USING HIGH PRESSURE TO STUDY THERMAL TRANSPORT AND PHONON SCATTERING MECHANISMS

BY

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DISSERTATION

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ABSTRACT

The aerospace industry studies nanocomposites for heat dissipation and moderation of thermal expansion, and the semiconductor industry faces a Joule heating barrier in devices with high power density. Be it for the nanocomposite frame of a satellite’s solar panel array, or a miniaturized high-power RF circuit, these industries share similar interests in thermal management in nanostructures. We can improve such designs by better understanding nanoscale heat transport by phonons across and away from material interfaces. The heat flux per unit temperature drop across an interface is quantified by the interface thermal conductance. This conductance is difficult to study, as it is comprised of at least three components: bond stiffness at the interface, non-equilibrium resistance near the interface, and some intrinsic conductance. Away from interfaces, phonon-defect scattering is arguably the most complex, and technologically relevant, thermally resistive scattering mechanism in nonmetallic crystals.

My primary experimental tools are the diamond anvil cell (DAC) coupled with time-domain thermoreflectance (TDTR). TDTR is a precise optical method well-suited to measuring thermal conductivities and conductances at the nanoscale and across interfaces. The DAC-TDTR method yields thermal property data as a function of pressure, rather than temperature. This relatively unexplored independent variable can separate the components of thermal conductance and serve as an independent test for phonon-defect scattering models.

I studied the effect of non-equilibrium thermal transport at the aluminum-coated surface of an exotic cuprate material $\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$, which boasts a tenfold enhanced thermal conductivity along one crystalline axis where two-leg copper-oxygen spin-ladder structures carry heat in the form of thermalized magnetic excitations. Highly anisotropic materials are of interest for controlled thermal management applications, and the spin-ladder magnetic
heat carriers ("magnons") are not well understood, even as they greatly enhance the thermal conductivity along the ladder axis. I found that below room temperature, the apparent thermal conductivity of $\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ depends on the frequency of the applied surface heating in TDTR. This occurs because the thermal penetration depth in the TDTR experiment is comparable to the length-scale for the equilibration of the magnons that are the dominant channel for heat conduction and the phonons that dominate the heat capacity. I applied a two-temperature model to analyze the TDTR data and extracted an effective volumetric magnon-phonon coupling parameter $g$ for $\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ at temperatures from 75 K to 300 K; $g$ varies by approximately two orders of magnitude over this range of temperature and has the value $g = 10^{15} \text{ W m}^{-3} \text{ K}^{-1}$ near the peak of the thermal conductivity at $T \approx 180$ K.

To examine intrinsic phonon-mediated interface conductance between dissimilar materials, I applied DAC-TDTR to measure the thermal conductance of a series of metal-diamond interfaces as a function of pressure up to 50 GPa. The thermal conductance of interfaces between metals and diamond, which has a comparatively high Debye temperature, is often greater than can be accounted for by two phonon-processes, and the nature of heat transport between such dissimilar materials is central to the thermal design of composite materials. The high pressures achievable in a diamond anvil cell can significantly extend the metal phonon density of states to higher frequencies, and can also suppress extrinsic effects by greatly stiffening interface bonding. I measured the interface thermal conductances of Pb, $\text{Au}_{0.95}\text{Pd}_{0.05}$, Pt, and Al films deposited on Type 1A natural [100] and Type 2A synthetic [110] diamond anvils, from ambient pressure to 50 GPa. In all cases, the thermal conductances increase weakly or saturate to similar values at high pressure. My results suggest that anharmonic conductance at metal-diamond interfaces is controlled by partial transmission processes, where a diamond phonon that inelastically scatters at the interface absorbs or emits a metal phonon.

Silicon is a highly studied material, and is known to transition from a semiconducting to several metallic phases at high pressures above 12 GPa. However, the thermal conductivity and absolute electrical resistivity of metallic silicon have not been measured previously. I performed regular and beam-offset TDTR to establish the thermal conductivities of Si and $\text{Si}_{0.991}\text{Ge}_{0.009}$ across the semiconductor-metal phase transition and up to 45 GPa. The
thermal conductivities of metallic Si and Si(Ge) are comparable to aluminum and indicative of predominantly electronic heat carriers. Metallic Si and Si(Ge) have a transport anisotropy of approximately 1.4, similar to that of beryllium, due to the primitive hexagonal crystal structure. I used the Wiedemann-Franz law to derive the associated electrical resistivity, and found it consistent with the Bloch-Grüneisen model.

Not all crystalline point defects are alike in how they scatter phonons and reduce the thermal conductivity of mixed crystals. Heat-carrying phonons in iron (Fe) doped MgO, or [Mg,Fe]O ferropericlase, are known to be resonantly scattered by interaction with a 3.3 THz electronic transition in the high-spin state of the Fe impurities. At sufficiently high pressures, the Fe atoms transition from a high-spin to a low-spin state, which eliminates the resonant interaction and reduces the Fe atoms to simpler point defect phonon scatterers. To study the behavior of phonon-defect scattering with and without this resonant scattering process, I measured the thermal conductivity of Mg$_{0.92}$Fe$_{0.08}$O ferropericlase up to and above the 40-60 GPa spin transition. Fe-doped MgO (ferropericlase) is also a model system relevant to geophysical modeling of the Earth’s core-mantle boundary, so data on its thermal transport under pressure is valuable in itself.
Everything is theoretically impossible, until it is done.

-R.A.H.
Thanks first to my Ph.D. advisor Professor David Cahill. I came in curious about thermal physics, having not learned much about it in the standard physics curriculum, and I’m exiting with a modest grasp of the field. Simply put, I could not have asked for a better or more professional research manager. Thank you for your patience and for setting a high standard.

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had more time with Dave. I also had great times dancing with the Illini Dancesport Team over the years; Kyong Noh, Elvan Ekiz, Yan Zhou, Xiang Deng, Lily Sacharow, Christen Mercier, Jeff Proulx, Allen Gehret, Alfred my love, Del, and all the rest of you, do keep in touch. And of course, Xiaojia, I’m glad for our friendship and the ridiculous variety of Chinese food we consumed. May your perseverance be unwavering, though now far away from David’s foxy smile.

Finally, abundant thanks to my parents for their steadfast support throughout this little adventure of mine. One of these years I will finish cataloguing that massive library of yours.

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# CONTENTS

Chapter 1  INTRODUCTION ............................................. 1
  1.1 Thermal Transport Basics ........................................ 1
  1.2 Relaxation time approximations for $\Lambda$ and $G$ ............ 3
  1.3 Independent Variables in Thermal Transport Experiments ...... 5
  1.4 Review of Recent High Pressure Thermal Transport Experiments 6
  1.5 Outline of Thesis ............................................. 9

Chapter 2  EXPERIMENTAL METHODS ............................. 12
  2.1 Time-domain thermoreflectance (TDTR) ......................... 12
  2.2 The diamond anvil cell ..................................... 16
  2.3 High pressure TDTR .......................................... 21
  2.4 Figures ..................................................... 25

Chapter 3  TDTR DATA ANALYSIS ................................. 29
  3.1 TDTR vH3: MATLAB data analysis system ....................... 29
  3.2 Interpreting picosecond acoustics in the case of a weakly- bonded interface ........................................... 30
  3.3 Figures ..................................................... 37

Chapter 4  MAGNON-PHONON COUPLING IN Ca$_9$La$_5$Cu$_{24}$O$_{41}$ SPIN LADDERS MEASURED BY TIME-DOMAIN THERMOREFLECTANCE ............................................. 40
  4.1 Introduction .................................................. 40
  4.2 Experimental Method ........................................ 42
  4.3 Magnon-phonon coupling via frequency-dependent apparent thermal conductivity ........................................... 43
  4.4 Two-Temperature Model for Time-Domain Thermoreflectance Data .................................................. 46
  4.5 Thermal Parameters ................................ .......... 47
  4.6 Data Analysis ................................................ 48
  4.7 Results ..................................................... 50
  4.8 Magnon-phonon relaxation-time model .......................... 51
  4.9 Discussion ................................................... 52
  4.10 Conclusion .................................................. 54
  4.11 Figures ..................................................... 55
<table>
<thead>
<tr>
<th>Chapter 5</th>
<th>THERMAL CONDUCTANCE OF METAL-DIAMOND INTERFACES AT HIGH PRESSURE</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>61</td>
</tr>
<tr>
<td>5.2</td>
<td>Methods</td>
<td>61</td>
</tr>
<tr>
<td>5.3</td>
<td>Brillouin spectroscopy</td>
<td>64</td>
</tr>
<tr>
<td>5.4</td>
<td>Pressure-dependent TDTR thermal parameters</td>
<td>66</td>
</tr>
<tr>
<td>5.5</td>
<td>Metal-diamond TDTR data analysis</td>
<td>67</td>
</tr>
<tr>
<td>5.6</td>
<td>Reflectance and thermoreflectance</td>
<td>71</td>
</tr>
<tr>
<td>5.7</td>
<td>Electron-phonon resistance</td>
<td>77</td>
</tr>
<tr>
<td>5.8</td>
<td>Irreversible interfacial stiffening and intermediate phases</td>
<td>81</td>
</tr>
<tr>
<td>5.9</td>
<td>Results</td>
<td>82</td>
</tr>
<tr>
<td>5.10</td>
<td>Discussion</td>
<td>89</td>
</tr>
<tr>
<td>5.11</td>
<td>Figures</td>
<td>94</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 6</th>
<th>THERMAL TRANSPORT ACROSS HIGH PRESSURE SEMICONDUCTOR-METAL TRANSITION IN Si &amp; Si$<em>{0.991}$Ge$</em>{0.009}$</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>Introduction</td>
<td>103</td>
</tr>
<tr>
<td>6.2</td>
<td>Experimental method</td>
<td>105</td>
</tr>
<tr>
<td>6.3</td>
<td>DAC sample preparation and pressure calibration</td>
<td>109</td>
</tr>
<tr>
<td>6.4</td>
<td>Pressure-dependent thermal modeling</td>
<td>110</td>
</tr>
<tr>
<td>6.5</td>
<td>Interface thermal conductance</td>
<td>113</td>
</tr>
<tr>
<td>6.6</td>
<td>Thermal conductivity - semiconducting</td>
<td>115</td>
</tr>
<tr>
<td>6.7</td>
<td>Thermal conductivity - metallic</td>
<td>118</td>
</tr>
<tr>
<td>6.8</td>
<td>Electrical resistivity</td>
<td>121</td>
</tr>
<tr>
<td>6.9</td>
<td>Conclusion</td>
<td>123</td>
</tr>
<tr>
<td>6.10</td>
<td>Figures</td>
<td>124</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 7</th>
<th>MAGNETIC VERSUS NON-MAGNETIC POINT DEFECTS IN MIXED CRYSTALS</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>Introduction</td>
<td>130</td>
</tr>
<tr>
<td>7.2</td>
<td>Resonant scattering in Mg$<em>{1-y}$Fe$</em>{y}$O</td>
<td>131</td>
</tr>
<tr>
<td>7.3</td>
<td>Sample preparation</td>
<td>133</td>
</tr>
<tr>
<td>7.4</td>
<td>Data collection and analysis: transient absorption, coherence, and reflectance</td>
<td>134</td>
</tr>
<tr>
<td>7.5</td>
<td>Transient absorption revisited</td>
<td>137</td>
</tr>
<tr>
<td>7.6</td>
<td>Discussion of preliminary results</td>
<td>138</td>
</tr>
<tr>
<td>7.7</td>
<td>Figures</td>
<td>140</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 8</th>
<th>CONCLUSION</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1</td>
<td>Summary</td>
<td>148</td>
</tr>
<tr>
<td>8.2</td>
<td>Next steps</td>
<td>150</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 9</th>
<th>BIBLIOGRAPHY</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>152</td>
</tr>
</tbody>
</table>
Chapter 1

INTRODUCTION

1.1 Thermal Transport Basics

Although it rarely takes center stage, thermal management is an essential design consideration for electronic devices, high-performance materials, and space satellite systems. The increased transistor density expected by Moore’s law implies an increase in power density, which causes Joule heating that must be dissipated lest the device overheat.\footnote{\textsuperscript{1}} This is also true for miniaturizing high-power RF circuits, which are sensitive to the dielectric coefficients of their surroundings, coefficients which vary with temperature. Miniaturization has reached a regime where heat sink materials are becoming inadequate, hence the rise of multicore computing designs that spread out the heat sources.\footnote{\textsuperscript{2}} Meanwhile in the aerospace industry there is a persistent demand for strong, lightweight materials with an array of thermal properties. Orbital launch vehicles need thermal insulation against atmospheric friction; to that end, researchers are developing nanocomposites.\footnote{\textsuperscript{3}} Satellites are exposed to dramatic temperature changes and gradients in space as they move between sunlight and Earth’s shadow, but can only rely on radiative cooling. Their designs require on-board heat spreaders for electronics and structural components, partly to prevent failures from nonuniform thermal expansion and contraction.\footnote{\textsuperscript{4}} Good thermal management is what enables long operating lifetimes for electronic components, and allows advanced composite materials to survive the extreme environments encountered by aerospace vehicles and satellites. Considering these and other motivations, there continues to be a wide range of active research into the physics of micro- and nano-scale thermal transport as it relates to thermal conductivity and interface thermal conductance at small length and time scales.\footnote{\textsuperscript{5,6}}

Whether the problem is macroscale or nanoscale, or the user is an engineer
or physicist, the most widely used and recognized governing equations for thermal transport are Fourier’s Law, followed by the heat diffusion equation. As we will see in the next section, Fourier’s law is a linearization, or first-order Taylor expansion, that describes the heat flux \( \vec{J} \) across a temperature gradient \( \vec{\nabla}T \). Simply put, Fourier’s law states that

\[
\vec{J} = -\Lambda \vec{\nabla}T, \tag{1.1}
\]

where \( \Lambda \) is the thermal conductivity of that material. Fourier’s law in fact defines thermal conductivity; in situations where Fourier’s law is invalid, there is no monolithic "thermal conductivity" in the problem.

