AB-INITIO CALCULATION OF PHASE STABILITY IN MECHANICALLY UNSTABLE PHASES

Undergraduate Honors Thesis

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Abstract

Ab-initio calculations have been hugely successful in the past decade in providing the necessary free energies to predict phase transformations and phase stability for elemental and alloyed materials. The application of ab-initio methods, however, is problematic when it comes to model metals and their alloys with mechanically unstable high-temperature phases, such as the bcc high-temperature phases of Ti, Zr, Hf, Sc, or U. Combining novel large-displacement phonon methods with strain calculations and a self-consistent phonon approach, the free energies and elastic constants of high-temperature phases of several transition and rare earth metals were calculated. These data were then used to calculate coefficients of thermal expansion and transition temperatures for a few model systems. With a few exceptions, calculated data agreed well with that obtained through experimental methods. Calculated elastic constants met the stability criterion for the cubic crystal system. Coefficients of thermal expansion matched experimental values where they existed, and calculated phase transition temperatures were within 100K of their experimental values. For future development of this method, research into a determination of the appropriate large displacement is necessary; without such a determination, separating data that matches experimental values from that which results from computational intricacies is not possible, and the methodology cannot be applied to unexplored material systems with any confidence.
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1 Introduction and objectives

The objective of this research is to determine the energetics of several high-temperature metallic phases and to use fundamental thermodynamic relations to calculate elastic and thermal properties of these high-temperature phases. The purpose of these calculations is the generation of data regarding phase properties that are not easily measurable by experiment but which would be necessary to calculate design parameters for these materials. Practical applications of this data include the design of titanium alloys for use in turbine engines and the modeling of solid metallic fuel systems for use in Generation IV nuclear reactors [1, 2].

1.1 Phase Transitions in High Temperature Systems

Figure 1.1 displays a scandium-zirconium phase diagram retrieved from the ASM phase diagram database [3]. A representative image of the phase’s crystal structure is illustrated in each single-phase region. This system is typical of the high-temperature systems investigated in this research study. Each system investigated goes through a crystal structure change as temperature is increased that results in a change in coordination number (CN), or the number of nearest neighbor atoms to each atom in the crystal structure; the high-temperature phase for all these systems is the body-centered cubic (BCC) crystal structure. Figure 1.2 displays a portion of the periodic table of elements comprising the transition metals, lanthanide series, and actinide series. The elements in this graphic have been color-coded according to their relevance to this study: yellow.

![Figure 1.1: The Sc-Zr phase diagram [3].](image-url)
elements were investigated in this study; red elements are elements that undergo a phase transition that results in a change in CN; dark gray elements are elements for which insufficient data exists to establish whether a phase transition occurs; and light gray elements are elements that do not undergo a phase transition that results in a change in CN [3]. For the transition metals, the low-temperature phase is typically the hexagonal close-packed (HCP) crystal structure; the lanthanide- and actinide-series elements typically adopt more complex low-temperature phases and may have several intermediate phases between their 0K configurations and the BCC structures investigated in this study [3]. For the purposes of this study, only the BCC structure of the investigated elements was modeled, except in cases where the energetics of the low-temperature HCP structure were to be compared to those of the high-temperature BCC structure.

The criteria for phase stability are discussed in depth in the next section, but it is instructive to understand conceptually why CN changes occur as the temperature of a material increases. Temperature measures atomic or molecular motion in a system,

![Figure 1.2](image-url)

**Figure 1.2:** Transition metals, lanthanides, and actinides divided into studied systems (yellow), other systems exhibiting a CN change (red), systems for which data are unavailable (dark gray), and systems exhibiting no CN change (light gray) [3].
Whether it be in the form of molecular collisions in a fluid or lattice vibrations in a crystalline solid [4]. In crystalline solids, this atomic motion is restricted around the equilibrium lattice positions of the atoms in the solid, but will increase as temperature increases. Thus, it is desirable to have a structure with lower atomic density (lower CN) such as BCC at high temperatures, because it will reduce the forces experienced by individual vibrating atoms by allowing a greater volume in which to vibrate without interacting with their nearest neighbors.

1.2 Criteria for Phase Stability

Thermodynamics defines a set of criteria for determining the stable configuration of a system under different sets of environmental conditions. For practical considerations, the most useful is typically the Gibbs free energy (symbolized by the variable $G$ or $F$), which determines the stable configuration under conditions of constant temperature and pressure [4]. Such environmental conditions are more reasonably achievable in experiment than others such as constant volume or constant number of particles. (Gibbs) Free energy is determined by an enthalpy contribution that is nearly independent of temperature and an entropy contribution that is dependent on temperature [4]. To determine the stable configuration of a system at a temperature $T$, the free energy of each configuration is determined at that temperature and the overall free energy of the system is minimized by

Figure 1.3: Schematic illustration of the determination of stable phase at a temperature $T$ by minimizing free energy, $G$ [4].
Choosing the lowest free energy configuration [4]. This calculation is illustrated schematically in Figure 1.3 over a temperature range in which several phase transitions occurs. The transition temperature is determined by the point at which both phases have the same free energy, i.e., both phases are stable.

