Density-Functional Theory Study of Materials and Their Properties at Non-Zero Temperature

DISSERTATION

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By

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Abstract

Density functional theory (DFT) has proven useful in providing energetic and structural data to inform higher levels of simulation as well as populate materials databases. However, DFT does not intrinsically include temperature effects that are critical to determining materials behavior in real-world applications. By considering the magnitude of critical energy differences in a system to be studied, one may select the appropriate level of additional theory with which to supplement DFT to obtain meaningful results with respect to temperature-induced behavior.

This thesis details studies on three materials systems, representing three distinct levels of additional theory used in the study of thermally-induced behavior. After introducing the concepts involved in extracting thermal data from atomistics and density functional theory in chapters 1 and 2, chapter 3 details studies on a Ni-base superalloy system and its behavior in creep testing at high temperature due to planar defects. Chapters 4 and 5 detail work on thermal stabilization of BCC phases which are unstable without temperature effects and the progress in calculating the thermodynamic stability of vacancies in these and other BCC systems. Chapter 6 describes a study of thermal effects coupling to magnetism in indium antimonide (InSb), which are the result of previously unobserved coupling between phonons and magnetic field in a diamagnetic material. All three of the systems studied exhibit materials properties which are strongly temperature-dependent, but the level of theory necessary to study them varies from simple ground state calculations to consideration of the effects of single vibrational modes within the
material. Since many of the approaches used and introduced here are computationally intensive and push the limits of publicly available computational resources, this thesis puts additional focus on optimizing code execution and choosing an appropriate level of theory to probe a given material system. An inappropriate level of theory can either be computationally wasteful (or unfeasible) or yield meaningless results; it is only by the inclusion of appropriate thermal effects, determined by system to be considered, that valid results can be obtained. Though much progress has been made in generalizing the approaches described in this thesis, further research will be necessary if we hope to fulfill the lofty goal of a universally applicable method of extracting thermal data from first principles in a way that guarantees valid and useful results.
Dedication

This document is dedicated to Thomas Wilson Tyl, who encouraged me to pursue an advanced degree.
Acknowledgments

I would like to acknowledge all the support I received from my fellow research group members, my advisor, my family and friends, and especially the help and support I received from the dedicated staff at the Ohio Supercomputer Center, without whom the computations conducted in this project would never have been possible.
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Chapter 1: Introduction

Data on variations in materials structure and behavior with temperature is critical to the design of materials for practical applications. When we consider the traditional materials tetrahedron in Figure 1.1,[1] it is clear that neither the properties nor the processing of a materials system can be thoroughly considered without knowledge of temperature effects such as phase transitions and diffusion. Indeed, even the structure of the system may vary with temperature via changes to the oxidation reactions and component solubilities, as well as phase changes.[2] As technology demands greater materials performance, filling gaps in our knowledge about thermal properties allows more precise tailoring of materials designs to an ever-increasing variety of applications.

If we contemplate the development of the ubiquitous iron-carbon system (phase diagram in Figure 1.2 [3]), the importance of thermal data becomes incredibly clear. Without data on the reduction of iron ore to iron with coke, the production of even rudimentary iron products was a prized art for thousands of years.[4] Without precise control of the carbon content of produced iron during processing, the production of steel was a carefully guarded secret process until the mid-19th century.[4] Without extensive knowledge of dislocation behavior as a function of temperature, brittle failure of steel at low temperatures continued to be a problem through the Second World War.[3] Even for a single massively important materials system, it has taken humanity thousands of years to
come close to understanding the iron-carbon materials tetrahedron without a complete set of thermal data. If one adds additional degrees of freedom to this task by the consideration of alloying, the problem quickly exceeds the scope of exploration by simple experimentation.

Figure 1.1: The traditional materials tetrahedron: an interplay of properties, processing and structure determines performance.

Fortunately, one does not have to rely on only guess and check to probe much of the materials tetrahedron. Computational materials science aims to guide and supplement experiment by providing functional relationships, testable hypotheses, and estimates of properties that may be difficult or expensive to directly access through experiment. Among the methods that allow examination of atomic level details, density functional theory (DFT) is currently widely used and demonstrates extreme versatility in treating a variety of dissimilar systems.
DFT, described in greater detail in chapter 2, is at its core a method to determine the ground state internal energy of an electron-ion system at zero temperature. For many materials systems, it will be sufficient only to compare the ground state energies calculated by DFT since the energy differences are great enough that thermal excitations of the atoms are unlikely to surmount them. The vast majority of published DFT work thus concerns only total internal energy calculations. As a rule of thumb, total energy differences that are in the range of $10k_B T$ or greater make the probability of a transition event occurring in the neighborhood of $10^{-5}$ and thus negligible. As an example for such a system, we describe our work on a planar fault system in Ni$_3$Al in which such ground
state energy comparisons are sufficient to demonstrate solute segregation and suppression of twin formation in chapter 3.

For materials systems exhibiting energy differences smaller than $10k_B T$, consideration of the full free energy at finite temperatures becomes relevant. This is often the case in phase transitions, where the ground state energies of competing phases may differ by $\sim 0.01eV$, as well as in systems containing point defects, where the free energy of formation may be significantly lower at high temperatures. Free energies require, in addition to the standard zero-temperature internal energies that are the results of DFT calculations, entropic contributions, as well as calculation of the pressure term for systems where non-zero pressures are relevant (which is not the case in the presented work). Entropic contributions come from various sources, from the electronic and configurational entropies, whose calculation is straightforward through analytical expressions, to vibrational entropies. For the latter, several computational approaches exist; however, since most of them are based on molecular dynamics (such as thermodynamic integration) and require a computational effort in excess of what is feasible with DFT molecular dynamics, the most commonly used framework used within DFT studies is the quasiharmonic approximation (QHA). QHA requires just calculation of the phonon density of states for different crystal volumes and works well for stable materials up to a large portion of melting temperature, in excess of 50% in most cases.[5,6] In this thesis, we make heavy use of QHA in calculating the thermodynamic properties of metallic phases and defects in BCC metals. However, we will show that some of the implicit assumptions of QHA typically used in calculating atomic
displacement-force relationships can influence its predictive abilities significantly. This especially concerns the magnitude of atomic displacements that can be rather large at elevated temperatures and thus introduce anharmonic effects that can go well beyond thermal expansion, as we will show in chapter 5. We particularly will show that such displacements may stabilize systems which exhibit a mechanical instability without the stabilizing effects of thermal excitations. Such systems challenge traditional atomistic approaches utilizing DFT because their configurations represent saddle points in the energy-displacement surface and perturbations to their structure will result in relaxation to a different atomic configuration. In order to address these issues, we have developed a simplified method for treating such systems that consists of determining the necessary atomic displacement to project the anharmonicity-dominated large displacement on the harmonic energy-displacement relationship assumed in QHA, which we describe in chapter 4. While other methods to achieve the same goal have been previously proposed, we found them to be inadequate for many purposes due to their excessive computational demands. Even after spending considerable work on optimizing the execution of our DFT codes on the available computational resources (appendix C), these demands could not be shrunk into the accessible range. We will show that our newly proposed large-displacement method and information about atomic displacements at finite temperature make the calculation of thermal properties accessible for a large number of strongly anharmonic systems that were previously inaccessible, and go on to investigate the thermodynamics of vacancy formation in a wide range of BCC systems with different levels of intrinsic displacement-amplitude generated anharmonic effects in chapter 5.
Having considered the energetic effects of thermal excitation and intrinsic anharmonicity, we then extend our discussion to extrinsic anharmonic effects, specifically the effects of an external field on atomic motion. Whereas coupling of atomic vibrations to electric fields is an effect that has been known for decades, such a coupling was not believed to exist for magnetic fields applied to non-magnetic materials. However, by studying the modification to the harmonic force constants of specific vibrational modes in InSb, we show in chapter 6 that atomic displacements create diamagnetic moments, which then couple to external magnetic fields. Using DFT, we predict the field-induced moments and their effect on thermal transport, which in non-metals is dominated by lattice vibrations and their interactions. We finally show that our predictions are in excellent agreement with experiments performed in collaboration with our work.

Thus, in summary (chapter 7), we show that thermal and anharmonic effects are well within the reach of modern DFT methods. We have applied existing methods to previously unstudied systems such as the full set of vacancies in BCC metals as well as total-energy dominated phase transformations in Ni-base superalloys. We then have proposed extensions over previous theory in the form of large-displacement modeling of anharmonic vibrational entropies, which allows order-of-magnitude faster calculations of vibrational entropies (or, equivalently, allows for considerably larger system sizes), which then is used to study phase stability and properties for mechanically-unstable high-temperature BCC phases and vacancies in them. We finally demonstrate how field-induced anharmonicities can be captured with DFT-based frozen-phonon calculations.
REFERENCES


Chapter 2: Overview of fundamentals and execution of density functional theory

Thorough discussion of density functional theory (DFT) necessitates a basic understanding of chemistry that is beyond the scope of this document. This description begins with the assumption that the reader is generally familiar with the role of electrons in bonding and the idea that one may determine the properties of an electron system using the Schrödinger equation.

2.1 MANY-BODY ELECTRONIC THEORY: THE SCHROEDINGER EQUATION

We start by assuming in a material system that we are dealing with a more-or-less time-independent electron-ion system, at least as far as the electronic structure is concerned. This approximation is termed the Born-Oppenheimer approximation: it implies that our electronic adjustment will occur nearly instantaneously in response to any ionic movement, and is an excellent representation of three-dimensional periodic systems.[1] We may then represent the energy $E$ and wavefunction $\Psi$ of a single electron in an external potential $V$ using the time-independent Schrödinger equation,

$$ -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi = E\Psi, $$

where the first term represents the kinetic energy of the electron and $m$ is the electron mass. Naturally, for an electron in a many-body electronic system, the external potential term $V$ must be broken down to include interactions with positively charged ion cores,
interactions with other negatively charged electrons, and any applied potential field. Thus, the previous equation may be expanded to reflect these contributions:

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) + \sum_j U(r, r_j) + V_{app}(r) \right] \Psi = E \Psi.
\]

In this expansion, we see that though interactions with ion cores and applied potentials are decoupled from other electronic states in the system, the electron-electron interactions represented by the summation term will become increasingly complex as we treat systems with multiple electrons. We may then consider the complete Schrödinger equation for a system of \( N \) electrons:

\[
\left[ -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(r_i) + \sum_{i=1}^{N} \sum_{j<i} U(r, r_j) + \sum_{i=1}^{N} V_{app}(r) \right] \Psi = \sum_{i=1}^{N} E_i \Psi = E_{sys} \Psi.
\]

As might be suspected from the complexity of the previous result, even a numerical solution for such a system of more than an extremely limited number of electrons exhausts current computational resources within approaches such as quantum Monte-Carlo calculations, necessitating an alternate approach.

### 2.2 FROM MANY-BODY TO EFFECTIVE FIELD: DENSITY FUNCTIONAL THEORY

As was mentioned above, the foremost candidate for simplification for calculation purposes in the Schrödinger equation is the electron-electron interaction term, which describes a many-body interaction that cannot be effectively solved for large numbers of electrons. Density functional theory is a relatively simple series of modifications that transform this intractable numerical problem into a merely difficult one. Of primary important is Hohenberg and Kohn's proof of one-to-one mapping between the ground-
state electron density and the ground-state energy,[2] which tells us that there is a unique solution to the numerical problem we wish to solve. A corollary to this proof is that an electron density which minimizes energy must represent the ground state as determined by the Schrödinger equation; this allows us to solve the complex multivariable differential equation by a minimization in one dimension, energy. The second major development in DFT is the Kohn-Sham equations allowing the treatment of the many-body Schrödinger problem as a series of single-electron interactions with the electron density of the atomic system being considered.[3] In the Kohn-Sham equations, the electron-electron interactions are broken down into two terms, $V_H$ and $V_{XC}$. The first term, called the Hartree potential, describes the interaction between the electron and the charge density of the system and takes the form

$$V_H(r) = e^2 \int \frac{n(r')}{|r - r'|} d^3r',$$

where $n(r')$ is the charge density arising from electrons in the system and $e$ is the fundamental electron charge. The second term, called the exchange-correlation potential, is defined such that it accounts for energy differences between the many-body electron system and the effective potential system considered in the Kohn-Sham equations. In our transition from a many-body system to a system of electrons interacting with an electron density, we will have lost a level of quantum detail if we do not have some way of accounting for interactions between specific elections (e.g. spin interactions), called exchange, and for interactions between large groups of electrons, called correlation. The physically correct form of this potential is not known, nor are there universal approximations that produce adequate results for all electronic systems.[4] A very basic
functional approximates this electron behavior as analogous to that of a homogeneous electron gas, and is known as the local density approximation (LDA), while more recent advances consider gradients within the electron density (GGA) or precisely calculate Hartree-Fock electronic interactions for a certain portion of the potential space.[4] For metallic systems, the GGA-type method of Perdew, Burke, and Ernzerhof [5] produces results in good agreement for lattice parameter and energy, and so this method is generally employed throughout this work.

The Kohn-Sham equations break down the many-body electronic problem into a series of single-electron interactions to allow the development of a tenable algorithm for the solution of a many-electron system: (1) take an initial charge density, which may be from a previous step or from some guess such as free-atom orbitals; (2) solve the Kohn-Sham equations to determine the single electron wavefunctions given this charge density; (3) calculate the charge density corresponding to the summation of the solved wavefunctions and (4) compare the initial and final energy and charge densities to determine if convergence criteria are met. It is this iterative process that is at the core of all DFT calculation methods.

Despite the numerical simplification that results from the derivation of DFT, inquiries into materials systems requiring highly converged calculations and/or large calculation cells present computational tasks that test the limits of publicly available computing resources. A high level of optimization is necessary to execute DFT software and effectively gather results for these calculations. Appendix C presents data on optimization that was conducted to facilitate the research presented in this thesis.
Thermodynamically, we know that inclusion of thermal effects is achieved by the addition of an entropy term to our energy calculation. We start our consideration with the complete Gibbs free energy of the system, defined to be \( G = E + pV - TS \), where \( E \) is the internal energy, \( pV \) (pressure times volume) describes work done to the system by external pressure, and \( TS \) defines the contribution of entropy \( S \) with temperature \( T \). In many DFT calculations, relaxation of a structure without external pressure is a prerequisite step to determining the internal energy; for all calculations performed in this work, we taken steps to minimize the importance of the pressure contribution to free energy. Therefore, we will focus on the Helmholtz free energy, \( F = E - TS \), which highlights the entropic contributions to the free energy.

We are able to consider three distinct contributions to the entropy of a material system: the electronic entropy arising from the probabilistic nature of the electron distribution in the material, configurational entropy arising from different atomic arrangements in the system, and vibrational entropy from the displacement of atoms from their equilibrium lattice positions at finite temperatures. The mathematical formulation for the electronic entropy is well understood and minimized in most DFT codes as a direct consequence of converging the electronic structure to a ground state configuration; thus, we may consider its contribution to be vanishingly small and uniform as a result of properly executed DFT methods. The formulation for configurational entropy is likewise well understood and its contribution may be thoroughly investigated by considering different possible atomic arrangements in the material system; however, configurational entropy contributions are
extremely small for non-alloy systems due to the high energy of alternatives to the perfect
crystal structure (defects) and small for systems in which the energy differences between
alternative atomic arrangements are large, e.g. the planar defect system considered in
chapter 3. As a result, we focus in this work on the contribution of vibrational entropy to
free energy.

To consider the vibrational entropy contribution in a material system, we need a method
to separate and characterize the random thermal motion of the individual atoms. This is
typically achieved by decomposition into Fourier space where we may consider distinct
displacement patterns of atoms, described below. Assuming that we have characterized
these coordinated atomic motions, we may then treat the crystal lattice as we would a
harmonic oscillator, and calculate the energy contributions from each independent
displacement pattern in terms of its characteristic frequency. This approach is known as
the harmonic approximation when the lattice dynamics are considered to be independent
of temperature and atomic volume. A more thorough approach, the quasiharmonic
approximation, allows the lattice dynamics to change as a function of crystal volume,
which will change as a function of temperature due to thermal expansion. Within the
quasiharmonic approximation (QHA), we can calculate the zero-point contribution to
energy $E_{ZP}$ at a given volume $V$ using the formula $E_{ZP}(V) = \frac{1}{N} \sum_{k,i} \frac{1}{2} h \omega_{k,i}(V)$, where
$\omega_{k,i}$ is the characteristic frequency of single displacement pattern and $N$ is the number of
particles in the system. Likewise, we can calculate the vibrational contribution to entropy
$S$ at a given $V$ using the formula

$$S(V) = -\frac{1}{N} \sum_{k,i} k_B \ln \left[ 1 - \exp \left( -\frac{h \omega_{k,i}(V)}{k_B T} \right) \right] + \frac{1}{N} \sum_{k,i} k_B \frac{h \omega_{k,i}(V)}{k_B T} \left[ \exp \left( -\frac{h \omega_{k,i}(V)}{k_B T} \right) - 1 \right]^{-1},$$
where \( k_B \) is the Boltzmann constant. QHA is a standard approach used with DFT to determine the contribution of vibrational entropy to a material system.

2.4 FROM ATOMISTICS TO THERMODYNAMICS: PHONON THEORY

If we consider the previously discussed random motion and its decomposition using a Fourier transform to the reciprocal lattice, we discuss patterns of these displacements in the form of standing waves with distinct frequencies that exist with various symmetries and periodicities that match the crystal lattice. We call each individual vibrational displacement pattern a phonon mode, and the atomic motion that is the superposition of all phonon modes operating simultaneously is the random thermal motion of atoms in the crystal lattice. Individual phonon frequencies may be found by finding the square root of the eigenvalues of the dynamical matrix

\[
D_{\alpha\beta}(k) = \frac{1}{\sqrt{M_s M_t}} \sum_{\mathbf{R}} \Phi_{\alpha\beta} e^{i\mathbf{k}\cdot\mathbf{R}},
\]

where \( M_s \) is the ionic mass of the atom under consideration, \( \Phi_{\alpha\beta} \) is the force constant matrix, and \( \mathbf{k} \) and \( \mathbf{R} \) are the reciprocal space point under consideration and Bravis lattice vector, respectively.

Three well documented approaches exist to achieve a thorough characterization of lattice dynamics from DFT: the frozen phonon method,[7] the finite-difference small displacement method,[8] and density functional perturbation theory (DFPT).[6,9]

In the frozen phonon approach, the ground-state energy is calculated using DFT as a function of atomic displacement. Lattice dynamics are then determined by comparing energies corresponding to various displacement patterns. In principle, a calculation cell can be constructed to determine the properties of any individual phonon within the Brillouin zone. However, Brillouin zone points corresponding to low-symmetry phonon
modes will require the use of extremely large supercells, limiting this approach to calculation of effects for displacement patterns with a high degree of symmetry.

In the finite-difference small displacement method, a series of small perturbations to symmetry-independent atomic positions in a calculation supercell are used to calculate the force response to atomic displacements in the material system. These symmetry-independent force calculations are then combined with the symmetries of the crystal lattice to construct a force constant matrix $\Phi$ by taking a numerical derivative and the eigenvalues of the related dynamical matrix are calculated. This method makes several numerical approximations that may decrease accuracy but has the advantage of requiring only a small number of symmetry-independent energy calculations to be performed.

Within DFPT, the response of a material system to an external perturbation such as a standing wave or external field is calculated by considering the Taylor expansion of the perturbing potential as it relates to the solution of the ground state electronic problem. The advantage of this approach is that it may be conducted on very small calculation cells with no loss of accuracy, provided that the mathematical form of the perturbing potential is known with sufficient accuracy to consider the important terms of the Taylor expansion. In practice, the mathematical form is likely approximate and will not accurately treat large deviations from the ground state (e.g. high-temperature atomic displacements) as accurately as small perturbations.

### 2.5 ENERGETIC TREATMENT OF DEFECTS

When we consider an atomic system containing a defect, it is necessary to consider the reference system for energy calculations such that the atomic compositions of the two
systems are equivalent. For an elemental system, we may therefore calculate the zero
temperature formation energy of a defect \( E_f = E_{\text{cell,defect}} - NE_{\text{perfect}} \), when \( E_{\text{cell,defect}} \) is
the internal energy of a calculation cell containing a defect from DFT, \( N \) is the number of
atoms in the defect calculation cell, and \( E_{\text{perfect}} \) is the internal energy per atom of the
perfect structure. We may likewise define the free energy of formation: \( F_f = F_{\text{cell,defect}} - NF_{\text{perfect}} \); then, using our thermodynamic relation \( F_f = E_f - TS_f \), we can
determine the entropy contribution of defect formation by calculating the free energy of
formation of the defect across an appropriate temperature range and performing a linear
fit to these data. The energy of formation \( E_f \) obtained from this approach is consistent
with that obtained by comparing the internal energies using the above equation for stable
systems, but may be significantly different for systems that exhibit anharmonic behavior.

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Chapter 3: Segregation and η phase formation along stacking faults during creep at intermediate temperatures in a Ni-based superalloy

This chapter represents a set of calculations performed on a material system in which thermal behavior is dominated by chemical effects instead of vibrational ones, allowing consideration of only ground-state energy differences. Nikolas Antolin performed all the DFT calculations for this work and performed subsequent analysis of strain and chemical effects on energetics. The following chapter contains verbatim excerpts from the corresponding publication by T.M. Smith, B.D. Esser, N. Antolin, G.B. Viswanathan, T. Hanlon, A. Wessman, D. Mourer, W. Windl, D.W. McComb, M.J. Mills, in Acta Materialia, Volume 100, pages 19-31, publish on 1 November 2015 marked by italic font.

3.1 INTRODUCTION

Polycrystalline nickel-based superalloys are essential materials for disks in the hot section of jet turbine engines due to their high strength and microstructural stability at elevated temperatures. Until recently, the fatigue performance of polycrystalline turbine disks has been a property of primary importance. As the operating temperature and engine hold times increase, developing a complete understanding of creep deformation becomes imperative. Recent studies have shown that the prominent deformation modes are strongly temperature-dependent. Operation of $\frac{1}{2}(110)$ dislocations in the $\gamma$ matrix and cutting of the $\gamma'$ precipitates by pairs of $\frac{1}{2}(110)$ dislocations (linked by an antiphase boundary or APB) is observed predominantly following lower temperature (400–600 °C)
testing,[1,2,3] for which the temperature dependence of the alloy strength is small.
Stacking fault shearing and microtwinning become active at higher temperatures (600–800 °C), particularly under low strain rate or creep conditions.[4,5,6] Understanding the rate-limiting process for these higher temperature deformation modes is important for creating more accurate models of creep behavior and for improving the temperature capability of future alloys.

The mechanistic reason for the onset of time- and temperature-dependence at intermediate temperatures is not obvious since both stacking faults and microtwins are created by the shear movement of partial dislocations on close-packed {111} planes. For example, Chen and Knowles [7,8] proposed a mechanism for creation of superlattice extrinsic stacking faults (SESFs) based on the passage of two different $\frac{1}{3}(112)$ superpartials on adjacent {111} planes. The $\frac{1}{3}(112)$ superpartials are created by the interaction of two like $\frac{1}{2}(110)$ dislocations at the γ/γ' interface:

$$\frac{1}{2}[110] + \frac{1}{2}[110] = \frac{1}{3}[12\bar{1}] + \frac{1}{3}[211] \quad (1)$$

There are several concerns with this mechanism: (a) the strong repulsive forces between the parent dislocations that would resist their interaction, (b) the two dissimilar $\frac{1}{3}(112)$ dislocations cannot simultaneously experience a large Schmid factor driving the shearing event, and (c) since this is a pure shear process, it should not be strongly temperature dependent.

In early work by Kear et al.[9] and more recently by Decamps et al.[10,11], a mechanism for the creation of intrinsic and extrinsic faults in $L1_2$ precipitates was
proposed that involves individual $\frac{1}{2}(110)$ dislocations initiating shearing of the $\gamma'$ precipitate, thereby forming an antiphase boundary (APB). This high energy fault is presumed to create a favorable situation for nucleation of $\frac{1}{6}(112)$ Shockley partial on the plane of (or adjacent to) the APB, and is equivalent to the net shear of $\frac{1}{3}(112)$ dislocation, which is a partial dislocation in the $\text{L1}_2$ superlattice. Kear [9] proposed that the nucleation of the partial loop could yield a temperature dependence. However, analysis by Zhou et al.[12] has criticized the Decamps model since the nucleation of the Shockley partial loop $\alpha B$ on the pre-existing APB would require overcoming a very large activation barrier.

The earliest proposed mechanism for forming superlattice extrinsic stacking faults (SESFs) was put forward by Kear et al.[13] who postulated that a the combination glide of three differently signed Shockley partials could create the $\text{D0}_{24}$ crystal structure of the two layer SESF in an $\text{L1}_2$ precipitate. Soon after, they introduced the possibility that like-sign Shockley partial pairs could create a SESF; however, this scenario required the interaction of a dipole displacement near the dislocation core.[14] The introduction of the dipole displacement was their attempt to account for the wrong nearest neighbors that would be created in the ordered $\text{L1}_2$ structure due to the movement of Shockley partials. However, this concept of a dipole occurring at or near the dislocation core was not developed further and is not supported by more recent high resolution TEM analysis of partial dislocation configurations.[15,16,17]
More recently,[18] the concept of “reordering” has been suggested as a rate-limiting process under the assumption that stacking faults are created by the movement of combinations of \( \frac{1}{6}(112) \) Shockley partials rather than \( \frac{1}{3}(112) \) superpartial. For instance, Decamps et al.[19] proposed that the dissociation of two like \( \frac{1}{2}(110) \) type dislocations at the interface leads to shearing of the precipitates by \( \frac{1}{6}(112) \) Shockley partials. These partials form a high energy, complex stacking fault (CSF) during the shearing process. Therefore, if two partials shear a precipitate on adjacent planes, forming a two-layer CSF, the reordering process described by Kolbe et al.[18], and later in more detail by Kovarik et al.[20] could occur, converting the high energy, two-layer CSF into a low energy SESF. Since reordering is a local, diffusion-mediated process, it could potentially be responsible for the onset of time- and temperature-dependent behavior at intermediate temperatures. Indeed, Kovarik et al. used DFT calculations to explore possible diffusion pathways for reordering, and the associated activation barriers.[3] A simple model of deformation based on reordering as the rate-limiting process was developed by Karthikeyan et al.[21]

These previous models have been challenged recently by several studies that have revealed the presence of compositional fluctuations at stacking faults in both Ni-base [22] and Co-base [23] superalloys-studies enabled by the advent of advanced, thin-foil, energy dispersive spectroscopy (EDX) capabilities. These results have lent important support to the earlier observation of increased intensity of atomic column positions at stacking faults in alloy ME3 [6] and CMSX-4.[24] For the Ni-base alloys, the indication
from initial EDX analysis is that the composition at superlattice intrinsic faults (SISFs) within the γ' tend toward that of the FCC γ matrix. In the case of the Co-base alloys, the proposed explanation by Titus et al.[20] is that the local D0₁₉ structure of the SISF is tending toward that of the thermodynamically favored Co₃Ti phase. Thus, Titus et al.[20] argue that the shearing process is the result of a displacive–diffusive transformation at the fault.

