±10
This work	TiNb ₇₅	208 ±3	130 ±4	15 ±10	156 ±4	22 ±10	64 ±10
This work	TiNb _{93.8}	242	134	18	170	28	81
This work	TiNb _{98.1}	242	134	18	170	28	81
This work	Nb	245	144	27	178	35	98
Expt 300 K [30]	TiNb ₂₉						67
Expt 300 K [30]	TiNb ₃₄						74
Expt 300 K [30]	TiNb ₄₄						84
Expt 300 K [28]	TiNb ₂₆						64

Table 5.3: First-principles calculations of the elastic stiffness constants, bulk modulus B , shear modulus G , and Young's modulus E in GPa for different atomic percent compositions of the bcc Ti-X binary systems at 0 °K. As well as experimental data for the Young's modulus obtained at 300 °K by the reference stated.

Reference	$Ti_{1-b}X_b$	\bar{C}_{11}	\bar{C}_{11}	\bar{C}_{11}	B	G	E
Expt 300 K [28]	$TiNb_{30}$						65
Expt 300 K [28]	$TiNb_{34}$						73
Expt 300 K [28]	$TiNb_{44}$						83
This work	$TiSn_{6.3}$	100	122	46	115	-10	-30
This work	$TiSn_{25}$	105 ± 5	114 ± 2	60 ± 4	111 ± 5	11 ± 5	31 ± 5
This work	$TiSn_{50}$	88 ± 9	93 ± 9	46 ± 4	91 ± 9	10 ± 9	29 ± 9
This work	$TiSn_{75}$	92 ± 9	55 ± 7	35 ± 8	67 ± 9	27 ± 9	72 ± 9
This work	Sn	50	52	29	51	7	21
This work	$TiTa_{1.9}$	100	115	39	110	-3	-9
This work	$TiTa_{6.3}$	116	113	30	114	11	32
This work	$TiTa_{12.5}$	120	121	39	121	11	32
This work	$TiTa_{25}$	167 ± 1	140 ± 3	45	149 ± 3	28 ± 3	78 ± 3
This work	$TiTa_{50}$	208 ± 1	159	51 ± 3	175 ± 1	38 ± 3	106 ± 3
This work	$TiTa_{75}$	239 ± 7	143 ± 5	62 ± 3	175 ± 7	56 ± 7	152 ± 7
This work	$TiTa_{93.8}$	257	158	72	191	62	168
This work	$TiTa_{98.1}$	264	163	72	197	62	169
This work	Ta	278	164	81	202	70	189
Expt 300 K [5]	$TiTa_{38}$						62
Expt 300 K [5]	$TiTa_{42}$						79
Expt 300 K [5]	$TiTa_{48}$						95
Expt 300 K [3]	$TiTa_{38}$						67
Expt 300 K [3]	$TiTa_{51}$						105
This work	$TiZr_{1.9}$	112	106	43	108	17	48
This work	$TiZr_{25}$	148 ± 14	82 ± 7	54 ± 7	104 ± 14	44 ± 14	116 ± 14
This work	$TiZr_{50}$	152 ± 17	76 ± 12	48 ± 12	101 ± 17	44 ± 17	115 ± 17
This work	$TiZr_{75}$	126 ± 12	82 ± 3	45 ± 3	97 ± 12	34 ± 12	91 ± 12

Table 5.3: First-principles calculations of the elastic stiffness constants, bulk modulus B , shear modulus G , and Young's modulus E in GPa for different atomic percent compositions of the bcc Ti-X binary systems at 0 °K. As well as experimental data for the Young's modulus obtained at 300 °K by the reference stated.

Reference	$\text{Ti}_{1-b}\text{X}_b$	\overline{C}_{11}	\overline{C}_{11}	\overline{C}_{11}	B	G	E
This work	$\text{TiZr}_{93.8}$	89	90	34	90	9	27
This work	Zr	86	91	32	89	6	16

Table 5.4. Predicted Young's modulus (in GPa) of higher order alloys in the bcc phase compared to experimental values found with both the weight percent and atomic percent listed. The predicted Young's modulus was found using the pure elements and binary interaction parameter data.

Alloy Name (%wt)	at %	Calc <i>E</i>	Expt <i>E</i>
Ti-35Nb-7Zr-5Ta [33]	Ti-24Nb-5Zr-2Ta	81	80
Ti-29Nb-13Ta-4.6Zr [33]	Ti-20Nb-5Ta-3Zr	76	75
Ti-29Nb-13Ta-6Sn [33]	Ti-21Nb-5Ta-3Sn	68	74
Ti-29Nb-13Ta-4.6Sn [33]	Ti-20Nb-5Ta-3Sn	67	66
Ti-29Nb-13Ta-4.5Zr [33]	Ti-20Nb-5Ta-3Zr	76	65
Ti-29Nb-13Ta-4.6Zr [32]	Ti-21Nb-5Ta-3Zr	76	64
Ti-30Nb-10Ta-5Zr [32]	Ti-23Nb-4Ta-3Zr	77	64
Ti-35Nb-10Ta-5Zr [32]	Ti-25Nb-4Ta-4Zr	80	65
Ti-24Nb-4Zr-7.9Sn [34]	Ti-15Nb-3Zr-4Sn	65	54
Ti-35Nb-2Ta-3Zr [34]	Ti-23Nb-1Ta-2Zr	69	61
Ti-29Nb-11Ta-5Zr [34]	Ti-20Nb-6Ta-2Zr	74	60
Ti-10Zr-5Ta-5Nb [34]	Ti-6Zr-1Ta-3Nb	64	52
Ti-29Nb-13Ta-2Sn [34]	Ti-20Nb-5Ta-1Sn	66	62

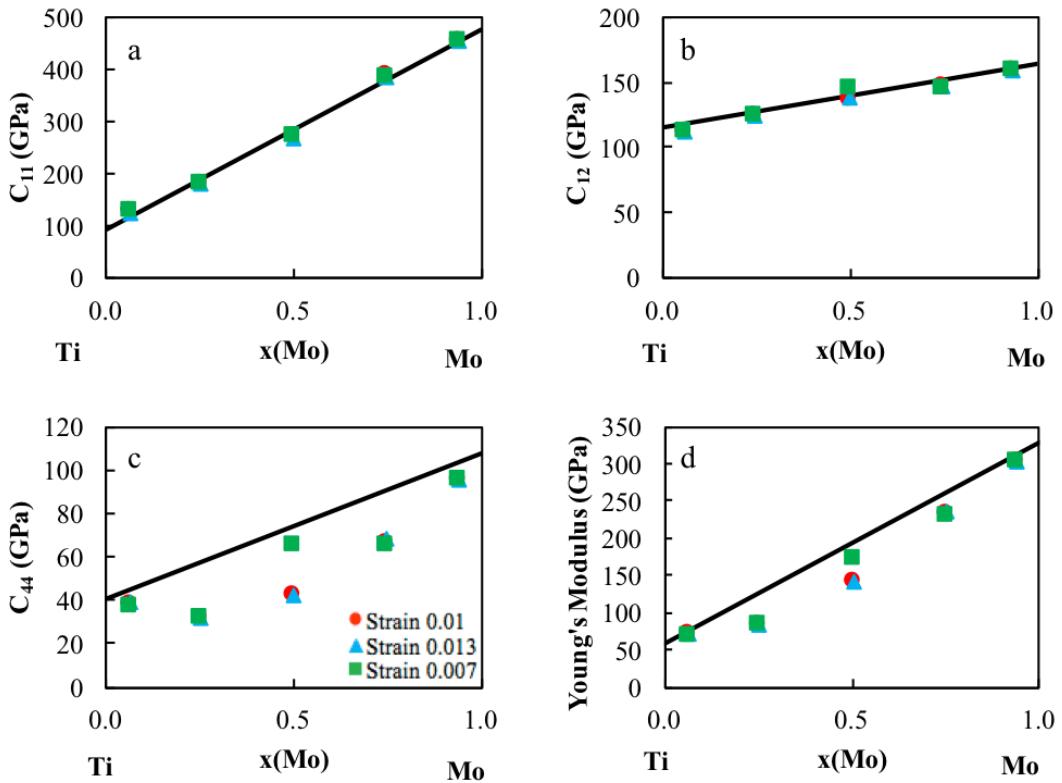


Figure 5.1. Elastic stiffness constants for the bcc Ti-Mo binary system calculated with strains, 0.01, 0.03 and 0.07, respectively, showing comparable results.

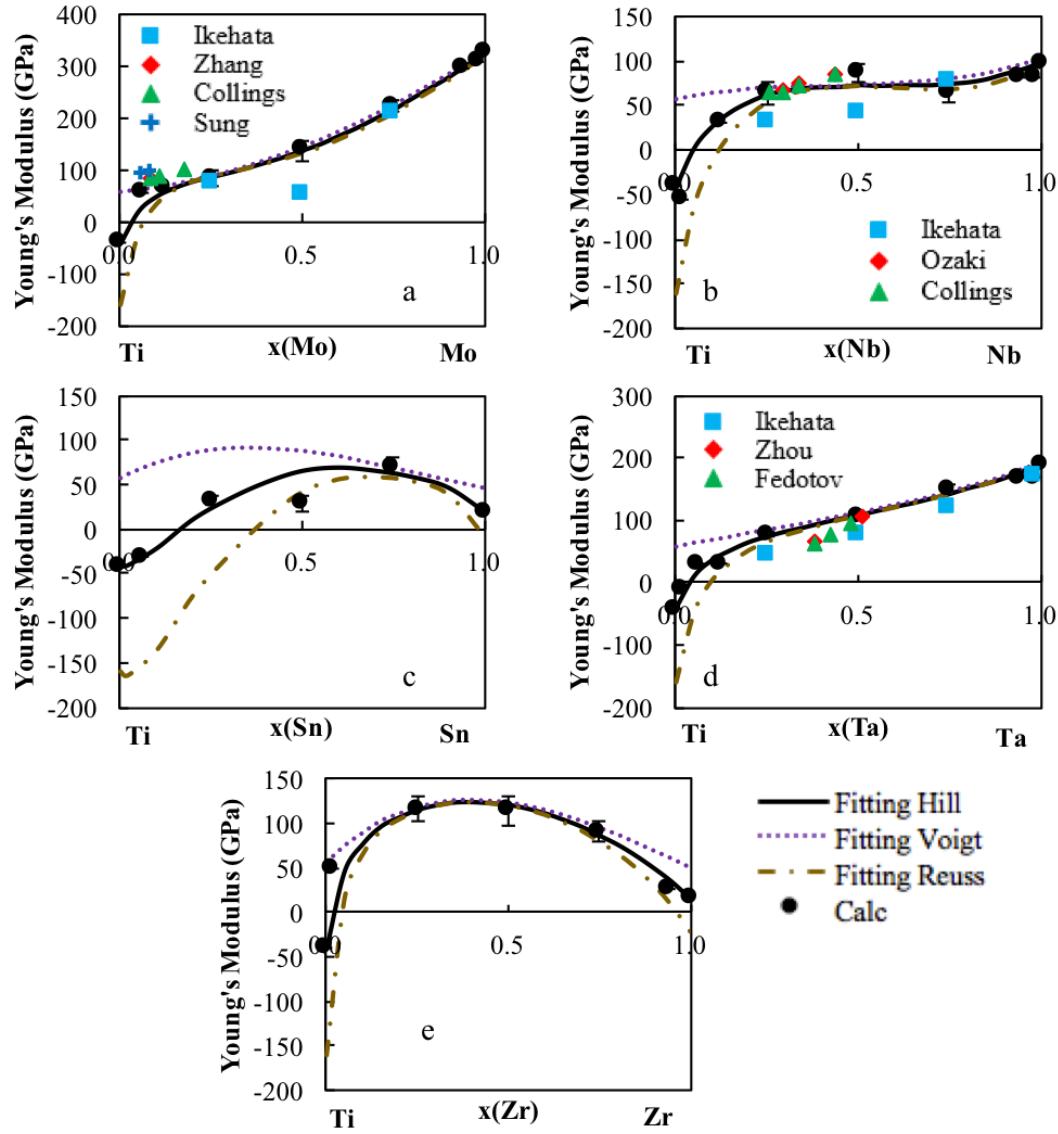


Figure 5.2. Young's modulus E of the Ti-X binary systems. The present calculations are plotted as the filled circles with the error bars. The dotted purple line is the Voigt upper Young's modulus bound, the gold dot dashed line is the lower Reuss Young's modulus bound and the black line is the Hill Young's modulus average. The experimental values [1–5, 27–31] are also included for comparison.

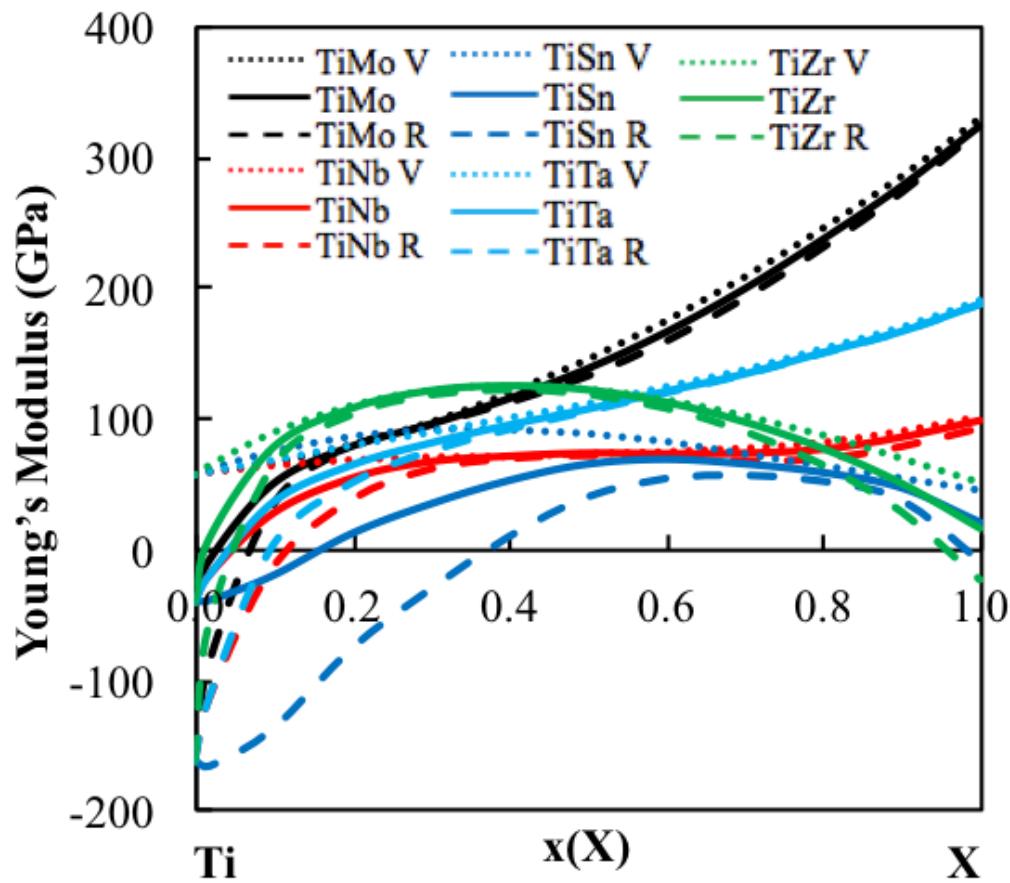


Figure 5.3. Young's modulus calculated from the model parameters (see ??) and Eq. Y as a function of composition from bcc Ti to bcc X.

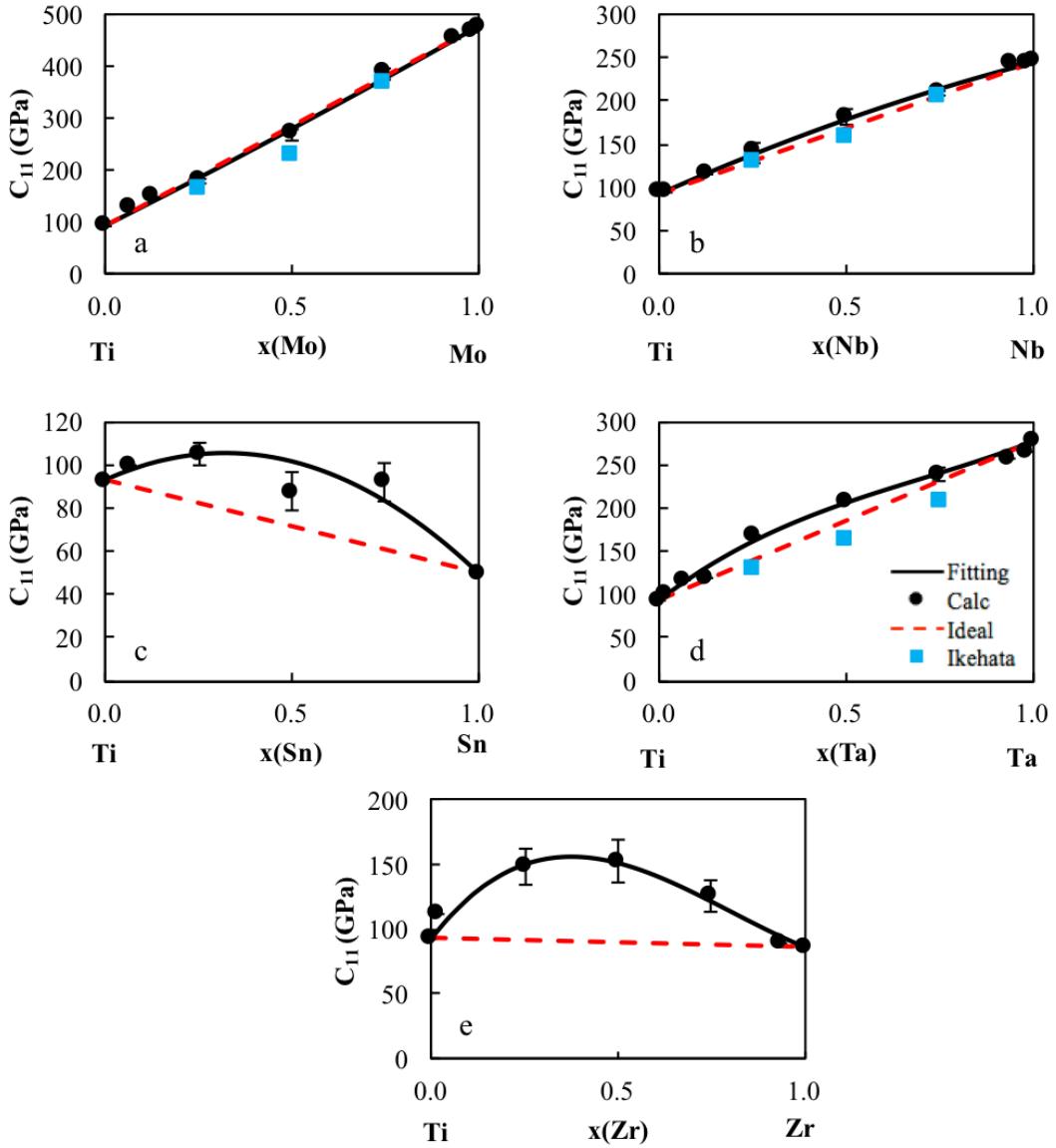


Figure 5.4. Calculated \bar{C}_{11} values (circles) plotted with their errors as well as the pure element extrapolation (red dashed line) and the present modeling (black dashed line) for five Ti-X binary systems ($X = \text{Mo}, \text{Nb}, \text{Ta}, \text{Sn}, \text{Zr}$). Ti-Mo, Ti-Nb, and Ti-Ta alloys are compared with previous calculations from Ikehata et al. [2].