The heat diffusion equation, meanwhile, is a statement of conservation of energy as heat flows in and out of a differential volume \( dV = dx dy dz \) over some time \( dt \). Without appeal to Fourier’s Law, the heat diffusion equation is:

\[
C \frac{\partial T}{\partial t} = -\nabla \vec{J} + S(\vec{r}, t). \tag{1.2}
\]

Here \( C \) is the volumetric heat capacity, and \( S(\vec{r}, t) \) represents an arbitrary heat source. Plugging in Fourier’s Law, and assuming \( \Lambda \) is constant in space, yields the familiar heat diffusion equation,

\[
C \frac{\partial T}{\partial t} = \Lambda \nabla^2 T + S(\vec{r}, t). \tag{1.3}
\]

This is fine for a bulk homogeneous material in the continuum limit, but between materials there are boundary conditions to consider. If two materials with different thermal properties are not in thermal equilibrium and are placed in contact with one another, there is in general an abrupt temperature drop \( \Delta T \) across the interface between them. The heat flow per unit area \( q \) across the interface is then described by a discrete form of Fourier’s Law:

\[
q = -G \Delta T. \tag{1.4}
\]

This is the definition of the interface thermal conductance \( G \), which is as much a property of the detailed structure and bonding at the interface as it is of the two materials on either side. Engineers will often invert \( G \) and consider the interfacial thermal resistance \( G^{-1} \) instead. \( G \) due to phonon transport across well-bonded solid-solid interfaces typically ranges from 50 to
200 MW m\(^{-2}\) K\(^{-1}\). The physical mechanisms resulting in this rather narrow range of phononic \(G\) are not well understood, and hence the subject of much current thermal physics research.

1.2 Relaxation time approximations for \(\Lambda\) and \(G\)

Our task as physicists is to build physical models that provide intuition and have predictive power, and then test those models against experimental data. Current theories of thermal conductivity and thermal conductance are built from a quantum mechanical picture of interacting (quasi)particles, mainly phonons and electrons. Specifically, much of our intuition for thermal transport comes from a class of models within the relaxation time approximation (RTA), the basis of which we will examine in the next section. For now, we introduce the necessary concepts and present the most basic RTA equations for \(\Lambda\) and \(G\).

In quantum theory the vibrational normal modes of a crystal, phonons, are treated as quasiparticles, each with a momentum \(\vec{Q}\) and branch index \(n\). The branch index marks a phonon as being, for example, a transverse acoustic mode or a longitudinal optic mode of the crystal. Each branch has a specific energy-momentum dispersion relation \(E_n(\vec{Q}) = \hbar \omega(\vec{Q}, n)\). Since crystals exist in three dimensions, even "two-dimensional" materials like graphene, every crystal has \(3m\) phonon branches, where \(m\) is the number of atoms per unit cell. Three of these are acoustic modes: one longitudinal and two transverse polarizations. The remaining \(3(m-1)\) are optical branches. Phonons are bosons, hence the number of phonons in a particular state \((\vec{Q}, n)\) in thermal equilibrium obeys Bose-Einstein statistics. The details of the phonon dispersion, as well as the phonon density of states, are determined by crystal structure, the mass of each atom, and interatomic bonding strengths.

Generally, acoustical phonons away from the Brillouin zone boundary have the largest group velocities \(v_g^a = d\omega_Q/d\vec{Q}\) and mean-free-paths \(l(Q, n)\), while optical phonons and acoustical phonons near the zone boundary have the highest phonon densities of states (inversely proportional to \(v_g\)) and energies \(E_n(Q)\). Hence the former group disproportionately influences the thermal conductivity \(\Lambda\), while the latter tend to dominate the heat capacity \(C\) at room temperature. All phonons can scatter with other phonons (and other
heat carriers, e.g. electrons) in ways that depend on temperature, energy conservation, crystal lattice symmetries, and so on.

We can imagine how thermal conductivity $\Lambda$ and conductance $G$ can be expressed in microscopic, quantum mechanical terms. The thermal conductivity of each phonon mode should depend on how much energy it picks up per unit temperature rise (heat capacity), how fast it propagates (group velocity), and how effectively it propagates despite interactions with other phonons, defects, and such. That last factor can be called the phonon mean-free-path $l$, or equivalently the thermal relaxation time $\tau$, where $l \equiv v_g \tau$. Without interactions, $l \to \infty$, the heat carriers are termed "ballistic", and the thermal conductivity is in theory infinite, ignoring the interactions by which heat enters those carriers in the first place. Since there is a broad spectrum of phonons, the contribution of each phonon mode at each frequency $\omega$ should be summed up to yield the total thermal conductivity $\Lambda$. It turns out that this picture, known as the relaxation time approximation (RTA), yields the following common expression for $\Lambda$,

$$\Lambda = \frac{1}{3} \int C(\omega) v_g^2(\omega) \tau(\omega) d\omega,$$

where the summation over phonon branches, each with their own $v_g(\omega)$, $\tau(\omega)$, and heat capacities $C(\omega)$ is implicit. To account for multiple resistive scattering rates such as by Umklapp ($\tau_U$) and defect ($\tau_d$) scattering, Matthiessen’s rule states that the effective resistive scattering rate $\tau_r^{-1}$ is the parallel sum of these, for example $\tau_r^{-1} = \tau_U^{-1} + \tau_d^{-1}$. Three-phonon normal scattering events, however, conserve momentum and are not directly resistive, but indirectly affect the thermal conductivity by redistributing phonons into modes that may be more or less prone to resistive scattering events. The Callaway, Callaway-Morelli, and Callaway-Allen RTA models are successive refinements of the RTA picture that include the influence of normal scattering $\tau_n^{-1}$ on the thermal conductivity.

Thermal conductance $G$ at an interface between materials is written similarly:

$$G = \frac{1}{4} \int C(\omega) v(\omega) t(\omega) d\omega,$$

where now the picture is simpler in that $t(\omega)$ is the transmission coefficient,
representing the probability for phonons carrying heat flux $C(\omega)v(\omega)$ to cross the interface and contribute to $G$. Here the interesting physics is contained in $t(\omega)$, and helpful models or limiting cases for $t(\omega)$ include: the acoustic mismatch model (AMM), which describes specular reflection and transmission of phonons at an interface; the diffuse mismatch model (DMM), which describes elastic scattering where $t(\omega)$ is weighted by the phonon densities of states on either side of the interface; the radiation limit, which assumes $t(\omega) = 1$ if possible; and the concept of a theoretical maximum conductance as a material property.$^{5,10,11}$

The central challenge of thermal transport physics is to discover the microscopic heat carrier dynamics leading to mean-free-paths, thermal relaxation times, and transmission coefficients in various material systems despite, for the most part, only having access to integral quantities such as $\Lambda$ and $G$.

1.3 Independent Variables in Thermal Transport Experiments

A universal part of the scientific method is the controlled experiment, whereby most relevant parameters are held constant and a physical property is measured as a function of some independent variable. In thermal transport experiments, that independent variable is very often temperature. Temperature determines the energy range available to the electrons and phonons that mediate heat flow in many materials. At low temperatures, phonons are said to be frozen out; their populations in different phonon modes decrease while the rates of phonon-phonon interactions also decrease. At high temperatures, crystalline nonmetals are recognizable by their $1/T$ temperature dependence due to dominant Umklapp scattering.

Thermal transport measurements as a function of temperature have revealed a great deal about the electron and phonon scattering mechanisms that determine thermal conductivity. Temperature-dependent transport data for pure and mixed crystals with varying defects, for glassy materials, and for metals have refined our models for how normal, Umklapp, and boundary phonon scattering occurs as a function of temperature, phonon frequency, and phonon dispersion. Such data has validated the minimum thermal conductivity model, based on Einstein’s vibrational model, for thermal transport.
in glassy materials. Temperature-dependent thermal conductivity and electrical resistivity data on metals have confirmed how and when these two properties are coupled through the Wiedemann-Franz law. More recently, electron-phonon thermal coupling has been probed at the sub-picosecond time scale with ultrafast lasers, and with the development of time-domain thermoreflectance (TDTR), the study of nanoscale thermal transport in thin films and at interfaces has come into its own. Systematic variation of temperature has been and continues to be a very informative avenue for thermal physics research.

Temperature, however, is not the only state variable that can be tuned experimentally for physical insight: pressure is another independent variable that can be controlled to reveal thermal transport physics. While temperature can control the thermal occupation of phonon modes, high pressure can directly alter the phonon dispersion and density of states by stiffening atomic bonds in the material. In some ways high pressure is analogous to low temperature, in that both can effectively cause parts of the phonon spectrum to be less accessible to thermally activated phonon modes. Pressure provides access to its own set of structural phase transitions that abruptly alter the transport properties of a material, and high pressure also directly stiffens interfacial bonding between materials. For these reasons pressure is an especially interesting independent variable for studying thermal transport, particularly at and near material interfaces.

1.4 Review of Recent High Pressure Thermal Transport Experiments

Before embarking on this brief review of recent thermal transport experiments at high pressures, the interested reader is advised to explore my predecessor Wen-Pin Hsieh’s similar review up to 2010 in his Ph.D. dissertation.

In the past it was difficult to apply sufficient pressure to significantly compress many solid state materials, but anvil cell techniques have seen progressive improvement in the past decades. Much of that improvement has been driven by the needs of geophysical research, which seeks to measure and accurately model planetary-scale mechanical, material, and thermal properties and dynamics. Geophysical models of planetary heat flow, notably near
the Earth’s core-mantle boundary where the pressure reaches 130 GPa, rely on knowledge of the thermal conductivity of minerals at high temperatures and pressures.\textsuperscript{14,15} The DAC has enabled laboratory study of geophysically relevant mineral physics, from elasticity and viscosity through phase transitions and thermal transport. The diamond anvil cell (DAC)\textsuperscript{16} is capable of producing static pressure on the order of 100 GPa in the laboratory, more than enough to achieve significant compression and alteration of thermal properties in most materials.

Insofar as thermal transport experiments at high pressure, researchers must contend with the fact that samples in the DAC are necessarily sub-millimeter in size, and are sealed in by two conical diamond anvils ringed by a metal gasket. The 5000 tonne multi-anvil apparatus at the Bayerisches Geoinstitut, completed in 2004,\textsuperscript{17} allows larger sample volumes than the DAC but is limited to pressures of about 20-30 GPa. In between the palm-sized DAC and massive 5000 tonne systems lie an ecosystem of specialized anvil cells that balance sample volume against maximum pressure, for instance the Paris-Edinburgh press.\textsuperscript{18} One advantage of larger cell volumes is enhanced stability for simultaneous high pressure, high temperature (HPHT) experiments that seek to replicate planetary interior conditions.