Our work provides the first structural and chemical analysis of superlattice extrinsic stacking faults (SESFs), which are the most prominent defect for the studied Ni-base superalloy under creep conditions at intermediate temperature. Definitive evidence for a local displacive–diffusive phase transformation, from faulted γ' to the η phase, is provided for the first time. In addition, evidence for the formation of a distinctive solute atmosphere surrounding the leading partials of the SESF is also obtained for the first time. In order to explore the origin of this mechanism and confirm that it is sensible, we perform density functional theory (DFT) [25] calculations and find that the observed segregation behavior of the solutes can be explained by a changed bonding environment around the SESF. The atomic structure used in the DFT calculations is validated by simulated HAADF images. Together, these results provide further evidence for the importance of long-range diffusional processes in association with shearing of γ' particles at intermediate temperatures.

3.2 MATERIALS AND EXPERIMENTAL METHODS

3.2.1 Sample Preparation
A single crystal analog of a disk alloy with minor compositional variations relative to the commercial alloy ME3 (with increases in Ta, Hf and Nb and decreases in Co and Cr as compared to ME3 which typically has 50.1% Ni, 20.6% Co, 13.0% Cr, 3.8% Mo, 2.1% W, 0.9% Nb, 2.4% Ta, 3.5% Al, 3.7% Ti, 0.04% C, 0.03% B, and 0.05% Zr) was obtained from GE Global Research Center in the form of a single, large casting after a heat treatment that formed a bimodal γ' precipitate microstructure. Before testing, microstructure analysis on this Alloy X was conducted to obtain volume fraction and average size for the secondary and tertiary precipitates. Samples were polished progressively down to a 1200 fine grit using SiC polishing pads and then further polished with a 0.05 μm colloidal silica finish. The alloy was then etched with a solution of 2 mL hydrofluoric acid, 30 mL nitric acid, and 50 mL lactic acid that preferentially etched the γ' precipitates. Using an FEI Sirion scanning electron microscope (SEM), backscattered electron micrographs of the alloy’s microstructure were obtained and then analyzed using ImageJ.[26] For statistical significance, multiple images were obtained and over a thousand particles were included in the analysis. Figure 3.1 shows an example of the microstructure present in Alloy X. The combined volume fraction of the secondary and tertiary γ' was approximately 55.5%. The average secondary precipitate diameter was 300 nm and the tertiary precipitate size was approximately 30 nm.

3.2.2 Creep sample orientation and preparation
Sections were prepared from the bulk single crystal casting and etched with a solution of Walkers etchant to validate that the casting was indeed a single crystal. Orientation Imaging Microscopy (OIM) was used to determine the orientation of the bulk crystal
prior to extracting compression samples. Surfaces were again polished to a 0.05 μm colloidal silica finish. An [001] oriented single crystal silicon sample was used for calibration to improve orientation accuracy.

![Back-scatter SEM image of the microstructure of Alloy X](image)

Figure 3.1: Back-scatter SEM image of the microstructure of Alloy X where the γ' precipitates have been etched away (black) from the γ channels (grey).

Compression cuboids with a 1:1:2.5 dimension ratio were extracted from the bulk crystal using Electrical Discharge Machining (EDM). The sides of the individual compression cuboids were then polished to a 1200 fine grit finish to reduce the damage layer created from the cutting process. A monotonic compression creep test was performed on an [001] oriented sample at 760 °C and 552 MPa until 0.5% plastic strain was reached. Linear variable displacement transducers (LVDTs) were used on an MTS 810 compression cage to directly record the displacement of the compression plattens. Temperature was recorded using two K thermocouples. After the desired plastic strain was reached, the test was stopped and the specimen was very quickly returned to room temperature using a fan. The compression sample remained under load in order to
preserve the deformation substructure that was present at the end of the test, and to minimize and changes to local structure and chemistry associated with dislocations and stacking faults. The maximum cooling rate was 4 °C/s from 760 °C to 450 °C.

3.3.3 Microscopy methods

Post creep samples were prepared by polishing off the oxidized layer and then extracting transmission electron microscopy (TEM) foils normal to the compression axis using an FEI Helios Nanolab Dualbeam 600 focused ion beam (FIB). Samples were thinned at 5 kV and then further cleaned using a Fischione Nanomill. Thin foils were analyzed using low annular angle dark field (LAADF) diffraction contrast on an FEI Tecnai F20 field emission 200 kV STEM. Dislocation analysis using STEM has many advantages over conventional TEM. It was shown by Phillips et al.[27,28,29] that conventional $g \cdot \mathbf{b}$ invisibility rules still apply for STEM and therefore images can be interpreted in the same fashion as conventional TEM (CTEM) images. STEM images exhibit decreased fringe and bend contour contrast and better signal to noise ratios when compared to CTEM.[30,31] Both traditional two beam conditions and higher-order $g$ imaging were employed in the present dislocation analysis.[27]

In CTEM, zone axis diffraction contrast imaging is rarely employed due to the low contrast images that correspond to these high absorption orientations. In STEM, the image intensity of the bright field (BF) and annular dark field (ADF) are averaged together allowing for high contrast defect micrographs. The ability to image on low index zone axes gives the capability to view multiple slip systems simultaneously for improved dislocation assessment.
Samples were also extracted normal to (110) orientations (longitudinal to the [001] compression axis) in order to view stacking faults edge-on using high angle annular dark field (HAADF) zone axis imaging conducted on a probe-corrected Titan3™ 80–300 kV. High resolution EDX mapping was conducted at 300 kV using an image-corrected Titan3™ 60–300 kV with a Super-X detector utilizing the Bruker Esprit software. The Super-X EDX detection system uses four silicon drift detectors that are located radially around the objective pole piece and specimen stage for improved collection performance. This technique has recently been used to observe segregation along edge-on stacking faults traversing through γ' precipitates.\cite{23,32} Integrated line scans were conducted and quantified through Cliff–Lorimer analysis \cite{33} using experimental $K_\alpha$ energies for Ni, Co, Al, Nb, Cr, Mo and Ti. The Cu specimen holder signal was avoided by using the $M_\alpha$ lines for Ta and W since the $L_\alpha$ Ta and W peaks corresponded too closely to a Cu peak to be accurately considered. Deconvolution for the W and Ta $M_\alpha$ peaks, as well as background subtraction was used to reduce the influence of Bremsstrahlung.

3.3 RESULTS

3.3.1 Diffraction contrast STEM

Post-creep STEM analysis illustrates that the deformation mechanisms primarily consist of precipitate shearing by stacking faults as well as dislocation build-up concentrated in the γ channels. In Figure 3.2, examples of these prominent deformation mechanisms are shown using [001] zone axis bright field and dark field images. Conventional $g \cdot R$ analysis utilizing diffraction contrast STEM confirms that the observed stacking faults are primarily extrinsic in nature, lying on inclined \{111\} planes. This is in agreement
with the observations by Decamps et al. [34]. The presence of SESFs on several \{111\} plane families demonstrates that multiple slip systems are active. It is noted that the dislocation and stacking fault content is very low in the as-heat-treated condition. Although most of the observed shearing events are isolated within the \(\gamma'\) precipitate, some shearing is also observed that extends through both \(\gamma\) and \(\gamma'\). High-resolution HAADF imaging has demonstrated that these are usually microtwins and not extended SESFs. Extensive \(g \cdot b\) analysis has revealed the existence of all 6 \(\frac{1}{2} (110)\) type dislocations; however \(\frac{1}{2} [10\bar{1}]\) and \(\frac{1}{2} [01\bar{1}]\) were the most prominent for the particular sample tested. Figure 3.3 shows an example of these two dislocation types together at the \(\gamma/\gamma'\) interface (determined from more complete \(g \cdot b\) analysis, not shown). In this particular example, these dislocations appear to cross each other, presumably at the interface.
3.3.2 Segregation and ordering along stacking faults

Observations along the [110] zone axis using high resolution HAADF imaging is used presently to characterize the local structure and composition variation at two-layer SESFs in Alloy X. As shown in Figure 3.4, Z-contrast HAADF-STEM imaging suggests heavy element segregation due to the appearance of a characteristic, grid-like pattern of brighter atomic columns at the fault.

Similar grid-like ordering has also been observed along SESFs in a CMSX-4 alloy crept at 750 °C.[24] This feature at the fault is distinctly different from the usual L12 ordering of the γ' precipitate which can also be observed in Figure 3.4 from the presence of the alternating contrast of the (001) atomic planes. The brighter planes correspond to the Al-sites where heavier elements such as Ta, Nb and W naturally replace Al; therefore, the
ordering seen along the SESF is predominantly caused by segregation of higher Z elements on the Al lattice sites. Since the bright contrast present in HAADF images does not prove segregation, nor quantify the segregating elements, EDX mapping was conducted on multiple SESFs in order to more completely specify the nature of the segregation. Figure 3.5 shows the elemental EDX maps along a SESF that had vertically sheared a $\gamma'$ precipitate.

![Figure 3.4: HAADF-STEM image obtained along the [110] zone axis revealing a grid-like ordering along a SESF inside a $\gamma'$ precipitate.](image)

Two fiducial markers, approximately 2 nm diameter holes, were “drilled” into the sample on each side of the SESF by positioning a converged electron beam with a high current density over a specific site for 30 s. These fiducial nanoholes aid the software correction for drift during the scan. EDX analysis consistently indicated Al and Ni to be
deficient along SESFs. Conversely Co, Nb, Ti and Ta (and to a lesser extent W) all segregated along the fault. The Cr elemental map, though not displaying segregation at the fault, does highlight the appearance of Cr rich particles (which are postulated to be $\gamma$ particles) averaging 2–6 nm in diameter inside the secondary $\gamma'$ precipitate. The influence of these particles on the creep strength of the alloy warrants further investigation as it is apparent that these small particles can be sheared and may be possible sources of Co within the secondary precipitates.

To quantify the compositional changes along the SESF, elemental profiles were created across the SESF, as shown in Figure 3.6. These intensity data were vertically integrated parallel to the fault in order to improve signal-to-noise, and then converted to composition using uncorrected k-factors. The results confirm the qualitative results obtained from the elemental maps. Both Ni and Al are deficient along the fault, while Ta, Nb, and Co are enriched at the fault as compared to the bulk precipitate. Both W and Ti also segregate slightly to the fault. It is expected that Co, having similar properties to Ni, would replace Ni along the SESF;[35] whereas, Nb and Ta are known $\gamma'$ formers that replace Al.[36] Higher resolution line scans were obtained in an attempt to determine which species were responsible for the grid-like ordering along the fault. These scans were not vertically integrated and were placed directly over the atomic columns exhibiting the higher intensity, grid-like ordering. The combined total intensities for Al and Ta from these scans are shown in Figure 3.7b. Ta was the only element that appeared to show statistically significant peaks in its line scan that correspond to the higher Z-contrast seen in the HAADF images, while Al was deficient across the fault,
although this trend is much clearer in Figure 3.6. Thus, Ta appears to be the only element to clearly correlate with the HAADF images since it has a relatively large cross-section for ionization, thereby producing a greater signal, as well as the fact that Ta is found in significantly higher concentrations along the fault (~5 wt%) when compared, for example, to Nb (~2 wt%) and W (~1 wt%).

*Figure 3.5: EDX elemental map of a vertical SESF showing segregation along the fault.*
For improved understanding of the mechanisms responsible for SESF formation, faults terminating inside a $\gamma'$ precipitate were also analyzed. For each terminated SESF, atomic resolution HAADF-STEM images of the leading partial(s) were recorded, and a Burgers circuit analysis was performed, as indicated in Figure 3.8a, in order to determine the type of dislocations responsible for creating the SESF.

Multiple examples revealed that two adjacent and identical $\frac{1}{6}(112)$ Shockley partials were responsible for forming the SESFs. Figure 3.8b, supports the conclusions from the Burgers circuit analysis indicating that a narrow (approximately 0.5 nm wide), one-layer fault is in the lead, then transitions to the two-layer fault. Since the leading partial is a
\(1/6 (112)\) partial, nearest neighbor violations must be created in their wake,[10,11] necessitating a re-ordering process in order to form a true SESF with a localized D0\(_{24}\) crystal structure.

Figure 3.7: (a) An example of an EDX line scan over the prominently segregated atomic columns. (b) The summed intensity for Ta (purple), Al (red) and the corresponding HAADF intensity profile (black) from the line scan.
Compositional EDX analysis was also conducted on these leading partials. Figure 3.9a shows examples of elemental maps for an SESF. Figure 3.9b, displays the integrated elemental profiles taken across the SESF very close to its termination within the precipitate at the leading partial.

Most remarkably, the local regions around the leading partials of the SESF are enriched in Cr, Co and Mo; whereas, the γ' formers (Al, Ti, Ta, and W) along with Ni, appear to be reduced near the partial. Another important observation is that the segregation present on this SESF is similar to that found on other SESFs (e.g. see Figure 3.6) far from the leading partials. This SESF exhibits segregation of Ta, Nb, Ti, and W along the fault while, Cr, Al, and Ni were either deficient or not detectably changed. Though it may appear that Mo has segregated along the SESF, further analysis indicates that the amount of Mo estimated to have segregated is within the error in measurement.
Figure 3.9: (a) The elemental maps of a terminated SESF. (b) A vertically integrated EDX line scan across the SESF present in Figure 3.10a.
3.4 DISCUSSION

3.4.1 SESF Formation

The experimental results have coupled diffraction-contrast and HAADF imaging with state-of-the-art EDX analysis to provide important new insights into the shearing of precipitates by stacking faults. To begin, the frequently observed interaction of different \( \frac{1}{2} (110) \) dislocations along the \( \gamma/\gamma' \) interface combined with the presence of isolated SESFs, leads to a new hypothesis for the formation of isolated SESFs, which expands on the models of Kear and Decamps for this process.\[11,37\] Figure 3.10a and b below illustrates this new model which is analogous to that presented recently by Vorontsov et al.\[24\] describing SISF formation:

The Decamps et al.\[19\] model assumes that the de-corrrelation of a \( \frac{1}{2} (110) \) type dislocation at the interface can lead to the shearing of the precipitate by a \( \frac{1}{6} (112) \) Shockley partial. This creates a CSF in the precipitate, which is energetically unfavorable and hence another \( \frac{1}{6} (112) \) Shockley partial is assumed to nucleate and shear the plane above the CSF. In essence, this is equivalent to the shear of a \( \frac{1}{3} (112) \) super-Shockley partial leaving behind a low energy SESF. However, their model ignores the nearest neighbor violations that would be created, and thus a two layer CSF would in fact be the result. Kolbe \[10\] realized that the wrong nearest neighbors at such a two-layer CSF could be eliminated by local diffusion (i.e. re-ordering), thereby creating an SESF.
Figure 3.10: (a) Two different full dislocations interact at the $\gamma/\gamma'$. (b) Leading, like-signed Shockley partials enter the precipitate forming a two-layer CSF, which re-orders (red circular arrow) to form a lower energy SESF. (c) Scenario incorporating new observations of both Cr and Co atmosphere surrounding the leading partials of the fault and the formation of $\eta$ phase immediately trailing the partials.

Figure 3.10 illustrates how this same scenario could occur involving two different $\frac{1}{2}(110)$ dislocations. As stated earlier, the two most prominent dislocations observed at the $\gamma/\gamma'$ interface were $\frac{1}{2}[10\Bar{1}]$ (BA) and $\frac{1}{2}[01\Bar{1}]$ (BC). In Figure 3.10a, both the BA and BC dislocations have become immobilized at the interface on parallel $(111)$ planes. The Shockley partial $\frac{1}{6}[11\Bar{2}]$ ($\delta b$), which experiences the highest Schmid factor (0.47) for a single crystal with a [001] stress direction, will shear the precipitate creating the reactions in Eq. (2) and the scenario illustrated in Figure 3.10b.
\[
\frac{1}{2}[10\bar{1}] \rightarrow \frac{1}{6}[2\bar{1}\bar{1}] + CSF + \frac{1}{6}[11\bar{2}] \quad (2a)
\]

\[
\frac{1}{2}[01\bar{1}] \rightarrow \frac{1}{6}[\bar{1}2\bar{1}] + CSF + \frac{1}{6}[11\bar{2}] \quad (2b)
\]

This will form a two layer CSF as described by Kolbe.\cite{Kolbe18} The operation of these partials has been supported through Burgers circuit analysis, as shown in Figure 3.8a. Reordering must occur in order to convert the two-layer CSF to an SESF and enable further extension of the fault.\cite{Kolbe18} This reordering mechanism, illustrated in Figure 3.10 and discussed in detail in Kovarik et al.\cite{Kovarik03} is potentially rate controlling. Local diffusion is required for reordering to occur. Kovarik et al. utilized VASP calculations to explore the possible diffusion paths, as well as the energy barriers associated with vacancy formation and migration near the SESF. It was found that the activation energy for reordering should be very similar to that for Ni self-diffusion. In this previous work, the effect of segregation and shear-induced phase transformation was not considered. An important new observation from the present work is the prominent Cr and Co segregation around the leading partials. The presence of a solute atmosphere of these elements is important in several respects. First, since these are elements favored in the \(\gamma\) (FCC) matrix, a higher concentration of them at the tip of the fault should significantly lower the CSF energy trailing the first Shockley partial, as well as the two-layer CSF trailing the passage of the second Shockley partial. Indeed, in the limit of a local FCC structure due to the high Cr and Co content, the faults trailing the partials would simply be intrinsic and extrinsic stacking faults containing no wrong nearest-neighbors, and consequently will have much lower energy than their CSF counterparts. The observation of the solute atmosphere therefore brings into question the concept of reordering as a
rate-limiting process. Instead, the movement the leading partials may be constrained by the diffusive motion of the solute atmosphere. This possibility has recently been proposed by Titus et al.[23] in the context of SISF propagation through γ' precipitates in Co base superalloys, although no direct evidence for a solute atmosphere was presented in their work.

3.4.2 η Phase Formation

It will now be shown that the segregation and structural features at the extrinsic faults within the γ' are actually consistent with the localized formation of η phase. Numerous experimental studies have demonstrated that formation of the η phase, exhibiting the hexagonal close packed (HCP) D02₄ crystal structure, has detrimental effects on the strength and durability of Ni-based superalloys. It has been shown that changing an alloy’s composition with respect to certain elements will promote the growth of η phase relative to the formation of γ', to the detriment of creep strength.[38,39,40,41,42] Bouse et al.[43] hypothesized that the η phase volume fraction will increase as the ratio of Ti + Ta + Hf + Nb relative to Al increases. Indirect support of this hypothesis can be derived based on the effect of carbon in both PWA1480 and IN792 + Hf alloys which promotes the formation of carbides involving η phase formers (Hf, Ta, Nb, and Ti). It was found that η phase formation was greatly reduced for both alloys. They further hypothesized that at lower temperatures a solid-state transformation from γ' to η phase can occur. In fact, it was concluded by Zhao et al.[44] through thermodynamic calculations that γ' was not an equilibrium phase above 750 °C and would transform to the η phase, which was in equilibrium for Nimonic 263. Asguri et al.[36] proposed that the passage of partials
through γ′ precipitates, and the consequent stacking sequence changes, could lead to a favorable local environment for η phase formation. This scenario is reasonable since the formation of an SESF inside a γ′ precipitate will locally form the D0$_{24}$ crystal structure that the η phase possesses;[13,45] however, no direct evidence for the connection between deformation-induced stacking faults in the precipitates and the formation of η phase has been reported prior to the present work.

Recently, variations in the structure and chemistry of the η phase have been recognized, where ordering of elements on the Al sites has been deduced based on high angle annular dark field (HAADF) Z-contrast imaging and diffraction simulations. Pickering et al.[46] reported the first instance where Nb atoms were ordering to certain Al sites, leaving Ti and Al to occupy randomly the other sites. Figure 3.11 shows a schematic of the unit cell of the η phase based on their observations.

![Figure 3.11: The structure of the Ni$_6$AlNb reportedly seen by Pickering et al.[23] in superalloy 718 plus.](image)

Figure 3.11: The structure of the Ni$_6$AlNb reportedly seen by Pickering et al.[23] in superalloy 718 plus.
As noted by Vorontsov et al.,[24] the grid-like ordering observed along SESFs in CMSX-4, and now in the present results on Alloy X, is similar to the local Z-contrast ordering observed for the η phase found by Pickering et al.[46] in Figure 3.11. The segregation revealed in the present EDX analysis is in agreement with this hypothesis. Numerous studies have reported Ta, Nb and Ti segregating to η phase at the expense of the γ′ phase.[39,40,43,45,47] Concurrently the absence of Cr and the reduction of Al along the faults aligns well with past chemical studies on η.[39,40,48] These observations, combined with the findings of Zhao et al.[44] leads to the hypothesis that the η phase has nucleated along the two-layer faults analyzed presently. The only difference between the η phase found in Alloy X and the one established by Pickering et al.[46] is the presence of Ta on the Wyckoff 2a sites along with Nb. Furthermore, the local D024 crystal structure along the SESF should be a local nucleation site for the η phase as suggested by Asguri et al.[45] Indeed no evidence for “bulk” η phase has been found at other lengthscales. It is still unknown what importance this γ′ → η phase transformation has on the shearing event, but the presence of segregation and local ordering along the SESFs terminated inside the γ′ precipitate indicates it may be rate-limiting, as suggested schematically in Figure 3.10c above.

3.4.3 Density Functional Theory Simulations

The DFT code VASP [25] was used to examine if the dependence of the chemical potentials of the solutes on ordering in the SESF would provide the necessary driving force for the observed segregation behavior, and also to explore whether the ordering is driven by strain-minimization or by chemical-bonding effects.
Cells containing 160 atoms were created consisting of 10 FCC-type \{111\} planes with Ni$_3$Al-type occupation of the lattice sites incorporating a SESF. Calculation cells contained solute atoms of Co, Nb, Mo, Ta, and W and combinations thereof, with compositions listed in Table 3.1. As suggested by experiment, Co occupied Ni superlattice sites, while all other solutes were placed on Al superlattice sites. This composition most closely matched the EDX data from the fault. In order to validate these choices, HAADF simulations as described in Section 3.4.4 were performed which reproduced the observed HAADF images very well, thus supporting the chosen structure. Structural relaxations were performed using a quasi-Newtonian algorithm with electron exchange treated with the generalized gradient approximation (GGA) including spin polarization in the formulation of Perdew, Burke, and Ernzerhof.[49] All calculations were performed using a 6×3×5 Monkhorst-Pack k-mesh with plane wave energy cutoffs at least 30% greater than the highest specified in the pseudopotentials used. For each composition calculated, two cells were relaxed: one with the solute atoms forming an η-phase at the defect boundary, and a second in which solutes were randomly dispersed at substitutional sites in the structure. The structures were first relaxed internally with no shape or volume change in the calculation cell, followed by expansion of the calculation cell perpendicular to the fault to minimize the stress in that direction. Energies of the internally relaxed cells as well as the out-of-plane lattice expansion percentages are listed in Table 3.2.
Table 3.1: Compositions of 160-atom SESF calculation cells.

<table>
<thead>
<tr>
<th>System</th>
<th>Composition</th>
<th>at%Co</th>
<th>at%Nb &amp;Ta</th>
<th>at%Mo&amp;W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>103Ni-22Al-17Co-18Nb</td>
<td>10.6</td>
<td>11.3</td>
<td>0</td>
</tr>
<tr>
<td>Mo</td>
<td>103Ni-22Al-17Co-18Mo</td>
<td>10.6</td>
<td>0</td>
<td>11.3</td>
</tr>
<tr>
<td>NbMo</td>
<td>103Ni-22Al-17Co-10Nb-8Mo</td>
<td>10.6</td>
<td>6.3</td>
<td>5.0</td>
</tr>
<tr>
<td>Ta</td>
<td>103Ni-22Al-17Co-18Ta</td>
<td>10.6</td>
<td>11.3</td>
<td>0</td>
</tr>
<tr>
<td>W</td>
<td>103Ni-22Al-17Co-18W</td>
<td>10.6</td>
<td>0</td>
<td>11.3</td>
</tr>
<tr>
<td>TaW</td>
<td>103Ni-22Al-17Co-10Ta-8W</td>
<td>10.6</td>
<td>6.3</td>
<td>5.0</td>
</tr>
<tr>
<td>NbTa</td>
<td>103Ni-22Al-17Co-10Nb-8Ta</td>
<td>10.6</td>
<td>11.3</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 3.12 and Figure 3.13 show the energy difference and the percentage out-of-plane expansion difference between the randomized and segregated relaxed structures, respectively. Energy differences suggest that the presence of the group 5 solutes (Nb and Ta) will result in strong segregation effects of solute to the SESF, even for solutes (e.g. W) that have very small driving force for segregation on their own. These energetics are consistent with the chemistry observed by EDX (Section 3.3.2). While both energy and strain are higher in the presence of group-5 solutes, differences in out-of-plane expansion do not correlate strongly to energy differences across atomic periods, leading us to conclude that the energy differences are not solely due to a strain effect that results from the localization of solute atoms. This is supported by studying the distribution of bond lengths in both structures: the average in both the segregated and randomized structures for atoms on each plane parallel to the SESF differs by less than 1% from the equilibrium bond length in Ni$_3$Al, and the standard deviation and range of bond lengths differs consistently at the limits of the SESF structure in both the segregated and randomized calculation cells.
Table 3.2: Relaxation results of 160-atom SESF calculation cells with segregated and randomized solute atoms.

<table>
<thead>
<tr>
<th>System</th>
<th>$E$ (eV)</th>
<th>Out of plane expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Segregated solute</td>
<td>Randomized solute</td>
</tr>
<tr>
<td>Nb</td>
<td>$-1003.20$</td>
<td>$-1002.55$</td>
</tr>
<tr>
<td>Mo</td>
<td>$-1005.31$</td>
<td>$-1004.96$</td>
</tr>
<tr>
<td>NbMo</td>
<td>$-1004.72$</td>
<td>$-1004.01$</td>
</tr>
<tr>
<td>Ta</td>
<td>$-1042.12$</td>
<td>$-1041.64$</td>
</tr>
<tr>
<td>W</td>
<td>$-1045.83$</td>
<td>$-1045.78$</td>
</tr>
<tr>
<td>TaW</td>
<td>$-1044.46$</td>
<td>$-1043.90$</td>
</tr>
<tr>
<td>NbTa</td>
<td>$-1020.48$</td>
<td>$-1019.85$</td>
</tr>
</tbody>
</table>

In order to determine if there is a chemical difference in bonding between calculation cells with solutes concentrated in the SESF and those with randomized solute positions, which should lead to electron rearrangements, Bader partial charges were calculated and plotted as a function of atomic position relative to the planar defect. Due to the limited number of solute atoms, it is most practical to study these effects on the most abundant species in the structures: Ni. Plotted in Figure 3.14 are the planar average Bader partial charges on Ni atoms as a function of atomic position for each of the solute systems. The red dash line represents the average Bader partial charge of the bulk structure. In these plots, we see that although the average Bader charge on Ni across the entire system changes insignificantly between the randomized and segregated calculation cells, there are significant changes in Ni charges between the SESF and the bulk phase when solutes are segregated to the SESF planes. From calculation, we find that the
Bader charge on Ni in bulk Ni$_3$Al is $\sim 0.61e$, which agrees well with the value we find in the bulk phase when solutes are confined to the SESF planes. On the other hand, the

![Figure 3.12: Energy difference between the randomized and segregated SESF calculation cells in eV.](image1)

![Figure 3.13: Percent difference in out-of-plane expansion in randomized and segregated SESF calculation cells.](image2)
charge on Ni is significantly smaller at the fault, indicating that the bonding is more “metallic” locally, and thus more tolerant to the presence of wrong (i.e. different from the correct neighbors in the ordered intermetallic) nearest neighbors and alloying species. Thus, chemical (bonding) energy gains come both from the decreased distortion of the ideal Ni₃Al-like charge transfer outside of the SESF (maximized charge) and decreased penalty from charged-atom interactions for the “wrong” bonding environment in the SESF (minimized charge).