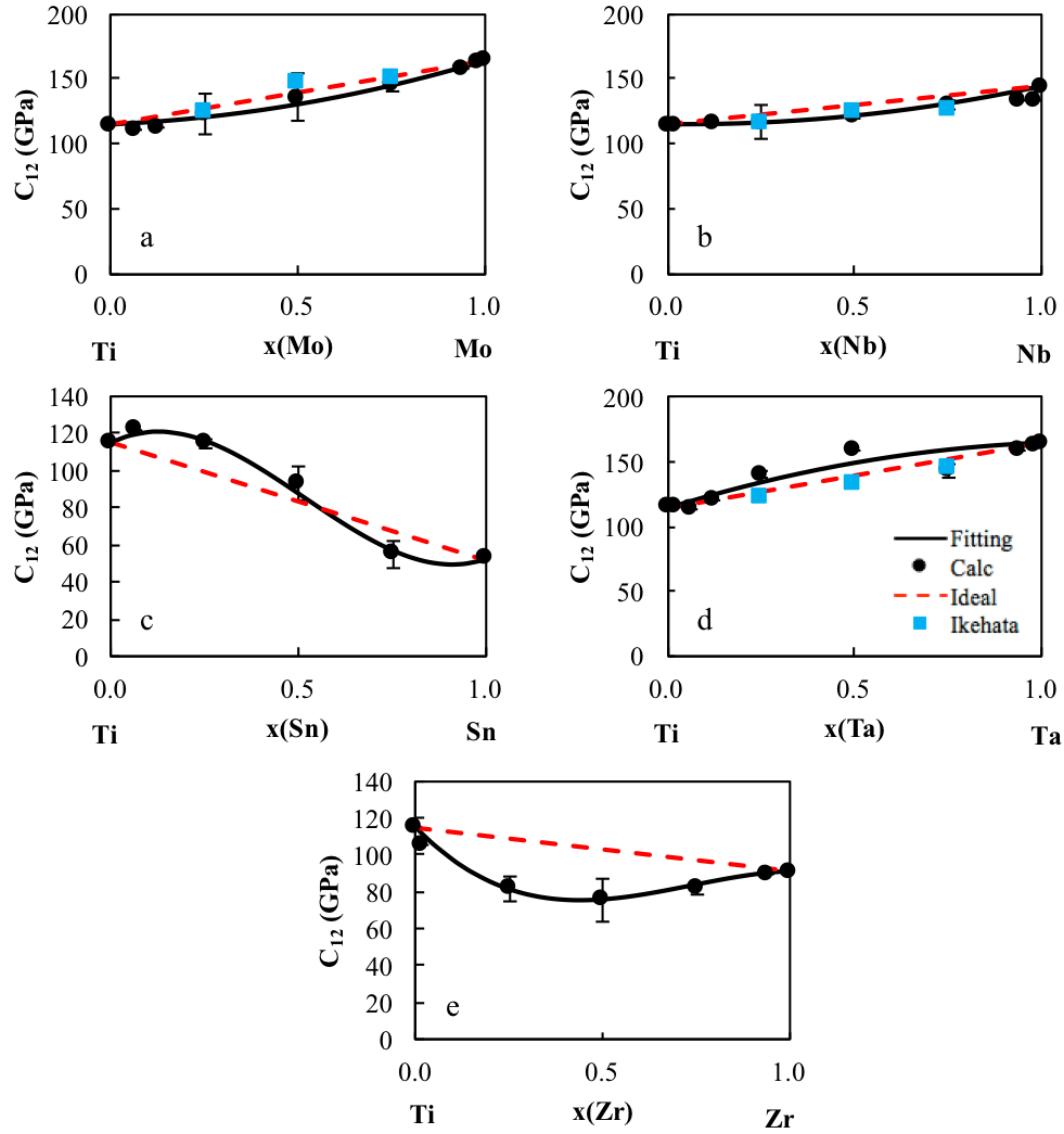


Figure 5.5. Calculated \bar{C}_{12} values (circles) plotted with their errors as well as the pure element extrapolation (red dashed line) and the present modeling (black dashed line) for five Ti-X binary systems ($X = \text{Mo}, \text{Nb}, \text{Ta}, \text{Sn}, \text{Zr}$). Ti-Mo, Ti-Nb, and Ti-Ta alloys are compared with previous calculations from Ikehata et al. [2].

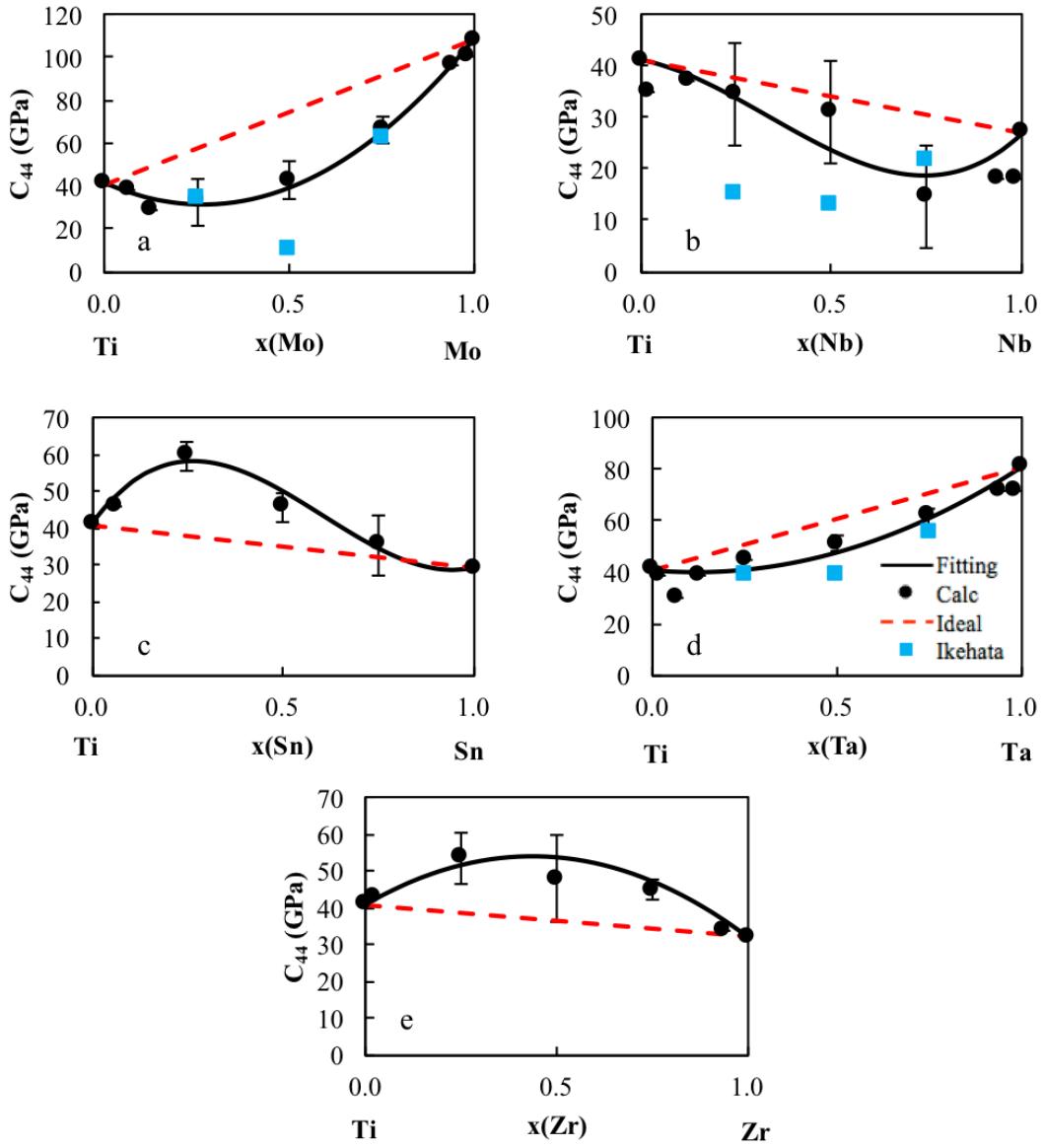


Figure 5.6. Calculated \bar{C}_{44} values (circles) plotted with their errors as well as the pure element extrapolation (red dashed line) and the present modeling (black dashed line) for five Ti-X binary systems ($X = \text{Mo}, \text{Nb}, \text{Ta}, \text{Sn}, \text{Zr}$). Ti-Mo, Ti-Nb, and Ti-Ta alloys are compared with previous calculations from Ikehata et al. [2].

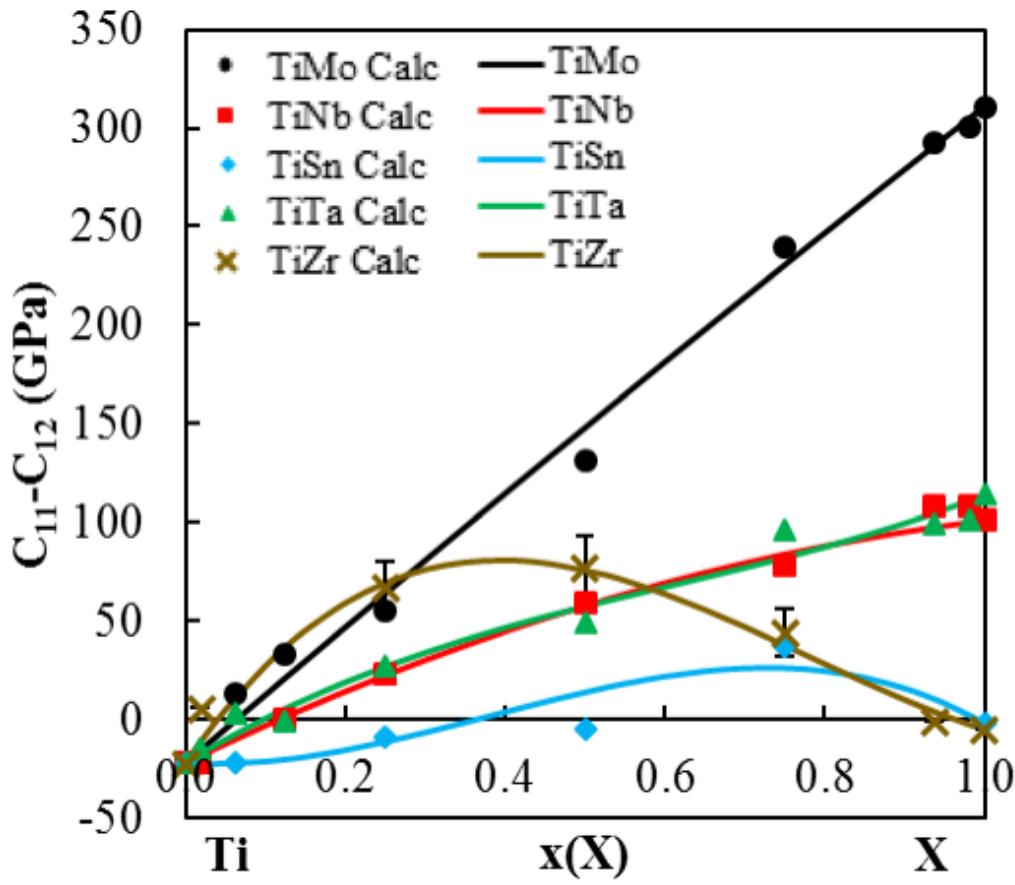


Figure 5.7. Calculated \bar{C}_{11} - \bar{C}_{12} values (circles) plotted with the present modeling (solid lines) for five Ti-X binary systems ($X = \text{Mo, Nb, Ta, Sn, Zr}$). The C_{11} - C_{12} shows the stability of the bcc phase. When the \bar{C}_{11} - \bar{C}_{12} value is negative the bcc phase is not stable in the corresponding compositions range.

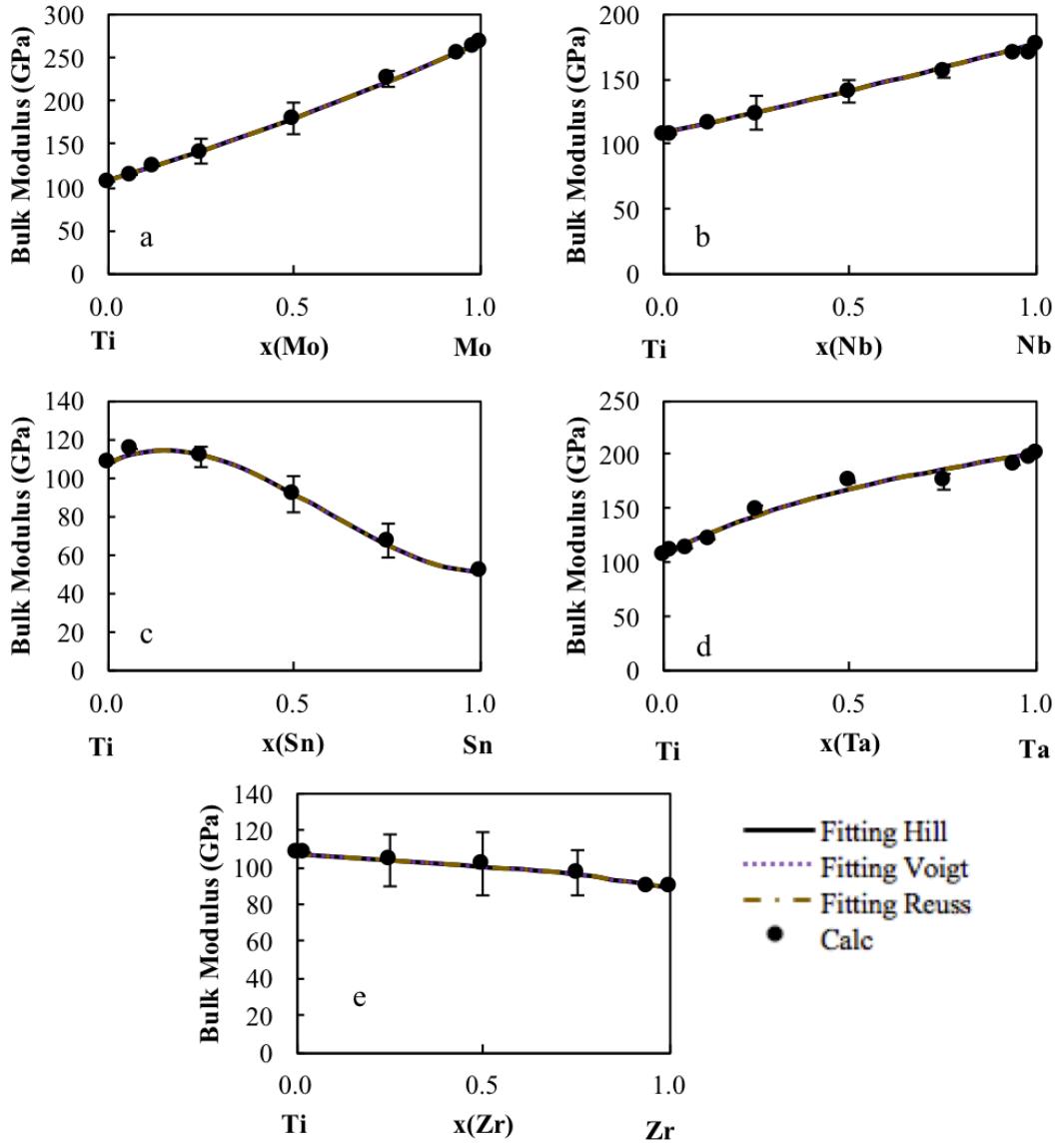


Figure 5.8. Bulk modulus B of the Ti-X binary systems. The present calculations are plotted as the filled circles with the error bars. The dotted purple line is the Voigt upper bulk modulus bound, the gold dot dashed line is the lower Reuss bulk modulus bound and the black line is the Hill bulk modulus average.