In the multi-anvil apparatus at the Bayerisches Geoinstitut, the Angström periodic heating method has been used to measure thermal diffusivity at pressures and temperatures as high as 26 GPa and 1273 K.\textsuperscript{19,15} An impulse heating method, where the sample is stacked with electric heater and thermocouple layers, has also been developed for thermal diffusivity and thermal conductivity measurements in larger anvil cells, up to approximately 10 GPa.\textsuperscript{20,21} Both methods require electrodes extending mechanically into the anvil cell chamber for heat input and temperature readout. This is challenging because the requisite metal leads must be simultaneously protected from the high pressure environment, electrically insulated, and in good contact with the sample. Stress gradients can build under pressure to damage or deform the metal leads, and the sample geometry will also change under compression or across phase transitions.\textsuperscript{22} Researchers have developed designer diamond anvils with embedded metal leads to perform electrical measurements in the DAC,\textsuperscript{23,24} but we are not aware of work using designer diamonds for thermal measurements in the DAC.

Recently, all-optical techniques have been developed for thermal trans-
port measurements at high pressure in the DAC. Optical techniques are less demanding in that the diamond anvils double as optical windows. For simultaneous high pressure, high temperature measurements in particular, high speed spectroradiometry is used to sample blackbody radiation from intensely laser-heated DAC samples. The resulting 2D temperature map is then fitted for thermal diffusivity.\cite{25-27}

Laser flash diffusivity is another set of optical thermal transport techniques where a sample is heated by a pump laser, and the resulting temperature excursion on the other side of the sample is monitored over time and fitted for the thermal diffusivity. At sufficiently high temperatures, the sample temperature can be monitored passively by collecting blackbody radiation.\cite{28} Alternately, the sample can be coated with a fluorescent material, so that the temperature rise is inferred from the fluorescent response.\cite{29}

In particular, researchers at the National Metrology Institute of Japan (NMIJ) have adapted a laser flash diffusivity technique using thermoreflectance to measure thermal diffusivity in the DAC.\cite{30;31} It is distinct from time-domain thermoreflectance (TDTR) in that the probe beam is continuous wave, and the probe is incident on a second transducer on the opposite side of the sample. Hence, information about the surface temperature over time is obtained with a high-speed detector rather than the relative delay of pump and probe pulses. In that geometry the method is sensitive to uncertainty in the sample thickness, while TDTR for a comparable sample is sensitive to the transducer thickness. In any case, the NMIJ used laser flash diffusivity to measure the diffusivity of Mg(OH)$_2$ to 57 GPa in 2011,\cite{31} and that of MgSiO$_3$ to 144 GPa in 2012.\cite{30}

Our approach has been to leverage time-domain thermoreflectance (TDTR), an established ultrafast pump-probe technique for measuring thermal transport properties.\cite{32;5;6} TDTR and its cousins\cite{33-35} have enabled fundamental work toward understanding heat flow in and across nanoscale thin-film materials. Over the past few years high pressure TDTR experiments have provided new insight into the role of weak interface bonding in suppressing the thermal conductance of an interface between two materials.\cite{36;37} TDTR has also verified theoretical predictions of the thermal conductivity in amorphous and crystalline solids at high pressure.\cite{38-40} However, there is little experimental data on the pressure scaling of the thermal conductivity of mixed crystals or metals. For metals, much of the existing data extends only to a few
Finally, high pressure thermal conductance studies have only just begun through my work and that of my predecessor Wen-Pin Hsieh.

1.5 Outline of Thesis

In this thesis, I combine time-domain thermoreflectance (TDTR) with diamond anvil cell (DAC) techniques to study high pressure heat transport, and infer nanoscale phonon scattering mechanisms. I have extended DAC-TDTR techniques to consistently higher pressures than before and answered unresolved questions in thermal transport physics. The following chapters describe the experiment, data analysis, and the four major projects I’ve completed over the course of my graduate research.

In Chapter 2, I describe the basics of my primary experimental techniques, time-domain thermoreflectance and the diamond anvil cell. Certain aspects of the TDTR optical setup become more important when dealing with DAC samples, and certain aspects of DAC sample preparation and loading have to match the requirements of TDTR. In other ways, DAC and TDTR techniques require little adjustment to be combined, since the optical access provided by DAC samples is well suited to the all-optical TDTR technique.

In Chapter 3, I go into more detail on TDTR data analysis in general and DAC-TDTR data analysis in particular. First, I explain my study of picosecond acoustics in the case of a weakly bonded interface, which I assembled as a service to the TDTR community. Very often, unless extraordinary care is taken to form material interfaces under ultra-clean conditions, TDTR samples carry a thin contaminant layer at the interface between the metal transducer and sample. This does not invalidate the thermal conductivity measurement, however, so long as the distorted picosecond acoustics from this soft interface are properly interpreted. Next, I discuss the detailed thermal model used to analyze TDTR data, as well as the length and time scales characteristic of TDTR that enable sensitivity to thermal properties and, at times, nanoscale thermal transport dynamics. I close this chapter with an introduction to the ecosystem of MATLAB scripts I developed and published online over the course of my research. Proper understanding of the TDTR measurement, and having efficient tools for data analysis and sensitivity calculations, are central to good experimental design, validation, and
Chapter 4 concerns my ambient pressure project on magnon-phonon thermalization in the spin ladder cuprate Ca$_9$La$_5$Cu$_{24}$O$_{41}$, where I used TDTR and an optical cryostat to measure, for the first time, the magnon-phonon coupling in this material as a function of temperature from 300 K down to approximately 60 K. This material provides a clean case study for how non-equilibrium dynamics between weakly coupled heat carriers, in this case magnons and phonons, can manifest as a nanoscale thermal resistance near an interface.

Chapter 5 presents my experiments on metal-diamond interface thermal conductance in the diamond anvil cell. At high pressures, the metal phonon density of states to higher frequencies, and the effect of weak bonding on interface conductance is suppressed. I measured Pb, Au$_{0.95}$Pd$_{0.05}$, Pt, and Al films deposited on Type 1A natural [100] and Type 2A synthetic [110] diamond anvils. In all cases, the thermal conductances increased weakly or saturated to similar values at high pressure. The results suggest that anharmonic conductance at metal-diamond interfaces is controlled by partial transmission processes, where a diamond phonon that inelastically scatters at the interface absorbs or emits a metal phonon.

Chapter 6 describes the results of my foray into thermal transport across a semiconducting to metallic phase transition at high pressure, specifically in silicon (Si) and Ge-doped silicon, Si(Ge). Though little was learned about thermal conductance, due to the large volume changes in Si and across its phase transitions, the lessons of this experiment will make future studies of thermal conductance in the presence or absence of electronic heat carriers more straightforward. Meanwhile my data on the thermal conductivity of metallic Si and Si(Ge), and the inferred Wiedemann-Franz electrical resistivity, adds to the sparse experimental literature on the pressure dependence of metallic thermal conductivity and electrical resistivity at very high pressures.

In Chapter 7, I present progress toward a more nuanced understanding of phonon-defect scattering in mixed crystals, specifically for cation substitutions in MgO. We know that the thermal conductivity of pure MgO to 60 GPa can be replicated by a Callaway model, but the thermal conductivity reduction in [Mg,Fe]O mixed crystals due to the Fe defects is greater than a Callaway model can plausibly reproduce with point defect scattering alone. This is due to magnetic scattering of phonons with the spin states of
Fe$^{2+}$ cations, and I have measured the thermal conductivity of single crystal Mg$_{0.92}$Fe$_{0.08}$O to high pressure to verify and quantify this effect.

Chapter 8 is the conclusion of my thesis, where I summarize what I have learned about high pressure thermal transport, and comment on what else might be learned by using pressure as an independent variable in thermal transport experiments. Following Chapter 8 is the full list of references for this thesis.
2.1 Time-domain thermoreflectance (TDTR)

Time-domain thermoreflectance (TDTR) is a well-established, ultrafast optical pump-probe technique for thermal transport measurements.\textsuperscript{32,42–44} The earliest forms of the technique were developed separately by Paddock and Eesley\textsuperscript{45} and by Humphrey Maris’s group\textsuperscript{46} in the late 1980’s. The technique was then adopted and developed by Cahill and others in the early 2000s,\textsuperscript{47} has seen widespread adoption in nanoscale heat transport research,\textsuperscript{6} and remains the workhorse for experiments in the Cahill group. Our research often produces or relies upon extensions of the technique.\textsuperscript{48,42,49,34}

In the TDTR experiment (Fig. 2.1), the 80 MHz, 785 nm mode-locked pulse train output of a Ti:sapphire laser is split into pump and probe beams by a polarizing beamsplitter. Before it reaches the sample, the pump beam passes through an electro-optic modulator (EOM) which imposes a square wave modulation at 9.8 MHz. This frequency can vary, but $1/f$ noise and the 80 MHz repetition rate result in a practical range of 1-20 MHz in most cases.

The pump and probe beams are both focused to the same spot on an optically smooth sample, which has previously been coated with a metal transducer film, typically 80 nm thick. The metal transducer is typically deposited by DC magnetron sputtering, and serves a dual purpose of absorbing some of the pump light and reflecting the subsequent probe pulses. The absorbed pump light goes to heating the electrons near the surface, the electrons rapidly thermalize with the phonons in the metal, and the heat proceeds to diffuse into the underlying sample over time.

The name "time-domain thermoreflectance" comes from the technique’s operating principles. First, thermoreflectance refers to a material property
whereby the optical reflectivity $R$ of a metal film changes linearly with a change in temperature: $\Delta R = (dR/dT) \Delta T$. As such, a metal film chosen for its large $dR/dT$ near 785 nm will reflect an amount of probe light that varies linearly with the surface temperature rise $\Delta T$. Meanwhile, the pump beam path contains a delay stage, whereby the time delay at the sample surface of each probe pulse, relative to the preceding pump pulse, can be controlled. The result is that the probe beam effectively measures, in the time-domain, the temperature rise and cooling of the sample in response to the pump light, thanks to the thermoreflectance effect. That cooling over time is then interpreted within a thermal model to extract unknown thermal properties from the data.

Before the reflected probe beam can be collected by the Si photodiode detector, care must be taken to ensure that reflected pump light does not also reach the detector. Our TDTR system relies on polarization, spatial, and two-tint wavelength filtering steps. An RF lock-in amplifier synchronized to the modulation frequency of the pump beam extracts a signal proportional to the change in reflectance of the transducer surface due to the pump heating.

Because of coherent pickup from the reference frequency generator electronics, not all of the modulation frequency signal detected by the RF lock-in is in fact the true signal originating from the reflected probe beam’s response to pump heating of the sample. To ensure this, we send the RF lock-in signal to a LabVIEW controller which has an acoustic lock-in stage implemented in software. The acoustic lock-in is referenced to the frequency of an optical chopper running near 200 Hz, which we place in the path of the probe beam before it reaches the sample. The 200 Hz probe modulation is irrelevant to the data analysis because it has no effect on the thermal response of the sample at the time scale of pump-probe delay time or the MHz pump modulation frequency.

Ultimately, time-domain data is taken by offsetting the pump and probe pulse trains with a delay stage. This signal is comprised of in-phase $V_{in}(t)$ and out-of-phase $V_{out}(t)$ components, relative to the pump modulation phase. The collected data is then compared to the output of our thermal model, which predicts the normalized ratio signal $r(t) = -V_{in}(t)/V_{out}(t)$ that is sensitive to the thermal properties of the sample. In its basic application, a single TDTR measurement can extract the thermal conductivity of the sample and the thermal conductance of its interface with the metal transducer.
See Chapter 3 for further details on thermal modeling and data analysis.

Because of the MHz heating frequency, TDTR only probes a microscale volume near a sample’s surface (see Chapter 3 for details). This simplifies thermal modeling in the diamond anvil cell, which can only pressurize microscale samples. Given optical access and an appropriate transducer, the TDTR technique is largely independent of the sample’s environment, whether in air, cryostat, or diamond anvil cell.

2.1.1 Beam shaping for TDTR

For the sake of TDTR practitioners, it is worthwhile to elaborate on the beam shaping considerations relevant to achieving stable, circular pump and probe beam spots on one’s samples in a standard TDTR measurement.

The spot size $w(z)$ of a Gaussian beam at any point $z$ along its path depends on three parameters: the laser wavelength $\lambda$, the distance to its beam waist $z - z_0$, and the radius of the beam waist $w_0$. The governing equation for the beam radius $w(z)$ is:

$$w(z) = w_0 \sqrt{1 + \left(\frac{z - z_0}{z_R}\right)^2}$$

(2.1)

where $z_R \equiv \pi w_0^2 / \lambda$ is the Rayleigh range. The divergence in $w(z)$ is quadratic near $z_0$ and asymptotically linear far from $z_0$.