1.3 Vibrational Modes in Crystal Lattices

Zero-temperature ab-initio calculations by design do not include the effects of finite temperature on the stability of the structures investigated. This is a simplification that allows calculation of energetics without the tedious calculation of atomic vibrations that occur at finite temperature and is a reasonable approximation for all cases where the difference in entropy between the structures that are compared energetically is negligible and would cancel when energy differences are calculated, such as for the formation energy of a point defect in a large, otherwise perfect system. However, as has been seen in the previous discussion of the origins of mechanical instability, it is necessary to include the effects of these vibrations to calculate reasonable results for mechanically unstable systems. Such vibrational effects at finite temperatures are calculated using the vibrational modes of the crystal, called phonons.

Phonons are collective excitations and correspond to vibration patterns where the atoms in a crystal vibrate with a given frequency and wavelength. The phonon dispersion is

![Figure 1.4](image)

**Figure 1.4**: Illustration of phonon vibrations in periodic materials: (a) displays a 0K structure with no vibrations but with interatomic interactions approximated as harmonic oscillators; (b) shows a longitudinal wave propagating through the material; and (c) shows a transverse wave propagating through the material [6]
important since any arbitrary lattice vibration can be Fourier decomposed into a superposition of phonons. Figure 1.4 displays a schematic illustration of the two types of fundamental polarization that occur in materials [6]. Longitudinal phonons result from the displacement of atoms in the direction of vibration propagation, while transverse phonons results from displacements perpendicular to the direction of wave propagation [6]. If a material has \( N \) atoms in the primitive cell, then for each wave vector \( \mathbf{k} \) there exist \( 3N \) vibrational frequencies in the phonon dispersion. Three of them go to zero in the long-wavelength limit (i.e. for \( \mathbf{k} \to 0 \)). Since they correspond to sound waves, they are called acoustic phonon branches. Atoms with more than one atom in the primitive unit cell also have \( (3N – 3) \) phonon branches that do not go to zero in the long wavelength limit. They are called optical phonons since they are excited by infrared light. Since all systems considered in the present work have a monatomic basis \( (N = 1) \), only acoustic phonons appear in the following discussion. Considering each phonon as a wave with frequency \( \omega \), we can consider each vibrational mode to have an associated energy of \( \hbar \omega \) according to the quantum mechanical relation. Summing these energies weight by their distribution function, the phonon density of states \( g(\omega) \), allows calculation of the zero-point energy, while an expression that compares the vibrational energy with the thermal energy allows calculating the vibrational entropy as a function of temperature. From that, the free energy for an elemental system can be calculated within the so-called quasiharmonic approximation (QHA) by [5]:

\[
F(p, T) = H(p) + \frac{1}{2} \int g(\omega(p)) \hbar \omega(p) d\omega + k_B T \int g(\omega(p)) \ln \left[ 1 - \exp \left( - \frac{\hbar \omega(p)}{k_B T} \right) \right] d\omega \quad (1.1)
\]

where the cell volume is varied to correspond to different pressures \( p \) for the calculation of enthalpy \( H \) and frequencies \( \omega \).

With a complete phonon dispersion of a crystal structure and its 0K enthalpy, it is thus possible to do a complete evaluation of the energetics of that crystal structure at a given temperature. Using the relation of the free energy to the temperature of the system via the entropy contribution to the free energy, it is possible to calculate and compare the free energies of two phases and determine the phase with the lowest free energy as show in Figure 1.3. By calculating the free energy of identical crystal structures with different
Calculation of Phase Stability in Mechanically Unstable Phases

At 0K, the entropy contribution to the Gibbs free energy of a phase is nil (apart from any non-classical zero-point energy), and the stability of that phase depends only on its enthalpy. This divides all phases that are stable at some finite temperature into two categories: (a) phases that area at a local enthalpy minimum at 0K; and (b) phases that are at a local energy minimum only when entropy contributions to free energy are included. A mechanically unstable phase falls into category (b), such that when stability calculations are performed at 0K without the inclusion of temperature effects, it is possible to decrease the enthalpy of the phase by displacing the atoms in certain directions. Figure 1.6 shows an energy calculation for such a mechanically unstable system as the structure is strained in the <110> crystallographic direction.

Mechanical instability creates a number of calculation problems that cannot be corrected using classical ab-initio methods. Firstly, because the enthalpy of a mechanically unstable

Figure 1.5: Illustration of showing the phonon branches corresponding to various elastic constants in the [001], [111], and [110] directions in a cubic crystal [7].
Introduction and objectives

Phase will decrease even as the atoms move from their high-temperature equilibrium positions, minimizing zero-temperature enthalpy by movement of atoms does not drive the system to its high-temperature equilibrium configuration. Furthermore, some elastic constants of the crystal, which are proportional to the second derivative of the energy versus lattice constant/strain curve, will be negative in directions in which the energy decreases as the crystal is strained. This is an indicator of mechanical instability in itself, since the tetragonal shear modulus in a cubic system such as BCC, given by \( \frac{1}{2}(C_{11} - C_{12}) \) and corresponds to a \((\varepsilon, -\varepsilon, 0, 0, 0, 0)\) strain. This elastic constant must be positive in a cubic crystal system. Finally, the square of frequencies of vibrational modes within the crystal, known as phonons, is proportional to the second derivative of the energy versus atomic displacement curve, which will result in imaginary (and thus physically meaningless) phonon frequencies for negative curvatures. Since phonons are used to calculate the temperature contribution to the free energy with the quasiharmonic approximation (QHA) typically used for solids, an incomplete phonon dispersion containing imaginary frequencies creates serious problems for calculating phase stability at finite temperatures [5].