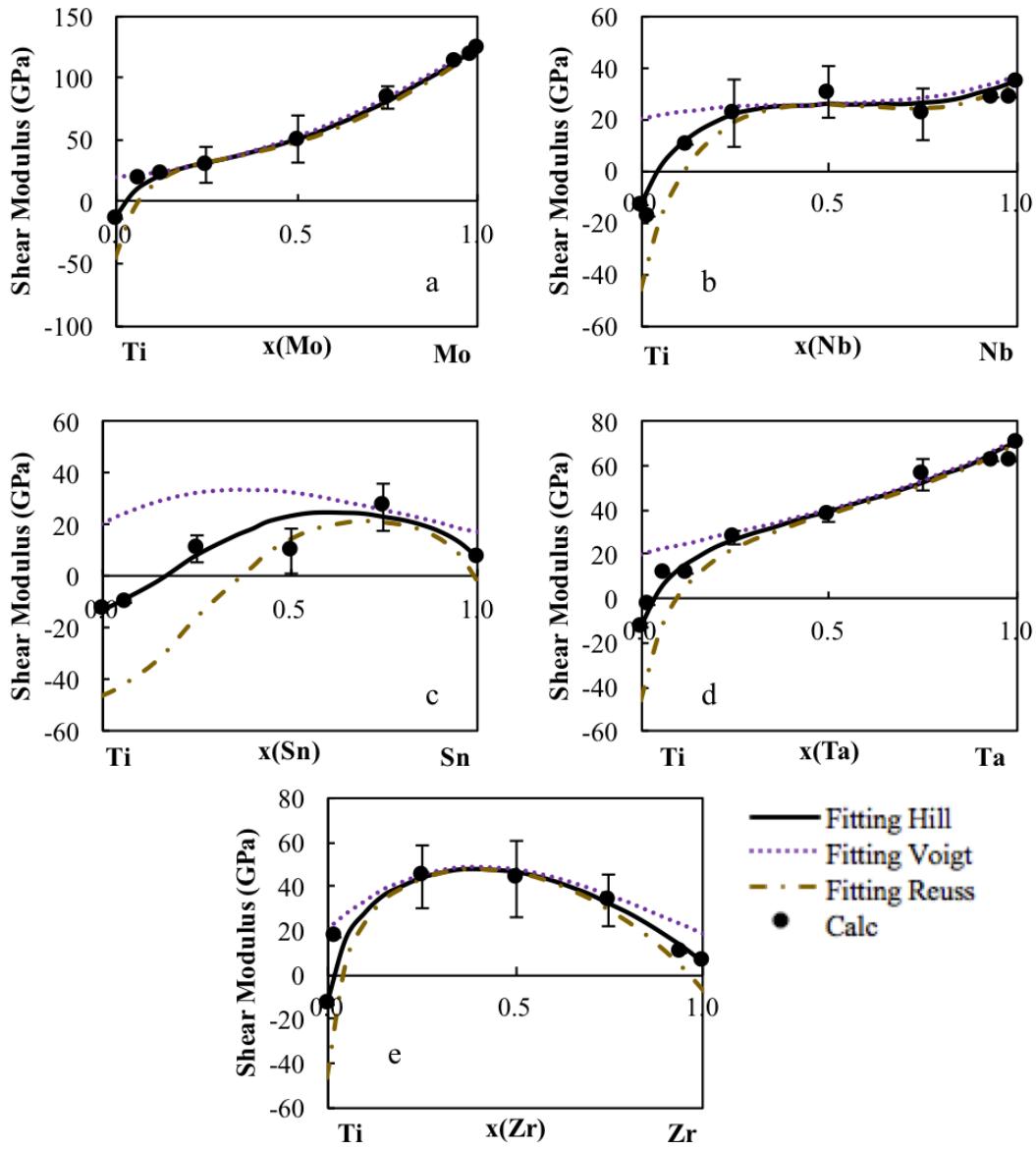


Figure 5.9. Shear modulus G of the Ti-X binary systems. The present calculations are plotted as the filled circles with the error bars. The dotted purple line is the Voigt upper shear modulus bound, the gold dot dashed line is the lower Reuss shear modulus bound and the black line is the Hill shear modulus average.

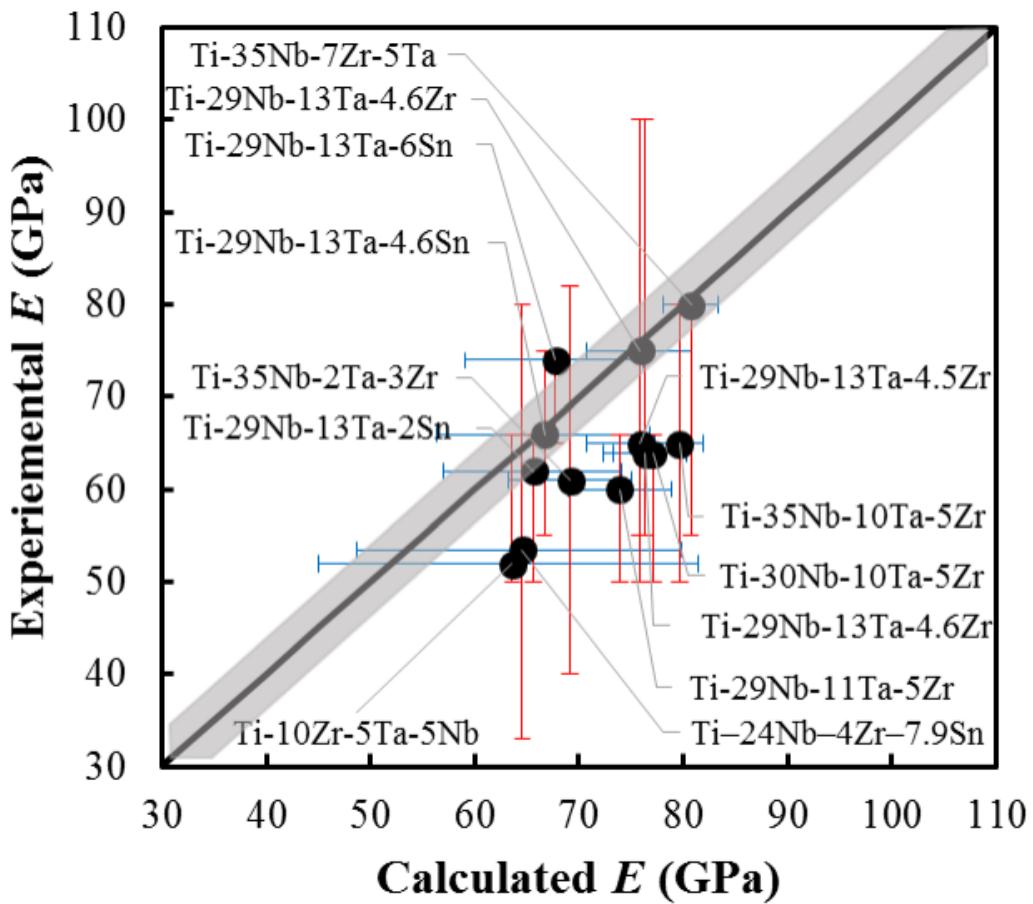


Figure 5.10. Young's modulus values of multicomponent bcc Ti alloys measured experimentally plotted against the predicted Young's modulus from the pure elements and binary interaction parameters with the black diagonal line showing the exact correlation between the experimental and calculated values. Error bars in the experiments and the bounds from Reuss and Voigt approximations are plotted as vertical and horizontal lines, respectively. The variance in the first calculations from Eq. Y-Eq. Y was averaged and plotted as the grey region to show the variance in the first-principles calculations. More information on the alloys is in Table ?? [32–34]

Chapter 6 |

Effects of alloying elements on the elastic properties of bcc ternary and higher ordered Ti-alloys

6.1 Introduction

In order to develop a better understanding about alloying effect on the elastic properties of Ti alloys, the present work is developing an elastic database for the Ti-Mo-Nb-Sn-Ta-Zr system. With the focus being on bcc Ti-alloys, the effects of alloying elements on the pure elements and Ti-X binary alloys in the bcc phase were calculated in chapter 5. After extrapolating to higher order systems, it was hypothesized that studying the effects of alloying on the elastic properties of ternary alloys would improve the database. The present work focuses on studying the elastic properties of the Ti-X-Y ($X \neq Y = Mo, Nb, Ta, Sn, and Zr$) ternary alloys in the bcc phase. The single crystal elastic stiffness constants ($c_{ij}\AA^2$ s) and polycrystalline aggregate properties are predicted across the composition range using Density Functional Theory (DFT) at 0 °K outlined in the methodology chapter. Based on the DFT results, the CALPHAD approach outlined in the methodology is used to evaluate ternary interaction parameters. The interaction parameters are then incorporated into the database and the database accuracy is again tested similarly to the testing in chapter 5. The completed database is used to map the elastic modulus as a function of composition.

6.2 Modeling and Calculations

6.2.1 Calculation details

To study the elastic properties of the ternary bcc Ti alloys in the Ti-Mo-Nb-Sn-Ta-Zr system, first-principles calculations based on density functional theory were completed using the VASP (Vienna ab-initio simulation package) [54, 55]. Four calculations were done for each ternary alloy Ti-X-Y, with the varying compositions of $X_{0.5}Y_{0.5}$ (16-atom supercell), $TiXY$ (36 atoms), Ti_2XY (32 atoms), Ti_6XY (64 atoms). The structures were all special quasirandom structures (SQS) that were previously generated by Jiang et al. [64, 65]. Due to instability of some of these structures in the bcc phase, different relaxation schemes were used to retain the strucutral symmetry while obtaining the lowest energy structure. These relaxation schemes are outlined in the methodology chapter under the SQS section. The projector augmented wave (PAW) method was used to describe the ion-electron interaction. Based on the work of comparing X-C functionals (Figure 2.1) the exchange-correlation functional of the generalized gradient approach depicted by Perdew, Burke, and Ernzerhof (PBE) was employed [51]. An energy cutoff roughly 1.3 times higher than the default value, 310, was used for all calculations. The valance configuration for each element was selected based on the VASP recommendations and is listed in the methodology chapter. The Brillouin zone sampling is done using the gamma centered Monkhorst-Pack scheme [72]. The elastic calculations were completed using a strain magnitude of ± 0.01 based on the study done in chapter 5 and the results seen in Figure 5.1.

6.2.2 Modeling details

The first-principles results are then used to model the elastic stiffness constants. The modeling was completed by plotting the binary interpolation from the working database build in chapter 5. The plots started at $X_{0.5}Y_{0.5}$ and plotted ot pure Ti. The difference between the binary interpolation and the first-principles results were calculated. The differences were then used to obtain a single fitting parameter using the mathematica code in appendix c. With the focus being Ti-rich alloys and wanting to follow the same modeling technique used on the binary alloys, the first-principles results with 70 at.% Ti or higher were weighted heavier (x6,

according to the authors' practices) than the other points for the fittings. The best fit was found and the ternary interaction parameters were incorporated into the database. The databases was then used to predict the moduli values of the ternary alloys.

6.3 Results and discussion

6.3.1 Elastic calcualtion results

The calculated elastic stiffness constants and moduli values are listed in Table 6.1 with the experimental values used for comparison. Figure 6.1 and 6.2 plot the Young's modulus calculations (circles) for each Ti-X-Y ternary system ($X \neq Y = Mo, Nb, Sn, Ta, Zr$) starting from a 50-50 mixture of the two alloying elements to Ti. The red dashed line is an interpolation from the binary interaction parameters shown in Table 5.2. The Voigt high bound is plotted as a purple dotted line with the Reuss low bound plotted as a gold dotted-dashed line and the Hill average is plotted as a solid black line. The Voigt and Reuss bounds vary more drastically when the bcc structure is unstable as opposed to when the bcc structure is stable. The database predicts the Hill average. When possible E data obtained experimentally is plotted for comparison.

The present E results for the Ti-Mo-Nb (Figure 6.1a) alloy system are compared with E data from Niinomi et al. [35] obtained experimentally. The error between the previous results and present results was calculated using Eq. Y. The E results from Niinomi et al. are closer to the Voigt bound than Hill average and has an error of 0.65. The present data shows that the E decreases from $Mo_{0.5}Nb_{0.5}$ to Ti. From the literature search, no bcc Ti-Mo-Sn (Figure 6.1b) experimental E results were available to compare with the present work. The E trend shows a decrease in value from $Mo_{0.5}Sn_{0.5}$ to Ti. The calculated E results for the Ti-Mo-Ta alloy system (Figure 6.1c) are compared with experimental data from Niinomi et al. [35] and Mohammad et al. [34] showing an error of 0.46 (Eq. Y). The E values from Niinomi et al. and Mohammad fit well with the present Voigt bound. The E data decreases in value from $Mo_{0.5}Ta_{0.5}$ to Ti. The Young's modulus of the Ti-Mo-Zr alloy system (Figure 6.1d) is compared with experimental E values from Mohammad et al. [34]. The experimental E from Mohammad et al. and the present

E vary by less than 6 GPa and shows the Young's modulus values decreases from $\text{Mo}_{0.5}\text{Zr}_{0.5}$ to Ti. Experimental E results from Niinomi et al. [35], Mohammad et al. [34], and Nozoe et al. [36] are compared with the present E calculations for the Ti-Nb-Sn alloy system (Figure 6.1e). The experimental E results from Niinomi et al., Mohammad et al. and Nozoe et al. fit within the present Voigt-Reuss bounds and have an error of 0.39 from the present Hill average E values. The data trend in the E values shows an increase in the E value from $\text{Nb}_{0.5}\text{Sn}_{0.5}$ to 50 at % Ti and then a decrease in value to Ti.

Figure 6.2 continues to plot the E of the Ti-X-Y ternary alloy systems. Figure 6.2a, plots the present E results for the Ti-Nb-Ta alloy system, versus the E results from Mohammad et al. [34]. The E results from Mohammad et al. fit along the Reuss bound and using Eq. Y have an error of 0.28 from the present E values. The Young's modulus decreases from $\text{Nb}_{0.5}\text{Ta}_{0.5}$ to Ti. The present E for the Ti-Nb-Zr (Figure 6.2b) alloy system is compared with E results obtained experimentally by Geetha et al. [33], Mohammad et al. [34], and Niinomi et al. [35]. The E results from Geetha, Mohammad and Niinomi fit well between the Voigt-Reuss bounds and have an error of 0.08 from the present Hill average E results. The E shows an increase in value from $\text{Nb}_{0.5}\text{Zr}_{0.5}$ to 70 at % Ti and then a decrease to Ti. The Ti-Sn-Ta, Ti-Sn-Zr and Ti-Ta-Zr alloy systems are not compared with any experimental data in Figure 6.2c, d and e respectively. The trend in the E data for the Ti-Sn-Ta alloy system shows that the E decreases from $\text{Sn}_{0.5}\text{Ta}_{0.5}$ to Ti. The Ti-Sn-Zr alloy system data shows an increase in the E values from $\text{Sn}_{0.5}\text{Zr}_{0.5}$ to 60 at % Ti and then the E decreases to Ti. The E values, for the Ti-Ta-Zr alloy system, show the E decreases to 15 at % Ti where the E begins increasing to 30 at % Ti and then decreases to Ti.

The error between the experimentally determined E and the present first-principles calculated E results is expected to occur due to the fact that the CALPHAD fittings are done using elastic stiffness constants calculations done at 0 °K on single crystal structures while the experiments are done measuring polycrystalline samples at 300 °K. While there is some error, the experiments fit well within the bounds set by Reuss and Voigt and the Hill average generally reproduces the experimentally determined E data for the Ti-X-Y ternary alloys.

The elastic stiffness constants, \bar{C}_{11} , \bar{C}_{12} , and \bar{C}_{44} are plotted in Figure 6.3 to Figure 6.8. The \bar{C}_{11} data showed similar trends for most of the Ti-X-Y systems

where the \bar{C}_{11} values decrease from $X_{0.5}Y_{0.5}$ to Ti (seen in Figure 6.3 and Figure 6.4). The data trends vary for the Ti-Sn-Zr and Ti-Ta-Zr alloy systems in Figure 6.4d and e, respectively. The \bar{C}_{11} values, for Ti-Sn-Zr system, increases to 60 at % Ti and then decreases to Ti, while the \bar{C}_{11} values, in the Ti-Ta-Zr system, increase to 35 at % Ti and then decreases to Ti.

The \bar{C}_{12} values plotted in Figure 6.5 and 6.6, decrease from $X_{0.5}Y_{0.5}$ to Ti similarly for the Ti-Mo-Nb, Ti-Mo-Ta and Ti-Nb-Ta systems. The Ti-Mo-Sn and Ti-Nb-Sn systems saw a decrease in \bar{C}_{12} value from $X_{0.5}Y_{0.5}$ to 15 at % Ti then and increase to 85 % Ti and then a decrease to Ti. The Ti-Mo-Zr and Ti-Nb-Zr systems show a decrease in \bar{C}_{12} value from $X_{0.5}Y_{0.5}$ to 60 at % Ti and then an increase to Ti. The \bar{C}_{12} values increase from $X_{0.5}Y_{0.5}$ to 70 at % Ti and then decrease to Ti for the Ti-Sn-Ta system. For the Ti-Sn-Zr system, the \bar{C}_{12} values increase from $X_{0.5}Y_{0.5}$ to Ti and the \bar{C}_{12} values, for the Ti-Ta-Zr system, decrease to 70 at % Ti and then increase.