In practice, the Ti:sapphire laser cavity is a sensitive optical system, and although the output pulse train has a Gaussian profile in space, its divergence is not uniform along the x- and y- axes relative to the optical table. The x- and y-axes of the beam will have beam waists $z_{0,x}$ and $z_{0,y}$ at different points within about a meter of the Ti:sapphire output, sometimes even inside the Ti:sapphire cavity. These beam waists will also have different spot sizes $w_{0,x}, w_{0,y}$, which means the ellipticity of the free space beam profile will vary over the optical path. If not corrected, the beam can diverge excessively, get clipped by the aperture of the electro-optic modulator (EOM), and produce an elliptical, non-uniform laser spot on the TDTR sample that varies dramatically with the position of the delay stage.

For TDTR we would like to impose certain constraints. First: the free space beam should be significantly smaller than the EOM aperture, to avoid
clipping and introduction of non-Gaussian elements.\textsuperscript{50} EOM aperture clipping is most visible in the free space beam profile measured when the pump delay stage is at a long time delay, corresponding to a short optical path from the EOM. Over longer distances, the non-Gaussian components are more divergent than the Gaussian mode, and eventually separate from the main beam.

Second: the last x- and y- beam waists before the TDTR sample should be the same size at that point in space, so that the divergences are equal and the beam remains circular. Otherwise the focused beam spot size must be approximated by its geometric mean \( \sqrt{w_x w_y} \) for thermal modeling, or an elliptical model applied. A significantly elliptical beam on the sample can also confuse beam-offset TDTR measurements, which focus on lateral heat spreading relative to the initial spot size.\textsuperscript{34}

Third: the final beam waist should be positioned immediately upstream of the objective lens when the delay stage is at its halfway point, so that the spot size varies weakly with time delay and is the same at the start and end of a TDTR scan. It is also strongly advised that the variation in pump spot size as a function of time delay (i.e., pump optical path length) be directly measured on the sample using beam-offset TDTR or another technique. Due to non-Gaussian elements in the free space beam, the user \textit{cannot} rely on an ideal conversion of the free space spot size to the focused spot size after the objective lens. Figure 2.2 shows how wrong that assumption can be, and how an apparently constant free space beam size nonetheless produces a nearly 20\% linear shift in pump spot size over delay time in our TDTR system \textit{after} beam shape optimization.

All three of these constraints can be implemented by placing cylindrical and spherical lenses near the output of the Ti:sapphire laser cavity, after the isolator. One will generally have to compromise between them for a "good enough" solution. An electronic beam profiler that can be inserted into the beam path at various points helps in characterizing the initial divergence. To guide lens placement and intuition, it is also useful to simulate the lens and propagation optical transfer matrices in MATLAB, based on data from the beam profiler.
2.2 The diamond anvil cell

This section serves both to introduce the diamond anvil cell as a technique, and to offer practical advice to the new DAC user based on my personal experience in high pressure research. For the most part, it takes a great deal of time, patience, hand/finger dexterity, and veteran advice to become a skilled DAC user. Before I begin describing the diamond anvil cell, I highly suggest that the reader take advantage of the following online resources. First, look up Stanislav Sinogeikin’s presentation slides on "Practical Aspects of High Pressure Experiments" from the September 15-18, 2010 Short Course on High Pressure Synchrotron Techniques, hosted by Argonne National Laboratory at the Advanced Photon Source. At this time the link to the slides is https://www.gl.ciw.edu/static/events/hpcatshortcourse/06Stas.pdf. The reader may also be interested in browsing through other HPCAT Short Course presentations. Sinogeikin’s presentation gives a very good visual introduction to the different types and design features of diamond anvil cells. Next, bookmark the COMPRES (Consortium for Materials Properties Research in Earth Sciences) website, in particular its COMPRES Technology Center (COMPTECH), which has a list of useful tools for high pressure experiments (the current live link is http://comptech.compres.us/tools/).

In my high pressure experiments I used a Boehler-Almax X-ray Plate DAC purchased from what is now Almax-EasyLab. The Boehler-Almax Plate DAC is designed with a wide, 140° aperture for optical access: this is important for X-ray experiments, and convenient for illuminating and focusing lasers on to DAC samples. Other DAC designs like the Japanese Syntek are popular as well. The diamond anvils are shaped according to the Boehler-Almax conical standard. The top of each anvil is polished flat to produce a surface known as the culet. The DAC consists of two palm-sized circular metal plates, held apart by three large set screws around the outer diameter. Along the middle diameter of the plates are holes for threaded pressure screws that pass through both plates. Tightening the pressure screws cause the centers of the plates to flex inward toward one another. A tungsten carbide seat is press-fitted into the center of each plate, and the seat contains a depression into which the back of a diamond anvil fits. To fix a diamond anvil to its seat, a tool known as a jig is used to firmly clamp a diamond anvil to the seat while an epoxy or ceramic adhesive is applied in a ring around where
the anvil fits into the seat. Once the diamonds are mounted, tightening the pressure screws can bring their culets into contact, although this should be done very gently to avoid diamond scratching diamond. Small adjustments are then made in the outer set screws of the Boehler-Almax DAC to ensure that the culets are precisely parallel to one another, using the Newton’s rings (optical interference) visible between lightly touching culets as feedback.

To actually apply pressure to a sample, it is necessary to contain it within the space between the diamonds as the diamonds are brought together by the DAC. Otherwise the sample would simply be crushed or escape laterally. A metal gasket is generally used to create a sample chamber between the anvil culets. I used 0.01" thick by 0.2" x 0.2" square rhenium plates from H Cross Company as my gasket material. In the past, I found rhenium from Almax-EasyLab to be too brittle for DAC use: it cracked during indentation. Other high pressure applications may require different gasket materials. Lower pressure experiments may make do with stainless steel, X-ray experiments may prefer X-ray transparent materials such as beryllium, a thermally or electrically insulated gasket may be necessary for laser-heating or electrical resistivity experiments, and so on. To prepare a sample chamber, the gasket is first placed between the diamond culets in an assembled DAC, and the diamonds are brought together to indent a region of the gasket to the thickness desired as the initial sample chamber height. The proper initial height varies depending on the gasket material, sample geometry, and maximum desired pressure, but for sub-50 GPa experiments like mine, an indentation to 50-100 microns is preferred. The indented gasket is then removed, and its thickness checked with a narrow-tipped micrometer. It is then taken to an electric discharge machining tool (EDM), which is capable of drilling a microscale hole in the center of the indentation. EDM proceeds by driving a high voltage between a metal needle (the "tool" or "electrode") in contact with the gasket to be machined, which sends a breakdown current across the gap and removes material from the gasket. The tool and resulting hole diameter should be 1/3 to 1/2 of the culet diameter to ensure gasket stability.

The maximum pressure achievable in any given DAC is controlled by the diamond culet diameter and initial gasket hole (sample chamber) dimensions. Essentially, a diamond can only sustain so much force, and a smaller culet area \( A \) implies higher pressure \( P \) for a given amount of force \( F \) through the
definitional equation $P = F/A$. The size of the diamond anvil as a whole must scale with the culet area to a certain extent, as the geometry of the DAC and anvils themselves are carefully designed to optimize the mechanical force distribution in the DAC under pressure. Single crystal diamond anvils cannot usually be made with culet diameters larger than a millimeter, and defects in a diamond anvil will cause premature cracking and breakage. Generally, 600 micron culets can sustain pressures up to 20 GPa, a 400 micron culet can reach 50 GPa, a 300 micron culet can reach 90 GPa, and culets as small as 30 microns (with appropriately designed bevels) have reached static high pressures near 200 GPa. In my experiments I used 400 micron diameter culets with bevels out to 450 microns. The bevels consist of a ring of 16 facets around the outer diameter of the culet surface, angled at a very shallow 5° from the horizontal culet plane; they help hold the gasket in place when the DAC is sealed. "Bevels out to 450 microns" from a 400 micron culet imply a bevel width of 25 microns around the culet, for a total "flat" diameter of 450 microns.

Loading a sample in a DAC is a delicate process. As described, the sample chamber formed by the gasket hole and the two opposing diamond culets is small, in my case at most 200 microns in diameter and 50 microns in initial height. Under pressure the chamber height will compress down to as little as 10-20 microns. The chamber diameter will generally also shrink, although if the gasket hole is too large it may expand out and approach the edge of the culet, ending the experiment. The sample itself must therefore be 10-15 microns thick and roughly 100 microns wide.

Loading proceeds first by placing the sample on one of the seated diamond culets. A ruby sphere is generally included as a pressure gauge (see next section); this sphere is typically 8-16 microns in diameter. Ruby and sample placement is done by hand under a stereomicroscope using special microtools, essentially stiff microscale needles. For DAC sample preparation and loading I relied on equipment in Professor Jay Bass’s geophysics laboratory at UIUC. Specifically, I used his group’s EDM tool, Leica MZ16 stereomicroscope, supply of ruby spheres, and other miscellaneous tools. I purchased my own microtools for sample and ruby placement from Electron Microscopy Sciences (EMS), specifically their smallest set of silicon carbide microtools. Those tool tips such as knives and spades are delicate and snap quickly, leaving behind a very useful, 20 micron diameter silicon carbide stub.
which I could use to cleave, pick up, and otherwise manipulate samples and ruby spheres.

To produce samples small enough to fit in the DAC chamber, one generally needs to polish the sample to the desired thickness, and then break or cleave what is now a thin sheet of material into pieces about 100 microns wide. Such small pieces are very lightweight and can be expected to recoil far away from the stereomicroscope from the released tension applied by one’s microtool to cut them. Hence DAC users are advised to either cut samples inside of a transparent bag, or immerse the samples in a fluid such as IPA, acetone, or water, so that the fluid viscosity will halt flying pieces before they escape. In addition, conventional TDTR requires the sample surface to be optically smooth and coated with a metal transducer film, so extra care must be taken to avoid scratching an appropriately sized piece while transferring it to the diamond culet.

Once the ruby and sample are secure on the culet, and the gasket is placed over them, the pressure medium is added to fill the space, and the top DAC plate is brought down so that the second anvil can seal the opening from above. A great deal can be said about the choice of pressure medium, but such media fall into four basic categories: solid (e.g., NaCl, KBr), liquid (water, silicone oil, methanol-ethanol:water mixture), cryogenic liquid, and high pressure gas. The latter two categories are for loading gases such as argon, nitrogen, or helium, which are far too compressible in their atmospheric gaseous state to properly fill the DAC chamber. Each method has its pro’s and con’s. Solid loading basically requires additional microtool work to form a medium-sample-medium sandwich on the culet. Liquid loading, depending on the surface tension, risks washing away the sample and ruby from the culet, and the liquid may evaporate before the DAC pressure screws can be tightened enough to seal the chamber. Cryogenic liquids tend not to disturb the sample, and the cell is sealed while immersed in the cryogen, but additional equipment is required to liquify the pressure medium. High pressure gas loading is a service provided by GSECARS at Argonne National Laboratory for certain DAC configurations, not including the Boehler-Almax plate DAC as of this writing.

As discussed, one or more ruby spheres are included in the sealed DAC sample chamber as a pressure gauge. The fluorescence spectrum of ruby has two-peaked structure, with the major R1 peak at 694.22 nm at atmospheric
pressure. The ruby spectrum shifts to longer wavelengths under pressure, and the center wavelength of the R1 peak has a precisely calibrated position to pressures in excess of 100 GPa. In the past irregular ruby flakes were used, but the initial R1 peak position varied depending on internal stresses due to crystalline defects; now, researchers generally use stress-free ruby spheres produced by one of two French companies, Crystal Solutions RSA (www.rubisrsa.com) and BETSA (www.betsa.fr). These companies do not presently do business with organizations that require a noticeable amount of paperwork, including UIUC, so it can be simpler to obtain a secondhand supply through a geophysical research group.

The ruby fluorescence spectrum is sensitive to non-hydrostatic behavior of the pressure medium, but the range of variations is small below 50 GPa. An ideal pressure medium is completely hydrostatic, which means that it cannot support shear stress that would lead to a pressure gradient across the sample chamber volume. Only fluids are entirely hydrostatic, and every material, including helium, solidifies under a few GPa of pressure. Some solids are softer than others: helium remains the most ideal pressure medium for hydrostaticity to very high pressures. The degree of hydrostaticity of pressure media are usually quantified and compared by reference to features in the ruby fluorescence spectra, such as peak FWHM's and R1 and R2 peak spacing.