In general, there are two physical reasons for mechanical instability in ab-initio calculations without temperature effects, which are both results from anharmonicity (the fact that truncating the Taylor expansion of the energy with respect to atomic

Figure 1.6: Total energy calculation for a mechanically unstable system when strained. In the \( c' \) direction, the energy of the system decreases with strain, indicative of mechanical instability.
displacements after the quadratic term is not sufficient to describe the vibrational frequencies reasonable well). The first is that without atomic vibrations resulting from the application of temperature effects, each atom at its equilibrium position “sees” only the unstable equilibrium of the directional energy maximum and not the outlying parabolic regime about the equilibrium that characterizes a stable atomic position. A second reason for mechanical instability is that the thermal vibrations in the material are large enough to invalidate the ab-initio premise that the other atoms in the crystal can be approximated as being at their equilibrium positions when one atom is displaced. This greatly complicates the matter of vibrational modes within the crystal at finite temperatures, since vibrations of atoms in any direction will interfere with those in other directions. The mechanical instability resulting from such phonon-phonon interactions is consequently much more difficult to correct for than that arising from simple non-parabolic behavior in the atomic potential.

1.5 **Density Functional Theory and Ab-Initio Treatment of Crystal Lattices**

Accurate quantum mechanical descriptions of solids can be achieved with ab-initio methods such as Density Functional Theory (DFT) [8,9]. In DFT all the physical properties of a system can be obtained from the knowledge of the ground-state density alone. Since the electronic density is the basic variable that needs to be computed (instead of the many-particle wavefunction), this allows a huge decrease in computational demands and makes the treatment of even large supercells (~1000 atoms) feasible. DFT calculates the interaction of individual electrons with the overall electron density of the material, not including the electron for which the calculation is performed. DFT has been known to predict accurately several properties such as lattice constant, total energies, elastic constants, among others for normal semiconductors and metals.

In performing order to calculate the properties of bulk materials, it is advisable to perform calculations on the largest available system so as to avoid surface effects. However, the complexity of ab-initio calculations, places a strict limit on the practical size of the system to be calculated. To correct for this, calculations are performed on the smallest cell that obeys periodic boundary conditions. This means that any behavior, such as electronic interactions, that would escape the cell through one of its boundary surfaces,
is wrapped around to the opposite surface of the cell so it is effectively present in the cell calculation. Practically, this has the effect of allowing realistic calculation of larger bulk systems.

### 1.6 Experimental Measurement of Calculated Phase Properties

It is important to determine the merits of any calculation method based on comparison to the experimental methods of collecting the same data. In the case of determining the energetics of high-temperature materials via collection of phonon dispersion data, the experimental method of data collection comprises use of a specialized neutron diffraction setup under high-temperature conditions and subsequent curve-fitting of a limited number of data point to fill in gaps in data. Such experiments are so difficult to conduct at high temperature that only one research group has collected data on four of the phases investigated in this study, and no research exists for the remaining five [10,11,12,13]. Additional restrictions on radioactive materials that comprise many of the elements of interest provide a further disincentive to experimental research. Alternative experiments for elastic constants and coefficient of thermal expansion at high temperature are no easier to conduct, although they require more common experimental equipment: only two of the systems investigated have been studied incompletely under these methods [14,15]. Given the difficulty of obtaining data and the large number of unexplored systems, calculation of the energetics of these systems makes sense as a method of quickly and reliably identifying systems that warrant further scientific investigation and collecting property data along the way.
2 Approach and experimental procedures

2.1 DFT Free Energy Calculations within the Quasiharmonic Approximation

All DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [16]. Three types of calculations were performed:

(a) Total energy calculations with fixed lattice and fixed atomic positions, where also the stress tensor for the cell is calculated. From such calculations with varying lattice vectors, also pressure, volume-pressure relationship, and elastic constants can be calculated at zero temperature.

(b) Relaxation runs, where the total energy is minimized with respect to atomic positions and/or lattice vectors.

(c) Finite-displacement calculations, where one atom at a time is displaced (traditionally by a small amount ~0.01 Å) in a large supercell, and the resulting atomic-force response is calculated. The matrix of the derivatives of the forces with respect to the displacements of all atoms is called the force constant matrix, from which the dynamical matrix can be formed [M. Born, K. Huang, Dynamical Theory of Crystal Lattices (Oxford University Press, 1954)]. Due to symmetry, not all atoms need to be displaced in all Cartesian directions. Diagonalizing the dynamical matrix allows calculating the phonon frequencies and eigenvectors. For the latter, the PHON phonon calculation program [17] was used. From the phonon density of states, the free energy can be calculated within the QHA as shown in Eq. (1.1).