3.4.4 HAADF Simulations

In order to validate the DFT-modeled structure, and thus further support the hypothesis that η phase is forming along the SESF, HAADF-STEM images of the SESF were simulated using the μSTEM program, based on the quantum excitation of phonons (QEP) model.[51] In the QEP model, a quantum mechanical approach is taken, whereby momentum and energy transfer are included through inelastic scattering: specifically through phonon excitation.

The crystal structure used as input for the image simulation was the relaxed Nb-Ta system described in Section 3.4.3 with out-of-plane expansion and solute atoms segregated to the SESF. As seen in Figure 3.15, the Ta and Nb atoms were segregated to the Al sites, while Co was segregated to the Ni sites within the SESF. The structure used was 8 atomic planes thick in the ⟨110⟩ direction and repeated to the appropriate thickness based on the experimental sample to allow for enough randomization of the solute positions, while still balancing computational demands. The black box represents the area sampled for the HAADF simulation shown in Figure 3.16.
The foil thickness was determined to be roughly 35 nm thick in the region of interest by comparison between experimental and simulated position averaged convergent beam electron diffraction (PACBED) patterns.[53] To ensure accurate representation of the experimental data in the simulations, the microscope variables from the FEI Titan 80–300 S/TEM with a probe corrector were used. Specifically, a convergence semi-angle of 12 mrad, Cₚ coefficient of 2 μm, and Cₛ of 1 mm were used at a zero defocus. Finally, a detection range from 55 to 372 mrad was used, which corresponds to HAADF image acquisition using a camera length of 91 mm on this microscope.

In order to minimize wrap-around errors during Fourier transforms, a 6×6 tiling of unit cells was used. The structure was sampled at discrete probe positions determined by twice the maximum spatial frequencies allowed by the probe-forming aperture. Images were interpolated via Fourier padding to provide a result that was both esthetic and representative without changing the simulated data. The temperature dependent mean square displacement term, 〈u²〉, was described by values of the elemental crystals of each species, as parameterized by Gao et al.[54]

From Figure 3.16, it can be seen that the fault structure, along with the effect of elemental segregation in the simulated and experimental images are in close agreement. The experimental HAADF image shown is the result of superimposing 12 periodic units of the images parallel to the fault in order to improve the signal-to-noise ratio in the image for comparison with the simulations. The experimental background is noticeably higher than that of the simulation, which could be due to factors such as amorphization at the surface or a thicker experimental sample than that which was simulated.
Figure 3.14: Planar average Bader charges on Ni as a function of atomic position for segregated and randomized calculation cells. The red dash line is the Bader partial charge of the bulk.
Figure 3.15: [110] view of the segregated SESF structure in $L1_2$. Ta and Nb are segregated to Al sites, and Co to Ni sites. The black box represents the area sampled for the HAADF simulation shown in Figure 3.16.

Figure 3.16: (a) Experimental and (b) simulated HAADF image of SESF. (c) Experimental and (d) simulated averaged intensity of grid-like ordering outlined by the dashed lines.

The excellent agreement between the observed and simulated images for the atomic structure based on the EDX-results, which has been found by the VASP simulations to be energetically favorable, provides additional validation for the $\eta$ phase structure,
including the elemental segregation and sublattice positions previously described. The similar intensity ratios between the high-Z and low-Z atomic columns for both the simulated and experimental cases establishes that the observed ordering is not a by-product of strain or diffraction contrast along the SESF. Therefore, the HAADF simulation confirms that the high intensity grid-like ordering along SESFs is a product of Ta and Nb segregating to those specific Al-sites forming the η phase revealed in Figure 3.11.

3.5 STUDY OF TWIN SUPPRESSION IN HL-11

3.5.1 Introduction

The push for energy efficiency has driven the need for high-performance materials to the forefront of materials science. Since turbine engine efficiency is directly related to the operating temperature, and high-temperature strength is limited by creep,[55] increased performance in this technology calls for a new generation of high-temperature structural materials that are creep resistant.

Currently three different strengthening mechanisms are employed to improve high temperature performance in disk Ni-base superalloys: solid solution strengthening, precipitation hardening, and grain boundary strengthening. Previous studies have examined how to maximize the potential from all three mechanisms, but as operating temperatures are increased the benefits from each changes. Therefore, there is a need for new work examining how to improve structural high-temperature alloys operating in higher temperature regimes.
Since the characterization of the $\gamma'$ phase by Bradley and Taylor in 1937,\cite{56,57} the development of superalloys proceeded in an incremental fashion with new progress focusing directly on the shortcomings of the current generation. Certainly, giant strides such as oxide dispersion strengthening in the 1950’s and crystal growth in the 1960’s and 1970’s have been made, but this progress represented the application of known materials principles to the deficiencies in existing alloy production. We report the observation of a novel high-temperature strengthening mechanism representing a leap forward in superalloy design, confirmed by experiment and supported density functional theory (DFT) calculations.

We show that the dominant mechanism of plastic deformation in this alloy system, twinning, is prevented by a temperature- and strain-induced phase transformation that makes twinning unlikely.

### 3.5.2 Results and Discussion

Figure 3.17 is the compression creep response for ME3 and HL-11 at 760 °C for both the [001] and [110] orientations (see methods and supplementary material in Appendix A for comparisons between the two alloys).

The creep curves in Figure 3.17(a) reveal two important results. One is the apparent anisotropic creep strength between the different orientations, with [110] oriented samples exhibiting strain hardening and [001] oriented samples strain softening. The other result is the improved creep resistance of HL-11 compared to ME3 for both orientations at 760 °C. For accurate evaluations in deformation mechanisms between the two alloys, the ME3 compression creep stress was reduced from 552 MPa, used for the HL-11 tests,
414 MPa to obtain comparable strain rates. Post-creep scanning transmission electron microscopy (STEM) analysis revealed multiple \( \frac{1}{2} \langle 110 \rangle \) dislocation types active in the \( \gamma \) matrix and faulting in the \( \gamma' \) precipitates for both alloys. Figure 3.17(b) and 1(c) show an [001] zone axis bright field (BF) STEM image of the deformation observed post-creep in ME3 and HL-11 respectively. Using high resolution high angle annular dark field (HAADF) STEM, it was established that the faults extending through both the \( \gamma \) and \( \gamma' \) phases observed in ME3 were microtwins and not extended stacking faults. The main observable differences found in the HL-11 deformation were the lack of twins and high frequency of isolated faulting that high resolution HAADF-STEM later revealed to be extrinsic in nature. Using electron channeling contrast imaging (ECCI) and STEM analysis, it was established that microtwinning was a much more prevalent deformation mode in ME3, contributing up to 50% of the accounted plastic strain compared to just 7% in HL-11 (See Figure A.2 in Appendix A).

Figure 3.18(a) and (b) are [110] zone axis HAADF-STEM images of isolated SESFs in ME3 and HL-11 respectively. As described by Smith et al.,[58] the ordering observed along the fault in HL-11 is attributed to a shear-induced phase transformation from \( \gamma' \) to \( \eta \) phase along the fault. Brighter contrast, attributed to heavier atomic weight, is also observed along SESFs in ME3; however, the lack of ordering implies that a different segregation event has occurred.[59,60,61] Figure 3.18(c) and (d) reveal the corresponding vertically integrated EDX line scans across the SESFs for ME3 and HL-11. The HL-11 line scan reveals the expected Nb, Ta, and Ti segregation along the fault, which supports previous work concluding that \( \eta \) phase has nucleated along the fault. In
contrast, the integrated line scan across the SESF in ME3 reveals a different type of segregation. Instead of the $\eta$ phase formers (Nb, Ti, Ta) replacing Al, the $\gamma$ formers (Cr, Mo) segregate along the fault and replace Al.[62] Not shown is the segregation of Co replacing Ni along the faults in both cases.

For the first time in a structural metal alloy, atomic resolution EDX maps show site-specific segregation of solute atoms along the nucleated $\eta$ phase in HL-11, as shown in Figure 3.19 below.

Within the $\eta$ phase, it can be seen that Ta and Nb preferentially segregate to the Wyckoff 2a positions in fairly high weight percentages (for Nb map see Figure A.5 in Appendix A). Furthermore, Al and Ti are shown to segregate to the Wyckoff 2d position, while Co can be seen to segregate to the Ni sublattice. Not only do these site-specific results account for the Z-contrast intensity observed in the HAADF-STEM images, they also confirm the assertion that the $\eta$ phase nucleating along the fault matches the ordering first described by Pickering et al.[46]

Multiple publications have found in single crystal creep testing that orientations which promote twinning result in poor creep performance.[63,64,65,66] In fact, twinning has been speculated as the source of the tension/compression anisotropy observed in single crystal creep tests for Ni-base superalloys, with the directions that encourage twinning exhibiting inferior creep strength.[67] This explains the poor creep strength exhibited by ME3 compared to HL-11, as twinning has been observed much more frequently in ME3. Karthikeyan et al.[21] first described a process for twin formation using like sign-Shockley partials that shear on adjacent planes creating twins in $\gamma'$ precipitates. This
model was further supported through experimental TEM findings on microtwin formation in Rene 88DT by Vismanathan et al.[68] Later it was postulated by Unocic et al. that the formation process for twins and SESFs were related. Several reports, this analysis included, have found twinning to occur in orientations that favor SESF formation.[65,67,7] This finding is understandable in reference to the recent model proposed by Smith et al.[58] on SESF formation which requires the shear of like-sign Shockley partials to form a SESF. Therefore, an isolated SESF may extend into a twin after two like-sign Shockley partials shear on adjacent \{111\} planes along the fault, the same process that formed the SESF previously. In order for a true SESF and twin to form a reordering process must occur to remove wrong nearest neighbors along the fault. Kovarik et al.[6] and Kolbe [18] both described the mechanism in which a fault trailing

![Figure 3.17](image.png)

Figure 3.17: (a) Compression creep curves of both ME3 and HL-11 for [001] (green and black respectively) and [110] (red and blue respectively) orientations. Stress is lower for ME3 tests (414Mpa compared to 552Mpa) to achieve comparable strain rates (5e-9) between the two alloys. (b) [001] Zone axis BF-STEM image revealing isolated SESFs and microtwins in a post-crept [001] ME3 crystal. (c) Zone axis BF-STEM image revealing isolated SESFs in a post-crept [001] HL-11 sample.
Figure 3.18: HAADF-STEM image obtained on a [110] zone axis revealing (a) segregation along a SESF in ME3 and (b) segregation and “grid-like” ordering of η phase along a SESF in HL-11. Integrated EDX line scans showing elemental segregation along a SESF for (c) ME3 and (d) HL-11, as indicated in (a) and (b), respectively.

The shear of like-sign Shockley partials on adjacent \{111\} planes in γ′ can reorder removing wrong nearest neighbor violations. This reordering process explains the presence of the SESFs and most twins observed in for this study. Yet, evidence of unlike Shockley partials and partials shearing on either side of SESFs (see Figure A.4 in Appendix A) points to new re-ordering configurations unknown at this time. Evidence does suggest though, that for SESFs to extend into a twin in HL-11, two Shockley partials are needed before a shearing process can occur in γ′.
Figure 3.19: Quantified atomic resolution EDX of $\eta$ phase in $\gamma'$ showing the HAADF-STEM image of the fault exhibiting characteristic ordering of intensity within the fault; Ni sublattice (green); Co (yellow) segregating to Ni sites; Ta (blue) segregating to the Wyckoff 2a sites; Al and Ti (red and magenta, respectively) segregating to the Wyckoff 2d sites. All EDX values are in wt%.

From the EDX line scans, it is clear that different segregation events are occurring in the two alloys. As previously shown, $\eta$ phase segregation and nucleation occurs along the faults in HL-11. However, the segregation in ME3 appears to be similar to a $\gamma$-like phase change (Cr and Mo replacing Al). To examine whether the different types of segregation affect whether the SESF is able to extend into a twin, DFT calculations were performed on cells created using knowledge gleaned from the site specific EDX scan in Figure 3.19 and HAADF-STEM images in Figure 3.18.[25] Two 176-atom calculation cells representing partial dislocation shearing adjacent to the SESF with and without nearest-neighbor reordering were created for pure Ni$_3$Al, HL-11 exhibiting solute segregation to
the SESF, HL-11 not exhibiting solute segregation, and ME3 exhibiting solute segregation to the stacking fault. After internal relaxation, the energetics of twin propagation was compared using previously obtained results from SESF calculations. Figure 3.20(a) displays the energetics of the twin formation process in the Ni-base superalloys studied. Following formation of the SESF configuration, it is necessary for two additional partial dislocations to shear adjacent planes to create the twin configuration; however, this action creates a plane of atoms with high-energy nearest-neighbor violations. We consider this configuration as an energy barrier for the propagation of twins in the Ni$_3$Al superlattice: for pure Ni$_3$Al, this barrier is 364 mJ/m$^2$, while for an HL-11 alloy the barrier is 743.2 mJ/m$^2$ or 480.5 mJ/m$^2$, for the ordered $\eta$ phase versus a random unsegregated SESF atomic configuration, respectively. Thus, the ordered $\eta$ phase observed at the HL-11 SESF presents a significant barrier to twin formation in this alloy system.[58] Following the hypothetical shearing of planes adjacent to the SESF, atomic reordering is necessary to create the low-energy fault that is typically associated with twinning.[6,18,24] In Figure 3.20(b), when we consider the energetics of this process we see large releases of energy associated with these atomic rearrangements: for pure Ni$_3$Al, this release is on the same order as the additional energy for shearing of partials 374.8 mJ/m$^2$, while for HL-11 alloys it is somewhat larger 856.4 or 938.1 mJ/m$^2$, for the random and ordered $\eta$ faults, respectively. Interestingly, for ME3 alloys, this process releases almost no energy at all: only 15.1 mJ/m$^2$, much less than the energy associated with twin formation. This small energy difference supports the theory that a $\gamma$-like phase transformation has occurred along the SESF removing the possibility of wrong
nearest neighbor violations. Thus, an additional creep deformation characteristic of the HL-11 alloy is that it strongly encourages the diffusion-controlled reordering process on twin formation, while in ME3 no reordering is necessary to propagate the twin to additional atomic planes. Therefore, this η phase formation along isolated SESFs represents a new strengthening mechanism by limiting the formation of twinning in HL-11, greatly improving creep strength and high temperature capabilities.

Figure 3.20: (a) Energetic cost of shearing along a SESF forming a twin that has not reordered yet in Ni₃Al, HL-11 where η has nucleated along the fault, and HL-11 without any segregation. Note the high energy cost necessary to form a twin along a SESF that has had η phase nucleate along it. (b) Difference in energy in an un-reordered twin vs. a reordered twin. The small difference found for ME3 suggests that the segregation of γ formers (Co, Cr, and Mo) replacing Ni and Al has removed nearest neighbor violations in the precipitate near the fault.
We may thus consider the high-temperature strengthening mechanism discussed here as a two-fold interaction: firstly, the nucleation of a secondary ordered phase at stacking faults that results in a two-fold increase in the energy required to shear additional partial dislocations; and secondly, the prevention of $\gamma$ formers from segregating to a fault creating a $\gamma$-like phase along it, which promotes twinning. This mechanism (tentatively named “phase transformation hardening”) operates in conjunction with the strengthening from secondary phase precipitates in $\gamma/\gamma'$ alloys, and is heretofore unidentified in literature characterizing high-temperature materials.

3.6 SUMMARY

In the Ni$_3$Al SESF system investigated in this chapter, DFT showed that the energy differences between systems with solutes concentrated at the SESF and those with solutes randomly distributed in the calculation cell ranged from 0.05 to 0.71 eV depending on the system considered. Relaxation of the calculation cell perpendicular to the planar defect additionally showed that these energy differences were not a consequence of strain concentration at the defect. Because the atomic configurations and volumes are essentially the same between the concentrated and randomized cells, differences in thermal excitations in this system will be minimal. This allows us to conclude, given the magnitude of energy differences between the two configurations, that a thermodynamic driving force for solute segregation to SESF exists for all the atomic species except W. Analysis of the metallic bonding in this system using Bader charges further supports a chemical origin to this effect in the reduction of partial charge on Ni atoms in the segregated SESF systems.
DFT showed that creep behavior of the two Ni$_3$Al systems investigated in this chapter, HL-11 and ME3, differed greatly as a result of different elements segregating to SESFs at elevated temperatures. In the HL-11 system, DFT showed a large increase in twin formation energy as a result of solute segregation to SESFs; this system also exhibited a very large driving force towards reordering if twinning were to occur. By contrast, the ME3 system, in which a large number of twins were observed (to the detriment of creep strength), exhibited almost no driving force for reordering after twin propagation. The energy differences calculated in this study are even more definitive than the results from the previous chapter: given the magnitude of the twin formation energy, it is almost inconceivable that twins will form in HL-11 as the result of dislocation shearing in the vicinity of an SESF. This effectively explains the much greater creep resistance of the HL-11 alloy system compared to the ME3 alloy system observed in experiment.

REFERENCES


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Chapter 4: Fast free-energy calculations for unstable high-temperature phases

This chapter represents an early attempt at calculating thermal properties for metallic phases that are not mechanically stable in traditional DFT calculations. Nikolas Antolin performed all the DFT calculations for this work with assistance from Oscar Restrepo and performed subsequent analysis with guidance from Prof. Wolfgang Windl. This paper was published as N. Antolin, O.D. Restrepo, and Windl, “Fast free-energy calculations for unstable high-temperature phases,” Physical Review B, Volume 86, 054119 on 27 August 2012 and is reported here in its unchanged form.

4.1 ABSTRACT

We present a fast and accurate method to calculate vibrational properties for mechanically unstable high-temperature phases that suffer from imaginary frequencies at zero temperature. The method is based on standard finite-difference calculations with optimized large displacements and is significantly more efficient than other methods. We demonstrate its application for calculation of phonon dispersion relations, free energies, phase-transition temperatures, and vacancy-formation energies for body-centered-cubic high-temperature phases of Ti, Zr, and Hf.

4.2 INTRODUCTION

Hexagonal-close-packed (hcp) to body-centered-cubic (bcc) phase transitions are characteristic of a number of transition and rare-earth metals, including titanium, zirconium, and hafnium. Although room-temperature applications of these materials are
limited by the expense of processing them, their high-temperature properties make them ideal candidates as the basis of high-temperature alloys. However, only limited experimental data [1,2,3] have been collected on the bcc high-temperature phase of these systems, and they are inaccessible to traditional zero-temperature *ab initio* calculations due to their mechanical instability.[4] Although the recently proposed self-consistent *ab initio* lattice dynamics (SCAILD) [5] and molecular dynamics (MD) [6] based approaches have proved successful in calculating phonon dispersions for these materials, convergence issues with free energy and phonon slopes in the long-wavelength limits prevent accurate calculation [7] of other phase properties relevant to high-temperature applications (e.g., elastic constants and formation energies of vacancies). As a result, the computational cost of these advanced calculation procedures sets limits to their applicability, and a supplemental calculation method is necessary for complete phase analysis. Thus, there is significant motivation to develop a simplified method of dealing with mechanically unstable systems of potentially large size that quickly produces reasonable *ab initio* results.

Current *ab initio* methods to deal with mechanical instability in these systems have focused on a simulated MD approach by displacing atoms around their equilibrium positions and using the resulting structures to calculate dynamical matrices for phonon calculations. The SCAILD method proposed by Souvatzis *et al.* [5] is limited by its high-symmetry requirement for reasonable calculation convergence and is thus inefficient at producing calculations beyond phonon dispersions for perfect structures.[7] A second calculation method proposed by Hellman *et al.* utilizes an MD approach to extract...
dynamical matrices, but it is computationally intensive due to the large number of MD steps it necessitates for convergence.[6] Due to their computational demands, neither method has been used to date to calculate the energetics of defects in mechanically unstable systems.

In this paper, we propose a method to calculate accurate thermodynamic properties of mechanically unstable high-temperature phases using \textit{ab initio} theory. This method utilizes large-displacement phonon calculations with a displacement determined by analysis of the phonon amplitude-energy curve. Because these calculations are computationally very economical, more complex calculations of defect energies, alloying effects, and transition temperatures are possible than using previous \textit{ab initio} methods. Furthermore, we find for the high-temperature bcc phases that we have studied that the agreement of phonon dispersions and phase-transition temperatures with experimental values is at least as good as with previously published \textit{ab initio} methods.

In high-temperature bcc phases, where the mechanical instability occurs as a result of decreased energy when a \((\varepsilon, -\varepsilon, 0, 0, 0, 0)\) strain is applied to the calculation cell,[4] the energy-strain response in this direction can be approximated by a quartic function with negative curvature at zero strain. The corresponding elastic constant \(c'\), given by that curvature, is thus negative. Due to the relationship between the slopes of the (acoustic) phonon branches and the elastic constants, especially for the transverse branch in the \([1\bar{1}0]\) direction, which is given by \((C_{11} - C_{12})/2\), the negative elastic constant corresponds to imaginary frequencies in the phonon dispersion, which is determined from the basic assumption that the energy versus atomic displacement curves have positive
curvature (minimum at the equilibrium position) and are parabolic (harmonic). Phonon frequencies and eigenvectors are determined by the curvature of the energy vs atomic displacement curve at the equilibrium position and can be determined by density functional perturbation theory [8] or small finite displacements.[9]

The appearance of imaginary frequencies interferes not only with determining phonons per se but also with free-energy-based calculations, which for solids are easiest obtained within the quasiharmonic approximation. There, the free-energy contribution to the total energy is calculated from the phonon density of states.[8] A small-displacement phonon calculation of the free-energy contribution to mechanically unstable structures is thus flawed through its inclusion of nonphysical frequencies.

The fundamental question at this point is why the high-temperature phases, despite being mechanically unstable, become stable at sufficiently high temperatures. As has been discussed previously, this is due to the fact that the vibrational amplitudes of the atoms increase with temperature. This has two consequences: first, an atom no longer moves in the potential landscape of the other atoms at or close to their equilibrium lattice positions but is displaced from them (phonon-phonon coupling). Second, the atom explores a larger part of the energy landscape through its higher vibrational amplitude (phonon anharmonicity). If the second effect dominated the first, a calculation that includes these anharmonic effects could be based on an improved displacement strategy around the equilibrium positions of the atoms. This would avoid the major computational overhead in the methods proposed to date,[5,6] which consist of relating displacements for the other atoms in the system to the atom displaced for a phonon calculation. Indeed, such a
strategy may be successful and not hampered by the instability in direct vicinity of the 
equilibrium position considering that an oscillating atom has its largest velocity when it 
passes through the equilibrium site, while its velocity decreases to zero at the turnaround 
points, where it thus spends the majority of its time. Therefore, we propose to use atomic 
displacements for the phonon calculations that are large enough to probe the curvature of 
the energy landscape far away from the equilibrium position. 
Indeed, at large displacements, the quartic term of the energy-strain function eclipses the 
negative quadratic term, leading to an approximately constant positive curvature at 
sufficient distance (e.g., at ~0.5 Å in Figure 4.1). Since a constant curvature corresponds 
to harmonic motion and enables the phonon concept, the shape of the curve can thus be 
approximated by only using a quadratic term with little loss of detail. This suggests that a 
phonon calculation of the free-energy contribution using a large displacement in the 
quartic dominated regime could be used with the quasiharmonic approximation to 
provide the free-energy contribution to the total structure energy and that the properties 
of a structure thus stabilized could be calculated using ab initio methods. By comparing 
the results of a large-displacement calculation to experiment, one then can also probe in a 
simple way if the dominating anharmonic effect comes from the large atomic 
displacements (with lesser effect from what the surrounding atoms do) or vice versa. 

4.3 METHODOLOGY
To calculate the approximate large displacement necessary to force the phonon 
calculation into the quartic-dominated regime, VASP [11] was used on a frozen-phonon- 
type supercell for N-point phonons [10] to calculate the internal energy of the structure as
a function of phonon displacement.[12] The $N$-point phonon was chosen since the transverse mode at the $N$ point is the primary marker of mechanical instability in bcc transition metals.[11] For these calculations, we used projector-augmented wave potentials [13,14] with a $10\times10\times10$ Monkhorst-Pack $k$-point mesh. Calculations were performed for bcc titanium, zirconium, and hafnium, as well as several mechanically stable bcc metals.

Figure 4.1: (a) The energy vs phonon amplitude curve and (b) its second derivative for an $N$-point frozen phonon cell [10] displacement of the bcc cell of Hf (solid) and Mo (dashed).
Figure 4.1(a) shows the calculated internal energy as a function of the $N$-point phonon amplitude in the chosen displacement direction for the Hf and Mo systems. To determine the appropriate phonon displacement for large-displacement calculations, second numerical derivatives of this internal energy data are calculated using a central-difference method, shown in Figure 4.1(b). In the case of Hf, these calculations give an indication of the point at which the amplitude-energy curve enters the quasiparabolic high-temperature regime (in this case between $\sim0.4$ and 0.7 Å, where the second derivative becomes approximately constant), allowing harmonic-type phonon calculations and use of the quasiharmonic approximation to determine the system’s free energy. By contrast, the second derivative for Mo is maximally positive at values around zero displacement, which therefore defines its quasiharmonic regime. For automatic detection of an appropriate displacement value, we found that the maximum value of the second derivative identifies well the necessary displacement to calculate a realistic phonon dispersion. This interpretation matches well with phonon approaches for stable materials, which exhibit maximum second derivative values at minimal displacements.

Alternatively, one can select the displacements just large enough that all the imaginary frequencies from the phonon dispersions are eliminated. Typically, the last frequencies to turn real are located not at the $N$ point, but close to the $\Gamma$ point.