The \bar{C}_{44} data plotted in Figure 6.7 and Figure 6.8 shows that the values similarly decrease from $X_{0.5}Y_{0.5}$ to Ti for the Ti-Mo-Sn and Ti-Ta-Zr systems. The Ti-Mo-Zr and Ti-Mo-Ta systems show that the \bar{C}_{44} values decrease from $X_{0.5}Y_{0.5}$ to 80 at % Ti and then increase to Ti. The \bar{C}_{44} values, for the Ti-Mo-Nb and Ti-Nb-Ta systems, show a decrease from $X_{0.5}Y_{0.5}$ to 65 at % Ti and then increasing to Ti. The \bar{C}_{44} values show an increase from $X_{0.5}Y_{0.5}$ to 80 at % Ti and then a decrease to Ti for the Ti-Nb-Sn and Ti-Nb-Zr systems. The \bar{C}_{44} values, for the Ti-Sn-Ta system, decrease from $X_{0.5}Y_{0.5}$ until 20 at % Ti, then increase to 50 at % Ti and then decrease to Ti. Finally the Ti-Sn-Zr system shows an increase in \bar{C}_{44} value from $X_{0.5}Y_{0.5}$ to 60 at % Ti and then decrease to Ti.

The $\bar{C}_{11} - \bar{C}_{12}$ is plotted in Figure 6.9. The $\bar{C}_{11} - \bar{C}_{12}$ plot shows the limit of mechanical stability of the bcc phase for each ternary alloy. Based on Borná Á Žs criteria when the $\bar{C}_{11} - \bar{C}_{12}$ values are negative then the phase, bcc in this case, loses mechanical stability. Based on the present results in Figure 6.9, the bcc phase loses mechanical stability in Ti-Mo-Nb, Ti-Mo-Ta, Ti-Mo-Zr, Ti-Nb-Zr, Ti-Sn-Zr, and Ti-Ta-Zr systems when the Ti concentration is more than 90 at %, with the values being 91, 92, 95, 93, 91, and 94 at % Ti respectively. The bcc phase loses mechanical stability at Ti concentrations of 87, 77, 89, and 80 at % Ti for Ti-Mo-Sn, Ti-Nb-Sn, Ti-Nb-Ta and Ti-Sn-Ta systems. The B and G moduli data are plotted similarly to the Young's modulus in Figure 6.10 to Figure 6.13. The

present B and G calculations (circles) are plotted with at interpolation from the binary interaction parameters (red dashed line), the Voigt (purple dotted line) and Reuss (gold dash-dotted line) bounds and the Hill average (solid black line). The B data showed the same trend, decreasing in value from $X_{0.5}Y_{0.5}$ to Ti, for all the Ti-X-Y ternaries except Ti-Nb-Sn, Ti-Sn-Ta and Ti-Sn-Zr seen in Figure 6.10 and Figure 6.11. The B data for the Ti-Nb-Sn and Ti-Sn-Ta systems, decrease in value from $X_{0.5}Y_{0.5}$ to 10 at % Ti and then increase to 55 at % Ti and then decrease to Ti. The B values, in the Ti-Sn-Zr alloy system, showed an increase in value from $X_{0.5}Y_{0.5}$ to 85 at % Ti and then a decrease to Ti. The G decrease in value from $X_{0.5}Y_{0.5}$ to Ti for all the ternary systems except Ti-Nb-Sn, Ti-Nb-Zr, Ti-Sn-Zr and Ti-Ta-Zr (Figure 6.12 and Figure 6.13). The G values increase from $X_{0.5}Y_{0.5}$ to 60 at % Ti and then decrease to Ti for the Ti-Nb-Sn, Ti-Nb-Zr systems. The G data for the Ti-Sn-Zr system increases in value and the G decreases in value from $X_{0.5}Y_{0.5}$ to 5 at % Ti and then increases to 35 at % Ti before decreasing to Ti for the Ti-Ta-Zr system.

6.3.2 Extrapolation to higher ordered systems

Using the completed database and interaction parameters in Table 5.2 and Table 6.2, the elastic stiffness constants can be predicted and then the moduli values can be calculated and mapped. Figure 6.14 and Figure 6.15 uses the global minimization tools in pycalphad [37] to map the Young's modulus based on composition for Ti-X-Y ternaries. The mapping can thus allow for regions with specific moduli values to be targeted.

The Young's modulus is predicted and compared with experimental results for higher order Ti alloys and the results are shown in Table 6.3 and Figure 6.16. The same comparison was made in chapter 5 but using only the pure elements and binary interaction parameters. As in Chapter 5, Figure 6.16 plots the calculated E versus the experimentally determined E [32–34]. The black diagonal line would be a perfect correlation between the predictions and experiments. The grey region is the average variance in the first-principles calculations when calculating the average elastic stiffness constants using Eq. Y-Eq. Y. The same higher order alloys were picked to compare the effect that introducing the ternary interaction parameters had. As discussed previously, the error bars plotted for the experiments come from

the variance that was seen when comparing the experimentally determined E at the same composition from Niinomi et al. [35], Geetha et al. [33], Tane et al. [32], and Mohammad et al. [34]. The horizontal error bars are the Voigt and Reuss bounds. Previously, with no ternary interaction parameters the predictions and experimental results varied anywhere between 0.69 and 14 GPa and on average by 7 GPa. This was attributed to the fact that the single crystal elastic stiffness constants that are fit to obtain the moduli values were at 0 °K while the experiments on the polycrystalline samples are done at 300 °K. It was predicted that introducing non-Ti containing binary interaction parameters and ternary interaction parameters would improve the database. The introduction of the ternary interaction parameters improved the predictions to vary anywhere from 0.39 to 13 GPa from the experimental values with an average variance of only 5 GPa. Thus the introduction of Ti-containing ternary interaction parameters improved the predictions and the database can accurately predict the Young's modulus of higher order Ti alloys.

6.4 Conclusion

The present work systematically calculates the elastic properties of the bcc Ti ternary alloys, including the elastic stiffness constants, bulk modulus, shear modulus, and Young's modulus. Six alloying elements, Mo, Nb, Sn, Ta and Zr were studied. The CALPHAD method was used to fit ternary interaction parameters. The fittings were done by calculating the difference between the first-principles calculations and the binary interpolations from the pure elements and binary interaction parameters previously determined. The differences were then used to determine the ternary interaction parameters. The present calculations showed that the bcc phase was mechanically stabilized at compositions less than 91, 92, 95, 93, 91, 94, 87, 77, 89, and 80 at % Ti for the Ti-Mo-Nb, Ti-Mo-Ta, Ti-Mo-Zr, Ti-Nb-Zr, Ti-Sn-Zr, Ti-Ta-Zr, Ti-Mo-Sn, Ti-Nb-St, Ti-Nb-Ta and Ti-Sn-Ta alloys respectively.

The Ti-Mo-Nb, Ti-Mo-Ta, Ti-Mo-Zr, and Ti-Nb-Ta alloys saw similar fitting trends. The ternary interaction parameters were combined with the previously determined pure elements and binary interaction parameters into one complete tdb database. The fittings were used to map some of the possible alloy compositions to find potential materials with a Young's modulus in the target range for biomedical load bearing implants. Overall, the introduction of the ternary interaction

parameters improved the database's ability to predict the Young's modulus of higher ordered alloys and the database is able to accurately predict the Young's modulus of Ti-alloys. It is hypothesized that the introduction of non-Ti containing interaction parameters would improve the database even further. The tdb file is attached in appendix d.

Table 6.1: First-principles calculations of the elastic stiffness constants, bulk modulus B , shear modulus G , and Young's modulus E in GPa for different atomic percent compositions of the bcc Ti-X-Y ternary systems at 0 °K. As well as experimental data obtained for the Young's modulus at 300 °K by the reference stated.

Reference	$Ti_{1-2b}X_bY_b$	\overline{C}_{11}	\overline{C}_{11}	\overline{C}_{11}	B	G	E
This work	Ti	93	115	41	108	-12.91	-40.34
This work	TiMo _{12.5} Nb _{12.5}	155	121 ±4	34 ±4	132 ±4	26 ±4	73 ±4
This work	TiMo _{25.0} Nb _{25.0}	222 ±3	129 ±3	33 ±3	160 ±3	38 ±3	105 ±3
This work	TiMo _{33.3} Nb _{33.3}	269 ±5	134 ±3	42 ±4	179 ±5	51 ±5	139 ±5
This work	Mo ₅₀ Nb ₅₀	414 ±6	165 ±3	68	248 ±6	87 ±6	233 ±6
Expt 300 K [35]	TiMo ₆ Nb ₂						110
This work	TiMo _{12.5} Sn _{12.5}	137 ±15	121 ±2	56 ±13	126 ±15	27 ±15	75 ±15
This work	TiMo _{25.0} Sn _{25.0}	160 ±3	130 ±8	71 ±2	140 ±8	39 ±8	106 ±8
This work	TiMo _{33.3} Sn _{33.3}	167 ±8	133 ±6	75 ±2	144 ±8	42 ±8	114 ±8
This work	Mo ₅₀ Sn ₅₀	192 ±28	130 ±36	40 ±31	151 ±36	36 ±36	100 ±36
This work	TiMo _{12.5} Ta _{12.5}	153 ±1	125 ±4	38 ±3	134 ±4	25 ±4	72 ±4
This work	TiMo _{25.0} Ta _{25.0}	222 ±2	136 ±1	45 ±3	165 ±2	44 ±3	122 ±3
This work	TiMo _{33.3} Ta _{33.3}	263 ±4	145 ±6	49 ±4	184 ±6	53 ±6	145 ±
This work	Mo ₅₀ Ta ₅₀	370 ±13	163 ±4	63 ±4	232 ±13	77 ±13	208 ±13
Expt 300 K [34]	TiMo ₇ Ta ₁						74
Expt 300 K [35]	TiMo ₇ Ta ₁						74
This work	TiMo _{12.5} Zr _{12.5}	125 ±1	109 ±8	35 ±1	114 ±8	20 ±8	55 ±8
This work	TiMo _{25.0} Zr _{25.0}	160 ±1	116 ±5	34 ±2	131 ±5	29 ±5	80 ±5
This work	TiMo _{33.3} Zr _{33.3}	182 ±1	116 ±2	31 ±8	138 ±2	32 ±8	89 ±8
This work	Mo ₅₀ Zr ₅₀	231 ±7	118 ±5	33 ±8	156 ±7	41 ±8	113 ±8
Expt 300 K [34]	TiMo ₇ Zr ₃						64
This work	TiNb _{12.5} Sn _{12.5}	115 ±4	118 ±3	55	117 ±4	14 ±4	41 ±4
This work	TiNb _{25.0} Sn _{25.0}	131 ±9	121 ±6	64 ±3	124 ±9	26 ±9	72 ±9
This work	TiNb _{33.3} Sn _{33.3}	134 ±2	122 ±3	67 ±6	126 ±6	28 ±6	78 ±6
This work	Nb ₅₀ Sn ₅₀	132 ±4	118 ±8	56 ±4	123 ±8	26 ±8	72 ±8
Expt 300 K [34]	TiNb ₂₂ Sn ₂						44

Table 6.1: First-principles calculations of the elastic stiffness constants, bulk modulus B , shear modulus G , and Young's modulus E in GPa for different atomic percent compositions of the bcc Ti-X-Y ternary systems at 0 °K. As well as experimental data obtained for the Young's modulus at 300 °K by the reference stated.

Reference	$Ti_{1-2b}X_bY_b$	\overline{C}_{11}	\overline{C}_{11}	\overline{C}_{11}	B	G	E
Expt 300 K [35]	$TiNb_{22}Sn_2$						50
Expt 300 K [36]	$TiNb_9Sn_3$						58
This work	$TiNb_{12.5}Ta_{12.5}$	130 ± 3	124 ± 4	37 ± 3	126 ± 4	15 ± 4	43 ± 4
This work	$TiNb_{25.0}Ta_{25.0}$	182 ± 1	129 ± 4	43 ± 6	147 ± 6	35 ± 6	98 ± 6
This work	$_{33.3}Ta_{33.3}$	208	135 ± 1	44 ± 1	159 ± 1	41 ± 1	113 ± 1
This work	$Nb_{50}Ta_{50}$	260 ± 2	148 ± 3	47 ± 3	185 ± 3	50 ± 3	140 ± 3
Expt 300 K [34]	$TiNb_{10}Ta_{19}$						55
This work	$TiNb_{12.5}Zr_{12.5}$	101 ± 2	113 ± 4	32 ± 3	109 ± 4	-2 ± 4	-6 ± 4
This work	$TiNb_{25.0}Zr_{25.0}$	122 ± 1	113 ± 3	28 ± 3	116 ± 3	14 ± 3	40 ± 3
This work	$TiNb_{33.3}Zr_{33.3}$	143 ± 2	107 ± 5	28 ± 3	119 ± 5	23 ± 5	66 ± 5
This work	$Nb_{50}Zr_{50}$	154 ± 5	110 ± 3	15 ± 2	125 ± 5	17 ± 5	50 ± 5
Expt 300 K [34]	$TiNb_8Zr_8$						77
Expt 300 K [34]	$TiNb_{12}Zr_9$						14
Expt 300 K [34]	$TiNb_{11}Zr_3$						50
Expt 300 K [35]	$TiNb_{17}Zr_5$						78
Expt 300 K [33]	$TiNb_8Zr_8$						81
This work	$TiSn_{12.5}Ta_{12.5}$	115 ± 6	121 ± 4	60 ± 2	119 ± 6	13 ± 6	39 ± 6
This work	$TiSn_{25.0}Ta_{25.0}$	138 ± 13	125 ± 4	75 ± 4	129 ± 13	31 ± 13	86 ± 13
This work	$TiSn_{33.3}Ta_{33.3}$	138 ± 6	131 ± 8	78 ± 1	133 ± 8	28 ± 8	79 ± 8
This work	$Sn_{50}Ta_{50}$	133 ± 8	130 ± 4	60 ± 4	131 ± 8	20 ± 8	57 ± 8
This work	$TiSn_{12.5}Zr_{12.5}$	97 ± 5	111 ± 4	55 ± 2	106 ± 5	4 ± 5	13 ± 5
This work	$TiSn_{25.0}Zr_{25.0}$	99 ± 12	103 ± 4	59 ± 7	102 ± 12	15 ± 12	42 ± 12
This work	$TiSn_{33.3}Zr_{33.3}$	96 ± 7	98 ± 3	55 ± 3	97 ± 7	15 ± 7	43 ± 7
This work	$Sn_{50}Zr_{50}$	85 ± 7	87 ± 9	42 ± 3	86 ± 9	11 ± 9	32 ± 9
This work	$TiTa_{12.5}Zr_{12.5}$	136 ± 36	103 ± 21	44 ± 5	114 ± 21	30 ± 21	82 ± 21
This work	$TiTa_{25.0}Zr_{25.0}$	130 ± 3	117 ± 4	42 ± 7	121 ± 4	20 ± 7	58 ± 7

Table 6.1: First-principles calculations of the elastic stiffness constants, bulk modulus B , shear modulus G , and Young's modulus E in GPa for different atomic percent compositions of the bcc Ti-X-Y ternary systems at 0 °K. As well as experimental data obtained for the Young's modulus at 300 °K by the reference stated.

Reference	$\text{Ti}_{1-2b}\text{X}_b\text{Y}_b$	\overline{C}_{11}	\overline{C}_{11}	\overline{C}_{11}	B	G	E
This work	$\text{TiTa}_{33.3}\text{Zr}_{33.3}$	148 ± 1	115 ± 2	44 ± 2	126 ± 2	30 ± 2	83 ± 2
This work	$\text{Ta}_{50}\text{Zr}_{50}$	157 ± 2	123 ± 3	35 ± 3	134 ± 3	26 ± 3	74 ± 3

Table 6.2. Evaluated interactions parameters (L_2 , Eq. Y) for the elastic stiffness constants of the Ti-containing ternary alloys.

Alloy	Interaction Parameter	\bar{C}_{11}	\bar{C}_{12}	\bar{C}_{44}
Ti-Mo-Nb	L_2	-29.97	13.97	9.72
Ti-Mo-Sn	L_2	-83.85	31.80	74.73
Ti-Mo-Ta	L_2	-106.53	-12.35	5.27
Ti-Mo-Zr	L_2	-245.27	50.43	-44.96
Ti-Nb-Sn	L_2	-41.52	25.52	67.85
Ti-Nb-Ta	L_2	-93.77	-15.80	4.25
Ti-Nb-Zr	L_2	-220.35	72.10	-55.29
Ti-Sn-Ta	L_2	-95.39	-10.94	67.85
Ti-Sn-Zr	L_2	-155.34	68.86	3.85
Ti-Ta-Zr	L_2	-149.67	-8.91	-23.70

Table 6.3. Predicted Young's modulus (in GPa) of higher order alloys in the bcc phase compared to experimental values found with both the weight percent and atomic percent listed. The predicted Young's modulus was found using the completed database with the pure elements, binary and ternary interaction parameters.