Wavefunctions and potentials in the DFT methods we used are expanded in terms of plane waves, $\exp[\mathbf{k} + \mathbf{G}) \mathbf{r}]$. Their number is determined by a cutoff energy which is a measure for the largest reciprocal lattice vector $\mathbf{G}$ being used in the expansion with $E_{\text{cut}} = \hbar^2 G^2/(2m)$. The cutoff energies used for the elements considered in this work guaranteed sufficient accuracy for the phonon calculations. Integrations over the electronic states in the Brillouin zone are performed with the help of Monkhorst-Pack special point meshes. For metals, a high integration grid density is necessary for converged calculations, since the Fermi energy converges only slowly with it. Finally, the number of atoms in the supercell for the finite-displacement calculations determines how
many phonon modes (standing waves) fit into the cell and thus are calculated accurately without interpolation.

Because all traditional QHA calculations require relatively little computational effort compared to the methods described in Sections 2.3 and 2.4, calculation cells containing large numbers of atoms and fine integration grids were used: typically 3x3x3 BCC supercells containing 54 atoms with 6x6x6 integration points and 3x3x2 HCP supercells containing 36 atoms with 9x9x6 integration points.

### 2.2 Large-Strain Elastic Calculations

Large strain calculations were performed using VASP and CASTEP DFT programs [18]. Since no atomic displacements breaking down crystal symmetry are applied to the structures in the calculations, primitive cells can be used and allow fast calculations. These calculations consisted of total energy calculations performed on BCC cells that had been deformed using positive and negative strains on the order of 1% to 10% in directions allowing the calculation of the three different elastic constants of the BCC crystal structure. The corresponding stress tensor was calculated and, in order to eliminate the next-order non-linear error, the elastic constant at a given strain was calculated using the formula:

\[
C = \frac{\sigma(\varepsilon) - \sigma(-\varepsilon)}{2\varepsilon}
\]  

where \(\sigma\) is the stress corresponding to the strain \(\varepsilon\). The resulting elastic constants were then plotted versus the strain at which they were calculated and a linear relationship fitted. For the purpose of calculating elastic constants at temperature using these linear relationships, strain was derived from the relative displacement of atoms due to vibration compared to the lattice parameter, as determined by SCAILD.
2.3 **Large-Displacement Phonon Calculations**

Large-displacement phonon calculations were performed using the same combination of VASP and PHON used to calculate phonon dispersions for mechanically stable phases. The same basic calculation procedure was used, with a single modification: the size of the atomic displacement used to calculate the phonon dispersion was increased by a factor of approximately 20 to 30 times. For example, a typical phonon dispersion for a mechanically stable configuration might use a calculation displacement of 0.03 Å, corresponding to approximately 1% of the lattice parameter, while a large-displacement phonon dispersion would typically use a displacement between 0.5 and 1.0 Å, corresponding to between 16 and 30% of the lattice parameter. The reasons for this large displacement are illustrated in Figure 2.1: while a small displacement is typically adequate for sampling the parabolic potential region in mechanically stable materials, a much greater displacement is necessary to sample this region in mechanically unstable materials due to the non-parabolic region surrounding the equilibrium lattice position. Large-displacement phonon calculations were conducted using 4x4x4 BCC primitive

![Figure 2.1](image)

**Figure 2.1:** Energy-displacement curve illustrating reasons for large-displacement phonon calculations. For parabolic potentials, small displacements of 0.01 are adequate to samples the parabolic region; for non-parabolic potentials (above), large strains of 0.15-0.3 are necessary to sample this regime.
cells containing 64 atoms with 6x6x6 integration points. Displacement size was increased until all calculated phonon frequencies were real, and the first displacement for which this occurred was used in all other large-displacement calculations of the same material. For reference, Figure 2.2 shows a schematic of the BCC Brillouin zone which defines the high-symmetry directions in which phonon dispersions will be plotted.

2.4 SCAILD Calculations
The self-consistent *ab initio* lattice dynamical (SCAILD) method is a method developed by Souvatzis et al. for the purpose of correcting anharmonic behavior in high-temperature phases [19]. The calculation is performed iteratively using VASP and PHON, and uses a code called SCPH to perform modifications to the calculation cell between iterations. The premise of the SCAILD method is that anharmonicity in high-temperature materials originates from phonon-phonon interactions, and that to correctly calculate the effect of these interactions, the atomic positions must be altered from the equilibrium positions to simulate the vibrational effects of temperature. To do this, the SCAILD method uses the QHA over the phonon density of states with imaginary frequencies to approximate the displacements of the atoms due to temperature, uses a random direction and a Gaussian distribution to displace the atoms in the calculation cell, and uses the displaced cell to calculate again the phonon dispersion. This process is conducted iteratively until the free energy calculated by this method stabilizes, indicating that a corrected phonon dispersion has been calculated and the mechanical instability eliminated. Figure 2.3 shows a
Figure 2.3: Schematic representation of the SCAILD method calculation process. 25 iterations separate the upper results from the lower ones.

schematic of the SCAILD method from the starting iteration to some stabilized iteration where a phonon dispersion containing only real frequencies has been calculated.
3 Results, analysis and discussion

3.1 β-Titanium Calculations

Figure 3.1 displays a calculated phonon dispersion of BCC-structure β-titanium using a large-displacement calculation (u=0.88 Å) in comparison to experimental data [10]. Figure 3.2 and 3.3 display calculated phonon dispersions of β-titanium using the SCAILD method, performed in the course of this study and from previous work, respectively [19]. Figure 3.4 displays the calculated minimum free energy lattice parameter versus temperature used to calculate the coefficient of thermal expansion. Figure 3.5 displays the calculated free energy of the BCC and HCP titanium phases in electron volts per atoms in the range from 900 to 1500 K. Table 3.1 displays the elastic constants, linear coefficient of thermal expansion, and phase transition temperature calculated from the phonon dispersion calculations alongside experimental data for the same quantities [10,14]. Figure 3.6 displays a total energy vs. displacement calculation.