Once the necessary displacement magnitude was determined for each system by eliminating all the imaginary frequencies from the phonon dispersion, force constants and dynamical matrices were determined from finite-displacement VASP calculations within $4\times4\times4$ supercells of the bcc primitive cells using the PHON code.[9] The calculations
were performed with 6×6×6 Monkhorst-Pack $k$-point meshes for a range of lattice parameters. Using the quasiharmonic approximation in PHON,[9] these calculations were used to determine the vibrational contribution to the system’s free energy over a temperature range that included the experimental transition temperature. For all materials considered, an additional calculation of the phonon density of states was conducted on relaxed supercells composed of 3×3×2 hexagonal unit cells with a $\Gamma$-centered 6×6×9 Monkhorst-Pack $k$-point mesh using a 0.03-Å phonon amplitude. The lattice parameter was then determined by minimizing the free energy with respect to volume. The minimum of the free energy versus volume curve at each temperature was then used to determine the phase transition temperature. The bulk modulus was calculated using a Birch-Murnaghan fit for temperatures across the literature range of phase stability and plotted to determine its temperature dependence.

To calculate the free energy of formation of a vacancy in the metallic bcc system, $F_f(T) = F_V(T) - \frac{N-1}{N} F_p(T)$, the free energy as a function of temperature for 3×3×3 54-atom bcc supercells with $(V)$ and without $(p)$ vacancies was calculated using a 6×6×6 Monkhorst-Pack $k$-point mesh and the large-displacement values from the perfect cells. For the demonstration here, the vacancy structures were not relaxed.

Table 4.1 shows the calculated transition temperature, lattice parameter, and bulk modulus obtained using the large-displacement phonon approach wherein no imaginary frequencies were present in the phonon dispersion, as well as experimental values. In addition, the displacements are displayed at which no imaginary frequencies appear in the
phonon dispersion and at which the second derivative of the phonon amplitude-energy curve was maximal.

<table>
<thead>
<tr>
<th></th>
<th>$u_{2d}$ (Å)</th>
<th>$u_{nl}$ (Å)</th>
<th>$T_{trans}$ (K)</th>
<th>$A$ (Å)</th>
<th>$B$ (GPA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>0.60</td>
<td>0.88</td>
<td>1200 (1155)</td>
<td>3.276 (3.33)</td>
<td>87.1 (87.7)</td>
</tr>
<tr>
<td>Zr</td>
<td>0.57</td>
<td>0.54</td>
<td>1050 (1136)</td>
<td>3.557 (3.551)</td>
<td>94.8 (96.7)</td>
</tr>
<tr>
<td>Hf</td>
<td>0.63</td>
<td>0.68</td>
<td>2100 (2016)</td>
<td>3.521 (3.625)</td>
<td>119 (112.3)</td>
</tr>
</tbody>
</table>

Table 4.1: Calculated vs. experimental values (in parentheses; Refs. 1–3, 15–17) of phase-transition temperature $T_{trans}$, bulk modulus $B$, and lattice parameter $a$ for the bcc high-temperature phases of Ti, Zr, and Hf. Also given are large-displacement values determined from maximum values of the second derivative of N-point frozen-phonon cells ($u_{2d}$) and from a no-imaginary-frequency condition ($u_{nl}$) used for these calculations.

4.4 RESULTS

For bcc titanium, the first displacement at which no imaginary frequencies were observed in the phonon dispersion was 0.88 Å; this value did not correspond to the absolute maximum of the second derivative, which occurred at approximately 0.6 Å but did correspond to a second local maximum of the second derivative which occurred at approximately 0.85 Å. The transition temperature was calculated to be 1200 K, which is within 4% of the experimental value of 1155 K (Ref. 15) and closer to experiment than that calculated using the SCAILD method, 1107 K.[7] The lattice parameter was calculated to be 3.234 Å at 0 K and 3.276 Å at the calculated transition temperature, while the experimental lattice parameter at this temperature was 3.33 Å. The coefficient of thermal expansion was calculated to be $6.7 \times 10^{-6} \text{ K}^{-1}$, compared to an experimental coefficient of thermal expansion for the bcc phase of $8.6 \times 10^{-6} \text{ K}^{-1}$.[19] The calculated phonon dispersion using the 0.88-Å phonon amplitude is displayed in Figure 4.2(a), with experimental data points from Ref. 1.
For bcc zirconium, the first displacement at which no imaginary frequencies were observed in the phonon dispersion was 0.54 Å; this value agreed well with the calculated maximum of the second derivative, which was approximately 0.57 Å. The transition temperature was calculated to be 1050 K, which is 8% lower than the experimental value of 1136 K,[15] whereas the transition temperature calculated using the SCAILD method, 916 K,[7] is more than 19% too low. The lattice parameter was calculated to be 3.557 Å at the calculated transition temperature and 3.562 Å at 1150 K, while the experimental lattice parameter near the transition temperature was 3.551 Å. The coefficient of thermal expansion was calculated to be $1.34 \times 10^{-5} \text{ K}^{-1}$ (no corresponding experimental measurements were found). The calculated phonon dispersion using the 0.54-Å phonon amplitude is displayed in Figure 4.2(b), in comparison to experimental data points.[2]

For bcc hafnium, the first displacement at which no imaginary frequencies were observed in the phonon dispersion was 0.68 Å; this value agreed well with the calculated maximum of the second derivative, which was approximately 0.63 Å. The transition temperature was calculated to be 2100 K, which is 4% higher than the experimental value of 2016 K,[16] while the transition temperature calculated using the SCAILD method, 1660 K,[7] is 18% too low. The lattice parameter at 2400 K was calculated to be 3.521 Å, which is 3% smaller than the experimental value of 3.625 Å at that temperature. The coefficient of thermal expansion was calculated to be $7.9 \times 10^{-6} \text{ K}^{-1}$, compared to an experimental coefficient of thermal expansion for the bcc phase of $11 \times 10^{-6} \text{ K}^{-1}$.[20] The calculated phonon dispersion using the 0.68-Å phonon amplitude is displayed in Figure 4.2(c), with experimental data points.[3] Additional phonon calculations were performed.
on the Hf bcc system using larger supercells to determine whether increases in cell size would improve the agreement of results with experimental values. Within the feasible limits of computational resources available for this study, no significantly better agreement was observed from increasing the calculation cell size past a supercell composed of $4\times4\times4$ bcc primitive cells. The results of expanding the supercell size from $4\times4\times4$ to $8\times8\times8$ bcc primitive cells are shown in Figure 4.2(c).

![Figure 4.2: Large-displacement calculated phonon dispersions for (a) Ti, (b) Zr, and (c) Hf vs experimental phonon energies from [1–3]. Solid lines are calculated with $4\times4\times4$ phonon supercells, and the dashed line for Hf is calculated with an $8\times8\times8$ supercell.](image)
The temperature dependence of bulk moduli for Ti, Zr, and Hf was calculated using the large-displacement method with Birch-Murnaghan fitting across a temperature range as previously described. The three temperature dependencies, displayed as normalized to each material’s transition temperature in Figure 4.3, exhibit nearly perfect quadratic relationships. Also plotted in Figure 4.3 are experimental data for the bulk moduli of the three materials, shown as solid points. Calculated values for Ti and Zr exhibit the typically expected decrease in bulk modulus with increased temperature. The experimental data for Ti [Figure 4.3(a)] show a large scattering and indicate significant error bars for the measured values, which are not reported in the experimental source [19]. Within these assumed error bars, our temperature dependence is in agreement for Ti and Zr, where values have been measured for more than one temperature. Calculated values for Hf indicate an anomalous increase in bulk modulus with increased temperature and show good agreement with the one experimental value available [3] for a temperature of 2073 K. While it is possible that this represents a calculation artifact or results from the Birch-Murnaghan fits used, if physically valid, it would indicate an internal structural change that may be related to the mechanism of the hcp-bcc phase transition.

The free energy of formation for unrelaxed vacancies in bcc Ti, Zr, and Hf was calculated using the large-displacement method with the displacements previously described. By fitting $F_f(T) = E_f - TS_f$ (Ref. 18) in the bcc stability range, the energy $E_f$ and entropy $S_f$ of formation of the vacancy were determined. In Ti, the vacancy energy of formation $E_f$ was 2.05 eV, and the entropy of formation $S_f$ was 8.15kB. In Zr, the vacancy energy of formation $E_f$ was 2.06 eV, and the entropy of formation $S_f$ was 2.76kB. In Hf, we found
Figure 4.3: Calculated temperature dependence of bulk modulus for (a) Ti, (b) Zr, and (c) Hf, normalized to the transition temperature of each metal, with corresponding experimental values from Refs. 2, 3, and 19.

\( E_f = 2.20 \text{ eV} \) and \( S_f = 0.89 \text{kB} \). The values for the formation energy determined in this way are smaller by 0.9%, 0.6%, and 5.9% than the zero-temperature formation energies of 2.07, 2.08, and 2.34 eV for Ti, Zr, and Hf, respectively. While the agreement between fit and zero temperature formation energy for Ti and Zr is similar to more harmonic bcc metals, where we calculate a decrease of 0.2%, 0.4%, and 1.0% for the examples of W, Mo, and Cr, respectively,[21] Hf shows a strong discrepancy coming from the fact that its phonon density of states shows a strong decrease in the high-frequency regime upon introduction of a vacancy which is not observed for Ti and Zr. Additionally, it would not
be possible to calculate the entropy of vacancy formation without a reliable temperature
dependence of free energy derived from a converged phonon density of states, as
calculated using this method. We find that the entropy of formation scales inversely with
the melting temperature of the three metals, which is sensible; since the melting
temperature is a measure for the influence of the lattice vibrations on the stability of the
lattice, the higher the melting temperature is, the smaller the effect of lattice vibrations is
on the order of the atoms with respect to their equilibrium position, and thus the smaller
the influence of vibrational disorder is on the formation of vacancies. In order to reliably
calculate the relative magnitude of these contributions for anharmonic structures at high
temperatures, full free-energy calculations are a necessity, and our results show that they
are well within the capabilities of the method proposed here.

4.5 CONCLUSIONS

In this paper, the large-displacement phonon approach has been shown to produce results
in good agreement with experimental values for a number of high-temperature metallic
systems. However, it cannot be expected to be applicable to all systems in the same way
presented here, as the causes underlying mechanical instability in these systems may
differ, although preliminary calculations for other systems up to now look promising. Our
methodology can only be applied to those systems in which a parabolic regime can be
reached by increased phonon amplitude, as determined in the displacement calculation
steps. For these systems, it produces results that have excellent agreement with
experimental values at a relatively low computational cost. For the other systems, large
displacement calculations can help to easily show that phonon-phonon interactions dominate the effect of a locally anharmonic potential.

In summary, the primary advantages of the large-displacement method for calculating the energetics of mechanically unstable high-temperature phases and defects are its speed and simplicity. Due to the computational demands of both the SCAILD [5] and MD [6] approaches, the cell volume is at best estimated from an extrapolation from a 0 K density functional theory relaxation, which can lead to large errors, as shown here. In contrast, the large-displacement method provides a fast self-consistent approach that allows phonon calculations on a number of different calculation cell volumes simultaneously, allowing for true incorporation of temperature effects due to lattice expansion and atomic vibration to yield more accurate values for thermodynamically determined quantities such as phase transition temperatures. The incorporation of these effects via the large displacement method seems to allow for results in the same range of accuracy as those obtained for mechanically stable phases. Additionally, the significantly reduced computational cost allows for more complex calculations to be performed, including defect calculations that were previously beyond the reach of ab initio methods.

REFERENCES


12) VASP and many other *ab initio* codes by default only allow calculations for small displacements. To avoid having the code override the input of a large displacement, it needs a simple modification.


Chapter 5: Thermodynamics of vacancies in body-centered cubic metals

5.1 INTRODUCTION

The vacancy may well be the most important point defect in elemental metals. Previous studies on defects in transition metals show self-interstitial formation energies to be a minimum of 0.8 eV greater than vacancy formation energies, making self-interstitial formation extremely unlikely outside highly defected systems such as irradiated materials.[1] Vacancies are also known to play a critical role in diffusion processes. Past research has shown great success in determining the vacancy formation energy, but attempts to determine the vacancy formation entropy have been more limited in scope.[1,2] Therefore, a more complete understanding of the thermodynamics of vacancy formation is would be very valuable to contemplating materials behavior at finite temperatures.

When contemplating the vibrational dynamics of a defect system, it is important to consider how a defect may change the atomic displacements such that they deviate from those in a perfect material. In a perfect material, we may typically assume that there will be some symmetry to the forces generated by a pair of displacements in equal and opposite high-symmetry directions. This symmetry allows one to average to forces from such pairs of displacements in order to eliminate anharmonicities from odd terms in the Taylor expansion of energy: \[ dE(u) = E'u + \frac{1}{2}E''u^2 + \frac{1}{6}E'''u^3 + \cdots. \] However, if we
consider a defect such as a vacancy, it is clear that the symmetry of forces for an equal
displacement approach is broken for certain directions, e.g. a displacement into the
vacancy itself. Under these conditions, one may no longer assume symmetry in the even
terms of the Taylor expansion, and it is more desirable to take an equal force approach
instead of an equal displacement approach, i.e. to calculate the forces by varying the
displacement such that they are approximately equal for such an asymmetric
displacement. We propose an efficient alternative in the form of a weighted average: for
the pair of equal displacements constructed according to a finite-differences method, one
may scale the second atomic force vector $F_2$ to match the atomic force vector of the first
displacement $F_1$ according to the ratio of the Euclidean norms of both vectors and
perform averaging of the original and scaled force vectors: $F_{avg,1} = \left\| F_1 \right\| \left( \frac{1}{\left\| F_1 \right\|} F_1 + \frac{1}{\left\| F_2 \right\|} F_2 \right)$. and likewise for the second force vector. This results an upper and lower limit for
the forces that may then be used in the quasiharmonic approximation to calculate the free
energy. It should be obvious that in the limiting case of materials in which an equal
displacement results in a symmetric force vector, this approach produces results identical
to the typical force averaging scheme.

Considering an equipotential displacement in an asymmetric oscillator system, we may
derive a different force averaging scheme. Given two oscillators with spring constants $k_1$
and $k_2$ with equal energy, we know that $k_1x_1^2 = k_2x_2^2$, so $x_1 = \sqrt{\frac{k_2}{k_1}}x_2$. We also know that
$F = kx$, so we can approximate $\sqrt{\frac{k_2}{k_1}} = \frac{F_2}{F_1}$ for a linear relationship between $F$ and $k$. A
more reasonable average value of the forces vector derived from such equipotential displacements may then be approximated by averaging the forces using the equation:

\[
F_{\text{avg}} = \frac{1}{\sqrt{\|F_{\text{min}}\|}} \left( \frac{1}{\sqrt{\|F_1\|}} F_1 - \frac{1}{\sqrt{\|F_2\|}} F_2 \right)
\]

where \(F_1\) and \(F_2\) are the two equal displacement atomic force vectors, \(\|F_{\text{min}}\|\) is the lesser of the two Euclidean norms of the force vectors (assessed to be more representative of forces near a vacancy), and \(F_{\text{avg}}\) is the averaged force vector. As with the previous approach, this result simplifies to the typical approach if a symmetric force matrix is obtained from the calculation. The magnitude of corrections obtained by this approach are typically less than 5% for highly stable systems but may be as large as 20% for systems that exhibit mechanical instabilities. This force averaging scheme was selected from among the proposed alternatives as it was shown to produce the most stable results and isolate anharmonic behavior in the phonon dispersion to a few non-interacting branches.

### 5.2 METHODS

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP) software package based on first-principles density functional theories (DFT).[3,4] Generalized gradient approximation as given by Perdew-Burke-Ernzerhof (GGA-PBE) was used as the electronic exchange correlation energy in the main part of the calculation.[5] All calculations were performed with a plane wave cutoff 30% higher than that specified by the pseudopotential. First-order Methfessel-Paxton smearing with a smearing width of 0.1 eV was used and was found to produce electronic entropy on the
order of 0.0002 eV/atom or less for relaxations and force calculations.[6] Spin polarization was only considered for bcc iron since all other systems exceed their Curie or Néel temperatures in the temperature range of interest.[7]

Each bcc system was relaxed using a 7×7×7 Γ-centered Monkorst-Pack k-point mesh and a 64-atom supercell constructed from 4×4×4 bcc primitive cells. A minimum of 1450 1 femtosecond timesteps of DFT molecular dynamics (MD) was performed on each bcc system using a 2×2×2 Monkorst-Pack k-point mesh and 54-atom cubic supercell at a temperature in the midpoint of its stability range as determined by experiment. Average displacements were calculated using displacements past the first 1000 timesteps except in the case of beryllium which exhibited excessive drift. Displacements for systems exhibiting mechanical instability at 0 K were also calculated using the large-displacement method developed in a previous work, and the larger of the two calculated displacements was used in subsequent calculations.[8]

Free-energy calculations were performed on each perfect bcc system using the same 64-atom supercell and k-point mesh from relaxation with series of linear expansions of 0.5% to determine the minimum energy volume at the midpoint temperature. Expanded lattice vectors were then used to construct 63-atom bcc vacancy cells, in which the first and second neighbor shells were internally relaxed using a 7×7×7 Γ-centered Monkorst-Pack k-point mesh. Using the displacements calculated from DFT MD, forces were calculated in response to each of the symmetry independent displacements in the relaxed vacancy supercell. The forces were then averaged using the previously described weighted-averaging scheme and the free energy of the vacancy cell calculated using the PHON
Finally, the free energy and entropy of vacancy formation was calculated by subtracting the previous results for expanded supercells and performing a linear fit of free energy versus temperature from 100 to 500 K for alkali metals and 200 to 1000 K for all other systems.

5.3 RESULTS

Table 5.1 displays the displacements calculated for each system using DFT MD and, in the case of mechanically unstable systems, the large-displacement method. While typically displacements in phonon calculations are limited to 0.03 to 0.05 Å (and indeed the VASP code must be modified to operate with displacements greater that 0.1 Å), none of the displacements obtained in this study fall in this range. Table 5.2 displays the midpoint temperatures used in calculations as well as the expanded lattice parameters and a percent error from the reported experimental value of the lattice parameter. The temperature reported in this table for magnesium represents the point at which the free energy of the bcc phase is lower than that of the hexagon close-packed (hcp) phase; this is above magnesium’s melting point and therefore not experimentally observed without additional pressure effects. Since these values are typically reported at room temperature for systems that are stable in that range, it is not unexpected that the lattice parameters for some of the high-temperature calculations differ by more than one percent from the experimental value. Indeed, studies of lattice parameters at high temperature in Mo, Nb, and Ta show significantly better agreement with the calculated values, with reductions in the percent error of 50% or greater. Table 5.3 reports the calculated formation energy
and formation entropy of a vacancy in the bcc systems in this study, as well as previously obtained results where available.

<table>
<thead>
<tr>
<th>BCC metal</th>
<th>DFT MD Disp., Å</th>
<th>Large Disp., Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td>0.34</td>
<td>0.35</td>
</tr>
<tr>
<td>Na</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.61</td>
<td>0.31</td>
</tr>
<tr>
<td>K</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>Sc</td>
<td>0.94</td>
<td>0.63</td>
</tr>
<tr>
<td>Ti</td>
<td>0.42</td>
<td>0.61</td>
</tr>
<tr>
<td>V</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.33</td>
<td>0.57</td>
</tr>
<tr>
<td>Fe</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>0.62</td>
<td>0.75</td>
</tr>
<tr>
<td>Zr</td>
<td>0.42</td>
<td>0.59</td>
</tr>
<tr>
<td>Nb</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>0.45</td>
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<tr>
<td>Eu</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td>0.47</td>
<td>0.69</td>
</tr>
<tr>
<td>Ta</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>0.19</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1: Displacements for BCC systems calculated with DFT MD and large-displacement method, in Å.
<table>
<thead>
<tr>
<th>BCC metal</th>
<th>Midpoint Stability Temp., K</th>
<th>Expanded Lattice Parameter, Å</th>
<th>Lattice Parameter Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>275</td>
<td>3.474</td>
<td>-0.992</td>
</tr>
<tr>
<td>Be</td>
<td>1550</td>
<td>2.575</td>
<td>0.927</td>
</tr>
<tr>
<td>Na</td>
<td>200</td>
<td>4.269</td>
<td>-0.512</td>
</tr>
<tr>
<td>Mg</td>
<td>(1000)</td>
<td>3.691</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td>175</td>
<td>5.365</td>
<td>0.822</td>
</tr>
<tr>
<td>Ca</td>
<td>925</td>
<td>4.499</td>
<td>0.428</td>
</tr>
<tr>
<td>Se</td>
<td>1700</td>
<td>3.703</td>
<td>-0.711</td>
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<tr>
<td>Ti</td>
<td>1550</td>
<td>3.294</td>
<td>0.366</td>
</tr>
<tr>
<td>V</td>
<td>1100</td>
<td>3.052</td>
<td>0.929</td>
</tr>
<tr>
<td>Cr</td>
<td>1100</td>
<td>2.864</td>
<td>-0.726</td>
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<td>Mn</td>
<td>1475</td>
<td>2.825</td>
<td>-8.27</td>
</tr>
<tr>
<td>Fe</td>
<td>600</td>
<td>2.844</td>
<td>-0.774</td>
</tr>
<tr>
<td>Rb</td>
<td>150</td>
<td>5.718</td>
<td>0.226</td>
</tr>
<tr>
<td>Sr</td>
<td>925</td>
<td>4.912</td>
<td>0.861</td>
</tr>
<tr>
<td>Y</td>
<td>1775</td>
<td>4.086</td>
<td>-0.337</td>
</tr>
<tr>
<td>Zr</td>
<td>1625</td>
<td>3.599</td>
<td>-0.270</td>
</tr>
<tr>
<td>Nb</td>
<td>1375</td>
<td>3.345</td>
<td>1.35</td>
</tr>
<tr>
<td>Mo</td>
<td>1450</td>
<td>3.190</td>
<td>1.38</td>
</tr>
<tr>
<td>Cs</td>
<td>150</td>
<td>6.249</td>
<td>1.76</td>
</tr>
<tr>
<td>Ba</td>
<td>500</td>
<td>5.091</td>
<td>1.36</td>
</tr>
<tr>
<td>Eu</td>
<td>550</td>
<td>4.517</td>
<td>1.43</td>
</tr>
<tr>
<td>Hf</td>
<td>2375</td>
<td>3.605</td>
<td>0.139</td>
</tr>
<tr>
<td>Ta</td>
<td>1650</td>
<td>3.366</td>
<td>1.91</td>
</tr>
<tr>
<td>W</td>
<td>1850</td>
<td>3.214</td>
<td>1.55</td>
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</table>

Table 5.2: Midpoint calculation temperatures in K and expanded lattice parameters in Å for BCC metals.[7]
<table>
<thead>
<tr>
<th>BCC metal</th>
<th>Calculated $E_f^V$, eV</th>
<th>Reported $E_f^V$, eV</th>
<th>Calculated $S_f^V$, $k_B$</th>
</tr>
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<tbody>
<tr>
<td>Li</td>
<td>0.574</td>
<td></td>
<td>2.04</td>
</tr>
<tr>
<td>Be</td>
<td>-0.765</td>
<td></td>
<td>-5.84</td>
</tr>
<tr>
<td>Na</td>
<td>0.391</td>
<td></td>
<td>0.483</td>
</tr>
<tr>
<td>Mg</td>
<td>0.718</td>
<td></td>
<td>3.32</td>
</tr>
<tr>
<td>K</td>
<td>0.340</td>
<td></td>
<td>4.09</td>
</tr>
<tr>
<td>Ca</td>
<td>0.994</td>
<td></td>
<td>2.71</td>
</tr>
<tr>
<td>Sc</td>
<td>1.39</td>
<td>1.21$^{[12]}$</td>
<td>1.28</td>
</tr>
<tr>
<td>Ti</td>
<td>1.40</td>
<td>1.63$^{[11]}$, 2.05$^{[8]}$</td>
<td>-5.61</td>
</tr>
<tr>
<td>V</td>
<td>2.81</td>
<td>2.51, 2.1-2.2$^{[1]}$</td>
<td>0.390</td>
</tr>
<tr>
<td>Cr</td>
<td>2.93</td>
<td>2.64, 2.0-2.4$^{[1]}$</td>
<td>3.60</td>
</tr>
<tr>
<td>Mn</td>
<td>1.47</td>
<td>1.51$^{[11]}$</td>
<td>-3.18</td>
</tr>
<tr>
<td>Fe</td>
<td>2.37</td>
<td>2.15, 1.6-2.2$^{[1]}$</td>
<td>5.89</td>
</tr>
<tr>
<td>Rb</td>
<td>0.297</td>
<td></td>
<td>4.16</td>
</tr>
<tr>
<td>Sr</td>
<td>0.908</td>
<td></td>
<td>2.79</td>
</tr>
<tr>
<td>Y</td>
<td>1.12</td>
<td>1.12$^{[11]}$</td>
<td>-38.0</td>
</tr>
<tr>
<td>Zr</td>
<td>1.54</td>
<td>1.68$^{[11]}$, 2.06$^{[8]}$</td>
<td>2.15</td>
</tr>
<tr>
<td>Nb</td>
<td>3.04</td>
<td>2.99, 2.6-3.1$^{[1]}$</td>
<td>1.28</td>
</tr>
<tr>
<td>Mo</td>
<td>2.99</td>
<td>2.96, 2.6-3.2$^{[1]}$</td>
<td>1.07</td>
</tr>
<tr>
<td>Cs</td>
<td>0.294</td>
<td></td>
<td>4.03</td>
</tr>
<tr>
<td>Ba</td>
<td>1.07</td>
<td></td>
<td>3.13</td>
</tr>
<tr>
<td>Eu</td>
<td>1.19</td>
<td></td>
<td>3.83</td>
</tr>
<tr>
<td>Hf</td>
<td>1.40</td>
<td>1.56$^{[11]}$, 2.20$^{[1]}$</td>
<td>-6.25</td>
</tr>
<tr>
<td>Ta</td>
<td>3.35</td>
<td>3.14, 2.8-3.1$^{[1]}$</td>
<td>3.83</td>
</tr>
<tr>
<td>W</td>
<td>3.45</td>
<td>3.56, 3.5-4.1$^{[1]}$</td>
<td>2.54</td>
</tr>
</tbody>
</table>

Table 5.3: Calculated and reported vacancy formation energies and calculated vacancy formation entropies of BCC metals.
5.4 DISCUSSION

Comparing the vacancy formation values calculated in this study to those that have been previously reported, we note that our values are generally in good agreement, especially given that other studies have used different relaxation algorithms and methods for calculating the electronic energy of the system. Even for the worst case, chromium, our vacancy formation energy differs from previous results by only 11%, much of which may be accounted for by our decision not to consider the antiferromagnetic structure above the Néel temperature. We note five cases in which our calculation method has produced results which are likely erroneous: Be, Ti, Mn, Y, and Hf. In three of these cases, the transition temperature into the BCC phase is greater than 90% of the metal’s melting temperature, meaning that these systems are significantly outside the scope of the quasiharmonic approximation we have used to calculate the free energy. Anomalous results in Ti and Hf may be attributed in part to our lack of consideration of thermal expansion in our calculation: both metals have thermal expansion coefficients on the order of $10^{-5}$ K$^{-1}$ in this regime and therefore thermal expansion is likely to play a strong role in stability in these metals.[11] We leave further investigation of these systems for future research.