Alloy Name (%wt)	at %	Calc E	Expt E
Ti-35Nb-7Zr-5Ta [33]	Ti-24Nb-5Zr-2Ta	78	80
Ti-29Nb-13Ta-4.6Zr [33]	Ti-20Nb-5Ta-3Zr	73	75
Ti-29Nb-13Ta-6Sn [33]	Ti-21Nb-5Ta-3Sn	68	74
Ti-29Nb-13Ta-4.6Sn [33]	Ti-20Nb-5Ta-3Sn	66	66
Ti-29Nb-13Ta-4.5Zr [33]	Ti-20Nb-5Ta-3Zr	73	65
Ti-29Nb-13Ta-4.6Zr [32]	Ti-21Nb-5Ta-3Zr	75	64
Ti-30Nb-10Ta-5Zr [32]	Ti-23Nb-4Ta-3Zr	74	64
Ti-35Nb-10Ta-5Zr [32]	Ti-25Nb-4Ta-4Zr	78	65
Ti-24Nb-4Zr-7.9Sn [34]	Ti-15Nb-3Zr-4Sn	62	54
Ti-35Nb-2Ta-3Zr [34]	Ti-23Nb-1Ta-2Zr	68	61
Ti-29Nb-11Ta-5Zr [34]	Ti-20Nb-6Ta-2Zr	72	60
Ti-10Zr-5Ta-5Nb [34]	Ti-6Zr-1Ta-3Nb	62	52
Ti-29Nb-13Ta-2Sn [34]	Ti-20Nb-5Ta-1Sn	65	62

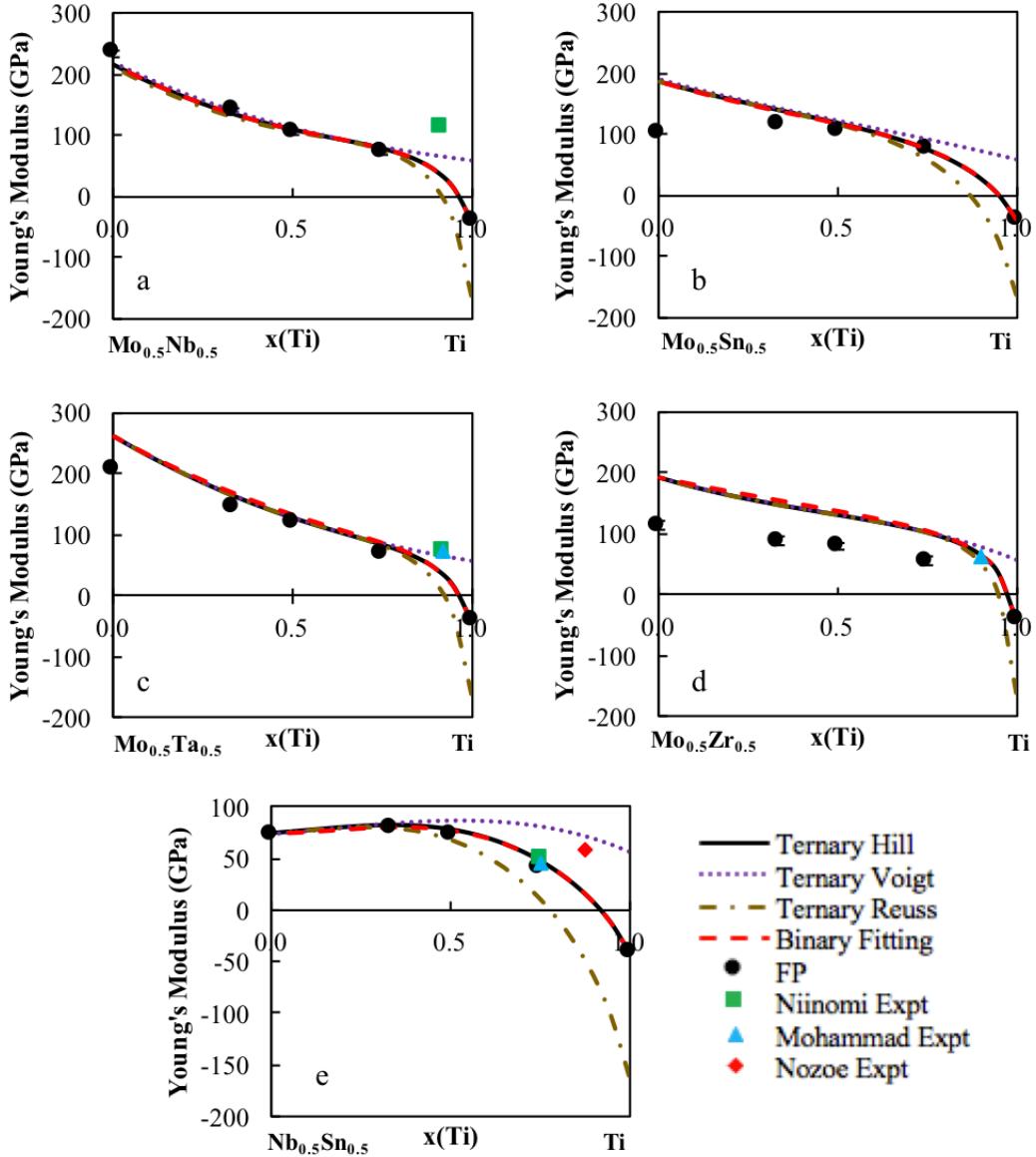


Figure 6.1. Young's modulus E of five of the Ti-X-Y ternary systems are plotted from a 50-50 mixture of the alloying elements to Ti in the bcc phase. The present calculations are plotted as filled circles with the error bars. The red dotted line is the extrapolation for the pure elements and binary interaction parameters only. The dotted purple line is the Voigt upper YoungâŽs modulus bound, the gold dot dashed line is the lower Reuss YoungâŽs modulus bound and the black line is the Hill YoungâŽs modulus average. Experimental values are included for comparison [33–36].

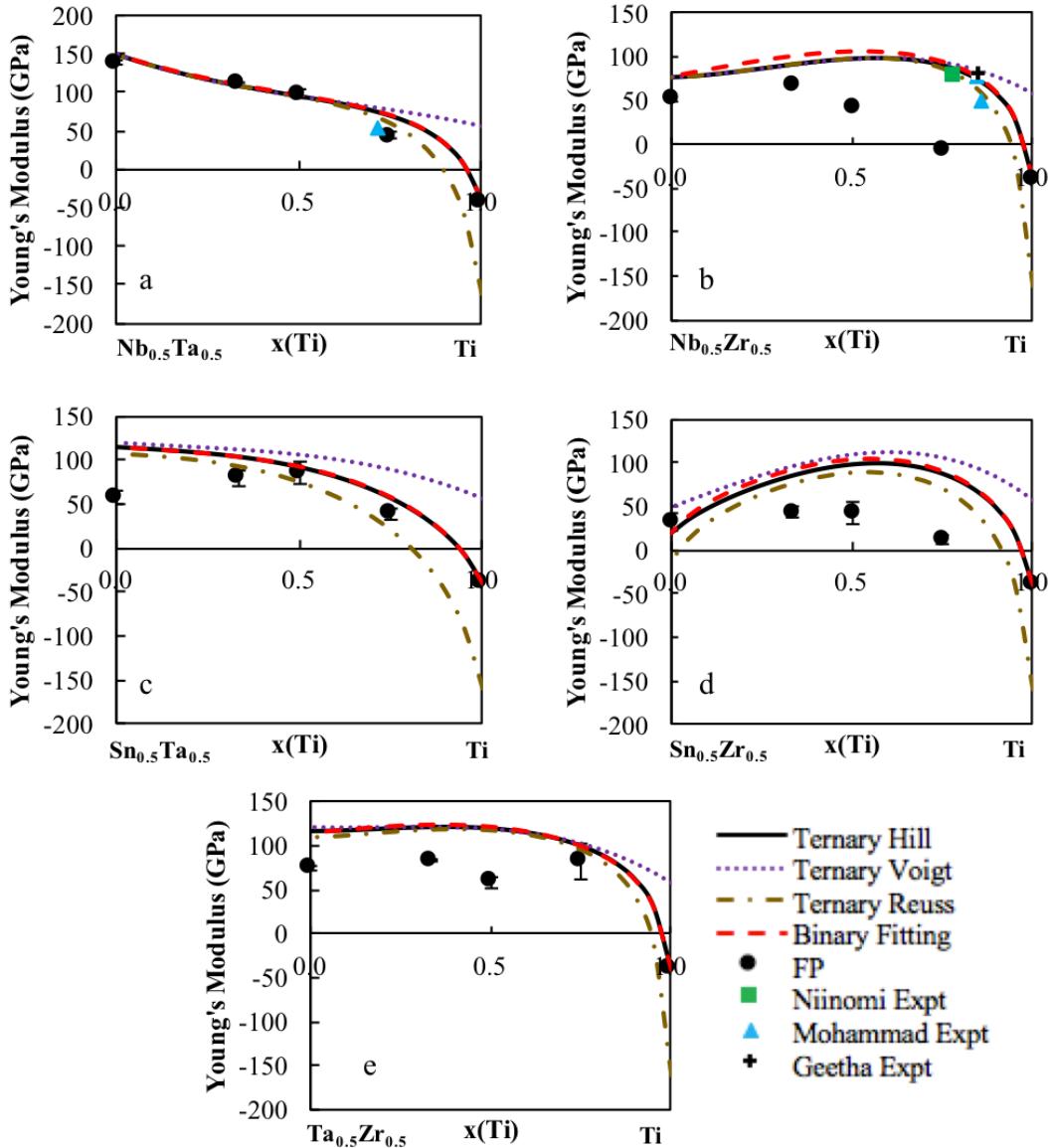


Figure 6.2. Young's modulus E of five of the Ti-X-Y ternary systems are plotted from a 50-50 mixture of the alloying elements to Ti in the bcc phase. The present calculations are plotted as filled circles with the error bars. The red dotted line is the extrapolation for the pure elements and binary interaction parameters only. The dotted purple line is the Voigt upper YoungâŽ's modulus bound, the gold dot dashed line is the lower Reuss YoungâŽ's modulus bound and the black line is the Hill YoungâŽ's modulus average. Experimental values are include for comparison [33-36].

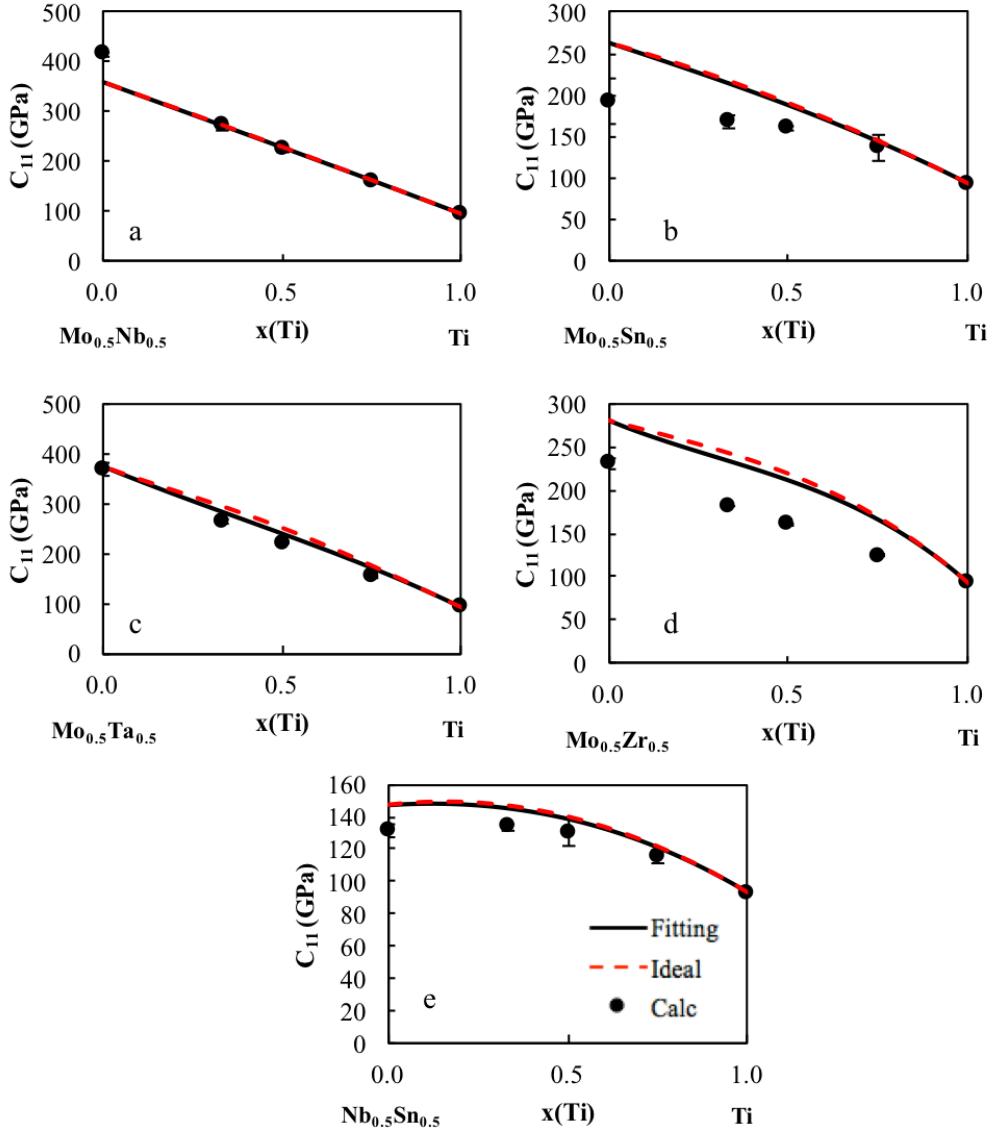


Figure 6.3. Calculated \bar{C}_{11} values (circles) plotted with their errors as well as the interpolation from the binary interaction parameters (red dashed line) and the ternary fitting (black dashed line) for five of the Ti-X-Y binary systems from a 50-50 mixture of the alloying elements X and Y to Ti ($X \neq Y = \text{Mo, Nb, Ta, Sn, Zr}$).

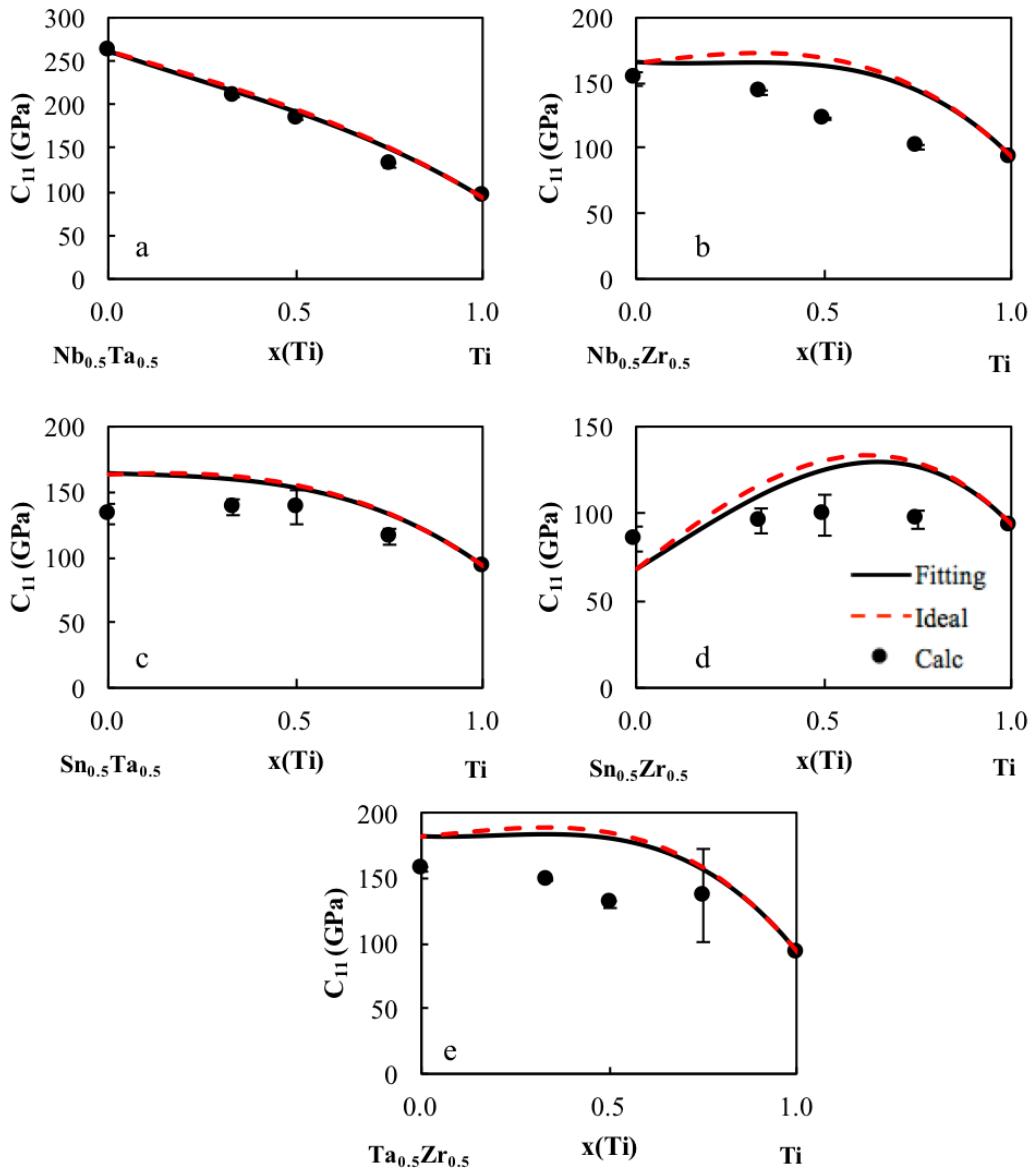


Figure 6.4. Calculated \bar{C}_{11} values (circles) plotted with their errors as well as the interpolation from the binary interaction parameters (red dashed line) and the ternary fitting (black dashed line) for five of the Ti-X-Y binary systems from a 50-50 mixture of the alloying elements X and Y to Ti ($X \neq Y = \text{Mo, Nb, Ta, Sn, Zr}$).