![Figure 3.1: Phonon dispersion of β-titanium calculated using the large-displacement method with a displacement of 0.88 Å. Diamond markers on the plot represent experimental data [10]](image)
for the β-titanium system with an atomic displacement pattern corresponding to the N-point of the phonon dispersion to determine the extent of anharmonicity in the system. In general, all calculations for β-titanium show excellent agreement with experimental values, although there is some decrease in phonon energies around the H-point in L-D calculations that raises questions about whether the displacement is appropriate for the system. The calculated lattice constant at high temperature also agrees well with the experimental value with less than 2% disagreement. There is excellent agreement between calculated and experimental values of the \( C_{11} \) elastic constant, with noticeably less agreement between the \( C_{12} \), \( C_{44} \), and \( K \) values. This disparity is somewhat expected since it is the phonon branch corresponding to the \( \frac{1}{2}(C_{11}-C_{12}) \) elastic constant that is initially problematic for this group of materials, resulting in low calculations of \( C_{12} \) and \( C_{44} \) elastic constants (see Figure 1.5). Additionally, calculated values for the coefficient of thermal expansion (CTE) and transition temperature agree well with experiment, with the CTE being nearly the same as that observed in commercial β-Ti alloys and the transition temperature calculated to the nearest 25 K within 50 K of the experimental value [20,3].
Figure 3.3: Phonon dispersion of β-titanium (THz) calculated using SCAILD method by the Souvatzis group [19]. Circles are experimental phonon values from [10].

Figure 3.4: Calculated minimum free energy lattice parameter of BCC β-Ti versus temperature, calculated with the L-D method.
Figure 3.5: Calculated free energy of HCP and BCC Ti phases using L-D method showing the transition temperature at approximately 1200K.

Figure 3.6: Energy in eV/atom versus atomic displacement in corresponding to N-point symmetry shows anharmonic behavior in the titanium potential space.
Table 3.1: Values of BCC β-titanium physical properties, calculated with L-D method, and experimental values.

<table>
<thead>
<tr>
<th>Property</th>
<th>Calc.</th>
<th>Expt.</th>
</tr>
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<tbody>
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<td>0K LP (Å)</td>
<td>3.234</td>
<td>-</td>
</tr>
<tr>
<td>LP</td>
<td>3.276</td>
<td>3.33</td>
</tr>
<tr>
<td>C_{11} (GPa)</td>
<td>114</td>
<td>115.3</td>
</tr>
<tr>
<td>C_{12}</td>
<td>60.7</td>
<td>73.9</td>
</tr>
<tr>
<td>C_{44}</td>
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<td>20.7</td>
</tr>
<tr>
<td>K</td>
<td>78.4</td>
<td>87.7</td>
</tr>
<tr>
<td>CTE (K^{-1})</td>
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<td>8.6x10^{-6}</td>
</tr>
<tr>
<td>Trans. T (K)</td>
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<td>1156</td>
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</table>

3.2 β-Zirconium Calculations

Figure 3.7 displays a calculated phonon dispersion of BCC-structure β-zirconium using a large-displacement calculation (u=0.54 Å) in comparison to experimental data [11]. Figure 3.8 displays a calculated phonon dispersion of β-zirconium using the SCAILD method from previous work [19]. Figure 3.9 displays the calculated minimum free energy lattice parameter versus temperature used to calculate the coefficient of thermal expansion. Figure 3.10 displays the calculated free energy of the BCC and HCP zirconium phases in electron volts per atoms in the range from 1000 to 1500 K. Table 3.2 displays the elastic constants, linear coefficient of thermal expansion, and phase transition temperature calculated from the phonon dispersion calculations alongside experimental data for the same quantities, where they exist [11]. Figure 3.11 displays a total energy vs. displacement calculation for the β-zirconium system with an atomic displacement pattern corresponding to the N-point of the phonon dispersion to determine the extent of anharmonicity in the system.

Calculations for β-zirconium show similar agreement with experimental values as those for β-titanium. Phonon energies calculated by the L-D method are in very good agreement with experimental values without the questionable energy deviations present in the titanium calculations. The calculated lattice constant at high temperature agrees almost perfectly with the experimental value. There is again excellent agreement between
calculated and experimental values of the $C_{11}$ elastic constant, with noticeably less agreement between the $C_{12}$, $C_{44}$, and $K$ values, which may be attributable to the same $\frac{1}{2}(C_{11}-C_{12})$ phonon branch. Calculated values for the transition temperature agree well with experiment, with the transition temperature calculated to the nearest 25 K within 100 K of the experimental value [3]. No experimental data on the coefficient of thermal expansion of β-zirconium was found. Interestingly, when plotting the displacement versus energy curve for zirconium, the energy appears be at a minimum at zero displacement; this indicates that there should be no mechanical instability in the zirconium potential space. It is unclear in the course of this study why this particular atomic potential has this form; however, there is a possibility that the deviation from a parabolic potential approximation is partially represented by the few outlier data points, and that greater deviations would appear in a larger calculation cell.