Figure 5.1 shows the calculated vacancy formation energy for all BCC systems with appropriate results, plotted by periodic group and period. Group 1 metals are very well-behaved with monotonically decreasing vacancy formation energy, while Groups 2, 3, and 4 appear to be in a sort of transition to the monotonically increasing vacancy formation energies of Groups 5 and 6. A sharp increase in vacancy formation energy is
Figure 5.1: BCC vacancy formation energy, plotted by periodic group (labels) and period (shading).

Figure 5.2: BCC vacancy formation energy plotted versus the experimental melting point of the metal.
noted between Groups 4 and 5, giving some indication that the mechanically unstable BCC phases in Groups 3 and 4 may behave more like alkali and alkaline earth metals than typical transition metals. Figure 5.2 shows the calculated vacancy formation energy plotted versus the experimental melting temperature of each BCC system. There is a clear trend of increasing vacancy formation energy with increased melting temperature, with some deviation for the mechanically unstable systems in Groups 3 and 4 between 1500 and 2500 K. It is not really possible to know whether this represents systems with anomalously high melting temperatures or with low vacancy formation energies. It is the suspicion of the authors that it is likely a combination of the two that is to blame for the magnitude of this deviation.
Figure 5.3 shows the calculated vacancy formation entropy for all BCC systems with appropriate results, again plotted by periodic group and period. There are no apparent trends in this data, an indication that rigorous consideration of the vibrational dynamics of a defect is highly system-dependent. This suggests that there are significant advances to be made in the computation of this thermodynamic parameter.

Figure 5.4 shows the calculated MD DFT displacement divided by the calculated expanded lattice parameter for BCC metals in this study, plotted by periodic group and period. There is a clear grouping of reduced displacements by periodic group, as well as a general trend for reduced displacements for elements in subsequent periods outside Group 1. Also evident is significantly increased displacements for mechanically unstable systems, which is likely analogous to observations of anomalous vacancy diffusion in systems such as BCC titanium.[13] The presence of such large displacements for these systems under perfect conditions lends credence to our choice of the large-displacement method for the calculation of free energy.

Table 5.4 displays the experimental melting point, calculated free energy of vacancy formation at the melting point, and corresponding vacancy concentration at the melting point for the BCC systems studied. It is worth noting that except for the very obvious problem systems of beryllium and yttrium, which are closest to the melting point of the metallic system, the calculated free energy of vacancy formation and vacancy concentration agree well with our intuitive expectations. This points towards lattice thermal expansion or force asymmetry as a source of error for the systems that do not currently give reasonable results.
Figure 5.4: DFT MD displacement divided by the calculated expanded lattice parameter for BCC systems.

5.6 SOURCES OF ERROR

Figure 5.5 shows the change in energy in eV versus atomic displacement in Å for three different displacements in the Mo vacancy system. Both the perfect system (solid line) and atom furthest from the defect in the vacancy calculation cell (dashed line) exhibit symmetric energy changes with respect to displacement, as is typically expected in a stable material system. However, the atom adjacent to the defect in the vacancy calculation cell (dot-dashed line) exhibits a distinct asymmetry in energy change with respect to atomic displacement. This supports our decision to use a force-averaging scheme in our free energy calculations; while this difference may not appear important
for the very stable Mo system, it is much greater in magnitude for other, less well-behaved systems.

Figure 5.6 shows the BCC vacancy formation entropy as a function of displacement magnitude for the Mo system. While the exact shape of this relationship has not been explored between the displayed data points, it is clear that there is a dramatic difference between a traditional small-displacement phonon calculation at 0.03 Å and any phonon calculation at a larger displacement. We may expect a small spread in displacement size as determined by DFT MD due to the stochastic nature of the calculation, but we see that as long as displacements are consistently large enough, we can expect significantly less error than would be encountered from assuming the small-displacement case.

Additionally, we find differences in DFT MD displacements from slightly different cell volumes and calculation parameters to be much less than the differences tested here, so we expect the error in vacancy formation entropy from this source to be significantly less than the ~20% obtained here.

Figure 5.7 shows the BCC vacancy formation entropy as a function of calculation cell volume for the Mo system. It is fairly well established [2] that the vacancy formation energy is sensitive to volume: for our study, we find it to be at most 10% for stable BCC systems. Vacancy formation entropy seems to be more sensitive, with a reduction of greater than 25% for even the stable Mo system between the thermally expanded and relaxed lattice volume. Also displayed in Figure 5.7 are vacancy formation entropies calculated for cells that were fully relaxed internally instead of limiting the relaxation to the first two neighbor shells. The error associated with this approximation is an order of
Figure 5.5: Change in energy $dE$ versus displacement $u$ for perfect BCC Mo atom (solid line), Mo atom far from vacancy (dashed line), and Mo atom adjacent to vacancy (dot-dashed line).

Figure 5.6: Mo vacancy formation entropy versus displacement magnitude.
magnitude less than that observed for deviations in the calculation cell volume. Thus, we may safely infer that the greatest source of error in this type of calculation is the thermal expansion of the thermal expansion of the atomic lattice, which we calculated and ideally minimized in our algorithm.
<table>
<thead>
<tr>
<th>BCC metal</th>
<th>Experimental Melting Point, K$^{[7]}$</th>
<th>Calculated $F_r^V$, eV</th>
<th>Vacancy Concentration at $T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>454</td>
<td>0.488</td>
<td>3.71x10$^{-6}$</td>
</tr>
<tr>
<td>Be</td>
<td>1560</td>
<td>0.066</td>
<td>6.12x10$^{-1}$</td>
</tr>
<tr>
<td>Na</td>
<td>371</td>
<td>0.364</td>
<td>1.13x10$^{-3}$</td>
</tr>
<tr>
<td>Mg</td>
<td>923</td>
<td>0.428</td>
<td>4.62x10$^{-2}$</td>
</tr>
<tr>
<td>K</td>
<td>337</td>
<td>0.211</td>
<td>6.89x10$^{-4}$</td>
</tr>
<tr>
<td>Ca</td>
<td>1115</td>
<td>1.04</td>
<td>1.93x10$^{-5}$</td>
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<tr>
<td>Sc</td>
<td>1814</td>
<td>1.17</td>
<td>5.64x10$^{-4}$</td>
</tr>
<tr>
<td>Ti</td>
<td>1941</td>
<td>2.53</td>
<td>2.66x10$^{-7}$</td>
</tr>
<tr>
<td>V</td>
<td>2183</td>
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<td>Fe</td>
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<td>1.37</td>
<td>1.53x10$^{-4}$</td>
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<td>Rb</td>
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<td>Sr</td>
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<td>3.55x10$^{-4}$</td>
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<tr>
<td>W</td>
<td>3695</td>
<td>2.62</td>
<td>2.69x10$^{-4}$</td>
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</tbody>
</table>

Table 5.4: Experimental melting point, calculated free energy of vacancy formation at the melting point, and corresponding vacancy concentration at the melting point for BCC metals.
5.7 CONCLUSIONS

We have shown in this work that the rigorous, self-consistent calculation of vacancy thermodynamics is a daunting but not insurmountable task. Using DFT MD, we determined that the typical displacements selected for phonon calculations are not representative of many metallic systems at reasonable finite temperatures. Our calculated displacements were then used to calculate lattice thermal expansion to a high degree of accuracy and subsequently to calculate the free energy of vacancy formation in a myriad of BCC systems. We also introduced a force averaging scheme that does not differ from the limiting case of a symmetric force matrix but allows for asymmetry in the displacement of atoms around a defect. Our results indicate several expected trends for vacancy formation energy but little predictability in vacancy formation entropy. While a possible next step might be to increase the self-consistency of the calculation by determining displacement and lattice expansion across a temperature range of interest, the additional computational effort expended in such a task is better spend optimizing a single material system than attempting to apply the same convergence criterion across the periodic table. With the algorithm developed in this study, we feel confident that the vast majority of systems for which DFT is properly applied can be probed to successfully yield thermodynamic data.

REFERENCES


Chapter 6: Phonon-induced diamagnetic force and its effect on the lattice thermal conductivity

This chapter represents a set of calculations performed on a material system in which thermal behavior is completely dominated by vibrational effects by design. Nikolas Antolin performed all the DFT calculations using the ELK code for this work and worked with Oscar Restrepo to perform the analysis of these results. This paper was published as Hyungyu Jin, Oscar D. Restrepo, Nikolas Antolin, Stephen R. Boona, Wolfgang Windl, Roberto C. Myers, and Joseph P. Heremans, Nature Materials, Volume 14, pages 601-606 on 23 March 2015 and is reported here in its unchanged form. Supplementary material for this paper is contained in Appendix B.

6.1 ABSTRACT

Phonons are displacements of atoms around their rest positions in a crystalline solid. They carry sound and heat, but are not classically associated with magnetism. Here, we show that phonons are, in fact, sensitive to magnetic fields, even in diamagnetic materials. We do so by demonstrating experimentally that acoustic phonons in a diamagnetic semiconductor (InSb) scatter more strongly from one another when a magnetic field is applied. We attribute this observation to the magnetic-field sensitivity of the anharmonicity of the interatomic bonds that govern the probability of phonon-phonon interactions. The displacements of atoms locally affect the orbital motion of valence band electrons, which, in the presence of an external magnetic field, spatially modulates the
orbital diamagnetism around the displaced atoms. The spatial gradient in magnetic moment results in an anharmonic magnetic force exerted on the displaced atom. The process is modelled by *ab initio* calculations that, without the use of a single adjustable parameter, reproduce the observed 12% decrease in the lattice thermal conductivity under a 7 T magnetic field at a temperature of 5.2 K.

6.2 INTRODUCTION

Electrons, phonons, and magnons (spin waves) are three elemental excitations in solids known to carry heat. Electrons are subject to a Lorentz force in the presence of an applied external magnetic field ($H$), giving rise to thermomagnetic effects.[1] The magnon density-of-states, heat capacity and thermal conductivity ($\kappa$) are affected by $H$ (ref. 2). In ferromagnetic crystals lacking inversion symmetry, $H$ can induce a Dzyaloshinskii–Moriya interaction that results in a magnon Hall effect.[3] It is only the phonon properties that are not conventionally considered to be sensitive to $H$, although some reports exist of thermomagnetic effects in insulating paramagnetic materials.[4,5] In contrast, we report here a magnetic response of the phonons in InSb, where the electronic states near the Fermi energy consist of only $s$- and $p$-electron shells, and attribute it to phonon-specific local diamagnetic moments on the atoms. These moments arise in the presence of an external magnetic field from phonon-induced changes in the valence band. Local and transient net moments then appear when phonon displacements are treated as effectively frozen in time (frozen-phonon approximation). They change continuously with time-dependent displacement, owing to the nearly instantaneous redistribution of electrons after changes in ionic-core position. Obviously, both the spatial and temporal averages of
this phonon-induced diamagnetic moment are zero. Yet, as we show, the spatial gradient in this transient moment alters the interatomic forces and results in magnetic-field-sensitive bond anharmonicities and phonon-phonon interactions; mechanisms that have

Figure 6.1: Magnetic-field dependence of lattice thermal conductivity in InSb. a, InSb tuning fork with a large arm of cross-section $A_L$ and a small arm of cross-section $A_S$. b, Principle of the tuning fork geometry: two heaters provide heat fluxes $Q_L$ and $Q_S$. The measurements are made when the temperature difference between the arms is zero ($\Delta T_{\text{DIFF}} = 0$)—that is, the condition $\kappa_L/\kappa_S = (Q_L/Q_S)/(A_L/A_S)$ holds. This gives an accurate measurement of the ratio $\kappa_L/\kappa_S$. c, Temperature dependence of $\kappa_L/\kappa_S$ at zero magnetic field and in a longitudinal magnetic field of 7 T (sample A). The inset shows $\kappa_L/\kappa_S$ over an extended temperature range. T denotes the average temperature of the sample, which, by the design of the tuning fork, is the same in the small and large arms. The error bars are standard deviations of the means, obtained as described in the Supplementary Information.
been at the root of the most recent progress in the design of thermoelectric materials.[6,7,8]

6.3 MAGNETIC-FIELD DEPENDENCE OF PHONON-PHONON INTERACTIONS

We used large InSb single-crystal samples with heat flow \( Q \) and \( H \) aligned along the [100] direction. Below 10 K, their thermal conductivity is \( \sim 200 \leq \kappa \leq \sim 2,700 \text{ Wm}^{-1}\text{K}^{-1} \) and entirely due to phonons, with the electronic thermal conductivity being 105 times smaller than the phonon conductivity (see Supplementary Information in Appendix B).

We mount each crystal in a tuning fork geometry (Figure 6.1a,b):[9,10] measuring the phonon conductivity ratio between the arms of a tuning fork sample allows one to isolate different phonon scattering mechanisms from boundary effects. The tuning fork has a large arm and a small arm of cross-sectional areas \( A_L \) and \( A_S \), through which heat fluxes \( Q_L \) and \( Q_S \) are sent, respectively. The tuning fork is the thermal equivalent of a galvanic potentiometer: when the ratio of the heat flows \( Q_L/Q_S \) is balanced so that \( \Delta T_{\text{DIFF}} = 0 \) (Figure 6.1b), the ratio between the lattice thermal conductivities of the large and small arms (\( \kappa_L \) and \( \kappa_S \), respectively) is \( \kappa_L/\kappa_S = (Q_L/Q_S)/(A_L/A_S) \).

This measurement of \( \kappa_L/\kappa_S \) is independent of the calibration of the thermometers, of their \( H \)-dependence (see Supplementary Information in Appendix B), and of eventual heat losses, assuming that both arms have the same losses. Only the amount of heat delivered by the heaters needs to be measured accurately, allowing a resolution of 1 part in \( \sim 10^4 \) or better. Most importantly, we will show that \( \kappa_S \) is mostly due to ballistic phonon transport below 8 K in our samples, which provides a reference to isolate the physics of phonon–phonon interactions in the measured ratio \( \kappa_L/\kappa_S \) (ref. 10).
Figure 6.2: Measurements on sample B with reduced thermal conductivity after thermal cycling.

a. Temperature dependence of $\kappa_L/\kappa_S$ at $H = 0$ T and in a longitudinal field $H = 7$ T. $\kappa_L/\kappa_S$ is an even function of magnetic field, as expected from symmetry.[25] c. Temperature dependence of $\kappa_S$ ($H = 0$ T), measured using the heater-and-sink method. The dashed line shows $\kappa_L$ calculated from $\kappa_S$ and the ratio in a. The yellow shaded region indicates the temperature range where the effect of magnetic field on $\kappa_L/\kappa_S$ is most pronounced. d. Temperature dependence of the specific heat of a piece of the same boule of InSb; the inset shows its relative change with field $\Delta C_p/C_p \equiv [C_p(7 \text{ T}) - C_p(0 \text{ T})]/C_p(0 \text{ T})$, which is less than 2%, but not resolved above the noise level. The error bars are standard deviations of the means, obtained as described in the Supplementary Information in Appendix B. $T$ denotes the average temperature of the sample.
The ratio $\kappa_L/\kappa_S$ is shown as a function of temperature in Figure 6.1c at $H = 0$ and 7 T for the first sample (A). The error bars were calculated in detail by taking possible random, systematic and fitting errors into account (Supplementary Information in Appendix B). The observed change in $\kappa_L/\kappa_S$ (12% at 7 T and 5.2 K) is well above the error bars. Figure 6.2a shows a repeat of the same measurement on sample B—the same sample after it had been cycled three times to room temperature and subjected to a considerable amount of thermal shock that induced dislocation strain fields in both arms that scatter phonons and strongly reduce $\kappa$. Both the ratio $\kappa_L/\kappa_S$ and its $H$-dependence (6% below 4 K) are smaller than in sample A (Figure 6.1c). The ratio $\kappa_L/\kappa_S$ is shown as a function of $H$ in Figure 6.2b to be a monotonic and even function of $H$.

The thermal conductivity of the small arm of sample B, $\kappa_S$, is shown in Figure 6.2c. The $H$-dependence of $\kappa_L/\kappa_S$ is observed in the temperature range between 3 and 8 K, where $\kappa_S(T)$ is limited primarily by scattering on the boundaries of our particular samples and phonon conduction is essentially ballistic.[11] Deviations from ballistic phonon transport start to occur first in $\kappa_L$ at these temperatures, and $\kappa_S$ serves as an internal reference for all material properties of the sample except phonon–phonon interactions. From 3 to 8 K, phonons are scattered [11] by other phonons at a rate of $\tau_\varphi^{-1}$, by dislocations at a rate of $\tau_D^{-1}$, by point defects at a rate of $\tau_{PD}^{-1}$, and by the sample’s boundaries at a rate of $\tau_{BS}^{-1}$ in the small arm and $\tau_{BL}^{-1}$ in the large arm. Assuming that these scattering mechanisms operate independently of each other (Matthiessen’s rule [11]), the total scattering rate is $\tau^{-1} = \tau_\varphi^{-1} + \tau_D^{-1} + \tau_{PD}^{-1} + \tau_B^{-1}$, where $\tau_B^{-1}$ is either $\tau_{BS}^{-1}$ or $\tau_{BL}^{-1}$ depending on which arm is considered. The kinetic formula [11] gives $\kappa = 1/3Cv\ell = 1/3Cv^2\tau$, where $C$ is the
specific heat, \( v \) the sound velocity, \( \ell \) the mean free path (\( \ell = v \tau \)) and \( \tau \) the scattering time. Rigorously, this formula has to be integrated over phonon modes and wavevectors \( q \). In our geometry and temperature range, heat is carried principally by one longitudinal acoustic (LA) and two transverse acoustic (TA) modes with propagation velocities along [100] and essentially linear dispersion relations. When these phonons interact with other phonons, \( \tau^{-1}_\varphi \) involves phonons throughout the Brillouin zone (BZ; ref. 13). For this simple analysis, we consider the kinetic formula to be a mode and frequency average, and write

\[
\frac{\kappa_L}{\kappa_S} = \frac{1}{3C_v^2} \left[ \frac{\tau^{-1}_\varphi + \tau^{-1}_D + \tau^{-1}_P + \tau^{-1}_BL}{\tau^{-1}_D + \tau^{-1}_P + \tau^{-1}_BL} \right] = \frac{\tau^{-1}_D + \tau^{-1}_P + \tau^{-1}_BL}{\tau^{-1}_D + \tau^{-1}_P + \tau^{-1}_BL} \tag{1}
\]

Thus \( \kappa_L/\kappa_S \) is independent of \( C \) and \( v \). We measure \( C(T, H) \) (Figure 6.2d) and observe that it is independent of \( H \) to within our experimental accuracy (2%). In the temperature range between 3 and 8 K, boundary scattering dominates in the small arm, but phonon-phonon scattering is more important in the large arm (\( \tau^{-1}_{BS} > \tau^{-1}_\varphi, \tau^{-1}_{BL}; \text{refs 9, 10} \)). Thus, equation (1) reduces to

\[
\frac{\kappa_L}{\kappa_S} \approx \frac{\tau^{-1}_D + \tau^{-1}_P + \tau^{-1}_{BS}}{\tau^{-1}_D + \tau^{-1}_P + \tau^{-1}_{BL}} \tag{2}
\]

\( \tau^{-1}_\varphi \) and \( \tau^{-1}_D \) are proportional [11] to the square of the Grüneisen parameter, which, for each mode \( i \) and frequency \( \omega \), is defined as \( \gamma_i(\omega) = \frac{d\ln \omega}{d\ln V} \), the logarithmic derivative of the phonon angular frequency \( \omega \) with respect to the volume \( V \) of the crystal. The thermal conductivity involves phonons and phonon interactions throughout the entire BZ. Therefore, \( \tau^{-1}_\varphi \) and \( \tau^{-1}_D \) depend on the mode- and frequency-averaged Grüneisen parameter \( \gamma \) weighted by the specific heat. \( \gamma \) quantifies the degree to which the bond
forces deviate from simple harmonic behavior and is temperature dependent: it changes
sign in InSb below 5 K (refs 14, 15). When two phonons collide in a solid with $\gamma \neq 0$, the
presence of the first phonon locally modifies the acoustic properties for the second
phonon, decreasing its transmission probability. The same reasoning applies to the
interaction between a phonon and the strain field around a dislocation. As a result, it is
given [11] that $\tau_{\phi}^{-1}, \tau_{D}^{-1} \propto \gamma^{2}$.

When dislocation scattering is less important than the other mechanisms (sample A),
equation (2) shows that the effect of $\gamma$ is limited to the denominator of $\kappa_{L}/\kappa_{S}$, even in the
presence of point defect and boundary scattering in the large arm. In the ideal case of
defect-free isotopically pure InSb with $A_{L} \to \infty$, $\tau_{\phi}^{-1} \gg (\tau_{PD}^{-1}, \tau_{D}^{-1}, \tau_{BL}^{-1})$ and $\kappa_{L}/\kappa_{S} \approx \tau_{BS}^{-1}/\tau_{\phi}^{-1} \propto \gamma^{-2}$, because $\tau_{BS}^{-1}$ is independent of temperature (as are the sample
dimensions and the sound velocity). Dislocation scattering (sample B) and the presence
of the other scattering mechanisms are expected to attenuate the effect of $\gamma$ on $\kappa_{L}/\kappa_{S}$, as
verified experimentally by comparing the effect on sample B (Figure 6.2a) against that on
sample A (Figure 6.1c). In the following ab initio theory section, we neglect the effects of
dislocations on sample A, and the resulting agreement between theory and experiment
will justify this approach a posteriori. Note that the temperature dependence of the effect
shown in Figure 6.1 and Figure 6.2 arises from our choice of material and sample
geometry. InSb was selected so that the observed effect would occur in a region where
the tuning fork geometry is able to distinguish the anharmonic regime from the boundary
scattering regime. The sample dimensions were then selected so as to isolate $\tau_{\phi}^{-1}$ above 3
K. The fact that the effect is most pronounced between 3 and 8 K is not intrinsic but
results from the selection of the experimental parameters, which is based on theoretical considerations given below.

We identify possible origins for the \( H \)-dependence of \( \kappa_L/\kappa_S \) as the electronic thermal conductivity or Peltier heat, phonon-electron interactions, an \( H \)-dependent phonon density-of-states, and an \( H \)-dependent phonon-phonon scattering rate via \( \gamma \). Considering first the Peltier heat, the electronic contribution to the thermal conductivity is measured and calculated in the Supplementary Information. This effect is limited to \( <6 \times 10^{-3} \) Wm\(^{-1}\)K\(^{-1}\), which is less than a 1:105 part of the total conduction. In the case of phonon-electron interactions, low-frequency phonons with wavevectors \( k_{\text{phonon}} \sim k_{\text{electron}} \) can be scattered by electrons as the temperature decreases (the reciprocal effect of phonon-drag [16], which we observe; see Supplementary Information in Appendix B). If this effect were important, however, \( \kappa_L/\kappa_S \) would increase with \( H \) because the electrons in InSb freeze out in magnetic fields at low temperature (see Supplementary Information in Appendix B), which is the opposite of what we observe. We also rule out an \( H \)-dependent phonon density-of-states, as we observe no significant \( H \)-dependence to the specific heat (Figure 6.2d). Indeed, at the temperatures of the experiment (<10 K) the LA and TA modes that contribute to the specific heat are also those that contribute to the thermal conductivity.[12]

We therefore put forward the last hypothesis; that the \( H \)-dependence of \( \gamma \) gives rise to the \( H \)-dependence of \( \kappa_L/\kappa_S \), such that

\[
\frac{\Delta \left[ \kappa_L/\kappa_S \right]}{\kappa_L/\kappa_S} = \left( \frac{\kappa_L}{\kappa_S} \right)_{H=7 \, T} - \left( \frac{\kappa_L}{\kappa_S} \right)_{H=0 \, T} = \frac{\Delta [\gamma^{-2}]}{\gamma^{-2}} = - \frac{(\gamma^{-2})_{H=7 \, T} - (\gamma^{-2})_{H=0 \, T}}{(\gamma^{-2})_{H=0 \, T}}
\]  

(3)
This hypothesis leads to a quantitative agreement between the experimental magnitude and temperature dependence of the effect and an \textit{ab initio} calculation of a phonon-induced magnetic moment (Figure 6.4). Because $\gamma$ depends fundamentally on the interatomic potential ($U$), the $H$-dependence of $\gamma$ must arise from an $H$-induced modification of $U$. Under the conditions where we observe $H$-dependent thermal properties, InSb contains negligible conduction electrons or valence band holes; it is insulating and without net spin. In such a solid, $H$ can induce changes only in orbital angular momentum ($L$) of core electrons and the filled valence band. Such changes give rise to the Langevin diamagnetism, as well as virtual magnetic dipole transitions between energy levels in an $LS$ multiple ($E(J) - E(J \pm 1)$), where $S$ is the spin angular momentum and $J$ the total angular momentum ($J = L + S$), which is known as Van Vleck paramagnetism.\cite{17,18} The magnetic susceptibility $\chi$, which is the ratio of the induced magnetization ($M$) to $H$, is therefore given by

$$\chi = -\frac{\mu_0 N Ze^2}{6m} \sum_{\text{core}} \langle r^2 \rangle - \frac{\mu_0 N Ze^2}{6m} \sum_{\text{valence}} \langle r^2 \rangle + 2N \mu_0 \mu_B^2 \sum_i \sum_{j \neq i} \frac{|\langle i | (L Z + g_0 S Z) | j \rangle|^2}{E_i - E_j}$$

with $\mu_0$ the magnetic permeability of free space, $\mu_B$ the Bohr magneton, $N$ the density of atoms, $Z$ the atomic number, $m$ the free electron mass, $r$ the atomic radius and $g_0$ the electronic $g$-factor. Considering the sensitivity of the three terms to phonon displacement, we can expect that the core susceptibility feels negligible influence. We expect the diamagnetic susceptibility, being driven by valence electron orbital motion, to be sensitive to the local bonding environment. Lande’s interval rule indicates that transitions between $E(J) - E(J \pm 1)$ are proportional to the magnitude of the spin–orbit coupling
(SOC; ref. 18). Our calculations show that the change in SOC with atomic displacements is negligible (<1%), from which we conclude that the Van Vleck paramagnetic term does not couple to phonons. One then expects a local change $\Delta \chi_\phi$ in $\chi$ due to the atomic displacements and bond distortions associated with a phonon. Accordingly, we label $\Delta \chi_\phi$ the phonon-induced diamagnetic susceptibility. Under an applied field $H$, the diamagnetic response of the solid is altered locally around phonons; that is, phonons exhibit a diamagnetic moment $H\Delta \chi_\phi$. However, phonon displacements are averaged to zero over time and space, which means the phonon moments must also sum to zero, although they can lead to magnetic-field sensitive local interactions with other phonons through these transient moments.