Alternatives to the ruby standard exist for certain situations. Under conditions where a ruby spectrum is not obtainable, one can use the second-order Raman spectra from the diamond anvil itself. High pressure X-ray synchrotron measurements of lattice constants for pressure-volume equations of state are often referenced against the lattice constants of heavy metallic standards such as Au and Pt. In addition, over the course of my experiments I found it possible to calibrate the stimulated Brillouin frequency of a pressure medium against the ruby standard, and later use the Brillouin frequency as my pressure gauge. See Chapter 3 for details.

For several reasons, one of the diamond anvils in a DAC can break during the course of a high pressure experiment. If the diamonds come into contact under pressure, they will break. This can happen if the gasket hole is too wide and drifts with pressure off the edge of the culet. If the gasket thickness becomes too thin, less than about 10 microns, excessive force may be transmitted to the diamonds. In my experience, even though ruby is softer than
diamond, if a ruby bridges (spans the space between) the diamond culets, generally a diamond will crack within a few more GPa of pressure. Ruby bridging is obvious because the ruby fluorescence spectrum will be distorted by the non-hydrostatic (uniaxial) pressure experienced by the ruby. Finally, excessively high laser power density through the diamond anvil, as can occur with high power ultrafast pulsed laser sources, will cause internal damage which may lead to diamond failure under pressure. To avoid this the diamond anvil must be selected for extremely low birefringence; Professor Jung-Fu Lin at UT Austin noted that only about 1 out of 10 synthetic Type 2A diamond anvils are qualified for high intensity pulsed laser DAC experiments.

After my TDTR experiments, which use comparatively low pulsed laser power, I have sent cracked diamond anvils for repolishing by my supplier (Technodiamant). They found a thin embedded column of powderized diamond inside each diamond, a few hundred microns below the center of the diamond culet. I have never observed diamond failure due to this type of damage by the amount of laser power used in TDTR experiments, however. Rather, diamond anvil cracks tend to form gradually, first as small rings immediately below and around the culet. Caught early, the anvil can be salvaged by sending it in for repolishing.

2.3 High pressure TDTR

2.3.1 Diamond anvil birefringence

There are a few other DAC considerations that come into play with TDTR measurements. First, birefringence: although the diamond unit cell has cubic symmetry, most diamonds have some small, observable degree of birefringence due to inhomogeneous stresses imposed by defects. This can be an issue in a TDTR system, because for TDTR we use polarizing beam splitters (PBS) to separate and redirect the pump and probe beams. Upon reflection from a TDTR sample, the probe beam is transmitted back through a PBS and into the Si photodiode detector. The pump beam, having a perpendicular polarization, is reflected away from the detector path. In this way the downstream PBS acts as a pump light filter, up to OD2 (two orders of magnitude filtering) if the pump arrives normal to the PBS surface. If the pump
and probe beams travel through a birefringent window in front of the sample, as in the diamond of a DAC, their polarizations will be rotated slightly, part of the probe signal will be lost at the PBS, and part of the pump will transmit toward the detector.

The amount of this leaked pump light can be observed qualitatively by the intensity of the pump beam in the CCD camera, which varies with the angular position of the DAC about the laser axis. Empirically, I have found that there are two angular positions, 180° apart, at which the CCD pump light is minimized. For beam propagation through a uniform material with perpendicular easy and hard birefringence axes, one might expect polarization rotation minima set 90° apart. The birefringence due to defects in diamond may not be uniform or have perpendicular axes, and if the pump is offset from the center of the objective lens, the incident and return paths for the pump through the diamond may not overlap. In any case, when the two-tint filtering on our TDTR system was less efficient, I have found that rotating the DAC to one of these 180° minimal angles (but still normal to the incident TDTR laser) reduces the amount of leaked pump light reaching the detector. Since we installed the current, sharp-edged Semrock shortpass and longpass filters on our TDTR systems, I have not observed, nor rigorously tested for, leaked pump light in my DAC experiments as a function of DAC angular position or diamond anvil birefringence.

The amount of birefringence in a diamond anvil can be specified when ordering it, although it is best to double-check under a polarizing microscope for birefringence or other flaws after receipt of the anvil. Type 1A natural diamond anvils can be chosen for "low" or "ultralow" birefringence, typically; these specifications are also quantified by the vendor. Type 2A diamonds, synthetic or natural, generally have ultralow birefringence. Low and ultralow fluorescence background options are available, depending on whether one needs a low Raman background for diamond Raman pressure calibration or other experiment.

2.3.2 Characterizing diamond anvil nitrogen content

The major differences between Type 1A and Type 2A diamond anvils are price and nitrogen defect concentration. Type 1A natural diamonds typically
contain 1000-1500 ppm nitrogen defect centers. These centers are categorized as A, B, or C centers depending on the pattern of nitrogen substitutions and carbon vacancies.

The nitrogen content can be quantified in two ways. First, one can observe broadening in the 1332 cm$^{-1}$ first-order diamond Raman line relative to pure Type 2A diamond; a 1 cm$^{-1}$ broadening correlates to about 1000 ppm A-type nitrogen. Second, one may measure the FTIR transmission spectrum. Relative to pure diamond, Type 1A natural will show absorption structures around 1000-1300 cm$^{-1}$ that depend on the A, B, and C-type nitrogen content.

Figures 2.3 and 2.4 show my results from characterizing the nitrogen content of a Type 1A diamond anvil by Raman and FTIR, respectively. Boyd et al. 1994 found that the absorption coefficient at 1282 cm$^{-1}$ in FTIR was linearly correlated with A-center defect concentration, at 16.5(1) ppm/cm$^{-1}$. Taking the maximum of 30 cm$^{-1}$ absorption in Fig. 2.4, that gives about 500 ppm A-centers. Meanwhile, Boyd et al. also studied B-type nitrogen defects, which similarly gave a linear fit of 94 ppm/cm$^{-1}$ for the absorption coefficient at 1282 cm$^{-1}$ in the B-type absorption spectrum. That overlaps with the A-type absorption, but referencing the Handbook of Industrial Diamonds, page 247, the small FTIR absorption peak near 1000 cm$^{-1}$ seems to scale with the peak calibrated by Boyd. From that I estimate a 10 cm$^{-1}$ peak absorption coefficient, which indicates ≈ 940 ppm B-centers. Hence the total nitrogen content adds to ≈ 1500 ppm, consistent with the Raman broadening in Fig. 2.3.

The thermal conductivity of diamond is also very sensitive to the nitrogen content. Type 2A diamond, with no measurable nitrogen content by FTIR, typically has a thermal conductivity of about $2200 \text{ W m}^{-1}\text{ K}^{-1}$. That of Type 1A diamond with 1500 ppm nitrogen is close to $800 \text{ W m}^{-1}\text{ K}^{-1}$, which is near the values I measured from my Type 1A diamond anvils.

2.3.3 TDTR transducers at high pressure

Aside from the diamond itself, high pressure TDTR requires a more careful choice of metal film transducer. For example, it may be advisable to choose a transducer with a bulk modulus and pressure-volume equation of state...
similar to that of your sample. In that way, applying high pressure does not lead to a strain mismatch between transducer and substrate that may cause the metal film to deform and possibly roughen as it seeks to relieve the mismatch. So for example, one might pair aluminum (Al) with silicon (Si), or platinum (Pt) with MgO.

A second, more critical concern is the thermoreflectance coefficient. While Al is the default transducer for ambient pressure TDTR experiments, it is not well-suited to high pressure because its thermoreflectance coefficient varies dramatically under pressure. Specifically, the $dR/dT$ of Al has a sharp zero-crossing near 6 GPa, followed by a gradual decrease in magnitude approaching another shallow zero crossing near 30 to 35 GPa. For further discussion of TDTR transducers at high pressure, see Chapter 5, Section 6, on reflectance and thermoreflectance.
2.4 Figures

Figure 2.1: Left: layout of the time-domain thermoreflectance system. A train of laser pulses from the Ti:sapphire laser is split into pump and probe beams, which sequentially heat and measure the change in reflectance of a metal transducer on the sample. Right: sketch of the high pressure sample chamber in the diamond anvil cell. The diamonds are truncated cones about 1.6 mm tall and 3 mm wide. Fluorescence from the ruby sphere is used to calibrate the pressure; associated optics not shown in the TDTR layout here.
Figure 2.2: **Focused spot size versus free space beam radius** The focused $1/e^2$ radius spot sizes were measured by fitting the beam offset profile of $V$(in) over delay time for an insulating Al/SiO2/Si reference sample, and the free space beam radii were measured at the back focal plane of the objective lens using a beam profiler. The focused spot size increases with delay time (left panel), while the product of the focused and free space beam radii (right panel) deviate from the ideal value (solid line) given by the laser wavelength and focal length of the objective lens. Here "5x" refers to an objective lens with a focal length of $f = 40$ mm. I interpret this effect as being influenced by partial clipping of the free space beam on the back aperture of the electro-optic modulator (EOM) in the TDTR system. Since the probe beam size does not change with delay time, a 10% increase in the correlated pump-probe spot size corresponds to a 20% change in pump spot size, which is accounted for in my MATLAB thermal model.
Figure 2.3: **Raman line broadening by nitrogen defects in Type 1A diamond anvils.** The Raman spectra were collected with a 532 nm excitation wavelength on a Raman spectrometer from Nanophoton in MRL. The broadened 1332 cm\(^{-1}\) diamond lines from the four Type 1A diamond anvils, relative to the Type 2A CVD diamond substrate from Element Six, indicate on the order of 1000 ppm nitrogen defects in the Type 1A anvils.\(^ {56} \) This conclusion is supported by FTIR data (Fig. 2.4). The shifts in the positions of the 1332 cm\(^{-1}\) line for different anvils may be a calibration error between measurements.
Figure 2.4: **Fourier Transform Infrared (FTIR) spectrum of a Type 1A diamond anvil.** The FTIR spectrum was collected from a Type 1A diamond anvil using the MRL Laser Facility’s Nicolet Nexus FTIR system in transmission mode. The blue dashed lines in the center represent the intrinsic Type 2A diamond spectrum; the nonzero absorption at shorter wavenumbers can be interpreted to quantify the concentration of nitrogen defects in the Type 1A diamond.\textsuperscript{57,58}
Chapter 3

TDTR DATA ANALYSIS

Parts of this Chapter were published in Review of Scientific Instruments 83:11 (2012) by Gregory T. Hohensee, Wen-Pin Hsieh, Mark D. Losego, and David G. Cahill.

3.1 TDTR vH3: MATLAB data analysis system

When I joined the Cahill group, the TDTR thermal model was implemented in a FORTRAN executable, which we used in conjunction with text input/output files and our favorite plotting software to analyze TDTR data, be it gnuplot, Origin, or MATLAB. Around the same time, Joseph Feser ported the FORTRAN thermal model into MATLAB, so that all the analysis could be done in one program.

In the course of my PhD research, I started from Joseph Feser’s foundation and built up a system of MATLAB scripts for efficient and flexible TDTR data analysis. I essentially built a framework around the thermal model in the TEMP and REFL scripts for ease of use, additional options, and documentation support. The user interacts only with front-end scripts, process and analyze, which allow the user to set modeling options and thermal parameters for all the data from that day’s TDTR session. Every TDTR session, with however many individual TDTR data sets, has its own permanent copies of the process and analyze scripts. That way, the user has a permanent record of that day’s analysis decision and results, which means the user can revisit the analysis later if necessary.

My system is capable of any of the thermal modeling tasks I have needed over the course of my PhD work. This includes isotropic, anisotropic, and bidirectional heat flow scenarios. It allows technical corrections, such as setting the pump beam spot size as a function of delay time in the TDTR
system owing to beam divergence. Setting the zero of time delay, correcting the RF lock-in phase that defines V(in) and V(out), picking out the picosecond acoustic echoes, and correcting for signal offsets are all easily handled. The system allows both manual and automatic (minimal root mean square deviation) fitting of the selected TDTR thermal parameter(s) to the TDTR data. The user can choose to model and fit various types of signals, including the ratio -V(in)/V(out), the normalized V(in) or V(out), and beam offset V(out) data at negative time delay. Sensitivity plots versus time delay can be generated for any scenario, including at any time during the manual fitting process. The latest version can also produce parametric sensitivity plots on demand, where the sensitivity of the chosen TDTR signal component, including the full-width-half-max (FWHM) of the beam-offset V(out) signal, can be plotted relative to an arbitrary TDTR system or thermal parameter, instead of time delay.