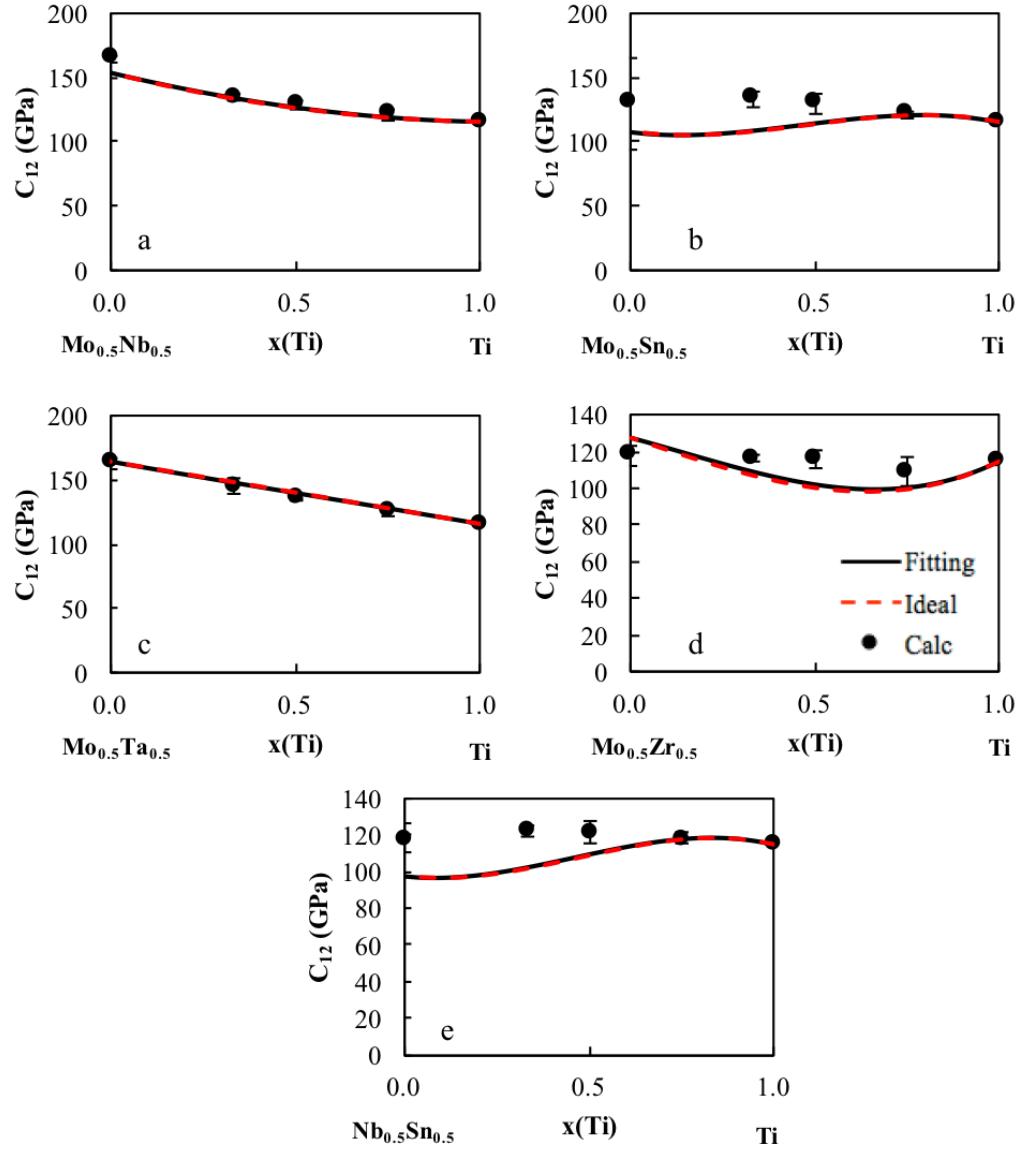


Figure 6.5. Calculated \bar{C}_{12} values (circles) plotted with their errors as well as the interpolation from the binary interaction parameters (red dashed line) and the ternary fitting (black dashed line) for five of the Ti-X-Y binary systems from a 50-50 mixture of the alloying elements X and Y to Ti ($X \neq Y = \text{Mo, Nb, Ta, Sn, Zr}$).

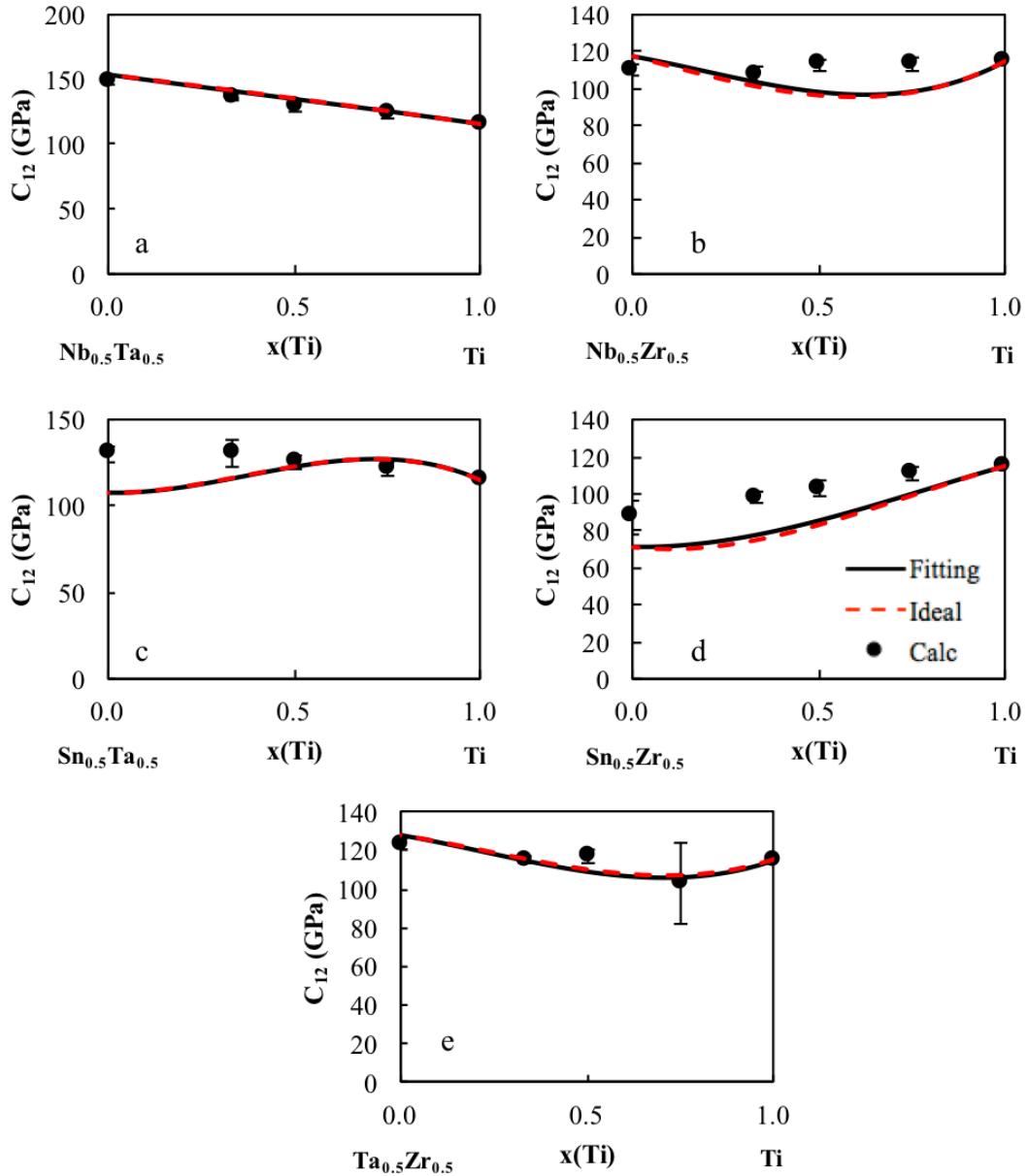


Figure 6.6. Calculated \bar{C}_{12} values (circles) plotted with their errors as well as the interpolation from the binary interaction parameters (red dashed line) and the ternary fitting (black dashed line) for five of the Ti-X-Y binary systems from a 50-50 mixture of the alloying elements X and Y to Ti ($X \neq Y = Mo, Nb, Ta, Sn, Zr$).

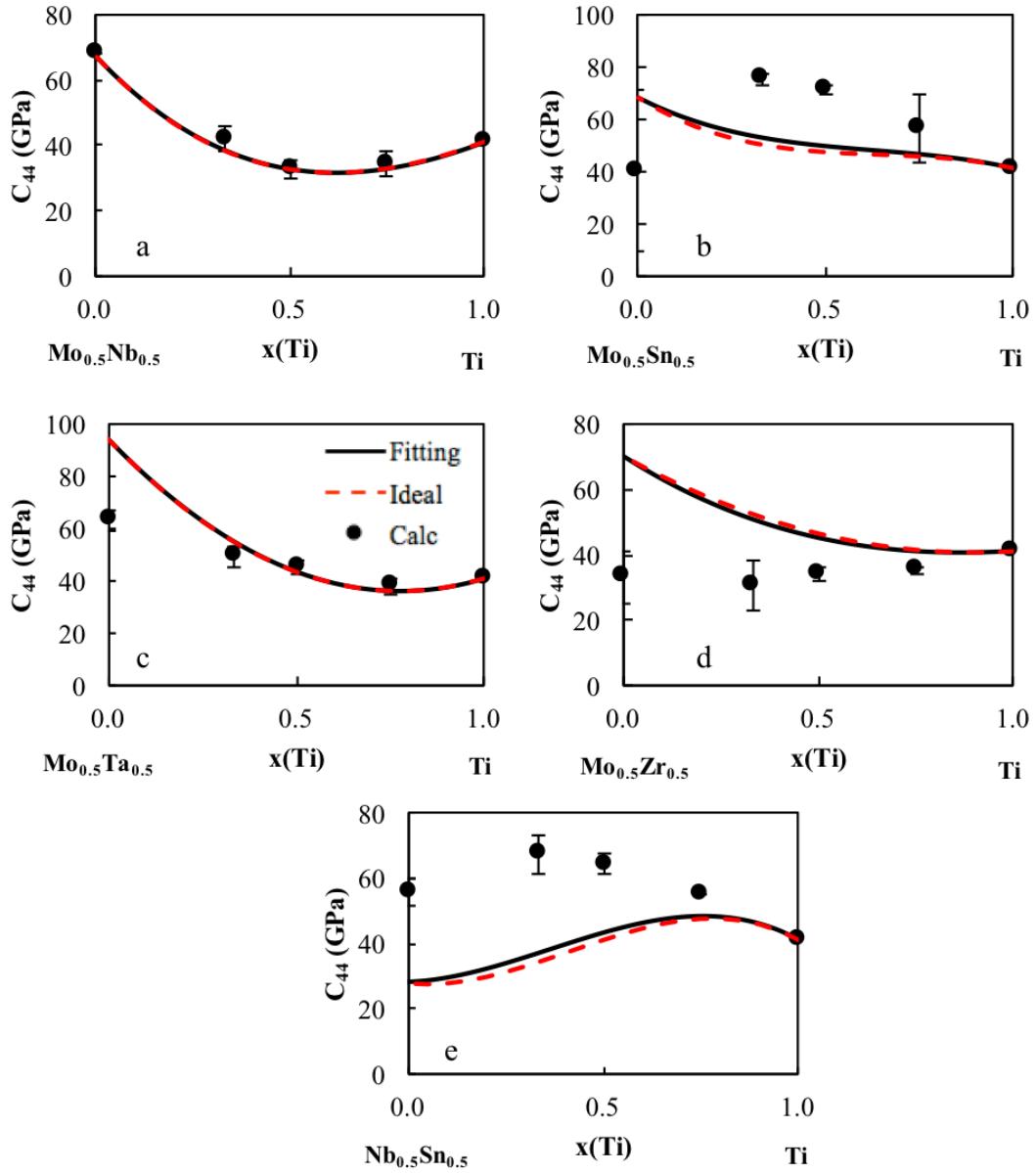


Figure 6.7. Calculated \bar{C}_{44} values (circles) plotted with their errors as well as the interpolation from the binary interaction parameters (red dashed line) and the ternary fitting (black dashed line) for five of the Ti-X-Y binary systems from a 50-50 mixture of the alloying elements X and Y to Ti ($X \neq Y = \text{Mo, Nb, Ta, Sn, Zr}$).

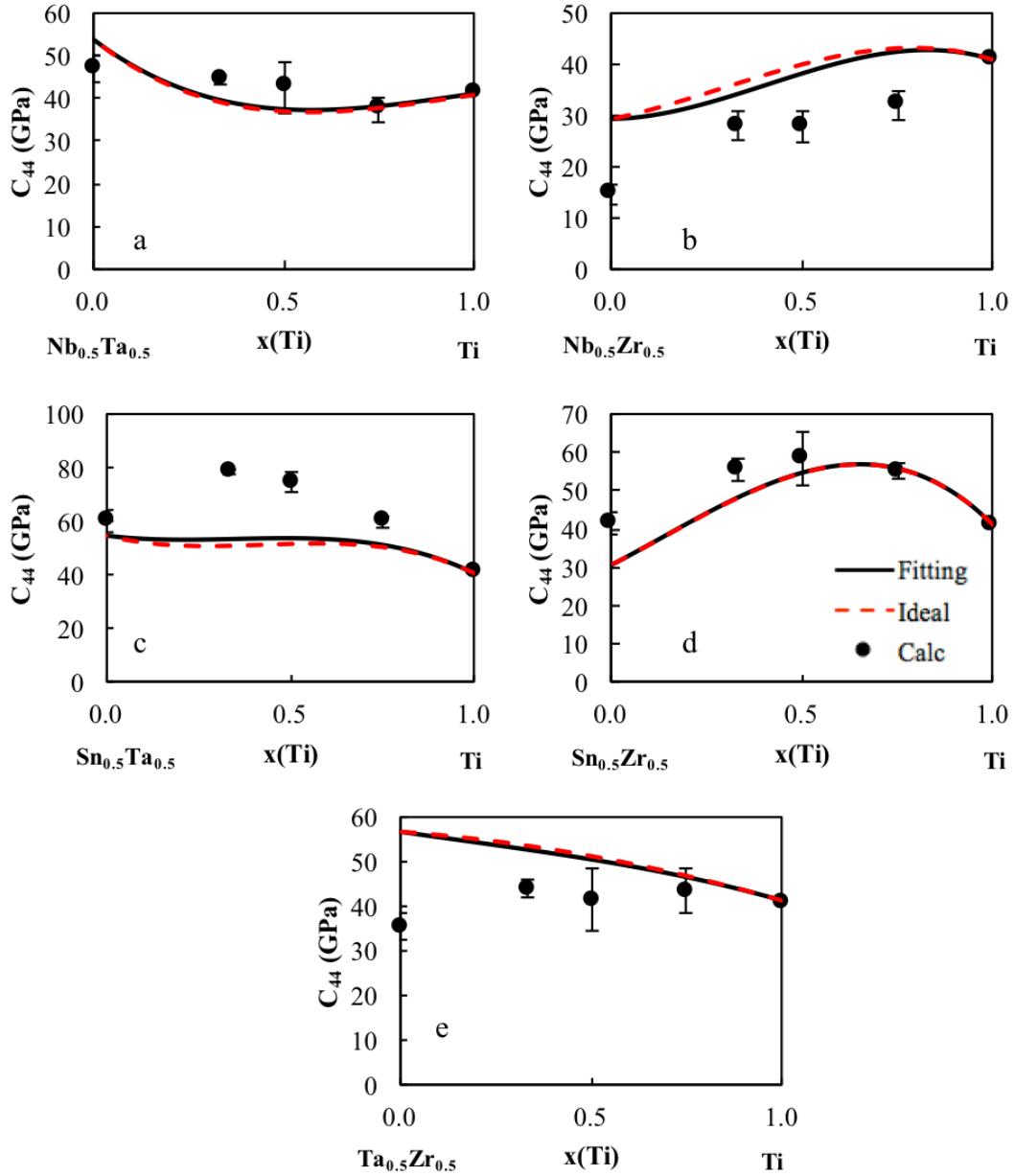


Figure 6.8. Calculated \bar{C}_{44} values (circles) plotted with their errors as well as the interpolation from the binary interaction parameters (red dashed line) and the ternary fitting (black dashed line) for five of the Ti-X-Y binary systems from a 50-50 mixture of the alloying elements X and Y to Ti ($X \neq Y = \text{Mo, Nb, Ta, Sn, Zr}$).

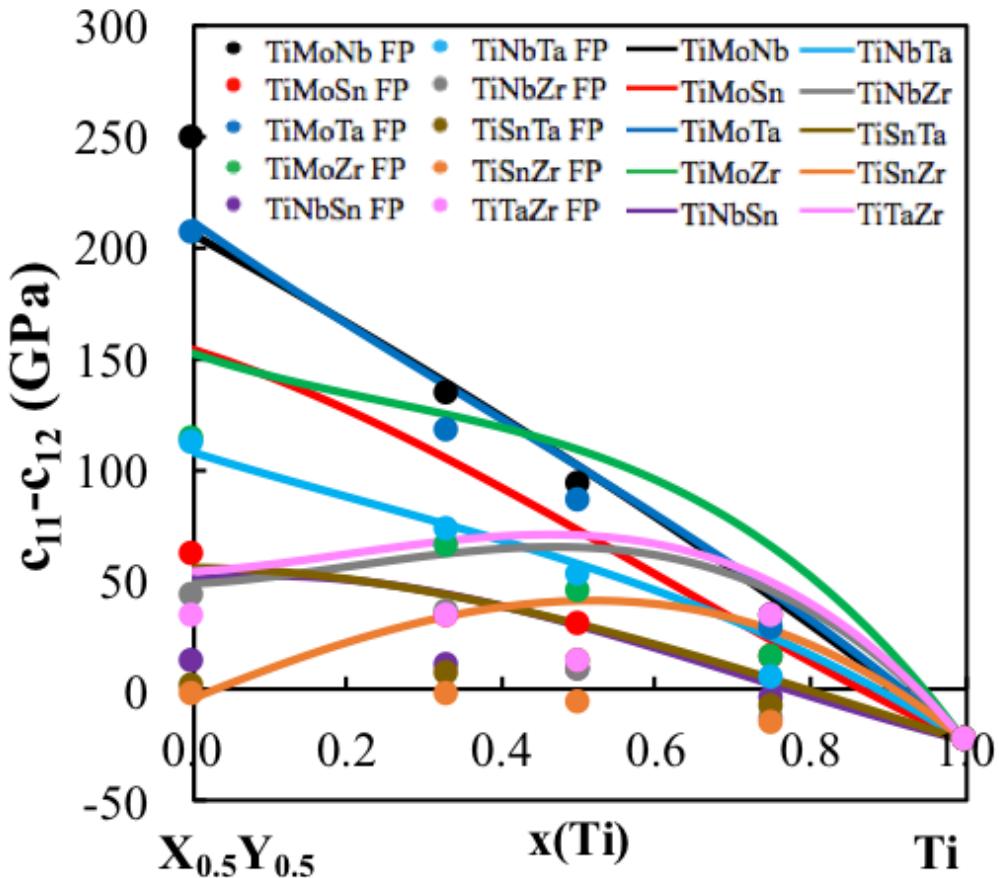


Figure 6.9. Calculated $\bar{C}_{11} - \bar{C}_{12}$ values (circles) plotted with the present modeling (solid lines) for the Ti-X-Y ternary systems ($X \neq Y = \text{Mo, Nb, Ta, Sn, Zr}$). The $\bar{C}_{11} - \bar{C}_{12}$ shows the stability of the bcc phase, when the value is negative the bcc phase is not stable in the corresponding composition ranges.