The quantitative picture we offer is based on the frozen-phonon model, whereby atomic motions occur at terahertz frequencies, which is a timescale much slower than that of electrons. The electrons therefore see the solid locally distorted by the phonon as a different crystal and develop a local perturbation of the band structure around the phonon. The conduction (CB) and valence bands (VB) are both affected. By considering equation (4) and the known sensitivity of $\chi$ to long-range Coulomb interactions, we postulate that the free electron mass in equation (4) can be replaced with the VB effective mass to approximate the effect of the VB structure on $\chi$. By this mechanism, the band structure distortion associated with the phonon is proportional to $\Delta \chi_\phi$ around the equilibrium position $r_0$ of an atom. This results in a local magnetic moment density $M(r) = H\chi(r)$ around that atom in an external applied magnetic field, and a magnetic force $F_M(r) = \nabla[M(r) \cdot H] = H^2 \nabla \chi(r)$ that adds to the interatomic force $F_0$. If we assume that $F_0$ is
harmonic and characterized by a spring constant $K (F_0 = K r)$ independent of $r$, then the total force $F = K r + F_M(r)$ is no longer harmonic, and an $H$-dependent contribution to $\gamma$ of the order $\Delta \gamma(H) \propto H^2 \nabla^2 \chi(r)$ is expected.

Figure 6.3: Ab initio calculation of the magnetic moment of frozen phonons in InSb. a, The frozen-phonon picture, showing the atomic displacements of the In atoms for a longitudinal acoustic [010] mode. The red arrow indicates the direction of the heat flux (Q) and applied field (H). b, Calculated VB maximum in $H = 20$ T (an unrealistically high value to visualize the effect), the blue lines with the atoms in their equilibrium positions, the red dotted lines with the atoms displaced by 0.07 Å as in a. c, Spatial distribution of the change in magnetic moment density (logarithmic mesh) in the plane normal to [101], calculated for an unrealistic 0.18 Å displacement of In atoms used to illustrate the effect. d, Calculated phonon-induced diamagnetic susceptibility $\Delta \chi_{\varphi}$, averaged over the unit cell as a function of atomic displacement $u$ (the In atoms are displaced along [010]).
The above model is tested using *ab initio* density functional theory (DFT) modelling in an applied magnetic field $H$ carried out in three steps considering the LA and two TA phonon modes described above. First, the average atomic displacements are calculated using *ab initio* molecular dynamics, and are found to be of the order [19] of 0.05 Å in the low-temperature limit ($T < 30$ K, numerical values given in the Supplementary Information in Appendix B). Second, band structure calculations in $H$ with the ELK (refs 20, 21) code (see Methods) for displaced frozen-phonon cells reveal changes in CB and VB. In the presence of the frozen phonon shown in Figure 6.3a with In atoms displaced by 0.07 Å, Figure 6.3b shows that the VB effective mass decreases by 5% in $H = 20$ T.

Finally, the magnetic moment $M(r)$, integrated over the unit cell, is calculated to be $M = -50m\mu_B$ for $H = 20$ T when the atoms are in their equilibrium positions. This corresponds well to the diamagnetic susceptibility ($\chi = -2.46 \times 10^{-7}$) of InSb. With the displacement of 0.07 Å, the value of $M$ increases by 8% to $M = -54m\mu_B$. Figure 6.3c shows that the local variation of $M(r)$ in the ([010], [101]) plane due to the atomic motion of Figure 6.3a is very localized around the In and Sb atoms: this creates a strong spatial gradient of $M(r)$. The vector potential $A$ in the Hamiltonian of the interaction (see Supplementary Information in Appendix B) is identified as the physical origin of the phonon-induced local diamagnetic moment. This can be specifically written as $\Delta\chi_\phi = -(Ne^2/4mc^2H^2)A^2(r_i)$. Figure 6.3d shows $\Delta\chi_\phi$ as a function of atomic displacement. At small, experimentally accessible displacements of $u < 0.1$ Å, both CB and VB move, but the gap does not close. The change $\Delta\chi_\phi$ is mainly phonon-induced Langevin diamagnetism (equation (4); ref. 17). At very high displacements ($u > 0.18$ Å, presently
beyond the reach of experiments), the frozen phonon can move the CB and VB so as to
close the energy gap. Free electrons and holes appear, resulting in additional Landau
diamagnetism. This observation relates the effect we describe here to the
magnetostriction observed at high field in diamagnetic solids,[22,23] to track the de
Haas–van Alphen effect. At the lower fields where the present experiments are carried
out, the field only insignificantly affects the bond lengths or the phonon frequencies
themselves, yet its effect on the derivative of the phonon frequencies is still important.
Effects of electronic properties that are insignificant on the phonon frequencies
themselves but strongly affect the Grüneisen parameters have been observed in both
semiconductors [8] and metals.[24]

Applying the procedure outlined above to the ab initio values of $M(r)$, we derive $H$-
dependent values of $\gamma$ integrated over the unit cell, and directly compare experiment and
theory. Figure 6.4 shows the ratio $\Delta[\gamma^{-2}] / \gamma^{-2}$ calculated ab initio using $\gamma(T)$ from ref. 14
with no adjustable parameters. This is compared (equation (3)) to the experimental $H$-
dependence of $\kappa_L / \kappa_S$. We submit that the agreement supports the hypothesis. Note that the
phonon-induced diamagnetic moment itself is, to the first order, independent of
temperature. Indeed, the movement of the atoms around their equilibrium positions below
10 K in InSb is due to a temperature-independent quantum effect—the zero-point
vibrations [19]—and diamagnetism arises from the valence band, which has no
temperature-dependence other than through atomic motion.[19] The relative effect of the
phonon-induced diamagnetic moment on $\gamma$ is most pronounced at temperatures where the
background $\gamma$ is small and the thermal expansion coefficient crosses zero—that is, $\sim 4$ K
in InSb (ref. 14). This determines the overall temperature dependence of the experimentally observed effect.

Figure 6.4: Agreement between \textit{ab initio} theory and experiment. Temperature dependence of the \textit{ab initio} calculated relative change in Grüneisen parameter with field ($\Delta[\gamma^{-2}]/\gamma^{-2}$) is compared against the experimentally observed change in ratio $\kappa_L/\kappa_S$, using equation (3). The field is changed from 0 to 7 T. The $\gamma(T)$ values are from ref. 14. The agreement, which involves no adjustable parameters, is evidence for the existence of phonon-induced diamagnetism and its role in phonon–phonon interactions. The error bars are standard deviations from the means.

\section*{6.5 Outlook}

We identify a magnetic-field response of the lattice thermal conductivity experimentally, and attribute it to a specific phonon-induced diamagnetic moment. This local diamagnetism is small and does not result in a net magnetic moment, because both spatial and temporal averages of this moment are zero. However, its very sharp spatial gradient
results in an anharmonic force applied to the atoms in the solid that is intense enough to be measured in the thermal properties. It is likely that this phonon-induced diamagnetism is a universal property of all solids, and it is plausible that it may be a yet undiscovered mechanism for coupling between phonons, heat and magnetic systems.

6.6 METHODS

The starting material for the samples is an InSb boule doped with Te to an electron concentration of $1.3 \times 10^{15} \text{ cm}^{-3}$ (measured by Hall effect at temperatures $3 \text{ K} < T < 50 \text{ K}$). Magnetization measurements on a piece of the same boule showed that no magnetic impurities are present in the samples down to our sensitivity limit of 16 ppb. The electronic transport and magnetic properties of the material are given in the Supplementary Information in Appendix B. The samples are cut into the tuning fork geometry shown in Figure 6.1. The large arm has a cross-section $A_L \sim 4 \times 3 \text{ mm}^2$, and the small arm has $A_S \sim 4 \times 1 \text{ mm}^2$. The length of both arms is 17.3 mm. The sample was mounted on a heat sink, with the small arm equipped with one 120 Ω heater and the large arm with three heaters. Each arm was equipped with $0.965 \times 0.762 \times 0.203 \text{ mm}^3$ Cernox thermometers, as shown, which were calibrated as a function of temperature (their field dependence was also previously characterized). We fixed the power $Q_L$ on the large arm and adjusted the heater power on the small arm ($Q_S$) until $\Delta T_{\text{DIFF}} = 0$ (see Figure 6.1b). At this value of $Q_S$, the thermal conductivity ratio $\kappa_L/\kappa_S = (Q_L/Q_S)/(A_L/A_S)$, where $\kappa_L$ and $\kappa_S$ denote the thermal conductivities, and $A_L$ and $A_S$ the cross-sectional areas of the large and small arms, respectively. The area ratio $(A_L/A_S)$ is determined accurately from the high-temperature asymptote of $Q_L/Q_S$. A detailed description of this method and an analysis of
the errors it accrues, which determines the error bars in Figure 6.1 and Figure 6.2, is provided in the Supplementary Information with a detailed description of how the magnetic-field dependence of the Cernox thermometers is eliminated from the measurements. The lowest temperature of all experiments is limited by the cooling power of the cryostat and the fact that the thermal resistance between the sample and the cryostat is much larger than that of the sample itself. Consequently, the heat flux necessary to create a gradient across the sample also increases the sample’s average temperature considerably above that of the cryostat. As a result, for example, the lowest temperature that could be reached on the sample B with dislocations (Figure 6.2a) is lower than that of the more pristine sample A (Figure 6.1c).

The thermal conductivity in Figure 6.2c was measured using the classical heater-and-sink method on the small arm of sample B, which is the sample that had the lowest $\kappa$ in the experiment, for the same reason: all other arms either require large heater powers or give small gradients. The thermal conductivity of the large arm ($\kappa_L$) of sample B was then calculated from $\kappa_S$ and the ratio in Figure 6.2a; more details are given in the Supplementary Information in Appendix B.

No transverse thermal gradient due to the phonon Hall effect [4] is expected to perturb the measurement, because in our configuration the magnetic field is parallel to the flux. In that configuration the transverse gradient was shown experimentally [4] to be zero, as expected theoretically from the Onsager relations.[25]

The ELK program is an all-electron, full-potential, linearized augmented-plane wave code.[20,21] It allows inclusion of non-collinear magnetism with arbitrary external
magnetic fields. We checked the convergence of our results by performing calculations with an increasing number of k-points in the BZ. We found that including 20 empty states in our calculations gives us an accuracy of better than 1%. To verify accuracy we used 31×31×23 k-point meshes. Our results show that the change in magnetic moment is less than 20% from 15×15×11 k-point meshes. We used the latter in our calculations as they represent a significant decrease in the computational demands and do not change our overall conclusions. We verify that the local magnetic moment $M(r)$ is linear in applied field (see Figure B.11, Appendix B), so that the susceptibility $\chi(r)$ is independent of field and the moment is given by $M(r) = H\chi(r)$. The calculated value of $\gamma$ is the mode and frequency average over the whole BZ, weighted by the specific heat (see Supplementary Information in Appendix B). We used the experimental value of Hass et al.[26] for the phonon linewidth and expressed it as an energy smearing equivalent to a temperature of 2 K (see Supplementary Information in Appendix B); this value affects the lineshape, but not the magnitude, of the calculated line in Figure 6.4. We point out that the agreement in Figure 6.4 would have had an offset along the x-axis of 2 K had we used the $\gamma(T)$ data of ref. 15, as also described in the Supplementary Information. Supplementary Movie 1 illustrates the local magnetic moments in the plane normal to the [101] axis around In and Sb atoms moving during the passage of a LA [010] phonon.

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20) Dewhurst, J. K. *et al.* Elk FP-LAPW code, version 2.2.9 (2004); http://elk.sourceforge.net


Chapter 7: Summary

In this dissertation we have explored macroscopic thermal properties of two metallic and one semiconductor system using atomistic modeling based on density functional theory. We have also seen that there is a range of thermal effects on the atomistic level, and that an appropriate level of detail must be used to effectively treat these effects in a meaningful way. For systems where total energy differences are large and the contributions of entropy are similar for the compared structures, we are safely able to approximate free energy differences with the internal energies calculated from DFT. For systems where total energy differences are small, it becomes necessary to consider the contributions of entropy to the free energy. In these systems, the quasiharmonic approximation (QHA), with its incorporation of anharmonicity through thermal expansion, is typically preferred to a more basic harmonic approximation. However, in our work, we see that even typical QHA approaches are not sufficient due to anharmonic behavior resulting from atomic displacements that are larger than typically treated in QHA. We develop a large-displacement (L-D) QHA approach to deal with systems where entropic stabilization results from these large displacements and show that even stable systems require displacements much larger than the common practice to probe high-temperature properties. We also find that finite difference averaging near
defects violates the assumptions of QHA and propose a force-scaling scheme based on equipotential atomic motion to compensate for this strongly anharmonic behavior. We started by exploring the properties of creep-induced defects in a Ni$_3$Al alloy system. This system exhibits solute segregation to stacking faults, an effect which we were able to characterize energetically; additionally, we showed that this effect arises from chemical differences in bonding within the defect and not solely as a response to strain concentration at the defect. The energy differences were large enough and the atomic configurations were similar enough in these alloy systems that we are able to conclude these effects will persist at high temperature without formally calculating free energies in this system. Having established a basis for the formation of these defects, we went on to explore their effect on creep behavior in this alloy system by comparing the energy necessary to extend the fault to additional atomic planes for this and another closely related alloy system. Working with experimentalists, we were able to show that segregation of several particular solute atoms to the stacking faults suppressed the ability of the stacking faults to extend into twins as is observed in previously developed commercial alloys. We anticipate this mechanism to exist in several related alloy systems and to be relevant in the further development of superalloys for high-temperature turbine applications.

In the case of mechanically unstable BCC metals, we see that it is possible to isolate the cause to of mechanical instability to inadequate sampling of a quasi-parabolic regime of the displacement-energy curve, resulting from small displacement methods typically used in phonon calculations. We propose a large-displacement method corresponding to a
stable range of the displacement-energy curve, and show that results using this method
are at least as accurate as those purporting to fully compensate for the origins of the BCC
phase instability and much more computationally efficient, allowing treatment of more
complex systems.

We go on to expand our work on BCC metal systems to encompass all elemental systems
for which DFT is reported to produce good results, calculating the vacancy formation
energy and entropy for each system using methods developed from the large-
displacement method. In the course of this work, we have shown that typical small
displacement phonon calculations are not representative of atomic displacements in
thermalized systems, and that adequate displacement magnitude is critical for calculation
of reasonable results. We also show that results are much less sensitive to displacement
magnitude past a critical point, and are insensitive to complete versus first- and second-
nearest-neighbor relaxation but extremely dependent upon calculation volume. Our
methods produce consistent results for all but a few high-temperature systems, and we
strongly suspect that these inconsistencies may be related to system properties. We are
able to show distinct trends in vacancy formation energy but not in vacancy formation
entropy, likely due to the single-point nature of our calculations.

Lastly, we explored a diamagnetic small bandgap semiconductor system (InSb) in which
an experiment was designed to determine the coupling between phonons and a magnetic
field. This coupling had previously only been theorized and was generally considered not
to exist. By examining the effects magnetic fields had on the energetics of individual
phonon branches in the crystal lattice, we were able to establish not only a theoretical
basis for the existence of coupling of phonons to magnetic field due to local magnetization of orbitals, but also to inform the experimental design for its observation. Theoretical results from these calculations are in excellent agreement with the measurements obtained from experiment, indicating the strong potential that exists to study the thermal properties of materials on this level. It should be noted, however, that the advanced analysis performed on this system would be not only impractical but unnecessary and wasteful for the other systems investigated due to the magnitude of the effects being studied. As might be expected, the universal applicability of density functional theory is a double-edged sword: only with knowledge of the appropriate level of detail to pursue can it be wielded effectively.
Appendix A: Supplementary Information for Chapter 3

Figure A.1 shows backscatter SEM images of the corresponding microstructures for ME3 and HL-11.

Figure A.1: SEM backscatter images of the (a) ME3 and (b) HL-11 microstructures.

Though both alloys experienced the same heat treatment the differences in alloying between the two resulted in different microstructures. HL-11 has a finer microstructure, but also a higher $\gamma'$ volume fraction. This higher volume fraction of secondary precipitates is a result of the greater amount of $\gamma'$ formers (Ta, Ti, Hf, and Nb).[1] These elements are also known $\eta$ phase formers.[2,3,4,5] Table A.1 shows the greater ratio of $\eta$ phase formers to Al that HL-11 possesses over ME3.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Wt% of η phase formers (Nb, Ta, W, Hf, Ti)</th>
<th>Ratio of wt% Al to η formers (Nb, Ta, W, Hf, Ti)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME3</td>
<td>9.1%</td>
<td>0.37</td>
</tr>
<tr>
<td>HL-11</td>
<td>13%</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table A.1: Alloying differences between ME3 and HL-11.

This higher amount of η formers in HL-11 (13% of total weight percent) may explain why η phase nucleates in HL-11 along SESFs while γ formers do so in ME3 (9% of total weight percent). Initial analysis using BF-STEM found microtwins to be more active in ME3 compared to HL-11, but the sample size reasonably obtained through STEM diffraction analysis of focus ion beam foils is not enough to conclusively make this assumption. Therefore, a technique called electron channeling contrast imaging (ECCI) was employed to create a larger deformation mode sample size.[6,7] By using the backscattered electron detector at low magnifications, electron channeling pattern lines can be observed. These lines indicate diffraction conditions, that when activated through tilting the bulk sample, can allow diffraction contrast imaging of dislocations and/or faults. The ability to image defects at low magnifications from large bulk samples allows for better statistical analysis. Therefore, this work was completed for the [001] ME3 and HL-11 samples to better understand the frequency of microtwins in both alloys. Below in Figure A.2 are two ECCI images showing defects in ME3 and HL-11.

Faults that extended through both γ and γ′ phases were classified twins; whereas, those that were isolated to just a precipitate were deemed SESFs. Table A.2 in Appendix A
contains the final statistics from the ECCI investigation. As was discovered in the STEM
diffraction work microtwins were much more prevalent in ME3 than in HL-11.

Viswanathan et al.[8] revealed a method to calculate the relative strain contribution from
twinning using the equation:

\[ \gamma = \frac{N_t \Delta_{avg}}{L} \]  

(1)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Twin avg.</th>
<th>Twin std.</th>
<th>Twin std. err.</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL-11</td>
<td>4.23</td>
<td>1.01</td>
<td>0.28</td>
<td>13</td>
</tr>
<tr>
<td>ME3</td>
<td>9.69</td>
<td>1.97</td>
<td>0.55</td>
<td>13</td>
</tr>
</tbody>
</table>

Table A.2: The twin occurrence rate for a 30μm² area for ME3 and HL-11. Twins are statistically
more prevalent in ME3 than HL-11.

Figure A.2: ECCI image of (a) ME3 showing 10 different twins and (b) HL-11 showing 4
different twins.

Using the ECCI images, for example those in Figure A.2, a line can be drawn across the
image with a length \(L\) that will cross a number of twins \(N_{twin}\). Using the average width
of twins \(\Delta_{avg}\) determined from high resolution HAADF-STEM images of edge-on twins,
the strain contribution from twins ($\gamma$) was calculated in both ME3 and HL-11 shown in Table A.3.

A large difference in the strain contribution from twins was found between HL-11 and ME3 due both from the fact that twins were observed with less frequency and the twins that were observed were significantly thinner. Though the contribution from twins in HL-11 is small, it may in fact be even less. Analysis on pre-creep test samples of HL-11 found twins inherent in the microstructure, possibly an artifact of the casting process. This suggests that the 7% contribution of strain from twins is most likely artificially high. Figure A.3 below shows an example of these twins.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Strain from twinning</th>
<th>% of Total strain from twinning</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME3</td>
<td>0.00343</td>
<td>50%</td>
</tr>
<tr>
<td>HL11</td>
<td>0.000455</td>
<td>7%</td>
</tr>
</tbody>
</table>

Table A.3: Strain contribution from twinning in ME3 and HL-11. A greater relative contribution is observed in ME3.

Previous studies have concluded that twin formation is an extension of SESF formation, where pairs of like-sign Shockley partials shear on adjacent $\{111\}$ planes along SESFs or twins to either form or extend them.[8,9,10,11,12] This scenario was observed numerous times in this HAADF-STEM analysis; however, it wasn’t the only scenario that was found to be possible. Below in Figure A.4 is an image of a SESF transitioning into a twin by the shearing of partials on either side of the fault.
Figure A.3: [001] zone axis BF-STEM image of as-cast HL-11. The long faults are twins most likely formed during the casting process.

Figure A.4: HAADF-STEM image of a SESF being sheared on either end to form a microtwin.
This scenario implies that there may be more ways for twins to form and the reordering of wrong nearest neighbors to occur. It was also observed that the formation/termination of twins occurred most frequently at $\gamma/\gamma'$ interfaces and not through de-correlation of full dislocations in the $\gamma$ channels as has been theorized in the past.[11]

As mentioned in the Methods section, 256 x 256 pixel atomic resolution EDX maps were collected in a region including an SESF in the HL-11 alloy. Given the fact that the SESF forms the $\eta$ phase, it can be asserted that site-specific segregation should exhibit the same periodicity dictated by the $\eta$ phase crystal structure.[2,4] Following on this, repeating units along the SESF can then be extracted from the total spectrum image and summed to improve the signal-to-noise ratio. Because the SESF was not oriented parallel to any side of the original spectrum image, the entire spectrum image was rotated using a bicubic interpolation from the Matlab 2015a Image Processing Toolbox.[13] As seen in Figure A.5, 11 repeating units, corresponding to two unit cells in the $[1120]$ projection were extracted from the total spectrum image and then summed. Given the limited amount of SESF length available, six sequential repeat units were taken (yellow boxes), with five additional repeat units taken midway between each of the previous six. This results in overlapping data sets; however, this is still a valid process because of the symmetry of the region contained. If, for example, this assumption were incorrect, and site-specific segregation were not occurring, the resulting summed data would exhibit a more uniform composition.

By summing the 11 regions mentioned above, the EDX spectra at each pixel were vastly improved. Figure A.6(a) shows a representative spectrum from the raw data with very
few counts per peak, which is typical of atomic resolution EDX data. Figure A.6(b) shows a representative spectrum from the summed spectrum image, displaying nearly an order of magnitude higher maximum peak counts and an even greater increase in total integrated peak counts. The summed spectrum image, with a better signal-to-noise ratio than the raw data, was then imported into Esprit and quantified using experimentally determined Cliff-Lorimer k-factors.

Figure A.5: EDX spectrum image, showing the HAADF layer with 6 repeating units along the SESF (yellow boxes) and 5 additional repeating units (red boxes) taken midway between the first 6.
Figure A.6: Representative EDX spectra from raw data (a) and summed data (b) showing a significant improvement in both counts per peak and signal-to-noise ratio.
K-factors were experimentally found by solutionizing the HL-11 alloy at 1210 °C for 1 hour, seen in Figure A.7. Some variation in HAADF-STEM image intensity suggests that there may be a compositional modulation that was not fully solutionized; however, the an EDX spectrum was then taken from a large area on a ⟨110⟩ zone axis just like the atomic resolution EDX data to ensure that the proper channeling condition was taken into account. Experimental k-factors (wt%) for this alloy and the associated error with each can be seen in Table A.4.

Figure A.7: HAADF-STEM image of HL-11 sample solutionized at 1210 °C for 1 hour.

After the summed spectrum image was quantified using the Bruker Esprit software package, along with the experimentally determined k-factors, the final atomic resolution
EDX maps were constructed, as seen in Figure A.8. Error in the EDX quantification is shown in wt% in Table A.5. Values displayed in Table A.5 are the minimum and maximum values (in wt%) and their associated standard deviations.

<table>
<thead>
<tr>
<th>Element</th>
<th>X-ray Series</th>
<th>(110) k-factor</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>K</td>
<td>1.0334</td>
<td>± 0.01</td>
</tr>
<tr>
<td>Co</td>
<td>K</td>
<td>0.8694</td>
<td>±0.005</td>
</tr>
<tr>
<td>Cr</td>
<td>K</td>
<td>0.8372</td>
<td>±0.005</td>
</tr>
<tr>
<td>Mo</td>
<td>L</td>
<td>1.6450</td>
<td>±0.02</td>
</tr>
<tr>
<td>Nb</td>
<td>L</td>
<td>3.9240</td>
<td>±0.18</td>
</tr>
<tr>
<td>Ni</td>
<td>K</td>
<td>1.0000</td>
<td>--</td>
</tr>
<tr>
<td>Ta</td>
<td>M</td>
<td>5.8734</td>
<td>±0.15</td>
</tr>
<tr>
<td>Ti</td>
<td>K</td>
<td>0.8507</td>
<td>±0.01</td>
</tr>
<tr>
<td>W</td>
<td>M</td>
<td>2.4190</td>
<td>±0.05</td>
</tr>
</tbody>
</table>

Table A.4: Experimentally determined k-factors for (110) HL-11.

<table>
<thead>
<tr>
<th>Element</th>
<th>Minimum value (wt%)</th>
<th>Maximum value (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.4 ± 0.4</td>
<td>8.3 ± 2.2</td>
</tr>
<tr>
<td>Co</td>
<td>1.8 ± 0.8</td>
<td>13.8 ± 2.5</td>
</tr>
<tr>
<td>Cr</td>
<td>0.2 ± 0.2</td>
<td>3.5 ± 1.3</td>
</tr>
<tr>
<td>Mo</td>
<td>0.5 ± 0.5</td>
<td>8.1 ± 3.0</td>
</tr>
<tr>
<td>Nb</td>
<td>1.1 ± 1.1</td>
<td>17.4 ± 7.0</td>
</tr>
<tr>
<td>Ni</td>
<td>33.2 ± 3.4</td>
<td>84.3 ± 7.9</td>
</tr>
<tr>
<td>Ta</td>
<td>2.3 ± 2.4</td>
<td>46.0 ± 14.6</td>
</tr>
<tr>
<td>Ti</td>
<td>0.4 ± 0.4</td>
<td>11.0 ± 2.3</td>
</tr>
<tr>
<td>W</td>
<td>0.8 ± 0.8</td>
<td>19.1 ± 6.4</td>
</tr>
</tbody>
</table>

Table A.5: Experimental error ranges for the atomic resolution EDX in Figure A.8.
Due to limitations in computational resources, a full convergence study of twin formation energy in ME3 and HL-11 with respect to calculation cell size was not possible. In order to establish that the relatively high twin formation energies were a result of cell size limitations, we conducted a partial convergence study on twin formation energy on the
simpler pure Ni$_3$Al system. Results are displayed in Figure A.9 and indicate that no fewer than 20 $\{111\}$ planes would be necessary to obtain converged formation energies consistent with twinning being a low energy defect in Ni$_3$Al.

Figure A.9: Twin formation energy in pure Ni$_3$Al calculated as a function of number of lattice planes in the calculation cell; the energetic cost of twinning decreases drastically as defects are separated by added lattice planes, as expected.