The interested reader is encouraged, and the interested TDTR user is strongly encouraged, to take a look at this system of MATLAB scripts and take from it what they find valuable. As of this writing the scripts are posted online on GitHub, under the name TDTR-vH3 by user gthohensee. Included in the TDTR-vH3 package is a readme and PowerPoint presentation slides to serve as an introduction and starting point to the use of these scripts. Nearly all the scripts have extensive header and in-line comments for user-friendliness, and there are example and template copies of the analysis and process scripts to help the new user get started.

3.2 Interpreting picosecond acoustics in the case of a weakly-bonded interface

Analysis of data acquired in time-domain thermoreflectance (TDTR) experiments requires accurate measurements of the thickness of the metal film optical transducer that absorbs energy from the pump optical pulse and provides a temperature dependent reflectivity that is interrogated by the probe optical pulse. This thickness measurement is typically accomplished using picosecond acoustics. The presence of contaminants and native oxides at the interface between the sample and transducer often produce a picosecond acoustics signal that is difficult to interpret. There is a need for heuristics to
address this common difficulty in interpreting picosecond acoustic data. The use of these heuristics can reduce the propagation of uncertainties and improve the accuracy of TDTR measurements of thermal transport properties.

Picosecond acoustics is a convenient, nondestructive and precise tool for measurement of the thickness and elastic constants of thin-films. Picosecond acoustics is particularly well-suited for opaque metal films which are difficult to characterize with conventional optical techniques based on interferometry or ellipsometry. In picosecond acoustics, an ultrafast optical pump pulse heats the surface of a layered sample, generating a strain pulse, and a delayed probe pulse monitors changes in optical reflectivity of the surface that are created when strain fields return to the surface after reflecting from interfaces in the sample. The return time and shape of the acoustic echoes mostly depend on the layer thicknesses and acoustic impedances, although additional information can sometimes be obtained on the acoustic attenuation, piezooptic coefficients, and hot electron transport by detailed comparisons between the data and simulations.

Often, as in Refs., the interfaces are clean and abrupt enough to produce echoes with a shape that is symmetric in the delay time; the return time of the echo can then be reliably determined from the maximum or minimum of the echo. (The sign of the echo depends on the relative values of the acoustic impedance and the sign of the piezo-optic coefficient that relates a strain in the near surface region to change in optical reflectivity.) A common problem arises, however, when a metal transducer is deposited on a sample whose surface is contaminated by a native oxide, organic film, or hydroxide layer. Producing a new sample with a clean interface may be impractical due to constraints. These layers typically have a small acoustic impedance \( Z = \rho v \), where \( \rho \) is the mass density and \( v \) the speed of sound. For an aluminum transducer and representative organic film, PMMA, \( Z_{Al}/Z_{PMMA} \approx 3.2 \); for native SiO\(_2\), \( Z_{Al}/Z_{SiO_2} \approx 1.3 \). The low interface stiffness changes the acoustic echo shapes, which can create significant errors in the identification of the echo return time \( \tau \). Direct simulation of the acoustic echo is often not possible because the thickness and acoustic properties of the interfacial layer are unknown.

Therefore, I present heuristics for analyzing picosecond acoustic data from a low stiffness interface between a transducer film and a elastically stiff substrate, using experimental case studies measured on our TDTR system and
analysis based on the approach described by Maris and co-workers.\textsuperscript{68}

3.2.1 Experimental Method

I use a Ti:sapphire laser to produce femtosecond pulses at 80 MHz repetition rate, split the beam into pump and probe beams, and use a delay stage to offset their arrival times at the sample. By measuring the reflected probe beam, I obtain the change in reflectivity $\Delta R(t)$ due to strain caused by a preceding pump pulse. Since $\Delta R(t)/R(t) \ll 1$, I modulate the pump beam (hence also $\Delta R(t)$) by a 10 MHz square wave, and use a lock-in amplifier to isolate $\Delta R(t)$.

The signal is comprised of in-phase and out-of-phase components $\Delta V_{in}$ and $\Delta V_{out}$, relative to the 10 MHz pump modulation. I phase-match the lock-in amplifier to the pump modulation, so the lock-in amplifier signal can be expressed as $S(t) = V_{in} + iV_{out} = A(t)(\cos(2\pi ft) + i\sin(2\pi ft))$, where $A(t)$ is the amplitude of the thermoreflectance change, $f$ is the pump modulation, and $t$ is the delay time of the probe signal with respect to the pump. Hence the period $1/f \approx 100$ ns. In Ref.\textsuperscript{69}, the first acoustic echo return time was $\approx 13$ ns after the pump pulse, over time which significant phase rotation occurs and $\Delta V_{in}$ and $\Delta V_{out}$ become comparable. The present discussion, in contrast, deals with the $\leq 0.05$ ns return times of first and second echoes from typical TDTR transducer films. There is no significant acoustic signal in the $V_{out}$ because at this time scale $\Delta V_{out} \ll \Delta V_{in}$ by a factor of $2\pi ft \approx 1/320$. Thus the picosecond acoustic signal resides in $\Delta V_{in}$, but to reduce common-mode laser noise and improve thermal measurement accuracy,\textsuperscript{70} one generally refers to the ratio signal $r(t) \equiv -V_{in}/V_{out}$. The timing and shape of acoustic echoes in $r(t)$ and $V_{in}(t)$ are identical at this time scale.

The sign of the piezo-optic coefficient of the absorbing layer determines whether a compressive or expansive strain on the sample surface is read as a positive or negative $\Delta V_{in}$, the thermoreflectance signal. For aluminum, the positive piezo-optic coefficient implies that when Al is laser-heated and expands, the reflectance increases, and one measures a positive thermoreflectance change. When this positive-strain wave reflects from an interface with a lower acoustic impedance medium, the reflected wave picks up a phase shift of $\pi$, and the observed sign of the return echo is negative. Contrariwise,
when a strain wave reflects from a higher impedance medium, the reflected wave picks up zero phase shift, and the observed sign of the return echo is positive. The signs of successive reflections can be predicted from this, keeping in mind the $\pi$ phase shift at the air/surface layer boundary.

### 3.2.2 Simulation Approach

Simulations of the picosecond acoustic signals are built by computing the strain field throughout a one-dimensional material multilayer, as created by the incident ultrafast optical pump pulse. The simulation approach is explained in Ref.\textsuperscript{67} and Ref.\textsuperscript{46}. Below, I describe how the model parameters enter into the algorithm.

Each material is specified by its mass density, sound velocity, dielectric constant at the pump and probe wavelengths, piezo optic coefficients at the probe wavelength, thermal expansion coefficient, electron diffusion length, and acoustic attenuation coefficient. The simulation algorithm first uses the dielectric constants to compute optical transfer matrices for the layers, subdivided into bins; from these matrices, it computes the distribution of pump pulse energy deposited in the system. Typically, this distribution is confined to the first layer, a metal transducer deposited specifically to absorb the pump. The algorithm makes no attempt to compute an absolute stress or strain field; instead, it assigns a strain $\epsilon = - (1/2) \alpha E$ to each bin, where $\alpha$ is an effective thermal expansion coefficient and $E$ is the energy deposited per unit length. In reality, the heat is first deposited in the electrons of the absorbing material; the algorithm accounts for this by relaxing the the preliminary strain $\epsilon$ in each bin across all the bins of that specific layer, according to the electron-phonon diffusion length of that layer. The result is a relative initial strain distribution. The algorithm then computes the sensitivity function for the probe beam reflectivity with respect to strain. From the sensitivity function for the probe beam reflectivity with respect to strain, the algorithm propagates the strain in time according to the acoustic properties of the layers. The final output is the acoustic component of the change in surface optical reflectivity over time, up to a scaling factor, as the strain distribution is not computed in absolute terms.

The standard application of picosecond acoustics is to adjust layer param-
eters in the simulation to obtain a good fit to the data. For example, Ref.\textsuperscript{71} refers to an industry sample where three film thicknesses are extracted from a four-layer system. To do this reliably, however, requires knowledge of the speed of sound and density for every layer. Often, a full simulation is unnecessary, as when the sample is a bulk substrate with one or two relatively thick surface films whose acoustic echoes are well separated in time and do not interfere. In that case, the return time $\tau = 2h/v$ of a strain pulse, where film thickness $h$ and $v$ are the film thickness and speed of sound, can be simply read off the raw data.

A common application of picosecond acoustics in many laboratories is measurement of the thickness of the metal film, typically Al, that is deposited on top of a bulk sample and provides an optical transducer for measurements of thermal conductivity by time-domain thermoreflectance (TDTR).\textsuperscript{32} Picosecond acoustics gives a precise thickness measurement, which helps minimize uncertainty in the areal heat capacity of the film, and therefore also in the thermal conductivity of the sample.

\subsection*{3.2.3 Results and Discussion}

Return times $\tau$ are measured relative to the arrival time of the pump beam; this is chosen at the mid-point of the initial abrupt increase in the thermoreflectance signal. In addition to the peak that is generated by echoes of the strain pulse launched from the transducer surface, picosecond acoustics data for Al also contain a peak that is created by the strain pulse created by a stress discontinuity at the Al/sample interface. This effect arises from hot electrons,\textsuperscript{68} i.e., energy deposition in the Al film extends over a much greater distance than the optical absorption length. For a clean interface, the aluminum film thickness is given by $h_{\text{Al}} = v_{\text{Al}}\tau_1/2$, where $\tau_1$ indicates the peak of the first echo after the hot electron peak, and the factor of 2 accounts for travel to-and-from the interface. Similar expressions are used to analyze subsequent echoes.

For a contaminated interface, $\tau_1$ is not easily determined: the goal is to choose $\tau_1$ so as to obtain the correct $h$ despite the influence of a low stiffness interface on echo shapes and return times, as seen experimentally in panels (a) of Figs. 1-2, where I vary interface thickness and stiffness, respectively.
Here I restrict the discussion to the case of an elastically stiff substrate with $Z_{\text{sub}} > Z_{\text{transducer}}$, as the high-low-high impedance layering offers more contrast for analysis and Al has a small impedance compared to many materials of interest.

A useful concept here is interface stiffness, defined as $s = C_{11}/h_i = \rho_i v_i^2/h_i$, where $C_{11}$ is the longitudinal modulus of the low stiffness interface material, and $h_i$ is its thickness. In panels (b) of Figs. 1-2, I inform my heuristics by simulating the picosecond acoustics from a range of interfaces for fixed aluminum thickness. The correct reading of the first and second echo return times are then always $\tau_1 = 25$ ps and $\tau_2 = 50$ ps, as labelled by solid colored circles. In Fig. 1b, I plot simulations of the first and second echoes for changes in $h_i$ while holding $\rho_i$ and $v_i$ constant. In Fig. 2b, I plot simulations of the echos for changes in $s$ holding interface transit time $h_i/v_i$ and $\rho_i$ constant. This is done by applying a dimensionless factor $\alpha$ such that $h_i = \alpha \times (1 \text{ nm})$ and $v_i = \alpha v_{\text{PMMA}}$. Varying $\rho_i$ and holding $v_i$ and $h_i$ constant has the same qualitative effects: as the interface stiffness $s$ decreases, the echo approaches the limit where the transducer is decoupled from the substrate, as if the transducer is suspended in air.

For a low stiffness interfacial layer, for example, $\approx 1$ nm of PMMA, the first echo is typically antisymmetric, with a negative peak in front of the original positive peak. Choosing the inflection point, or the “zero crossing” with respect to the background thermal signal, I get a result within $\approx 0.5$ ps of the actual $\tau_1$. As the layer gets thicker, the negative peak becomes stronger, and $\tau_1$ should be chosen between that peak and the inflection. Beyond a thickness of 2–3 nm, see Fig. 1, the echoes of the low stiffness layer and substrate are sufficiently separated in time that the negative going peak marks the interface between the Al film and the low stiffness layer.

In Fig. 1b, as the low stiffness interface becomes thicker and the Si substrate echo shifts to later times, there is a gradual separation of a small peak after the first echo, which represents the creation of a second interface. In Fig. 2b, however, I simulate the effect of decreasing interface stiffness for fixed echo return time, so that the interface stiffness scales linearly with the parameter $\alpha$. Here the overlap in time of the echoes from the low stiffness layer and the SiC remains fixed, and instead the echoes increasingly take on the character of reflections from a low impedance wall, decoupled from the SiC substrate. This is the distinction between a well-bonded but thick low
stiffness interface layer, on the one hand, and an increasingly low impedance or weakly bonded yet thin interface layer, on the other.