**Figure 3.7:** Phonon dispersion of β-zirconium calculated using the large-displacement method with a displacement of 0.54 Å. Diamond markers on the plot represent experimental data [11]
Figure 3.8: Phonon dispersion of β-zirconium (THz) calculated using SCAILD method by the Souvatzis group [19]. Circles are experimental phonon values from [11].

Figure 3.9: Calculated minimum free energy lattice parameter of BCC β-Zr versus temperature, calculated with the L-D method.
Figure 3.10: Calculated free energy of HCP and BCC Zr phases using L-D method showing the transition temperature at approximately 1050K.

Figure 3.11: Energy in eV/atom versus atomic displacement corresponding to N-point symmetry shows an absence of anharmonic behavior in the zirconium potential space.
Table 3.2: Values of BCC β-zirconium physical properties, calculated with the L-D method, and experimental values.

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<td>3.551</td>
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<tr>
<td>C_{11} (GPa)</td>
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<td>104</td>
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<td>C_{12}</td>
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<td>93</td>
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<td>K</td>
<td>86.5</td>
<td>96.7</td>
</tr>
<tr>
<td>CTE (K^{-1})</td>
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</tr>
<tr>
<td>Trans. T (K)</td>
<td>1050</td>
<td>1136</td>
</tr>
</tbody>
</table>

3.3 β-Hafnium Calculations

Figure 3.12 displays a calculated phonon dispersion of BCC-structure β-hafnium using a large-displacement calculation (u=0.68 Å) in comparison to experimental data [12]. Figure 3.13 displays a calculated phonon dispersion of β-hafnium using the SCAILD method from previous work [19]. Figure 3.14 displays the calculated minimum free energy lattice parameter versus temperature used to calculate the coefficient of thermal expansion. Figure 3.15 displays the calculated free energy of the BCC and HCP hafnium phases in electron volts per atoms in the range from 1500 to 2500 K. Table 3.3 displays the elastic constants, linear coefficient of thermal expansion, and phase transition temperature calculated from the phonon dispersion calculations alongside experimental data for the same quantities [12,15]. Figure 3.16 displays a total energy vs. displacement calculation for the β-hafnium system with an atomic displacement pattern corresponding to the N-point of the phonon dispersion to determine the extent of anharmonicity in the system.

Calculations for β-hafnium also show similar agreement with experimental values as those for β-titanium. Like zirconium, phonon energies calculated by the L-D method are in very good agreement with experimental values without the questionable energies present in the titanium calculations. The calculated lattice constant at high temperature is somewhat smaller than the experimental value but still only 3% different. There is decent
agreement between calculated and experimental values of the $C_{11}$ elastic constant, with noticeably less agreement between the $C_{12}$, $C_{44}$, and $K$ values. Calculated values for the coefficient of thermal expansion are about a factor of two different and the transition temperature agrees well with experiment, with the transition temperature calculated to the nearest 25 K within 100 K of the experimental value [15,3]. Unlike zirconium, anharmonic potential behavior was definitely observed for the hafnium system, those in a much more mild form than for the titanium system. Additionally, due to the speed with which it may be calculated, the hafnium system was chosen to test calculations of larger cells using the L-D method; such calculations did not appear to provide any benefit in terms of agreement with experimental phonon data.

**Figure 3.12:** Phonon dispersion of β-hafnium calculated using the large-displacement method with a displacement of 0.68 Å. Diamond markers on the plot represent experimental data [12]
Results, analysis and discussion

Figure 3.13: Phonon dispersion of $\beta$-hafnium (THz) calculated using SCAILD method by the Souvatzis group [19]. Circles are experimental phonon values from [12].

Figure 3.14: Calculated minimum free energy lattice parameter of BCC $\beta$-Hf versus temperature, calculated using the L-D method.
Figure 3.15: Calculated free energy of HCP and BCC Hf phases using L-D method showing the transition temperature at approximately 2100K.

Figure 3.16: Energy in eV/atom versus atomic displacement corresponding to N-point symmetry shows anharmonic behavior in the hafnium potential space.
3.4 β-Scandium Calculations

Figure 3.17 displays a calculated phonon dispersion of BCC-structure β-scandium using a large-displacement calculation (u=0.74 Å) in comparison to experimental data [13]. Figure 3.18 displays calculated a phonon dispersion of β-hafnium using the SCAILD method from previous work [19]. Table 3.4 displays the elastic constants calculated from the phonon dispersion calculations alongside experimental data for the same quantities [13].

Agreement of calculated properties for β-scandium with experimental values is much poorer than for previously-calculated high-temperature phases. Phonon energies are only approximately 60% of what they should be near their peak values, and all elastic constants are extremely low compared to experimental values. It is believed that is disagreement with experiment represents an incomplete stabilizer of the β-scandium phase, possibly indicating the formation of a third phase in a limited temperature regime between the two known phases. This suggestion is further evidenced by the β-scandium calculated phonon dispersion at 0.8 Å, depicted in Figure 3.19, in which phonons in the system have clearly destabilized and resumed their anharmonic behavior as a result of mechanical instability.