REFERENCES


Appendix B: Supplementary Information for Chapter 6

B.1 EXPERIMENTAL METHODS

The starting material was Te-doped InSb purchased from Wafer Technology Ltd [1] as 51 mm diameter, 4 mm thick Cz-cut wafers oriented along [100] ± 0.1°. The tuning fork geometry shown in Figure 6.1a was cut with a wire saw out of the plane of the wafers. The long axis of the tuning fork is oriented along a [010] axis. The large arm has a cross section $A_L \sim 4 \times 3 \text{ mm}^2$, the small arm has $A_S \sim 4 \times 1 \text{ mm}^2$. The sample was then etched with HF (49%):H$_2$O$_2$ (30%):C$_4$H$_6$O$_6$ (10%) = 1:42:54 (volumetric ratio) for 3 minutes to remove surface damage. Four 120 Ω resistive heaters were attached on top of gold-plated copper sheets using silver epoxy. Three of these were indium-soldered on top of the large arm and one on the small arm. This was done to ensure uniform heat flow. Cernox thermometers (Lakeshore CX-1050-BR) were attached on each arm equidistant from the top of the sample, as shown in Figure 6.1b. The bottom surface of the sample was indium-soldered to the thick, copper block heat sink. All contacts on the sample were made using 6N indium to minimize contact thermal resistances and thermal stresses during heating/cooling cycles. Thermal conductivity measurements were made using the heater and sink method in a modified Thermal Transport Option in the Physical Properties Measurement System (PPMS) by Quantum Design. Radiative and convective
losses were minimized by using a fully gold-plated cryopumped sample chamber. Conductive losses were minimized by using manganin wiring.

For temperature readings, Cernox thermometers were calibrated before the thermal conductivity measurements. The Cernox thermometers’ resistance has a magnetic field dependence below 20 K that is known from prior calibrations on a copper reference sample. We will show in section B.2.2 that the effect of the thermometer field sensitivity is eliminated in the differential thermal conductivity measurement via the tuning fork geometry. Therefore, it is only relevant to the analysis for estimating the error bars (section B.2). For differential conductivity measurements, the principle of the thermal potentiometer was applied. To operate the thermal potentiometer at any given value of the PPMS base temperature, we fixed the power \( Q_L \) on the large arm, and stepped the heater power on the small arm \( Q_S \), while monitoring the temperature difference \( \Delta T_{LS} \) \( (\Delta T_{LS} = T_L - T_S, \text{where } T_L \text{ and } T_S \text{ are temperatures of the large and small arms, respectively, measured by the upper thermometers}) \). Traces showing \( \Delta T_{LS} \) as a function of time for different values of \( Q_S \) are shown in Figure B.1a. \( Q_S \) was adjusted such that the measured \( \Delta T_{LS} \) are approximately symmetric with respect to zero. After the heater was turned on or off, the temperature was recorded for a sufficiently long time to ensure that a steady-state condition was reached in the temperature traces, but not so much time that the measurement was affected by thermal drift (typically related to the change in liquid helium level). We then plotted the steadystate value of \( \Delta T_{DIFF} \) \( (\Delta T_{DIFF} = \Delta T_{LS} - \Delta T_R \) where \( \Delta T_R \) corresponds to the residual \( \Delta T_{LS} \) when no heat is applied) versus \( Q_S \) and interpolated the value of \( Q_S \) for \( \Delta T_{DIFF} = 0 \) (Figure B.1b). At this value of \( Q_S \), the
Figure B.1: Principle of thermal potentiometer measurements. (a) The time-dependence of the differential temperature $\Delta T_{LS}$ measured between large and small arm in the thermal potentiometer for different amounts of heat dialed into $Q_L$ and $Q_S$. At left and at right, $Q_L = Q_S = 0$ and the trace represents the zero value, including the effects of drift and offset. These effects determine the residual temperature difference $\Delta T_R$. A fixed value of $Q_L$ is then dialed in and $Q_S$ is stepped, giving the various red traces. The deviation of $\Delta T_{LS}$ with respect to its zero ($\Delta T_R$, the dashed green line), which we define as $\Delta T_{DIFF} = \Delta T_{LS} - \Delta T_R$, is plotted versus the value of $Q_S$ in (b). (b) The interpolation value of $Q_S$ for $\Delta T_{DIFF} = 0$ gives the value where the relation $\kappa_L/\kappa_S = (Q_L/Q_S)/(A_L/A_S)$ holds. Purple crosses are experimental data, and the red cross indicates a value of $Q_S$ when $\Delta T_{DIFF} = 0$, obtained by a linear interpolation. The solid line is a linear fit to the data points.

Longitudinal temperature differences in both arms were equal ($\Delta T_L = \Delta T_S$), such that $\kappa_L/\kappa_S = (Q_L/Q_S)/(A_L/A_S)$, where $\kappa_L$ and $\kappa_S$ denote the thermal conductivities of the large and
small arms, respectively. The area ratio \( A_L/A_S \) was determined accurately from the high-temperature asymptote of \( Q_L/Q_S \). For absolute thermal conductivity measurements on the small arm, the temperature difference was measured between the upper and lower thermometry with a fixed heater power. Absolute thermal conductivity measurements in a longitudinal 7 T magnetic field lack a sufficient level of accuracy, as compared to the differential measurement. This is due to uncertainty in the magnetic field dependence of the thermometry.

For both differential and absolute measurements, actual temperature differences were obtained by calculation. We subtracted the residual temperature differences (measured with the heater off) from the experimental temperature differences (measured with the heater on). The major difficulty in all static heater-and-sink measurements of thermal properties on materials with high thermal conductivity and large dimensions is that a large amount of heat must be applied in order to establish a measureable temperature gradient. Here, the InSb samples have a high thermal conductivity of >100 Wm\(^{-1}\)K\(^{-1}\) and dimensions on the order of 10\(^{-3}\) m or larger. This difficulty arises because the thermal contact resistance between the sample and the cryostat can be several orders of magnitude larger than the thermal resistance across the sample itself. This means that the heat current required for generating a measureable temperature difference (or voltage difference in thermopower and Nernst effect measurements) will tend to increase the average temperature of the sample. This temperature increase can be 1000 times larger than the magnitude of the steady-state temperature difference produced across the sample as a result of the heat flux. Low temperature measurements are thus especially difficult,
since thermal conductivity tends to peak below 50 K, and since any rise at all in the absolute sample temperature will constitute a relatively large percentage change. The problem generally is minimized by using malleable, highly thermally conductive materials that remain soft at cryogenic temperatures for the contacts (e.g. indium solder, as in our experiment), and careful design of the thermal cell. Still, the problem remains present regardless of the experimental design. This forces the experimentalist to compromise between the lowest possible measurement temperature (which depends on how much the average sample temperature rises from the base value) and the signal-to-noise ratio (which depends on the magnitude of the temperature gradient itself). These parameters are inversely related to each other through the amount of heat flux through the sample.

Thermal properties that are particularly difficult to measure under such circumstances include absolute thermal conductivity, thermopower, and Nernst-Ettingshausen coefficients. The tuning fork geometry relies on the sensitivity of the thermometers rather than on their absolute accuracy, thereby greatly reducing the problem. Yet even in differential measurements, the accuracy is affected by the intensity of the heat flow. For example, a lower temperature could be achieved in Figure 6.2a than in Figure 6.1c because the dislocations in the Figure 6.2a sample lower the thermal conductivity enough to get larger gradients while not increasing the base temperature as much as the Figure 6.1c sample. Great care was taken for accurate measurements of the residual temperature differences. Those differences become only one order of magnitude smaller than the temperature differences under applied heat at low temperatures, due to the problem
mentioned above. For the same reason again, residual temperature differences were separately measured after adjusting the base temperature to the same temperature at which the sample had been measured with the heater on. This problem is also the reason why we were not able to accurately measure the thermal conductivity of the large arms directly, but instead calculated it from the conductivity ratio (Figure 6.2c).

For specific heat measurements, a small parallelepiped sample ~ 2 mm x 2 mm x 3 mm was cut from the same starting InSb slab used for the other measurements. The specific heat was measured using the Heat Capacity option in the PPMS from 300 K to 1.8 K in 0 T and 7 T magnetic fields. The magnetic field was applied along the [100] direction of the sample, which replicates the conditions used in the thermal conductivity measurements.

B.2 ERROR ANALYSIS

The error bars shown in Figures 1, 2, and 4 were calculated by taking random, systematic, and fitting errors into account. We report details about how each error contribution is calculated.

B.2.1 Random errors

A main source of random errors in the measurement of $\Delta T_{\text{DIFF}}$ stems from noises in the temperature signals. For each trace in Figure B.1a, standard deviations of the means (or standard errors) can be calculated for $\Delta T_{\text{DIFF}}$. Each trace determines one data point in Figure B.1b, and is divided into three regimes: no-heat, heater-on, and heater-off. We first build a histogram for each regime to assess whether or not these fluctuations can, in
fact, be described by a simple normal distribution function, which then determines our approach for calculating standard errors.

Figure B.2 shows an example of the random error calculation process performed for measurements at 10 K. For heater-on and heater-off regimes, only data points after saturations are taken. All three histograms show highly centered distributions with respect to the mean values due to small standard deviations, \( \sigma \). The goodness-of-fit test [2] is performed for each histogram. The resulting Chi-squared value (\( \chi^2 \)) for a given degree of freedom is typically so small that \( P(\chi^2) < 2\% \). This means that over 98\% of the discrepancy between the histogram and the assumed distribution is due only to random variations, and thus assures a very good fit of the data to the assumed normal distribution.

We checked that a change of the sample (bin) size negligibly affects the results of goodness-of-fit test. The standard deviation \( S_x \) for \( \Delta T_{\text{DIFF}} \) is given as a sum of squared standard deviations of the three regimes:

\[
S_x = \sqrt{(0.116)^2 + (0.158)^2 + (0.131)^2} \approx 0.236
\]

Since we are interested in the deviation of the sample mean from the true mean in one set of multiple measurements, it is more reasonable to use standard errors than standard deviations to set the error bars. The standard error \( S_{\bar{x}} \) for \( \Delta T_{\text{DIFF}} \) is calculated by \( S_{\bar{x}} = S_x / \sqrt{N} \approx 0.012 \), where \( N \) is the total number of data points for all three regimes.

Therefore, for this specific measurement at 10 K, the random error is estimated to be on the order of 10 \( \mu \)K. This is the typical magnitude for random errors throughout the whole measured \( \Delta T_{\text{DIFF}} \) in this study. It is noted that \( \Delta T_{\text{DIFF}} \approx 5 \)mK for this measurement, and the random error is thus 1/500 of \( \Delta T_{\text{DIFF}} \). This fraction tends to become smaller as
measurement temperature increases due to a larger $\Delta T_{\text{DIFF}}$, and vice versa as temperature decreases.

![Diagram](image)

Figure B.2: Temperature differences between large and small arm ($\Delta T_{\text{LS}}$) as a function of time at 10K, and histograms for no-heat, heater-on, and heater-off regimes. $n_j$ denotes the number of data points for jth interval, and $\sigma$ the standard deviation.

**B.2.2 Systematic Errors**

Here, we show how the magnetic field dependence of thermometry is canceled out by the thermal potentiometer approach. If not for this canceling effect, this magnetic field
dependence would be the most significant source of systematic error. In real measurements, although both Cernox thermometers can exhibit quite significant magnetic field dependences (Figure B.4a), it is important to note that the temperature difference between them ($\Delta T_{LS} = T_L - T_S$) is almost field-independent: $T_1(0T) - T_S(0T) \approx T_1(7T) - T_S(7T)$. Figure B.3a is included to provide a general qualitative demonstration of the magnetic field dependence of Cernox thermometers, where the field dependence of the thermometers is shown to be varied for different temperatures. Note that there is always a finite difference in temperature reading between the two thermometers at the same sample temperature: $T_{1,L} \neq T_{1,S}$ and $T_{2,L} \neq T_{2,S}$ (See Figure B.4a for the actual measurement wherein $T_{R,L} \neq T_{R,S}$, even though the difference is very small).

Now, as heater powers $Q_L$ and $Q_S$ are adjusted, the temperature of each arm changes such that $T_L = T_{1,L}$ and $T_S = T_{1,S}$ for $Q_L/Q_S$, and $T_L = T_{2,L}$ and $T_S = T_{2,S}$ for the other $Q_L/Q_S$.

Then, we can define $\Delta T_{LS,i} = T_{1,L} - T_{2,S}$ and $\Delta T_{LS,ii} = T_{2,L} - T_{1,S}$ (Figure B.3a). Relative errors in $\Delta T_{LS,i}$ and $\Delta T_{LS,ii}$ induced by the 7T magnetic field can be expressed for both cases as $e_i = \Delta T_{LS,i}(7T) - \Delta T_{LS,i}(0T) = [T_{1,L}(7T) - T_{2,S}(7T)] - [T_{1,L}(0T) - T_{2,S}(0T)]$ and $e_{ii} = \Delta T_{LS,ii}(7T) - \Delta T_{LS,ii}(0T) = [T_{2,L}(7T) - T_{1,S}(7T)] - [T_{2,L}(0T) - T_{1,S}(0T)]$. Therefore, according to Figure B.3a, $e_i > 0$ and $e_{ii} < 0$. In case $T_L = T_{1,L}$ (or $T_{2,L}$) and $T_S = T_{1,S}$ (or $T_{2,S}$), $e_i \sim 0$ (or $e_{ii} \sim 0$). Figure B.3b illustrates how these errors shift the measured $\Delta T_{LS,i}$ and $\Delta T_{LS,ii}$ with respect to the true values. An important question is whether they will also shift point A, which corresponds to a value of $Q_L/Q_S$ when $\Delta T_{LS} = 0$. We can see that the position of point A is not affected by the shifts of $\Delta T_{LS,i}$ and $\Delta T_{LS,ii}$, because of the symmetry between $e_i$ and $e_{ii}$. Thus, the thermal potentiometer technique allows us to
effectively eliminate magnetic field effects in $\Delta T_{LS}$ measurements, based on the assumption that $e_i$ and $e_{ii}$ perfectly cancel.

![Diagram](image)

Figure B.3: Schematic diagrams for magnetic field dependence of Cernox thermometers. (a) Variation of temperature readings as a function of magnetic field $H$. It is assumed that the heater power ratio $Q_L/Q_S$ is adjusted such that for one measurement, $T_L = T_{1,L}$ and $T_S = T_{2,S}$, and TL $T_L = T_{2,L}$ and $T_S = T_{1,S}$ for the other measurement. (b) Effect of the magnetic field induced errors $e_i$ and $e_{ii}$ on measured temperature differences $\Delta T_{LS}$.

However, in actual measurements, the residual temperature differences $\Delta T_{R,i}$ and $\Delta T_{R,ii}$ before heat is applied should be measured separately and subtracted from the temperature differences $\Delta T_{LS,i}$ and $\Delta T_{LS,ii}$, respectively. When heat is applied, magnetic field
Figure B.4: Experimentally measured magnetic field dependence of Cernox thermometers. (a) Variation of temperature readings as a function of magnetic field $H$. $T_{R,L}$ and $T_{R,S}$ denote temperature readings when no heat is applied. (b) $\Delta T_{\text{DIFF}}$ as a function of heater power on the small arm, $Q_S$. $\Delta T_{\text{DIFF}}$ is the temperature difference between the large and small arms after subtracting the residual temperature difference. Two circled points are determined by processes shown in (c): left and right columns correspond to left and right circled points, respectively, as pointed by arrows.

dependencies are significantly different than when it is not (Figure B.4a). We can consecutively calculate $\Delta T_{LS} = T_L - T_S$, $\Delta T_R = T_{R,L} - T_{R,S}$ and $\Delta T_{\text{DIFF}} = \Delta T_{LS} - \Delta T_R$ for $T_L > T_S$, shown in the left column in Figure B.4c. The same calculations for $T_S > T_L$ are
shown in the right column. It is observed that $\Delta T_{\text{DIFF},i} > 0$ and $\Delta T_{\text{DIFF},ii} < 0$. The data points corresponding to $\Delta T_{\text{DIFF},i}$ and $\Delta T_{\text{DIFF},ii}$ are circled in Figure B.4b. As in Figure B.3, $e_i$ and $e_{ii}$ can be calculated by $e_i = \Delta T_{\text{DIFF},i}(7T) - \Delta T_{\text{DIFF},i}(0T)$ and $e_{ii} = \Delta T_{\text{DIFF},ii}(7T) - \Delta T_{\text{DIFF},ii}(0T)$. We see that $e_i < 0$ and $e_{ii} > 0$ by referencing the plots. However, since the magnitudes of $e_i$ and $e_{ii}$ are slightly different in this case, they do not perfectly cancel. This requires adjusting the slope of the linear regression line in Figure B.4b, introducing a systematic error. The typical order of residual $e_i - e_{ii}$ is 10 μK at all measured temperatures, which is similar to that of random errors.

B.2.3 Fitting Errors

We find a value of heater power on the small arm $Q_S$ when $\Delta T_{\text{DIFF}} = 0$ by taking a linear regression through four measurement data points, as shown in Figure B.4b. Because there are almost always small random and systematic errors that can slightly shift each data point, the regression fit is not always perfect. The small sample size can also reduce the fitting accuracy. The standard error of the fit $S_{yx}$ is calculated for each regression fit to take this fitting error into consideration. The $S_{yx}$ can be computed by

$$S_{yx} = \sqrt{\frac{\sum_{i=1}^{N} (y_i - y_{ci})^2}{N - 2}},$$

where $N$ is the number of data points, $y_i$ the dependent variable, and $y_{ci}$ the value of the polynomial evaluated at the data point $(x_i, y_i)$. At all measurement temperatures, $N = 4$, and $x_i$ and $y_i$ correspond to $Q_S$ and $\Delta T_{\text{DIFF}}$, respectively.

2.4 Total Errors

The total errors that directly determine the error bars in Figure 6.1 and Figure 6.2 can be calculated by combining the three different error components discussed thus far. Note
that both random and systematic errors result in shifts of the data points, such as those in Figure B.4b, even before those points are fitted to a linear regression function. An error bar set by those two errors for each data point is typically of the same order of magnitude or smaller than that set by a fitting error. In addition, based on the fact that the linear regression assumes a normal distribution of each dependent variable,[2] we can safely state that random and systematic errors are already included in fitting errors. Once we find a value of $Q_S$ where $\Delta T_{\text{DIFF}} = 0$, an error bar for the corresponding $Q_L/Q_S$ is determined by

$$\text{err}(\frac{Q_L}{Q_S}) = \frac{Q_L}{Q_S} \sqrt{\frac{S_{xy}}{Q_S}^2}.$$ 

B.3 ELECTRONIC, THERMOELECTRIC, THERMOMAGNETIC, AND MAGNETIC PROPERTIES OF THE InSb BOULE USED

As mentioned earlier, a single-crystal wafer [1] of Te-doped InSb 51 mm in diameter and 4 mm thick was purchased. The classical galvanomagnetic and thermomagnetic transport properties of the material in the wafers were fully characterized on samples cut from the same wafer used for the tuning fork measurements. These samples were oriented so that the heat flux and temperature gradients in the experiments are parallel to [100]. We use the notations defined in Ref [3].

To perform galvanomagnetic measurements, a different parallelepiped sample (~ 4 mm x 3 mm x 8 mm) with the same [100] orientation was cut from the same starting InSb slab used for the tuning fork. The electrical resistivity, Hall resistivity, and Shubnikov - de Haas oscillations were measured using the AC Transport option in the PPMS and a Lakeshore 370 AC bridge. The resistivity at zero field and in a perpendicular magnetic
Figure B.5: Galvanomagnetic transport in the InSb material used. (a) The temperature dependence of the resistivity at zero magnetic field and in a magnetic field of 7 T. (b) The Hall resistivity versus magnetic field at the temperatures indicated.

Field $H = 7$ T (// [001]) is shown in Figure B.5a. In Figure B.5b, we report the magnetic field dependence of the Hall resistivity data in a perpendicular field (i.e. $H$ // [001]). The low-field Hall data give the electron concentration of about $1.3 \times 10^{15}$ cm$^{-3}$ at 10 K. The ratio of zero field resistivity to Hall coefficient gives the mobility, which is on the order of 160,000 cm$^2$V$^{-1}$s$^{-1}$ at 10 K. From the temperature dependence of these quantities,
Figure B.6: Electron concentration and mobility. The temperature dependence of the electron concentration (a) and mobility (b) calculated from the low-field Hall coefficient. Shubnikov-de Haas oscillations in the low-field resistivity (c) and Hall resistivity (d).

shown in Figure B.6 a and b, we conclude qualitatively that the mobility is limited by ionized impurity scattering below 80 K. Shubnikov-de Haas oscillations are also observed in resistivity (Figure B.6c) and Hall resistivity (Figure B.6d). Both the period of
the oscillations and the position of the ultra-quantum limit are consistent with the electron concentrations.

In contrast to the low-field data, the high-field Hall data in Figure B.5b clearly show the onset of magnetic freeze-out,[4] which begins at magnetic fields above approximately 3 T and at temperatures of 10 K and below. If the magnetic field effects observed in the main text were due to phonon scattering on free carriers, the fact that these carriers freeze out in magnetic fields above 3 T implies that they should result in a decrease of the phonon scattering rate at high magnetic field, and an increase in thermal conductivity of the large arm. This is the opposite of what is observed.

The electrical resistivity, Hall effect, and thermoelectric power were measured as a function of temperature and magnetic field in order to prove that there is almost no electronic contribution to the thermal conductivity (see section B.4). Figure B.7 shows the thermoelectric power $\alpha$ measured on the small arm of the tuning fork sample. The small arm’s thermal conductivity is studied in the main text in Figure 6.1 and Figure 6.2. The problem with obtaining a good signal-to-noise ratio on highly thermally conducting samples (discussed above in section B.1) is exacerbated in measurements of thermopower in the phonon drag regime. The noise level on the small arm is quite high because of the small temperature gradients used. The noise level on the measurement in magnetic fields exceeding a few Tesla field is higher yet, not only because the gradient is small, but also because the sample becomes extremely resistive (see Figure B.5a). This adds significant electrical noise to the measurements. The maximum in absolute value of $\alpha$ around 8 K is likely due to the dominance of phonon-electron drag. These measurements should be
taken as simply an order of magnitude estimate for $\alpha$, and are reported only because this number is necessary to estimate the amount of heat carried by electrons.

To examine whether or not there are any para- or ferro-magnetic impurities in our InSb samples, the magnetic moment ($M$) of a piece of the same starting boule was measured in

Figure B.7: Temperature dependence of the thermoelectric power $\alpha$ of the small arm of sample B (Figure 6.2), at zero field and in a longitudinal magnetic field ($H // [100]$).
a Quantum Design Vibrating Sample Magnetometer (VSM). While there is a small
temperature dependence of $M$ in $H = 7$ T as shown in the enlarged scale in Figure B.8a,
we state that the $M$ remains almost constant with the negative sign over a temperature
range of 2 K to 300 K, exhibiting a typical diamagnetic behavior. The measurement of $M$
as a function of $H$ at $T = 2$ K (Figure B.8b) reveals linear dependence ($r^2 = 0.999993$)
without any traces of the Brillouin function that would indicate the presence of free spins
or hysteresis loops that could signify the presence of small ferromagnetic clusters. We
confirmed that the same trend persists up to 40 K. These observations indicate that no
detectable magnetic impurities are present in our InSb samples within the resolution of
the measurement. The error bars from the measurement were used to set an upper limit
for the possible amount of magnetic impurities, since there were none detected due to the
resolution limit of the measurement. For instance, the standard error in $M$ is given as
1.4x10-9 μB/Å³ at 2 K in $H = 7$ T. Assuming that all impurities are Fe⁶⁺, which

Figure B.8: Magnetic moment (M) data of the InSb material used. (a) The temperature
dependence of $M$ in $H = 7$ T. (b) The magnetic field dependence of $M$ at $T = 2$ K.
contribute 5.9 μB per ion, the estimated maximum amount of Fe$^{3+}$ in the sample is about 16.4 ppb (parts-per-billion).

**B.4 ELECTRONIC CONTRIBUTIONS TO HEAT CONDUCTION**

In the main text, we report that the thermal conductivity of InSb is sensitive to an applied external magnetic field. We attribute that to phonon-phonon interactions. Obviously, because of the magnetic freeze-out (Figure B.5b) and the formation of Landau levels (Figure B.6c), it would be natural to suspect that the magnetic-field dependence of the thermal conductivity ratio reported in the main text could be due to a magnetic field dependence of the electronic properties. We calculated here that the electronic contributions to heat conduction are 5 to 6 orders of magnitude smaller than the observed thermal conductivity (200 – 2700 Wm$^{-1}$K$^{-1}$; see Figure 6.2c in Chapter 6) in the temperature range of interest (T < 10 K). There can be two such electronic contributions. The Onsager relations (in a scalar notation, since heat transport in this case is one-dimensional along the length of the sample) linearly relate the electrical current density $J$ and the heat flux $Q$ to the electric field $E$ and the temperature gradient $\nabla T$:

$$J = L_{EE}E + L_{ET}\nabla T$$

$$Q = L_{TE}E + L_{TT}\nabla T$$

The quantities $L_{EE}$, etc., are the kinetic coefficients, but in practice we do not observe them directly. Instead, they relate to experimental quantities like resistivity $\rho$, thermoelectric power $\alpha$, and electronic thermal conductivity $\kappa_E$. During resistivity measurements, the sample is held isothermally, so that the first Onsager relation becomes
\[ J = L_{EE}E, \] and therefore \( L_{EE} = 1/\rho. \) During a measurement of thermoelectric power, no electrical current flows, and the first Onsager relation can be solved for \( J = 0. \) For the thermopower \( \alpha, \) the equation reduces to the defining ratio \( E/\nabla T, \) such that \( \alpha = -L_{ET}/L_{EE}. \) During thermal conductivity measurements, the sample is electrically insulated and no current flows through it while a temperature gradient is applied. The first Onsager relation is solved for \( J = 0. \) The resulting \( E \) field is put into the second Onsager relation to yield the heat flux \( Q \) as a function of \( \nabla T. \) The electronic thermal conductivity \( \kappa_E, \) given by the ratio \(-Q/\nabla T, \) is then \( \kappa_E = -(L_{TT} - (L_{TE}L_{ET})/L_{EE}). \) Thus, we have \(-\kappa_E = L_{TT} - \alpha^2 T/\rho, \) given the Kelvin-Onsager relation \( L_{ET} = -L_{TE}/T \) and the definitions of the other transport coefficients. Here, the \( L_{TT} \) term can be estimated using the electrical resistivity and the Wiedemann-Franz law, which relates the electrical conductivity and electronic thermal conductivity proportionally. Using the free electron value for the Lorenz number, \( L_{TT} = \) \( L_0 T/\rho, \) with \( L_0 = \left(\pi^2/3\right)(k_B/e)^2. \) The maximum value \( L_{TT} \) can take is \( L_{TT} < 8 \times 10^{-4} \) Wm\(^{-1}\)K\(^{-1}\) at temperatures below 10 K and given the lowest resistivity reported in Figure B.5a (30 m\(\Omega\) cm at zero field). The second term, \( \alpha^2 T/\rho, \) can be viewed as the Peltier heat carried by the electrons. In the presence of a 7 T field, the maximum value of the absolute value of the thermopower \(|\alpha| < 3 \times 10^{-3} \) V K\(^{-1}\) at 6 K but \( \rho > 2000 \) m\(\Omega\) cm, resulting in \( \alpha^2 T/\rho \leq 4 \times 10^{-3} \) Wm\(^{-1}\)K\(^{-1}\). At zero field, \(|\alpha| < 5 \times 10^{-4} \) V K\(^{-1}\) at 6 K, and \( \rho > 35 \) m\(\Omega\) cm, resulting in \( \alpha^2 T/\rho \leq 5 \times 10^{-3} \) Wm\(^{-1}\)K\(^{-1}\). We conclude that the electronic system’s thermal conductivity is limited to at most \( 6 \times 10^{-3} \) Wm\(^{-1}\)K\(^{-1}\). This is more than 5 orders of magnitude smaller than the lattice thermal conductivity of the same material (1.5 \times 103 Wm\(^{-1}\)K\(^{-1}\) on the small arm at 6K).
B.5 NUMERICAL METHODS AND CALCULATIONS

B.5.1 Calculation of Magnetic Properties

The magnetic properties of InSb were calculated using the ELK code. This is an all-electron full-potential linearized augmented plane wave (FPLAPW) code [7] that allows introduction of magnetic effects by variational perturbation theory.[8] As a first variational step, a Hamiltonian containing only the scalar fields is solved. The scalar states obtained by this solution serve as the basis for a second variational step, where the magnetic terms are included. In ELK, the magnetic energy \( E_M \) of a system of interacting electrons in the presence of an external magnetic field \( \mathbf{H}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r}) \) is represented as a function of the electron density \( \rho(\mathbf{r}) \), the magnetization density \( \mathbf{m}(\mathbf{r}) \), and the paramagnetic current density \( \mathbf{j}_p(\mathbf{r}) \),[9]

\[
E_M = -\int \mathbf{m}(\mathbf{r}) \cdot \mathbf{H}(\mathbf{r}) d^3r + \frac{1}{c} \int \mathbf{j}_p(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) d^3r - \frac{1}{2c^2} \int \rho(\mathbf{r}) \cdot \mathbf{A}^2(\mathbf{r}) d^3r
\]

where the first term is the Pauli paramagnetic term, the second term is the paramagnetic current density coupling to \( \mathbf{A} \), and the last term models diamagnetism. The Pauli paramagnetic term is the result of the interaction of the external magnetic field with spin up and spin down electrons. Here, since InSb is an insulator, this term is zero. The second term will affect the magnetic susceptibility by giving rise to a paramagnetic Zeeman-type interaction. We have tested the effect of this Zeeman term by excluding it in our calculations. We found it does not significantly affect the total magnetic moment (a relative change of \( 10^{-5} \) is observed for the displacement of 0.07 Å). Thus, the last term is the only term that generates a magnetic response. Therefore, atomic displacements
generate a diamagnetic response through changes in the charge density $\rho(r)$ (changes in the electronic effective masses and $\langle r^2 \rangle$). This term is at the origin of phonon-induced diamagnetism in InSb.