The second and later echoes from a low stiffness interface are more complex than the first. The low interface stiffness inverts the sign of the second echo and produces troughs on either side. If the echo has an asymmetric positive-to-negative shape (the inverse of a slightly contaminated first echo), $\tau_2$ is best taken slightly before the positive-going peak. If the second echo is symmetric, $\tau_2$ is halfway up the leading edge of the symmetric positive peak. If the leading negative trough is stronger than subsequent features, $\tau_2$ is closer to the bottom of that trough.

The low stiffness interface layers in Fig. 2a are about 2 nm or less in thickness with symmetric second echo shapes; these features best match the $\alpha = 0.5$ thin interface simulated in Fig. 2b. Hence, these real-world interface layers have the stiffness of a simulated 2 nm of PMMA.

### 3.2.4 TDTR Error Analysis

Misreading the return time of the picosecond acoustic echo leads to an error in film thickness $\delta h$; this error is in addition to any uncertainty in the speed of sound in the film. If the acoustics measurement is followed by a thermal measurement such as TDTR, this error will propagate through the fitting parameters of the thermal model. The thermal signal from TDTR is sensitive to both the thermal conductivity $\Lambda$ and thickness $h$ of the metal film transducer. If $\Lambda$ is determined by a four-point resistivity measurement and the Wiedemann-Franz law, $\Lambda$ will be uncertain in proportion to $\delta h$. Typically, however, the largest source of error in a thermal conductivity measurement is the heat capacity per unit area of the transducer $C_v h$, where $C_v$ is the volumetric heat capacity of the transducer. The error in $C_v h$ is in proportion to $\delta h$.

Working through an example will show the reduced error from following my heuristics. Suppose, conservatively, that I misread the acoustics from an 80 nm Al transducer by 1 ps. Using $v_{Al} = 6.42$ nm/ps, I have $\delta h_{Al} \sim 3.2$ nm, or $\delta \ln h_{Al} \sim 4\%$. This error propagates to the fitting parameter according to the relative sensitivities of the fit to each parameter. These sensitivities are defined as $S_\alpha \equiv \partial \ln r / \partial \ln \beta$, where $r = -V_{in}/V_{out}$ is the quantity plotted in
Figs. 1a, 2a – again, the absolute value of the ratio of in-phase and out-of-phase of the lock-in amplifier of the TDTR system. Here $\beta$ is a parameter in the thermal model, e.g., the aluminum thickness or substrate thermal conductivity.\textsuperscript{72} Restricting ourselves to uncertainty in $h$ and $\Lambda_{Al}$ for the Al/Si geometry, the error in the fitting parameter is just the sum in quadrature of the (independent) uncertainties in the other parameters:

\begin{equation}
(S_{\Lambda_s} \delta \ln \Lambda_s)^2 = (S_{\Lambda_{Al}} \delta \ln \Lambda_{Al})^2 + (S_{h_{Al}} \delta \ln h_{Al})^2.
\end{equation}

Typical sensitivities for short delay time (100 ps) in the Al/Si geometry are $S_{\Lambda_{Al}} \approx 0.03$, $S_{h_{Al}} \approx -1$, and $S_{\Lambda_{Si}} \approx 0.5$, so $\delta \ln \Lambda_s \approx 0.8$, a 8% uncertainty. Picking the return time according to a good heuristic can reduce its uncertainty to 1/2 ps, or 4% in $\Lambda_{Si}$ for Al/Si.

### 3.2.5 Summary

Slight interface contamination, if acoustically distinct from the media on either side, markedly changes the return echo shapes and procedure for accurately picking the return echo times. Briefly, for a typical low acoustic impedance interface between a moderate-impedance transducer and high-impedance substrate, one reads the inflection point of the first echo and leading features of the second. As the interface becomes less stiff for fixed acoustic travel time, it effects a smooth transition from clean interface echoes to the case of a completely decoupled transducer, as if suspended or on a very low impedance substrate. Without knowing the particulars of the low stiffness interface but with the appropriate heuristics, the uncertainty in picking the return time of low stiffness interface echoes may be significantly reduced.

### 3.3 Figures
Figure 3.1: Picosecond acoustics (a) data and (b) simulation for the Al / PMMA / Si system. In (a), the Si wafers also carry a 2 nm native oxide. The thickness of the Al film is not constant in the different data sets and varies between 70 and 85 nm. The PMMA thicknesses were measured independently by ellipsometry. The time delay that correctly marks the first echo return time from the interface moves smoothly from the up-peak for clean Al/Si to the down-peak for the thickest PMMA layer. The simulation in (b) is for 80.25 nm Al on Si for increasing PMMA interface thickness; the correctly interpreted Al echo return times are 25 and 50 ps (solid circles). In general, the first echo becomes antisymmetric and the second echo develops troughs and a pronounced positive peak. In contrast to Fig. 2b, the Al/PMMA and PMMA/Si echoes separate with increasing PMMA thickness.
Figure 3.2: Picosecond acoustics (a) data and (b) simulation for the Al / low stiffness layer / SiC system. In (a), SiC anvils with and without native oxide and graphene were coated with Al of varying thickness. The SiC native oxide thickness was measured by XPS, and the graphene layer was transfer printed after being grown by CVD on Cu foil. The stiffnesses of thin interfaces (a) are to be compared against simulation (b), which presents 80.25 nm Al on Si for decreasing interface stiffness \( s = \rho_i v_i^2 / h_i \). The correctly interpreted Al echo return times are 25 and 50 ps (solid circles). The decreasing interface stiffness is obtained by varying \( v_i = \alpha v_{PMMA} \) and \( h_i = \alpha \times (1 \text{ nm}) \) for fixed interface transit time \( h_i / v_i \) and density \( \rho_i \). In contrast to Fig. 1b, the echo from SiC begins to fade by \( \alpha = 0.2 \) as the interface stiffness decreases.
Chapter 4

MAGNON-PHONON COUPLING IN $\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ SPIN LADDERS MEASURED BY TIME-DOMAIN THERMOREFLECTANCE

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4.1 Introduction

Although heat transport in materials is typically mediated by phonons and electrons, materials with strong magnetic coupling can also carry heat through collective excitations of the spin degrees-of-freedom, broadly referred to as “magnons”.\textsuperscript{75,76} Interest in magnons as heat carriers has been bolstered by the prediction that the energy current in one-dimensional spin-1/2 Heisenberg magnets could be a conserved quantity and support ballistic heat transport at finite temperature.\textsuperscript{77} Recently, researchers have studied a diverse set of cuprate materials where magnons are the dominant heat carrier.\textsuperscript{78–82}

In particular, the two-leg spin ladder system with prototypical composition $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}\text{88–83}$ exhibits a dominant contribution to its room temperature thermal conductivity from magnons, exclusively along the spin ladder axis.\textsuperscript{82,84}

The unit cell of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ contains four copper-oxide ladders running along the $c$-axis with rungs in the ac-plane; the magnetic interaction between adjacent ladders is relatively weak.\textsuperscript{85} The magnons are based on the Cu-O-Cu “rungs” of each ladder. Each rung has two electrons that interact in the strong-coupling limit as spin-1/2 particles to form a singlet ground state or one of three triplet excited states. Although the paired electrons have integer spin that implies Bose statistics, each pair is pinned to a rung. As such, each rung is a two-level quantum system with at most unitary occupancy in each of its spin states, which suggests fermion-like statistics.\textsuperscript{84} Due
to this subtlety, magnons in two-leg spin ladders with closer to isotropic coupling such as $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ are often referred to as “triplons”,\(^8\) in reference to the triplet excitation. They have also been called “hard-core bosons” to emphasize their limited occupancy and distinguish their two-level energy states from the archetypical Bose excitations in the harmonic oscillator spectrum.

Substitution of a 3+ ion on the Sr site enhances the magnon thermal conductivity near room temperature by reducing the local hole concentration along the spin ladders.\(^8\) The composition $\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ has a nearly minimal hole concentration along the ladders and has been reported to possess a room temperature thermal conductivity as high as 90 W m\(^{-1}\) K\(^{-1}\) along the ladder axis, a factor of 40 greater than the estimated phonon contribution.\(^8\)

Magnon-defect scattering has been explored using non-magnetic Zn impurities along the ladders.\(^8\) Recent work suggests a magnon-phonon mean-free-path in $\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ as large as 300 nm at low temperatures.\(^4;8\)

The mechanisms that limit the magnon mean-free-path in the cuprates are not yet established. Extrinsic defects probably play an important role at low temperatures but the decrease in conductivity with increasing temperature at $T > 200$ K suggests that interactions between excitations, i.e., magnon-magnon or magnon-phonon scattering,\(^9\) are most important near room temperature.

My work concerns the strength of magnon-phonon interactions. In a pioneering work, Sanders and Walton\(^7\) described how a two temperature model for magnons and phonons could lead to an apparent suppression of the magnon thermal conductivity measured by steady-state heat flow experiments at cryogenic temperatures when the magnon-phonon coupling is sufficiently weak. This effect originates from the fact that magnons cannot leave the host material, so there exists an adiabatic (zero heat flow) boundary condition at the interface with other materials.

Recently, these ideas have been applied to thermal conductivity data acquired on $\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ at room temperature using a combination of steady-state and laser-flash methods.\(^9\) More can be learned with the application of time-domain thermoreflectance (TDTR), which is a well-established pump-probe technique for thermal transport measurements.\(^4;4\) TDTR is also sensitive to more subtle dynamics, such as ballistic phonon effects\(^9\) and electron-phonon coupling.\(^9\) In this chapter I report the use of TDTR to directly measure an effective, volumetric magnon-phonon coupling in the two-leg spin
ladder cuprate $\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ from 70 K to 300 K.

### 4.2 Experimental Method

The two bulk $\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ samples I studied were grown by the group of A. Revcolevschi, of the Laboratoire de Physico-Chimie de L'Etat Solide at the Université Paris-Sud, France, by the traveling solvent floating zone (TSFZ) method. The structure was verified by cleaving a fragment of one of the samples and analyzing it by X-ray diffraction in transmission using a Mo source and two-dimensional detector. The spectrum is consistent with the lattice parameters of $\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ and a grain size $> 500$ µm, much larger than the measurement volume of this time-domain thermoreflectance (TDTR) experiment. To prepare the sample for TDTR measurement, I polished the surface normal to the $c$-axis with colloidal alumina down to 0.05 µm particle size, and annealed the samples at 600°C for 10 min in air to alleviate any polishing damage in the near-surface region of the sample and remove organic contaminants. Each sample was then coated with approximately 90 nm of Al by magnetron sputtering. Repetition of the annealing procedure does not produce an additional increase in the interface thermal conductance or the thermal conductivity.

The samples were measured by TDTR at temperatures from 70 K to 580 K. Below room temperature, the samples were mounted in vacuum in a helium-cooled cryostat with optical access; above room temperature, the samples were mounted on a resistively heated stage in air. Data was taken in both cooling and heating sweeps. The temperature of the sample during the measurement was taken as the sum of the measured temperature of the sample state and the contribution of steady-state heating by the pump and probe laser, which is computed directly from the TDTR thermal model. Above 100 K the steady state heating was 6–7 K; the highest value was 9.5 K, at the lowest temperature measured.
4.3 Magnon-phonon coupling via frequency-dependent apparent thermal conductivity

The standard TDTR data analysis produces a fitted value for the thermal conductivity $\Lambda$ of a simple substrate described by a single heat diffusion equation. Fig. 4.1 shows the result of fitting my raw TDTR data to this one-channel model. The solid curves are literature data from conventional steady-state thermal measurements for other Ca$_9$La$_5$Cu$_{24}$O$_{41}$ samples, showing the ladder-axis and a-axis thermal conductivities. With decreasing temperature, my data shows an increasing TDTR modulation frequency dependent suppression in the apparent ladder-axis thermal conductivity relative to the steady state reference. As confirmed for additional TDTR modulation frequencies in Fig. 4.2, the suppression increases with increasing modulation frequency.