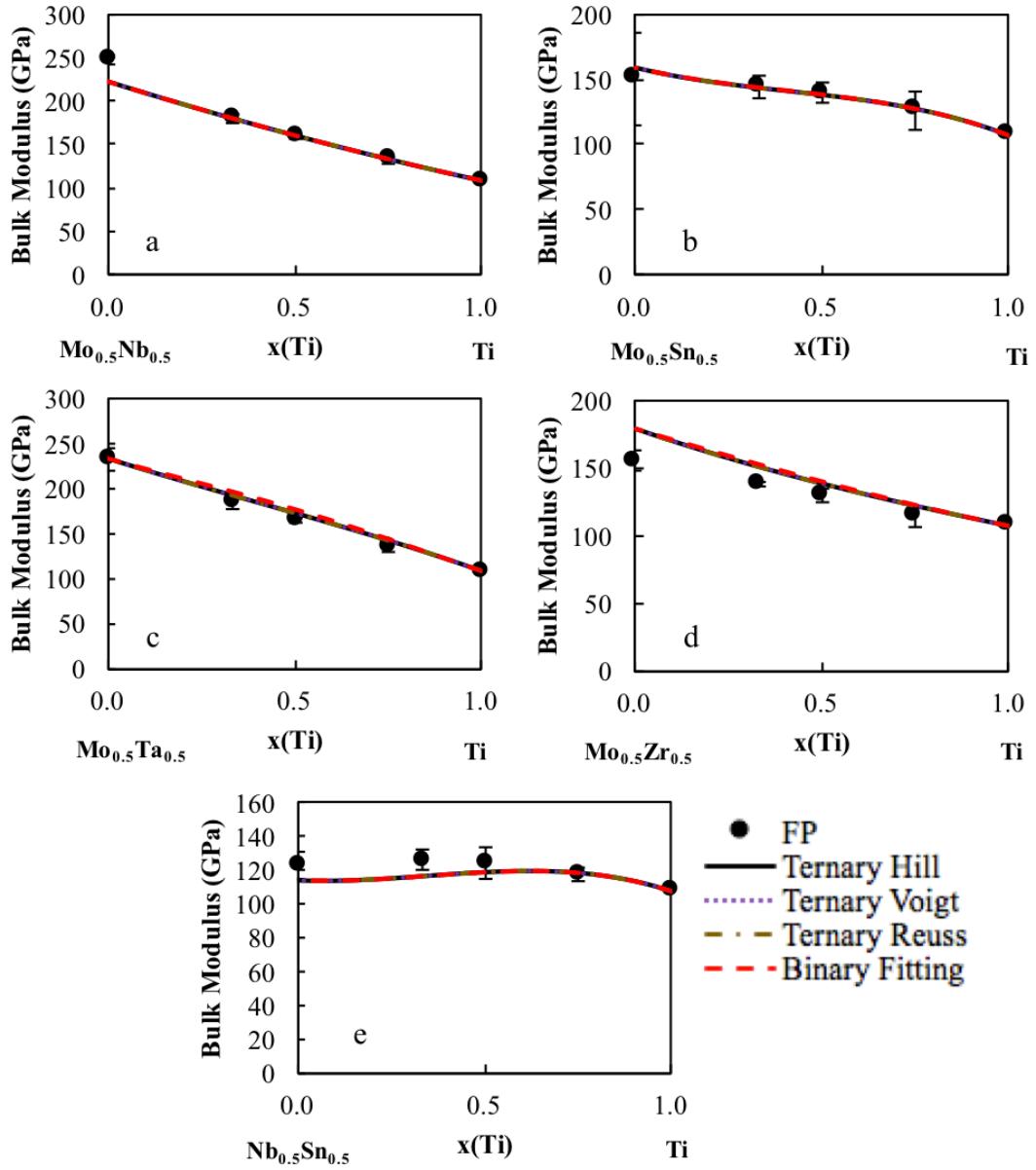


Figure 6.10. Bulk modulus B calculations of five of the Ti-X-Y ternary systems ($X \neq Y = \text{Mo, Nb, Ta, Sn, Zr}$). The present calculations are plotted as the filled circles with error bars as well as the interpolation from the binary interaction parameters (red dashed line). The dotted purple line is the Voigt upper bulk modulus bound, the gold dashed line is the lower Reuss bulk modulus bound and the black line is the Hill bulk modulus average plotted from a 50-50 mixture of the alloying elements X and Y to Ti.

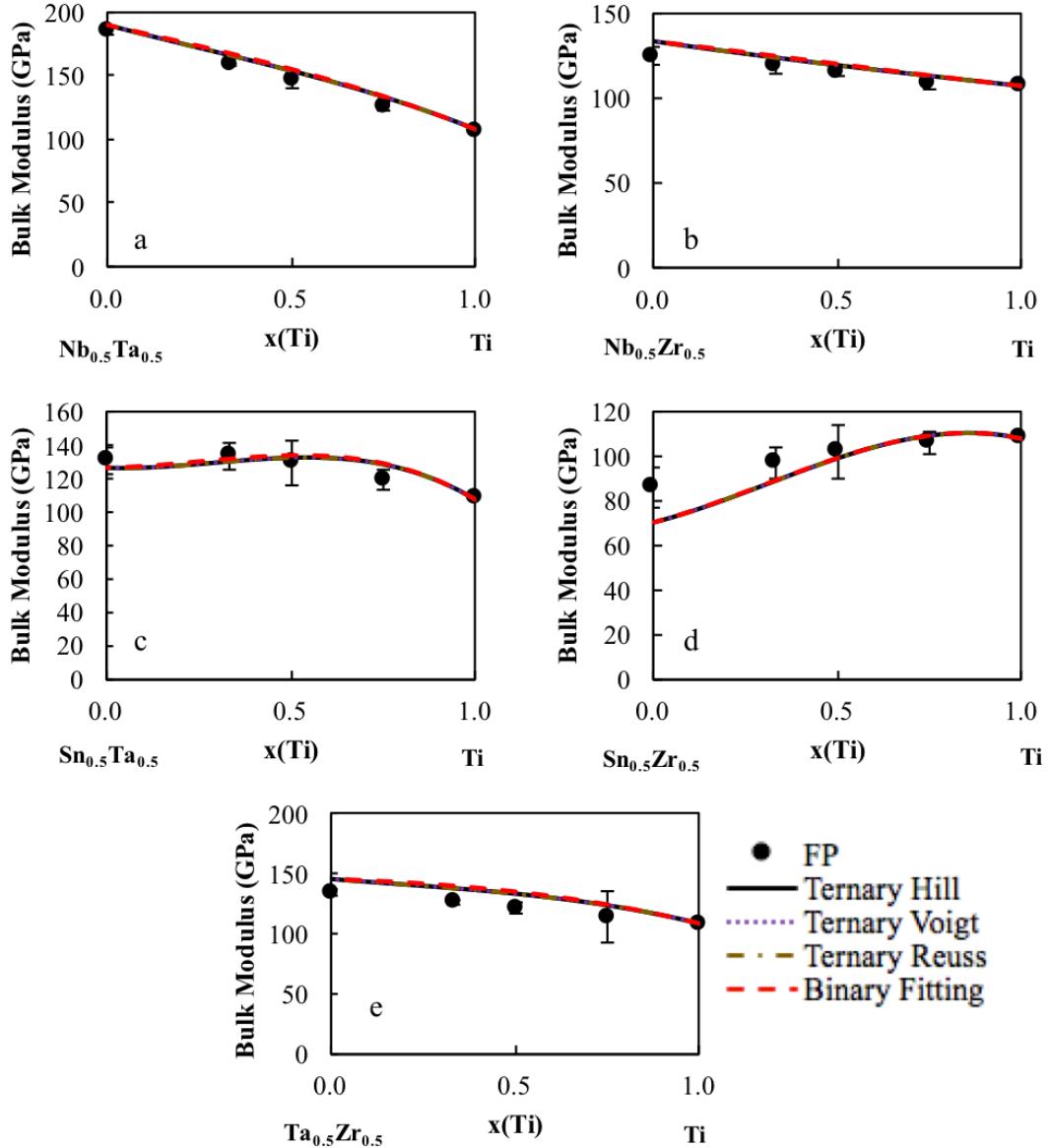


Figure 6.11. Bulk modulus B calculations of five of the Ti-X-Y ternary systems ($X \neq Y = \text{Mo, Nb, Ta, Sn, Zr}$). The present calculations are plotted as the filled circles with error bars as well as the interpolation from the binary interaction parameters (red dashed line). The dotted purple line is the Voigt upper bulk modulus bound, the gold dashed line is the lower Reuss bulk modulus bound and the black line is the Hill bulk modulus average plotted from a 50-50 mixture of the alloying elements X and Y to Ti.

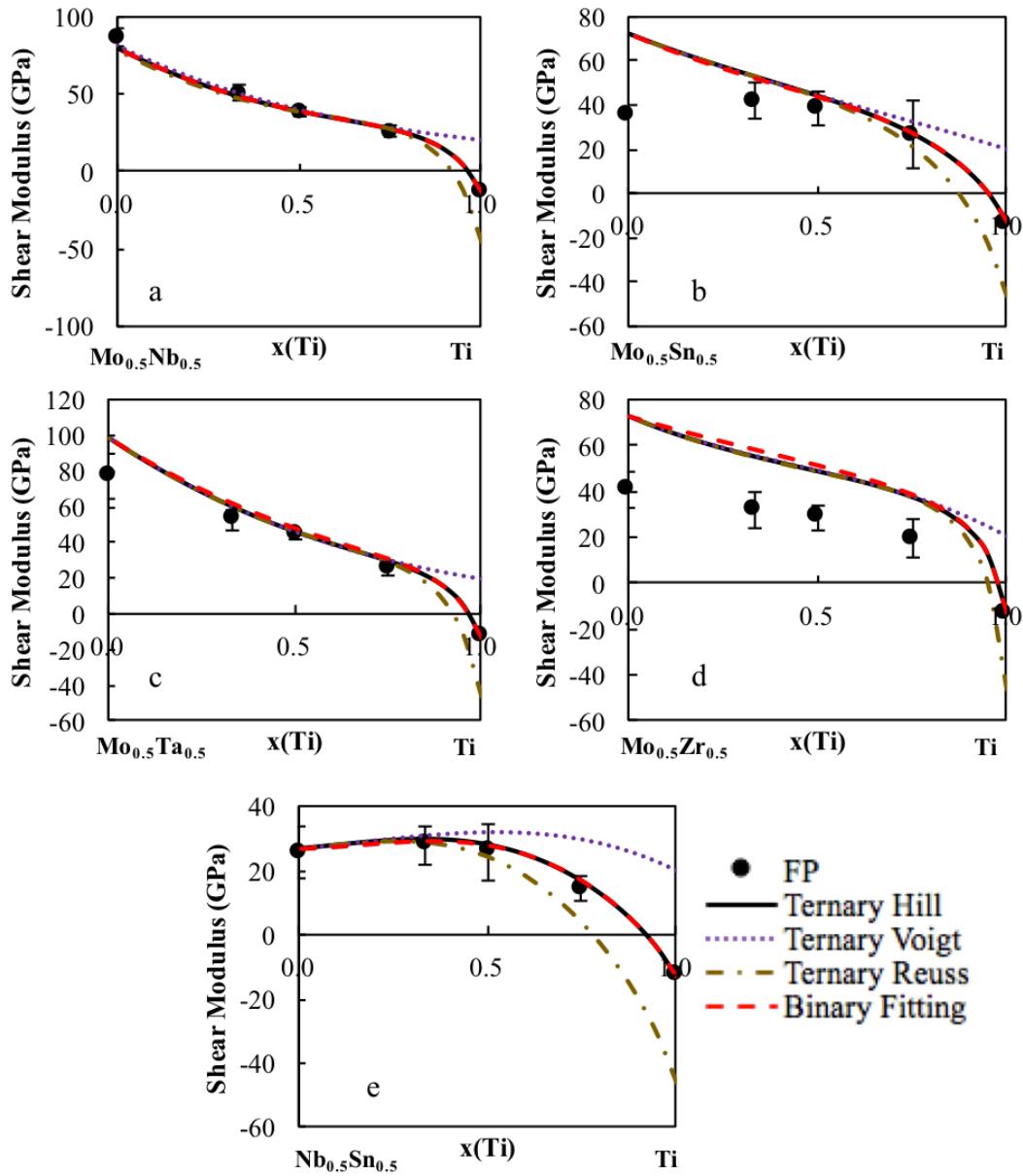


Figure 6.12. Shear modulus G calculations of five of the Ti-X-Y ternary systems ($X \neq Y = \text{Mo, Nb, Ta, Sn, Zr}$). The present calculations are plotted as the filled circles with error bars as well as the interpolation from the binary interaction parameters (red dashed line). The dotted purple line is the Voigt upper shear modulus bound, the gold dashed line is the lower Reuss shear modulus bound and the black line is the Hill shear modulus average plotted from a 50-50 mixture of the alloying elements X and Y to Ti.

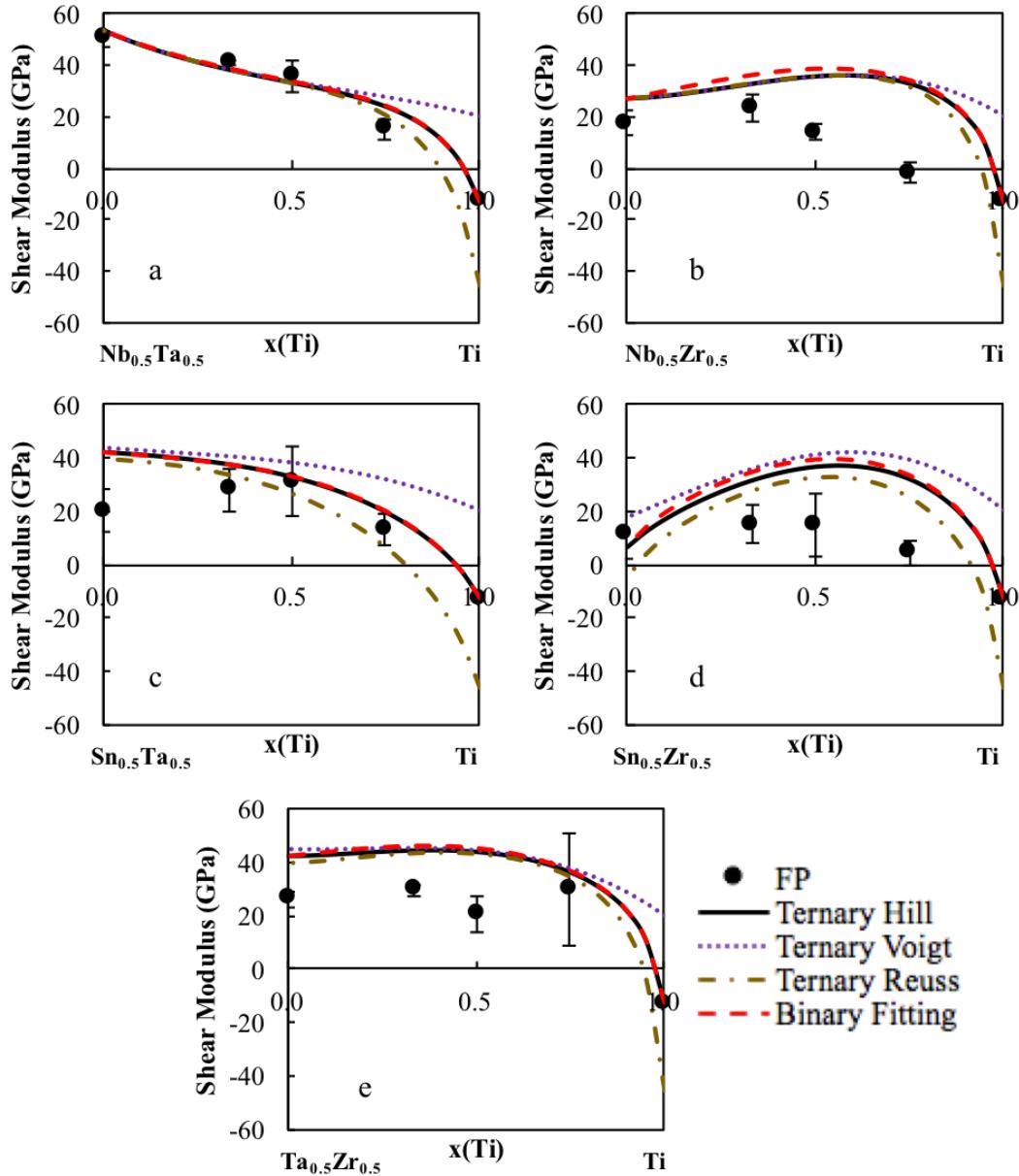


Figure 6.13. Shear modulus G calculations of five of the Ti-X-Y ternary systems ($X \neq Y = \text{Mo, Nb, Ta, Sn, Zr}$). The present calculations are plotted as the filled circles with error bars as well as the interpolation from the binary interaction parameters (red dashed line). The dotted purple line is the Voigt upper shear modulus bound, the gold dashed line is the lower Reuss shear modulus bound and the black line is the Hill shear modulus average plotted from a 50-50 mixture of the alloying elements X and Y to Ti.