All frozen phonon calculations completed using the ELK code incorporated spin polarization and spin-orbit coupling. These calculations were performed with basic convergence parameters corresponding to the high-quality settings, with a few modifications to improve calculation consistency and speed. Convergence criteria for the Kohn-Sham potentials and total energy were set to $10^{-8}$ and $10^{-7}$ H, respectively. No additional benefit was observed in lowering these criteria. Twenty empty states per atom and spin were used as testing showed that empty states from 10 to 50 per atom and spin resulted in stable results for energy and a difference of less than 4% in magnetic moment. Reciprocal space meshes with a density of approximately 11 points per unit lattice vector were chosen such that the Γ-point was always included in the calculation. Convergence testing of the reciprocal space mesh density showed good convergence in total energy, but large changes in magnetic moment. When the mesh density was doubled in each reciprocal space direction, a 30% reduction in calculated magnetic moment was observed. However, such a calculation would not have been computationally feasible for the large number of frozen phonon cells investigated. Further, the mesh density chosen for the calculations accurately yields the order of magnitude of the magnetic effect and its size, relative to the other magnetic effects in the system.

B.5.2 Change of the Grüneisen Parameter in the Presence of a Magnetic Field

The mode Grüneisen parameter $\gamma(q,i)$ is given by
\[ \gamma(q, i) = -\frac{V}{\omega(q, i)} \frac{\partial \omega(q, i)}{\partial V} \]

for any given phonon mode \( i \) with wavevector \( q \) and frequency \( \omega(q, i) = \sqrt{K(q, i)/\mu} \).

Within that frequency definition, \( K(q, i) \) is the spring constant, \( \mu \) the effective atomic mass, and \( V \) the volume of the cell. Thus, \( \gamma(q, i) \) can be expressed as

\[ \gamma(q, i) = -\frac{V}{\omega(q, i)} \frac{\partial \omega(q, i)}{\partial V} = -\frac{V}{\sqrt{K(q, i)}} \frac{\partial \sqrt{K(q, i)}}{\partial V} = -\frac{V}{2K(q, i)} \frac{\partial K(q, i)}{\partial V} \]

where \( K(q, i) = K_0(q, i) + K_m(q, i) \). Within that spring constant definition, \( K_0(q, i) \) is the spring constant without an external magnetic field and \( K_m(q, i) \) is the change in spring constant due to an external magnetic field \( H \).

We can then calculate \( \gamma(q, i) \) in the presence or absence of an external magnetic field by finite-differences for the derivatives,

\[ \gamma(H = 0, q, i) = \frac{1}{2K_0(V_1, q, i)} \frac{K_0(V_1, q, i) - K_0(V_2, q, i)}{V_1 - V_2} \]
\[ \gamma(H \neq 0, q, i) = \frac{1}{2K(V_1, q, i)} \frac{K(V_1, q, i) - K(V_2, q, i)}{V_1 - V_2} \]

We can more explicitly visualize the effect of a magnetic field on \( \gamma(q, i) \) by considering that \( K_m(q, i) \ll K_0(q, i) \) (see below for numerical values). Then, the previous equation becomes simply

\[ \gamma(H \neq 0, q, i) = \gamma(H = 0, q, i) + \gamma_m(q, i) \]

where \( \gamma_m(q, i) \) is the magnetic contribution to \( \gamma(q, i) \) and is given by

\[ \gamma_m(q, i) = \frac{1}{2\frac{V_1}{V_1 - V_2}} \frac{K_m(V_1, q, i) - K_m(V_2, q, i)}{K_0(V_1, q, i)} \]
The macroscopic Grüneisen parameter can be calculated from the mode Grüneisen parameters through a weighted average over the Brillouin zone, \( \gamma = \frac{\sum_{q,i} \gamma(q, i) C_V(q, i)}{\sum_{q,i} C_V(q, i)} \), where \( C_V(q, i) = \frac{\hbar \omega(q, i) n'(q, i)}{V} \) is the contribution to the total specific heat of mode \( i \) at point \( q \) in the Brillouin zone and \( n'(q, i) = \frac{\partial}{\partial T} \left[ e^{\frac{\hbar \omega(q, i)}{k_B T}} - 1 \right]^{-1} \).

In our experiment, the ratio between the thermal conductivities of the large and small arm \((\kappa_L/\kappa_S)\) changes with magnetic field as \(1/\gamma^2\) (see Eq. (3) in the main text). Thus, we are interested in the relative variation of \(1/\gamma^2\) with \( H \),

\[
\frac{\Delta[Y^{-2}]}{Y^{-2}} = \frac{\partial}{\partial Y} \left( \frac{1}{Y^2} \right) \Delta Y = -2 \left[ \frac{\gamma(H \neq 0) - \gamma(H = 0)}{\gamma} \right] = -2 \frac{\gamma_m}{\gamma}
\]

To calculate \( \gamma_m(q, i) \), we obtain the spring constants \( K_0(q, i) \) and \( K_m(q, i) \) from first-principles calculations by fitting a parabola to the total and magnetic energies for sufficiently small atomic displacements, and have values of \( K_0 = 16.31 \text{ eV/Å}^2 \) and \( K_m(H = 7 \text{ T}) \sim 10^{-6} \text{ eV/Å}^2 \) for the L1 (LA) phonon. For \( H = 7 \text{ T} \) and taking the finite-difference derivative for a volume decrease of \( \Delta V = V_1 - V_2 = 0.6 \% \), we get \( \frac{V_1}{V_1-V_2} = 168.6 \) and \( [K_m(V_1) - K_m(V_2)]/K_0(V_1) = -8 \times 10^{-10} \), obtaining \( \gamma_m(L1) = 0.65 \times 10^{-7} \). The choice of \( \Delta V \) does not affect our numerical results.

We are interested in the behavior of \( \gamma \) in the temperature range 3-10 K, which is where the major differences in \( \kappa_L/\kappa_S \) with and without magnetic field are observed. Different experiments report \( \gamma \) for \( H = 0 \) to be linearly proportional to the temperature, and note that it crosses zero at a certain temperature. This could lead \( \gamma \) to be comparable in magnitude to \( \gamma_m \) for a certain range of temperatures. Three different experimental findings
have been reported in literature (Figure B.9). Gibbons [10] reports very low values of $\gamma$ on the order of -0.1 at 21 K. Sparks et al.[11] give values that change linearly from -0.93 at 10 K to -0.2 at 5 K. In the presence of a magnetic field, this trend can increase $\Delta[\gamma^2]/\gamma^2$ (previous equation). At 4 K, $\gamma$ becomes zero, which would appear to be a singularity. However, the physical reality is that this is an average and has a finite linewidth. Cetas et al.[12] reported corrections to the data given by Gibbons. From the data presented by Cetas, $\gamma = 0$ at 2 K. In order to compare with the thermal conductivity experiments that show a decrease of $\kappa_L/\kappa_S$ after applying a magnetic field of 7 T, we plotted in Figure 6.4 in Chapter 6 the ratio $\Delta[\gamma^2]/\gamma^2$ as extracted from the experiment, and by using the previous equation and the $\gamma$'s reported by Sparks. We performed a convolution of the function $\Delta[\gamma^2]/\gamma^2$ with a normal distribution $\exp\left(-\frac{\tau^2}{2\sigma^2}\right)/\sigma\sqrt{2\pi}$, where $\sigma = 2$ K is the temperature associated with the phonon linewidth due to anharmonicity in InSb.[13] Since the convolution mathematically becomes infinite at the temperature at which $\gamma = 0$, which is unphysical, $1/\gamma$ needs to have a finite linewidth such that it corresponds to the phonon linewidth. This leads $1/\gamma$ to behave as a delta function $\delta_\gamma/(\gamma^2 + \delta_\gamma^2)$ when $\gamma \to 0$, where $\delta_\gamma = 10^{-9}$. Figure 6.4 shows good agreement between $\Delta[\gamma^2]/\gamma^2$ and the change with $H$ of $\kappa_L/\kappa_S$. Obviously, the magnetic field sensitivity of $\gamma$ is best detected when the background value of that $\gamma$ is small, i.e. in solids where the bonds have little anharmonicity.
B.5.3 Pre-calculation Setup

Prior to conducting frozen phonon calculations, an undistorted cell is typically constructed and relaxed to minimize interatomic forces. The ELK code does not allow volume relaxation of structures, and use of the experimental lattice parameters for InSb gave results that were inconsistent with existing experimental observations, particularly electronic structure and bandgap. We anticipate these properties being important in determining the magnitude and mechanism of any magnetic vibrational effects. As such, the electronic structure of primitive cells of InSb in the zinc blende configuration at several different lattice parameters was calculated, paying close attention to the size and

Figure B.9: Grüneisen parameter $\gamma$ as a function of temperature from Spark [11] and Cetas [12].
character of the electronic bandgap. The cubic lattice parameter was then adjusted to find
the lattice constant where the experimental band gap of 0.25 eV could be reproduced.
This resulted in a lattice parameter of 6.144 Å. A plot of the calculated direct bandgap as
a function of lattice constant is included below in Figure B.10.

![Figure B.10: DFT results for the direct bandgap of InSb as a function of lattice parameter. The
dashed lines indicate the lattice constant for which the experimental band gap can be reproduced.](image)

**B.5.4 Modes Tested and Results**

For the frozen phonon calculations, high symmetry reciprocal space points were selected
that yield calculation cells of eight or fewer atoms because of calculation capability
constraints. The frozen-phonon cells were created with the SMODES package.[14] Both
individual modes and linear combinations of modes were investigated where appropriate. When linear combinations were considered, only unitary addition of modes was considered. This is anticipated to be a reasonable physical approximation due to the small mass difference between indium and antimony, leading to an expected displacement difference of less than 3% based on mass dependence. Magnetic fields were applied in various \( \langle 100 \rangle \) directions, according to the symmetry of the displacement pattern. Each distinct frozen phonon cell was calculated with and without displacements applied to establish the relative magnetic contribution of the phonon mode to the system. The symmetry information for the different modes is listed in Table B.1.

![Magnetic Moment vs Magnetic Field](image)

Figure B.11: Magnetic moment as a function of applied magnetic field for two different atomic displacements for the X3 phonon.
<table>
<thead>
<tr>
<th>Q</th>
<th>IRep</th>
<th>Cell Vect.</th>
<th>At.</th>
<th>Position</th>
<th>D1</th>
<th>Vectors</th>
<th>D2</th>
<th>Vectors</th>
</tr>
</thead>
<tbody>
<tr>
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<td>X1</td>
<td>-0.5,0,0.5</td>
<td>Sb</td>
<td>0.0,5,0,25</td>
<td>1</td>
<td>0,0,1</td>
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<td></td>
<td>Sb</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>In</td>
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<td>3</td>
<td>1,-1,0</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>In</td>
<td>0,0,0,25</td>
<td>4</td>
<td>-1,-1,0</td>
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<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td>In</td>
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<td>4</td>
<td>1,1,0</td>
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</table>

Table B.1: Description of frozen phonons. [continued]
The magnetic moment depends linearly on the applied magnetic field, as shown in Figure B.11 for two different displacements (\( u \)) for the X3 phonon. Because the magnetization is linear in the applied magnetic field, all further calculations use the magnetic...
susceptibility only, which is reported in Table B.2 for different phonon branches, and magnetic field and displacement directions.

<table>
<thead>
<tr>
<th>Phonon Branch</th>
<th>Pattern Number</th>
<th>Field Direction</th>
<th>Disp. Dir.</th>
<th>Disp. Atom</th>
<th>Susceptibility</th>
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<tr>
<td>X-L</td>
<td>1</td>
<td>(010)</td>
<td>(010)</td>
<td>Sb</td>
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<td>X-L</td>
<td>2</td>
<td>(010)</td>
<td>(010)</td>
<td>In</td>
<td>1.26E-07</td>
</tr>
<tr>
<td>X-T</td>
<td>1</td>
<td>(010)</td>
<td>(110)</td>
<td>Sb</td>
<td>1.29E-07</td>
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<td>X-T</td>
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<td>(001)</td>
<td>(110)</td>
<td>Sb</td>
<td>1.14E-07</td>
</tr>
<tr>
<td>X-T</td>
<td>2</td>
<td>(010)</td>
<td>(110)</td>
<td>In</td>
<td>1.29E-07</td>
</tr>
<tr>
<td>X-T</td>
<td>1&amp;2</td>
<td>(010)</td>
<td>(110)</td>
<td>InSb</td>
<td>1.28E-07</td>
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<tr>
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<td>(010)</td>
<td>(111)</td>
<td>Sb</td>
<td>2.48E-07</td>
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<tr>
<td>L-L</td>
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<td>(010)</td>
<td>(111)</td>
<td>In</td>
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<td>(010)</td>
<td>(111)</td>
<td>InSb</td>
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<td>(010)</td>
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<td>L-T</td>
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<td>(001)</td>
<td>(-110)</td>
<td>Sb</td>
<td>1.84E-07</td>
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<tr>
<td>L-T</td>
<td>1&amp;2</td>
<td>(010)</td>
<td>(-110)</td>
<td>InSb</td>
<td>1.87E-07</td>
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<td>L-T</td>
<td>1&amp;2</td>
<td>(001)</td>
<td>(-110)</td>
<td>InSb</td>
<td>1.87E-07</td>
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<tr>
<td>Δ-L</td>
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<td>(010)</td>
<td>InSb</td>
<td>1.32E-07</td>
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<tr>
<td>Λ-L</td>
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<td>(010)</td>
<td>(111)</td>
<td>InSb</td>
<td>1.55E-07</td>
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<tr>
<td>Σ-L</td>
<td>1,2,3,4</td>
<td>(010)</td>
<td>(110)/(001)</td>
<td>InSb</td>
<td>1.31E-07</td>
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</table>

Table B.2: Susceptibility results.

REFERENCES


Appendix C: Parallelization and Convergence of VASP DFT Code

C.1 Introduction

With recent developments in parallel computing, a number of codes have added features to further distribute calculation tasks over multiple processors. In the commonly used academic and commercial density functional theory (DFT) code VASP, this functionality was fully implemented over both integration points of the k-mesh and bands as of version 5.3.2, released in November 2012; however, initial versions did not consistently produce the same results as those without parallelization. With the release of version 5.4.1 in June 2015, the features have been tested and found to produce reliable results that are consistent with those obtained without parallelization. With this development, one can now confidently use VASP parallelization flags to produce significant performance gains with minimal effort expended on checking validity of results. As such, it now make sense to expend effort on fully optimizing the VASP code to work at optimal efficiency.

The nature of a DFT calculation makes it an ideal problem to parallelize. In the normal DFT algorithm, the code selects an initial input for the electron density based either upon the input structure or the results of the previous calculation step, solves the Kohn-Sham equations to find the wave functions of electrons given the initial density, calculates the electron density based upon the solved wave functions, and finally compares this final result to the initial input to determine if the differences are less than a convergence parameter. It is not difficult to see that this algorithm can be branched into independent
calculations in the second step and merged after the third step to obtain an equivalent result. Further branching may be obtained if one performs calculations at reciprocal space integration points independently. Because of the nature of the density functional in the Kohn-Sham equations, these calculations should in principle be independent and at most require minor adjustment after completion to be consistent with the density functional theory.

Given this potential for parallelization, one should not be surprised at the options offered by the VASP code for separating the DFT problem into independent parts. The NPAR flag, available since at least version 4.6, allows the code to distribute the calculation of electron wavefunctions over multiple compute cores. The KPAR flag, implemented in version 5.3.2, allows calculation of multiple integration points simultaneously. Additional flags such as LPLANE, LSCALAPACK, and LSCALU control the communication of compute cores and nodes during steps which involve simultaneous consideration of the entire system, and their effect is likely highly dependent on relative communication speeds in the cluster on which optimization is being performed. Additionally, choices such as electronic relaxation algorithm will affect both the number of calculation steps necessary to achieve convergence and the speed at which those steps will be executed; these must be balanced depending on the system selected to offer optimum speed and convergence of calculations.

C.2 Methods

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP) software package version 5.4.1 based on first-principles density functional theories.
Generalized gradient approximation as given by Perdew-Burke-Ernzerhof (GGA-PBE) was used as the electronic exchange correlation energy in the main part of the calculation. Three calculation systems were selected: a 64-atom FCC supercell of aluminum, a 54-atom B1 supercell of magnesium oxide, and a 54-atom BCC SQS supercell of a TiZrVCuBe alloy. The FCC and B1 supercells were selected to illustrate the effects of parallelization on high-symmetry systems which are generally well-behaved, while the BCC special quasirandom structure (SQS) supercell was selected as an illustration of a “worst-case” scenario in which symmetry is not present and the presence of electronic states at the Fermi level complicates convergence. A 7x7x7 gamma-centered Monkhorst-Pack k-mesh was selected for all three systems on the basis of providing adequate energy convergence for the highly-symmetric systems and a computational challenge for the asymmetric system.

In order to minimize differences in the number of calculation steps necessary to meet convergence criteria in the different systems, the number of electronic calculation steps was arbitrarily set to be greater than that necessary for the system with slowest convergence (NELMIN = 40 or 100, depending on algorithm); likewise, the number of wave functions to be solved was arbitrarily set to be higher than the number calculated in the system with the most electrons (NBANDS = 400), and the plane wave cutoff energy was arbitrarily set to be greater than that necessary for the system with the highest default cutoff (ENCUT = 500 eV). These options reduced the advantages one system might have over another vis-à-vis its composition, allowing the calculations to focus solely on the performance gains from parallelization flags.
All calculations were performed on OSC’s Ruby cluster; 8 nodes were utilized for all calculations not testing node distribution and partial node distribution. Two electronic relaxation algorithms were tested: a blocked Davidson iteration scheme (IALGO = 38 or ALGO = Normal) and a hybrid blocked Davidson/RMM-DIIS scheme (IALGO = 68 or ALGO = Fast). It was noted that all calculations were extremely well-converged: energy differences between different algorithms and parallelization flags were generally confined to $10^{-6}$ eV or less.

C.3 Discussion

Figure C.1 displays the convergence testing of the two high-symmetry systems with respect to k-mesh size. Note that past 7x7x7, the error between subsequent k-mesh sizes is on the same order as the total calculation error; denser meshes may be necessary to ensure accuracy depending upon the scale of the effect being studied. Figure C.2 shows the CPU time for various values of KPAR for a 40-step calculation on the MgO system using both relaxation algorithms; it should be noted that while IALGO = 68 is always capable of executing this number of steps faster, it does not guarantee that convergence may not be achieved faster with IALGO = 38. Most importantly, this plot (along with many of the subsequent ones) shows that KPAR parallelization is generally independent of algorithm choice.

Figure C.3 shows the results of independent KPAR and NPAR parallelization on CPU time using IALGO = 38. The default value in each case is highlighted with a dashed box for comparison purposes. Notable here is the saturation of KPAR value for the high-symmetry systems as opposed to the clearly optimal range for the asymmetric system.
Figure C.1: Convergence of total energy of FCC Al (circles) and B1 MgO (diamonds) with k-mesh size

Figure C.2: CPU time usage for 40-step calculation of B1 MgO with various KPAR parallelization using IALGO = 38 and IALGO = 68
Additionally, it is observed that KPAR parallelization alone is capable of reducing CPU time by a factor of up to 17 while NPAR parallelization alone is capable of reducing it by a factor of up to 5. Thus, primary emphasis should be placed first on KPAR parallelization, especially since it is more flexible to changes in calculation requirements than NPAR parallelization (for instance, changes in k-mesh due to symmetry changes).

Figure C.4 shows the results of NPAR parallelization after KPAR = 4 parallelization on CPU time for both IALGO = 38 and IALGO = 68. It is clear that there is not any significant gain in computation speed for simultaneous parallelization in high-symmetry systems, nor any when IALGO = 38 is used. Interestingly, about 45% less CPU time is used when simultaneous optimization of NPAR and KPAR is performed on the asymmetric system using IALGO = 68; however, examining Figure C.3 in more detail, one sees an analogous gain by fully optimizing KPAR, and independent parallelization results for KPAR using IALGO = 68 indicate that this gain can be duplicated using KPAR = 8 without adjusting NPAR from its default value. These results further the previous conclusion that KPAR parallelization should be the first plan of attack.

When considering communication flags for parallelization in VASP such as LPLANE, LSCALAPACK, and LSCALU, testing was performed using both default and KPAR = 10 parallelization values and both IALGO = 38 and IALGO = 68. While some reduction (up to 12%) in CPU time was observed using these flags with default values, no significant reduction was observed for calculations in which KPAR was already optimized; indeed, slight increases in CPU time were observed for most KPAR = 10 calculations. Thus, it is recommended that these flags be ignored unless a system for
Figure C.3: CPU time usage for calculations utilizing independent KPAR and NPAR parallelization flags for an asymmetric BCC system (triangles), FCC Al (circles), and B1 MgO (diamonds) using IALGO = 38

Figure C.4: CPU time usage for calculations with NPAR parallelization with KPAR = 4 for an asymmetric BCC system (triangles), FCC Al (circles), and B1 MgO (diamonds) using IALGO = 38 and IALGO = 68
which KPAR is not useful is encountered, e.g. a system in which only the Γ-point is considered.

Figure C.5 shows the results of expansion of calculations to different numbers of requested nodes for a calculation using KPAR = 10 and IALGO = 38. It is clear from the relationship between CPU time and the number of requested nodes that the smallest “sufficient” number of nodes is the optimal accounting choice, since resources are charged roughly according to the amount of CPU time used. However, should faster real-time progress be necessary, the relationship between wall time and the number of requested nodes shows that an acceleration of 40% or more is possible by requesting additional nodes with minimal increase in resource usage; the efficacy of such a request is left to the user to contemplate given the scheduling conditions at OSC when the request is made.

Figure C.6 shows the results of requesting partial nodes on CPU and wall time as well as the average time to complete the blocked Davidson algorithm for each computation step for the same. Here the same KPAR and IALGO settings were used as for Figure C.5, but the number of cores per node requested was adjusted such that the total number of requested cores was 80. It is unexpected that the CPU time used here should decrease as the number of nodes increases as greater numbers of nodes should require additional bandwidth to communicate (typically the bottleneck for DFT calculations). However, in this case the bandwidth on the Ruby cluster is more than adequate to handle the load; the decrease in computation time is thus best attributed to either more efficient memory usage or the generation of additional parallel threads in when executing the blocked
Figure C.5: CPU time usage and wall time for calculations of FCC Al (circles) and an asymmetric BCC system (triangles) using KPAR = 10 and IALGO = 38 requesting different numbers of nodes.

Figure C.6: CPU time, wall time, and average blocked Davidson algorithm execution time for FCC Al requesting partial nodes for a total of 80 requested cores.

Davidson algorithm. Since no memory issues were observed thus far in this study and memory logs do not indicate significantly different usage between these tests, it is reasonable to conclude that a compilation of VASP making use of multi-threading on
individual nodes would result in greater computational efficiency. Unfortunately, the tools to create such a compilation are in the beta testing phase at writing, making testing of this hypothesis impractical at the present.

\textit{C.4 Conclusions:}

Given the results of this study, a clear algorithm exists for parallelization of the VASP code on the Ruby cluster at OSC: one should optimize KPAR for the system being calculated, and then adjust NPAR to determine if there are additional performance gains. All other optimization flags can safely be ignored once KPAR and NPAR have been optimized if satisfactory convergence has been obtained. A simple starting point for KPAR optimization is the lesser of the number of requested nodes or the number of integration points in the irreducible Brillouin zone; NPAR may then be selected by considering options such that the number of requested cores is evenly divisible by KPAR*NPAR. If the number of integration points in the irreducible Brillouin zone may change during the calculation, for instance if some crystal symmetry will be broken, NPAR should not be changed from the default value to ensure that the calculation will not end prematurely. Even in complex cases where initial guesses about appropriate parallelization flag settings are not optimized a suboptimal KPAR value will significantly improve calculation speed with no effect on results, and accordingly a KPAR value should always be selected if applicable.
References

References from Chapter 1


References from Chapter 2


References from Chapter 3

180


References from Chapter 4


12) VASP and many other ab initio codes by default only allow calculations for small displacements. To avoid having the code override the input of a large displacement, it needs a simple modification.


References from Chapter 5


References from Chapter 6


*References from Appendix A*


References from Appendix B

1) Wafer Technology Ltd., 34 Maryland Road, Tongwell, Milton Keynes, MK158HJ, England, UK, [http://www.wafertech.co.uk](http://www.wafertech.co.uk).


12) Cetas, T. C., Tilford, C. R. and Swenson, C. A. Specific heats of Cu, GaAs, GaSb, InAs, and InSb from 1 to 30K. *Phys. Rev.* 174, 835 (1968).