Table 3.3: Values of BCC β-hafnium physical properties, calculated with the L-D method, and experimental values.

<table>
<thead>
<tr>
<th>Property</th>
<th>Calc.</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0K LP (Å)</td>
<td>3.436</td>
<td>-</td>
</tr>
<tr>
<td>LP</td>
<td>3.521</td>
<td>3.625</td>
</tr>
<tr>
<td>$C_{11}$ (GPa)</td>
<td>112</td>
<td>131</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>78.1</td>
<td>103</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>60.1</td>
<td>45</td>
</tr>
<tr>
<td>$K$</td>
<td>89.5</td>
<td>112.3</td>
</tr>
<tr>
<td>CTE (K$^{-1}$)</td>
<td>2.8x10$^{-5}$</td>
<td>1.1x10$^{-5}$</td>
</tr>
<tr>
<td>Trans. T (K)</td>
<td>2100</td>
<td>2016</td>
</tr>
</tbody>
</table>
Figure 3.17: Phonon dispersion of β-scandium calculated using the large-displacement method with a displacement of 0.74 Å. Diamond markers on the plot represent experimental data [13].

Figure 3.18: Phonon dispersion of β-scandium (THz) calculated using SCAILD method by the Souvatzis group [19]. Circles are experimental phonon values from [13].
Figure 3.19: Phonon dispersion of $\beta$-scandium calculated using the large-displacement method with a displacement of 0.80 Å showing continued mechanical instability.

Table 3.4: Values of BCC $\beta$-scandium physical properties, calculated with the L-D method, and experimental values.

<table>
<thead>
<tr>
<th>Property</th>
<th>Calc.</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0K LP (Å)</td>
<td>3.581</td>
<td>(3.73)</td>
</tr>
<tr>
<td>$C_{11}$ (GPa)</td>
<td>44.4</td>
<td>73.3</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>26.4</td>
<td>60.5</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>32.8</td>
<td>26.4</td>
</tr>
<tr>
<td>$K$</td>
<td>32.4</td>
<td>64.8</td>
</tr>
</tbody>
</table>
3.5 **High-Temperature Rare Earth Calculations**

Figure 3.20 displays a calculated phonon dispersion of BCC-structure $\beta$-yttrium using a large-displacement calculation ($u=0.76$ Å). Figure 3.21 displays a calculated phonon dispersion of $\beta$-yttrium using the SCAILD method from previous work [19]. Figure 3.22 displays a calculated phonon dispersion of BCC-structure $\beta$-neodymium using a large-displacement calculation. Table 3.5 displays the elastic constants calculated from the phonon dispersion calculations for these two systems. These systems are a good example of viable systems for calculation of physical properties: neither is well explored, nor are they likely to be unless a promising set of material properties is determined to exist.

However, calculations on both materials pose challenges for the use of phonon methods to determine properties. As with $\beta$-scandium, relatively low phonon energies are observed for both systems, raising the possibility that the phonon dispersions are not representative of the real material and would not match experimentally collected data. This necessitates the development of a set of criteria for selecting a displacement using the large-displacement method, or at least for accepting or rejecting the phonon dispersions generated by this approach. At this time, this study has not generated such a relationship, although it would be a logical direction for this research to proceed in the future.
Results, analysis and discussion

Figure 3.20: Phonon dispersion of β-yttrium calculated using the large-displacement method with a displacement of 0.76 Å.

Figure 3.21: Phonon dispersion of β-yttrium calculated using SCAILD method by the Souvatzis group [19].
Figure 3.22: Phonon dispersion of $\beta$-neodymium calculated using the large-displacement method with a displacement of 1.05 Å.

Table 3.5: Values of BCC rare earth phase physical properties, calculated with the L-D method.

<table>
<thead>
<tr>
<th>Property</th>
<th>Y</th>
<th>Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>0K LP (Å)</td>
<td>3.905 (4.10)</td>
<td>4.125 (4.13)</td>
</tr>
<tr>
<td>$C_{11}$ (GPa)</td>
<td>36.8</td>
<td>42.5</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>29.9</td>
<td>41.4</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>38.0</td>
<td>25.9</td>
</tr>
<tr>
<td>$K$</td>
<td>32.2</td>
<td>41.8</td>
</tr>
</tbody>
</table>
3.6 \textit{γ-Uranium Calculations}

Because of the complexity of its electron orbitals and the degree to which phonon-phonon interactions play a role in it anharmonicity, it was not possible to perform large-displacement phonon calculations on the uranium system. Displacement size was increased to the point at which nearest-neighbor collisions became a calculation issue, after which alternative calculation methods were utilized. Figure 3.23 shows the results of a large-strain calculation on BCC \(γ\)-uranium, used to determine the strain dependence of the elastic constants of this system. Figure 3.24 shows a Murnaghan fit for bulk modulus using SCAILD pressure data from cells of different volumes; similar fits were used with strained cells to determine the \(C_{11}\) and \(C_{12}\) elastic constants. Figure 3.25 shows calculated phonon dispersion for \(γ\)-uranium using the SCAILD method. Table 3.6 displays the elastic constants determined from the large-strain and SCAILD calculations on \(γ\)-uranium, calculated using an average strain from phonon displacements. Due to curvature issues near the high-symmetry points in the phonon dispersion calculated using SCAILD, calculation of elastic constants using this method was not performed on this system.