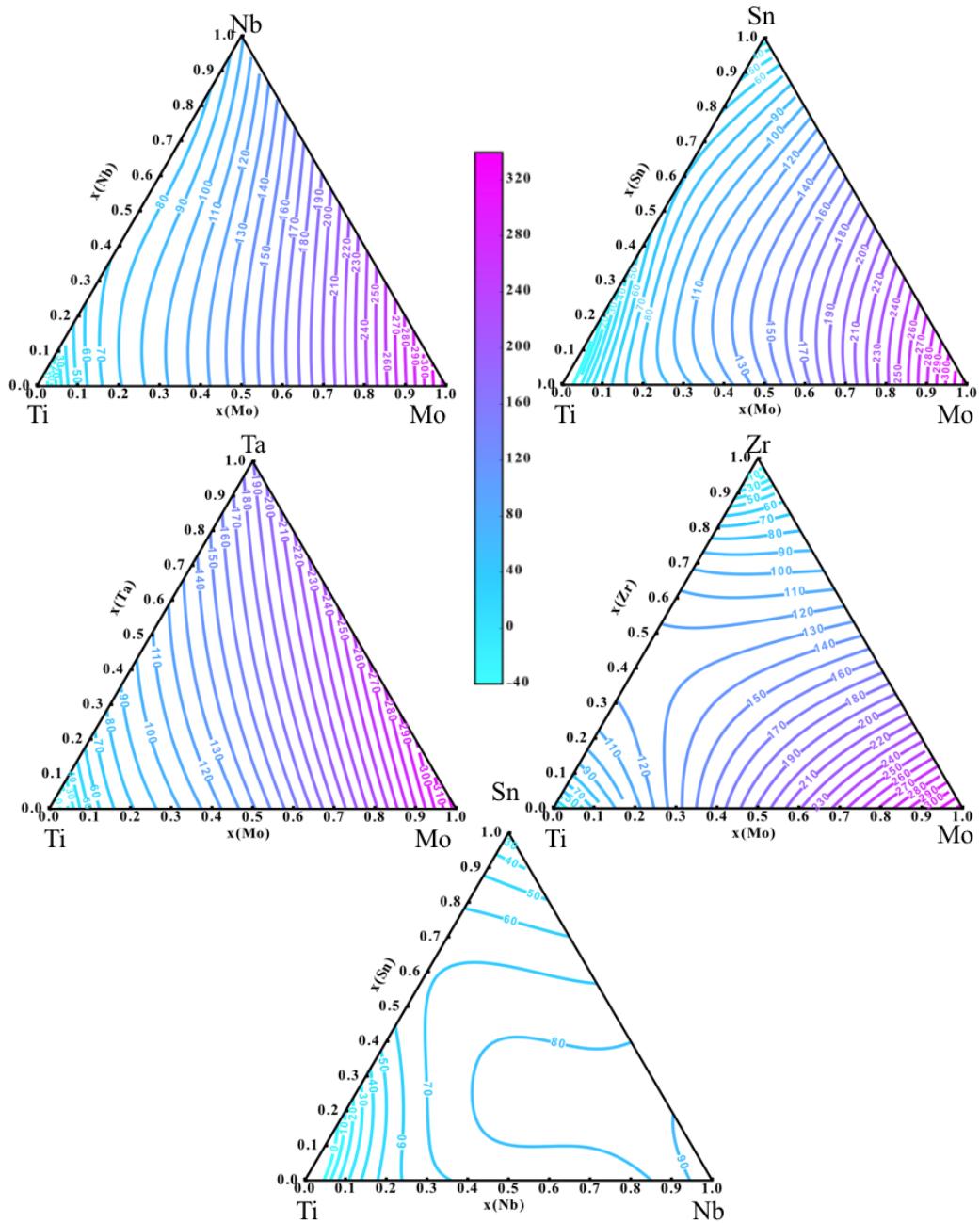


Figure 6.14. The Young's modulus is mapped as a function of composition in GPa for the Ti-Mo-Nb, Ti-Mo-Sn, Ti-Mo-Ta, Ti-Mo-Zr and Ti-Nb-Sn alloy systems using pycalphad [37].

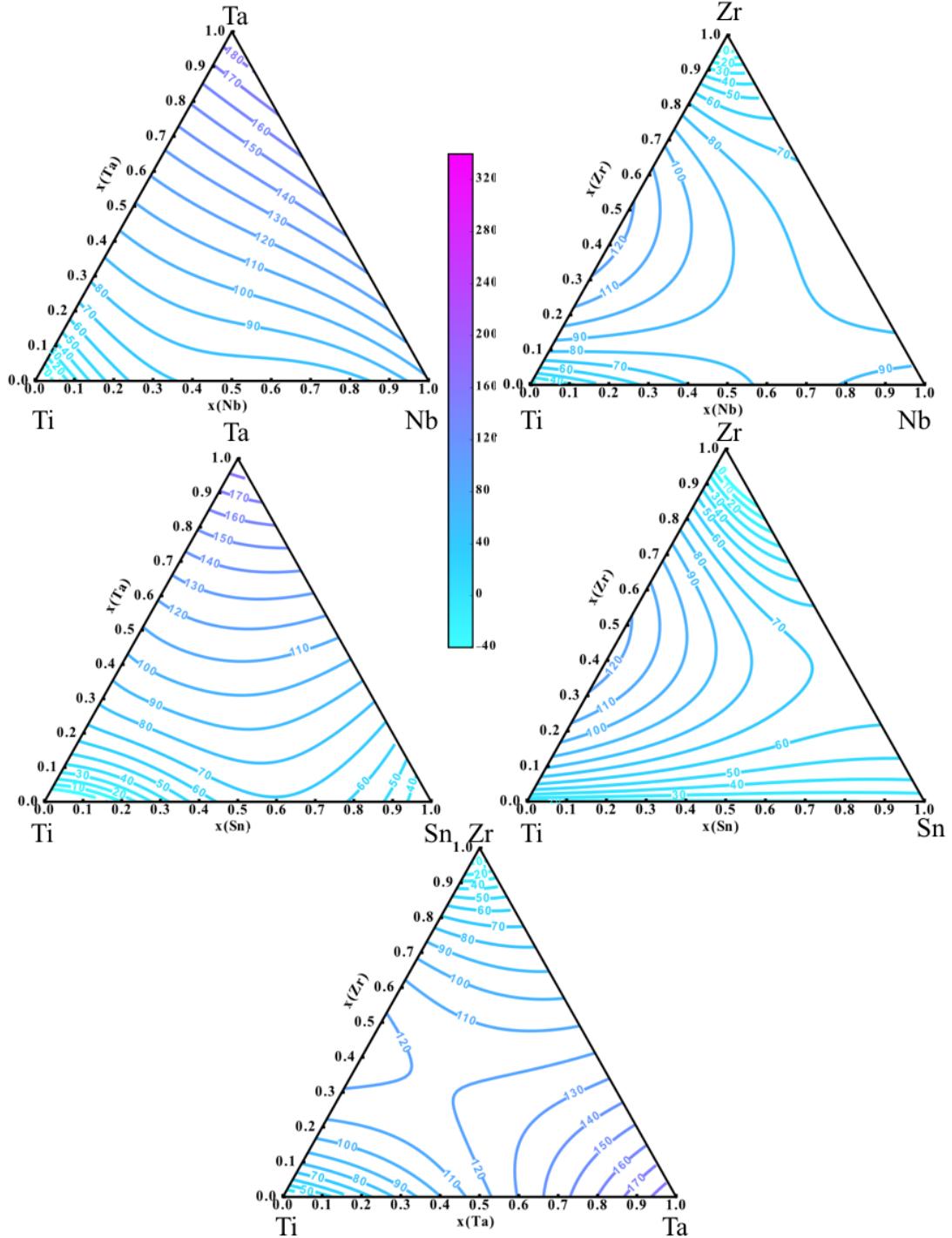


Figure 6.15. The Young's modulus is mapped as a function of composition in GPa for the Ti-Mo-Nb, Ti-Mo-Sn, Ti-Mo-Ta, Ti-Mo-Zr and Ti-Nb-Sn alloy systems using pycalphad [37].

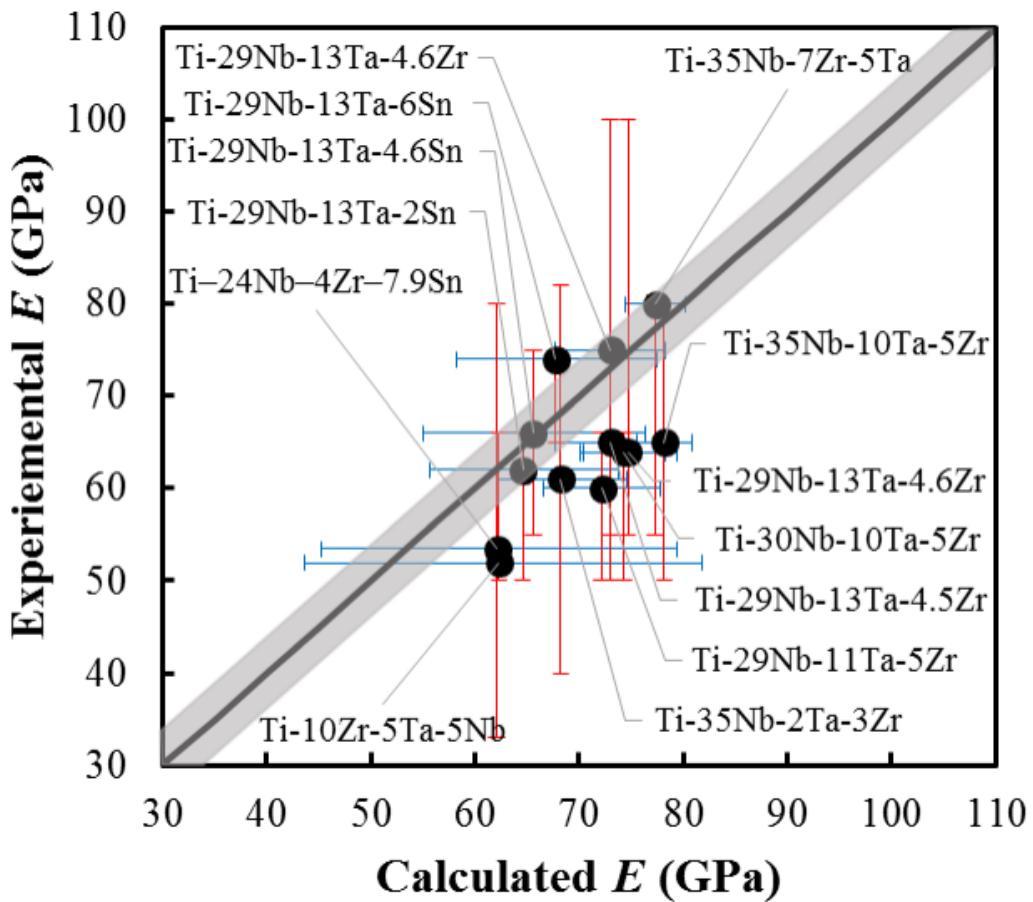


Figure 6.16. E of multicomponent bcc Ti alloys predicted from the completed database are compared with measured experimental results. Error bars plotted are from the variation in experimentally determined YoungâŽs modulus values for the specific multicomponent alloy. The grey region refers to the error in the first-principles calculations. More information on the alloys is Table 6.3 [32â€”34].

Chapter 7 |

Phase stability and elastic properties study of the Ti-Ta and Ti-Nb systems

7.1 Introduction

ADD

7.2 Modeling and Calculations

7.2.1 Computational details

ADD

7.2.2 Modeling details

ADD

7.3 Results and discussion

7.3.1 First-principles calculations at 0 K

ADD

7.3.2 Elastic properties

ADD

7.3.3 Neutron scattering results

7.3.3.1 Phonon density of states at 300 K

7.3.3.2 Diffraction patterns at 300 K

7.3.3.3 Temperature dependent phonon density of states

7.3.3.4 Temperature dependent diffraction patterns

7.3.4 Partition function approach results

7.3.4.1 Phase fractions

7.3.4.2 Mixed force constants

7.3.5 Comparison of elastic properties

7.4 Conclusion

Chapter 8 |

Conclusions and Future Work

8.1 Conclusions

ADD

8.2 Future Work

ADD

Appendix A |

Sn-Ta Database

Appendix B |

Title of the Second Appendix

B.1 Introduction

When in the Course of human events, it becomes necessary for one people to dissolve the political bands which have connected them with another, and to assume among the powers of the earth, the separate and equal station to which the Laws of Nature and of Nature's God entitle them, a decent respect to the opinions of mankind requires that they should declare the causes which impel them to the separation.

B.2 More Declaration

We hold these truths to be self-evident, that all men are created equal, that they are endowed by their Creator with certain unalienable Rights, that among these are Life, Liberty and the pursuit of Happiness. —That to secure these rights, Governments are instituted among Men, deriving their just powers from the consent of the governed, —That whenever any Form of Government becomes destructive of these ends, it is the Right of the People to alter or to abolish it, and to institute new Government, laying its foundation on such principles and organizing its powers in such form, as to them shall seem most likely to effect their Safety and Happiness. Prudence, indeed, will dictate that Governments long established should not be changed for light and transient causes; and accordingly all experience hath shewn, that mankind are more disposed to suffer, while evils are sufferable, than to right themselves by abolishing the forms to which they are accustomed. But when a long train of abuses and usurpations, pursuing invariably the same Object evinces

a design to reduce them under absolute Despotism, it is their right, it is their duty, to throw off such Government, and to provide new Guards for their future security. —Such has been the patient sufferance of these Colonies; and such is now the necessity which constrains them to alter their former Systems of Government. The history of the present King of Great Britain [George III] is a history of repeated injuries and usurpations, all having in direct object the establishment of an absolute Tyranny over these States. To prove this, let Facts be submitted to a candid world.

Appendix C|

Title of the Third Appendix

C.1 Introduction

When in the Course of human events, it becomes necessary for one people to dissolve the political bands which have connected them with another, and to assume among the powers of the earth, the separate and equal station to which the Laws of Nature and of Nature's God entitle them, a decent respect to the opinions of mankind requires that they should declare the causes which impel them to the separation.

C.2 More Declaration

We hold these truths to be self-evident, that all men are created equal, that they are endowed by their Creator with certain unalienable Rights, that among these are Life, Liberty and the pursuit of Happiness. —That to secure these rights, Governments are instituted among Men, deriving their just powers from the consent of the governed, —That whenever any Form of Government becomes destructive of these ends, it is the Right of the People to alter or to abolish it, and to institute new Government, laying its foundation on such principles and organizing its powers in such form, as to them shall seem most likely to effect their Safety and Happiness. Prudence, indeed, will dictate that Governments long established should not be changed for light and transient causes; and accordingly all experience hath shewn, that mankind are more disposed to suffer, while evils are sufferable, than to right themselves by abolishing the forms to which they are accustomed. But when a long train of abuses and usurpations, pursuing invariably the same Object evinces

a design to reduce them under absolute Despotism, it is their right, it is their duty, to throw off such Government, and to provide new Guards for their future security. —Such has been the patient sufferance of these Colonies; and such is now the necessity which constrains them to alter their former Systems of Government. The history of the present King of Great Britain [George III] is a history of repeated injuries and usurpations, all having in direct object the establishment of an absolute Tyranny over these States. To prove this, let Facts be submitted to a candid world.

Appendix D |

Title of the Fourth Appendix

D.1 Introduction

When in the Course of human events, it becomes necessary for one people to dissolve the political bands which have connected them with another, and to assume among the powers of the earth, the separate and equal station to which the Laws of Nature and of Nature's God entitle them, a decent respect to the opinions of mankind requires that they should declare the causes which impel them to the separation.

D.2 More Declaration

We hold these truths to be self-evident, that all men are created equal, that they are endowed by their Creator with certain unalienable Rights, that among these are Life, Liberty and the pursuit of Happiness. —That to secure these rights, Governments are instituted among Men, deriving their just powers from the consent of the governed, —That whenever any Form of Government becomes destructive of these ends, it is the Right of the People to alter or to abolish it, and to institute new Government, laying its foundation on such principles and organizing its powers in such form, as to them shall seem most likely to effect their Safety and Happiness. Prudence, indeed, will dictate that Governments long established should not be changed for light and transient causes; and accordingly all experience hath shewn, that mankind are more disposed to suffer, while evils are sufferable, than to right themselves by abolishing the forms to which they are accustomed. But when a long train of abuses and usurpations, pursuing invariably the same Object evinces

a design to reduce them under absolute Despotism, it is their right, it is their duty, to throw off such Government, and to provide new Guards for their future security. —Such has been the patient sufferance of these Colonies; and such is now the necessity which constrains them to alter their former Systems of Government. The history of the present King of Great Britain [George III] is a history of repeated injuries and usurpations, all having in direct object the establishment of an absolute Tyranny over these States. To prove this, let Facts be submitted to a candid world.

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The details of my childhood are inconsequential.