There are no experimental data for \(γ\)-uranium properties beyond the temperature range of its phase stability. Thus, it is especially important to confirm any calculated values with multiple approaches. In this case, it appears that both the large-strain and SCAILD approaches give approximately the same calculated values, thus validating the large-strain approach in this case and increasing confidence that these data are correct.
Figure 3.23: Large-strain calculation showing the dependence of elastic constants in γ-uranium on cell strain.

Figure 3.24: Murnaghan fit for bulk modulus using SCAILD calculations of pressure in various cell volumes.
Figure 3.25: Phonon dispersion of $\gamma$-uranium calculated using SCAILD method at 1173K.

Table 3.6: Values of BCC $\gamma$-uranium physical properties, calculated with large-strain and SCAILD methods.

<table>
<thead>
<tr>
<th>Property</th>
<th>Large-Strain</th>
<th>SCAILD</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP (Å)</td>
<td>3.43</td>
<td>3.48 (3.52)</td>
</tr>
<tr>
<td>$C_{11}$ (GPa)</td>
<td>148</td>
<td>143</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>127</td>
<td>126</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>53</td>
<td>-</td>
</tr>
<tr>
<td>$K$</td>
<td>135</td>
<td>131</td>
</tr>
</tbody>
</table>
3.7 Evaluation of Approaches

The applicability of various computational approaches and quality of results for the different systems investigated in this study provide excellent incentive for further research in this area.

Large-strain approaches were largely ineffective in determining the elastic properties of the systems in this study. This is not entirely surprising given the simplicity of this approach. The only realistic results achieved were those for uranium from the CASTEP DFT package. Other systems displayed incorrect relationships between elastic constants under this method (i.e., increasing rather than decreasing relationship between $C_{11}$ and $C_{12}$ with increasing strain), and even the uranium large-strain calculations could not be duplicated using the more advanced VASP DFT program. Therefore, any potential benefit from the calculation simplicity of large-strain calculations is negated by the uncertainty in the results, and they should only be considered as an area for possible future investigation.

Large-displacement phonon approaches in most cases produced phonon dispersions that matched well with experimental results. While elastic constants calculated from these phonon dispersions were somewhat different from experimental values, it appears that

![Figure 3.26: Phonon dispersion of β-titanium calculated using SCAILD method at 1200K.](image-url)
this is more likely the result of sensitivity to the displacement size than a fundamental issue with the methodology. Attempts to determine the appropriate displacement size for a system based on its physical properties have thus far failed; Figure 3.26 displays a log-log plot of displacement size versus mass, temperature, and cell size, which shows the lack of strength in linear fits for all these parameters. The development of a formula for the appropriate displacement or at least a set of criteria for accepting or rejecting an L-D calculated phonon dispersion is one of the future research objectives of this group. This development would be particularly valuable since L-D calculations can be performed in hours, as opposed to the weeks it takes to complete SCAILD calculations with any realistic results.

SCAILD results are generally the standard to which other calculations of mechanically-unstable phases must be held, but pose a host of problems for the purpose of calculation. Since SCAILD is an iterative method, cell sizes are extremely limited, as each iteration is at least computationally equivalent to a single large-phonon calculation. This high computational cost also limits the SCAILD method to high symmetry systems. Additionally, convergence of free energy values in SCAILD calculations typically takes more than 100 iterations, much longer than simply calculating a physically valid phonon dispersion. Finally, due to the averaging process that occurs in the SCAILD method between iterations, phonon curvature tends to occur near high-symmetry points where elastic constants would generally be calculated, making calculation of these properties impossible without some sort of correction. In the experience of this study, if it is possible to avoid calculating properties of a system using SCAILD, it is desirable to do so due to the complexity of the program and the high probability of convergence issues.
4 Conclusions

The results of this study have shown that it is possible to calculate the properties of mechanically unstable phases using a number of different methods. Using the previously established SCAILD method, successful calculation of some of the elastic properties of $\gamma$-uranium was achieved. However, problems with SCAILD led to testing of other simpler and less tedious calculation methods. The large-strain method for calculating elastic constants was successful in duplicating SCAILD results for uranium but could not be successfully applied to other systems. This method does not seem to hold future potential for accurate calculations. The large-displacement method for calculating phonon dispersions produced reasonable results quickly and in good agreement with experimental data for most systems. The largest issue with its widespread application appears to be calculation of the displacement necessary to stabilize the phonon dispersion calculation. However, a thorough investigation into the topic of this displacement would have immense benefits to this type of computational method as it would eliminate the need to use the restrictive SCAILD method to calculate the properties of unstable high-temperature materials. Without the necessity of high symmetry, small cells, it may be possible in the future to calculate defect energies and alloy properties of materials that were in the past inaccessible to the advances of computational materials science.
References

3. ASM Alloy Phase Diagrams Center, maintained by ASM International <www1.asminternational.org/asmenterprise/apd/>.