Since both magnons and phonons carry heat along the ladders in Ca$_9$La$_5$Cu$_{24}$O$_{41}$, a single heat diffusion equation seems inadequate to describe the thermal transport. To properly interpret my data, I used a two-temperature model, as is widely used to rationalize magnon-phonon coupling\textsuperscript{75} and electron-phonon coupling\textsuperscript{95;93}. The model is comprised of two linearly coupled heat diffusion channels. For magnons and phonons, these equations are:

$$C_p \frac{\partial T_p}{\partial t} - \frac{\partial}{\partial x} \left( \Lambda_p \frac{\partial T_p}{\partial x} \right) + g(T_p - T_m) = 0$$  \hspace{1cm} (4.1)

$$C_m \frac{\partial T_m}{\partial t} - \frac{\partial}{\partial x} \left( \Lambda_m \frac{\partial T_m}{\partial x} \right) + g(T_m - T_p) = 0.$$  \hspace{1cm} (4.2)

The boundary conditions depend on how heat enters the system. In a TDTR experiment, the pump laser heats the electrons of the Al metal film transducer which rapidly transfer their thermal energy to the Al phonons on time-scales $< 1$ ps. Phonons in the spin-ladder are coupled to the Al phonons through a disordered interfacial layer with a thermal conductance $G$. The magnon temperature has an adiabatic (zero heat flow) boundary condition at the Al-cuprate interface. Heat enters the magnon system solely through the magnon-phonon coupling $g$.

For large $g$, $T_m = T_p$ and the equations collapse to a single heat diffusion equation, with $\Lambda_{tot} = \Lambda_m + \Lambda_p$ and $C_{tot} = C_m + C_p$. For small $g$, the magnon
channel receives negligible heat, so it is irrelevant, $\Lambda_{\text{tot}} = \Lambda_p$, and $C_{\text{tot}} = C_p$. Thus the extent to which the apparent TDTR conductivity deviates from the upper and lower bounds set by the steady state data, is the extent to which $\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ deviates from the strong and weak coupling limits in my measurement. It also correlates with the extent to which the TDTR signal is sensitive to $g$.

Physically, the TDTR signal has sensitivity to $g$ if and only if one of two conditions are met. Either TDTR has a time-scale comparable to the magnon-phonon relaxation time, or TDTR has a length-scale comparable to a magnon-phonon relaxation length-scale. The first condition can be rejected immediately based on the raw TDTR data. The time-scale for the decay of the in-phase signal $V_{in}(t)$, which is the cooling rate of the transducer surface, is controlled by the rates at which heat crosses the interface and escapes into the substrate. The interface time-scale is $\tau_G = h_{Al}C_{Al}/G$, where $h_{Al}C_{Al}$ is the transducer areal heat capacity and $G$ is the conductance. Even for epitaxial phonon-mediated interfaces $G < 700 \text{ MW m}^{-2} \text{ K}^{-1}$, and more typically $G \approx 100 \text{ MW m}^{-2} \text{ K}^{-1}$, such that for an 80 nm Al transducer $\tau_G$ is typically 1-2 ns. Meanwhile, the time-scale for heat flow into the cuprate, assuming just the phonon conductivity $\approx 3 \text{ W m}^{-1} \text{ K}^{-1}$, is $\approx 8 - 10 \text{ ns}$. If the magnon-phonon relaxation time were comparable to or longer than the TDTR modulation time-scale $\tau_{\text{mod}} = 1/(2\pi f) > 16 \text{ ns}$, the magnon channel would not couple into the phonon channel within the 4 ns of delay time accessed by the raw $V_{in}(t)$ signal. Since I observed exponential decay times of $\approx 4 - 5 \text{ ns}$ in the $V_{in}(t)$ at all temperatures, that alone, before any modeling, sets the magnon-phonon time-scale to be on the order of 1 ns or less. If the TDTR measurements shared a time-scale with the magnon-phonon relaxation, I could not possibly have results dependent on the modulation frequency between 1-10 MHz, but that is exactly what Fig. 4.1 shows.

As the sensitivity does not come from comparable time-scales, it must come from comparable length-scales. In TDTR the modulated pump pulses drive a periodic heat flux into the sample, creating an oscillating temperature gradient with a length-scale set by the thermal penetration depth $L_{\text{th}} = \sqrt{\Lambda/(\pi f C)}$, where $\Lambda$ can be taken as the apparent conductivity from Fig. 4.1. As the spin ladders are one-dimensional, this is the only relevant TDTR length-scale. Meanwhile the magnon-phonon coupling also has a characteristic length-scale that derives from the adiabatic (zero heat flow)
boundary condition on the magnons at the Al-cuprate interface. Immediately below the interface, the phonon temperature must be higher than the magnon temperature, as heat is flowing into the phonons but not the magnons. In the steady-state limit of Eqns. (1–2), the length-scale over which this temperature difference is resolved is

\[ L_{mp}^{-1} = \sqrt{g(\Lambda_p^{-1} + \Lambda_m^{-1})}. \]

In Fig. 4.3, I illustrate the solutions of the full, time-dependent Eqns. (1–2) for the relative amplitudes of \( T_m \) and \( T_p \) with a periodic heat flux boundary condition for the phonon channel and a thermally insulating boundary condition on the magnon channel. I used values of the parameters that are typical of the experiments, as discussed in Section 4.5. The thermal penetration depth is \( L_{th} \approx 600 \) nm at both high and low temperatures, the parameters \( C_m, C_p, \Lambda_m, \Lambda_p \) were chosen as described in Section 4.5, and \( g \) was extracted from the TDTR data using the two-temperature model. I found that \( L_{mp} \) was within an order of magnitude of \( L_{th} \) at room temperature, and within a factor of 2 at 120 K.

The TDTR experiment accesses the interesting case where \( L_{mp} \approx L_{th} \). When \( \Lambda_m > \Lambda_p \), this establishes a region of depth \( L_{mp} \) at the sample surface with a greater thermal resistance than the bulk. Because heat must first flow into the magnon channel before being transported with conductivity \( \Lambda_m \), the TDTR experiment observes \( \Lambda_p < \Lambda < \Lambda_p + \Lambda_m \), where the exact value of \( \Lambda \) depends on how \( L_{mp} \) compares to \( L_{th} \).

This situation is reminiscent of Sanders and Walton’s 1977 theoretical paper,\(^{75}\) in which they explored the conditions under which a conventional steady state heat transport measurement may measure magnon-phonon relaxation. They found that finite magnon-phonon coupling is only observable in steady-state for very weak coupling or very thin samples, when \( L_{mp} \) is comparable to the sample thickness. For a 1 mm thick sample of Ca\(_9\)La\(_5\)Cu\(_{24}\)O\(_{41}\), a steady-state measurement would only observe magnon-phonon relaxation if the coupling were of order \( 10^7 \) W m\(^{-3}\) K\(^{-1}\) or smaller. The advantage of TDTR is that the temperature gradient \( (L_{th}) \) is sub-micron, much shorter than the sample thickness, and comparable to \( L_{mp} \) even when the coupling is of order \( 10^{16} \) W m\(^{-3}\) K\(^{-1}\).
4.4 Two-Temperature Model for Time-Domain Thermoreflectance Data

To incorporate the two-temperature model into the TDTR data analysis and extract $g$, I formulated the usual cylindrical solution to the heat diffusion equation,\textsuperscript{32} except now with two channels governed by the full time-dependent Eqns. (1–2) and the Al-cuprate interface boundary conditions. The complete two-temperature TDTR model is presented in Ref.\textsuperscript{97}. In this case the model layers are the 100 nm Al transducer on top of the Ca$_9$La$_5$Cu$_{24}$O$_{41}$ substrate. The substrate layer incorporates both magnon and phonon heat channels. The magnon channel is one-dimensional, whereas the phonon channel is isotropic; this model accounts for any deviations from one-dimensional heat transport due to heat spreading relative to the laser spot size. The model does not make any assumption about relative time or length-scales of the TDTR measurement and magnon-phonon dynamics.

By choosing a two-temperature diffusive heat flow model I assume the absence of ballistic effects, where the mean-free-paths of dominant heat carriers are longer than the length-scale of the temperature gradient. With regard to the phonons, the complex crystal structure lead to many optical phonons and a low, glass-like phonon thermal conductivity. I therefore assume ballistic effects were negligible.

A recent estimate for the magnon-phonon mean-free-path in Ca$_9$La$_5$Cu$_{24}$O$_{41}$, based on magnon-defect scattering experiments, peaks near 300 nm at temperatures below 120 K.\textsuperscript{88} This estimate was based on the original steady-state data of Ref.\textsuperscript{84} which is over a factor of 2 larger than the more recent steady-state data I cite in Fig. 4.1. In my measurements, the thermal penetration depth is $> 600$ nm at all temperatures, using the apparent (one-channel) thermal conductivities in Fig. 4.1. So even at the lowest temperatures, the magnon mean-free-paths seem to be less than half the TDTR thermal penetration depth; therefore, I can also discount ballistic magnon effects. A diffusive/diffusive two-temperature model and a diffusive/ballistic two-channel model are equivalent in the limit where the high diffusivity or ballistic channel has an adiabatic boundary condition at the transducer-sample interface.\textsuperscript{97}
4.5 Thermal Parameters

Each substrate channel has its own heat capacity, thermal conductivity, and interface conductance, and the channels are linearly coupled through $g$ as described in Eqns. (1–2). All of these parameters are temperature dependent. The phonon heat capacity $C_p$ is taken from a Debye model, where the atomic density and Debye temperature are $N \approx 8.01 \times 10^{28} \text{ m}^{-3}$ and $\theta_D = 500 \text{ K}$, the latter chosen to mimic the temperature dependence of measured heat capacities of other oxides (Fig. 5.2). This gives $C_p = 2.89 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$ at $T = 295 \text{ K}$, within 1% of the room temperature value measured by Montagnese et al.

The measurement is insensitive to $C_m$ because $C_m \ll C_p$. Nevertheless, I estimate the magnon heat capacity starting from the relation $C_m = (d/dT) \int c_m(\epsilon) D_m(\epsilon) d\epsilon$, where $n_m(\epsilon)$ is the occupancy and $D_m(\epsilon)$ is the energy density of states for the magnon system. The magnons are built from a two-level system with threefold degeneracy in the excited state, so their statistics are $n_m(\epsilon) = 3 \left[3 + \exp(\epsilon/k_B T)\right]^{-1}$. I take the magnon dispersion relation $\epsilon(k)$ as the one-triplon dispersion measured by inelastic neutron scattering on La$_4$Sr$_{10}$Cu$_{24}$O$_{41}$.

The lattice parameters for Ca$_9$La$_5$Cu$_{24}$O$_{41}$, provide the number density of ladder rungs: $n \approx 7.10 \times 10^{27} \text{ m}^{-3}$. The result for $C_m$ is

$$C_m(T) = 3nk_b \int_0^1 \frac{x^2(q)e^{x(q)}}{(3 + e^{x(q)})^2} dq,$$

(4.3)

where $q \equiv kc_L/2\pi$ is the reduced wavenumber, $c_L = 0.393 \text{ nm}$ is the measured rung spacing of the two-leg ladder, and $x(q) \equiv \epsilon(q)/k_B T$. The calculated magnon and phonon heat capacities are plotted versus temperature in Fig. 4.4.

At $T = 295$ K, $C_m \approx 1.6 \times 10^4 \text{ J m}^{-3} \text{ K}^{-1}$, $\approx 0.6\%$ of the lattice heat capacity. $C_m$ peaks at $\approx 2.5\%$ of $C_p$ near 900 K. $C_m$ is limited at high temperature by the two-level, “hard-core boson” statistics: at sufficiently high temperature, each site has $3/4$ probability of hosting a triplet, and most magnon modes cannot exist. The suppression of the slope of the $C_m$ vs. $T$ curve near 200 K is caused by the form of the magnon dispersion. Montagnese et al. report their calculated room temperature magnon heat capacity as $1.5 \times 10^5 \text{ J m}^{-3} \text{ K}^{-1}$, citing Ref. without elaboration. This value is $10\times$ larger than ours, and about half the classical limit $3nk_B \approx 3 \times 10^5 \text{ J m}^{-3} \text{ K}^{-1}$.
but still only 5% of the lattice heat capacity. The impact of $C_m < 5\%$ of $C_p$ on the data analysis is negligible compared to uncertainties imposed by other parameters, as I will discuss in Section 4.6.

I take the total $c$-axis thermal conductivity $\Lambda_c = \Lambda_m + \Lambda_p$ from recently published steady-state measurements of Ca$_9$La$_5$Cu$_{24}$O$_{41}$ by Naruse et al.$^{82}$ Note that steady-state measurements of the $c$-axis thermal conductivity near the magnon peak sometimes show variations in the thermal conductivity with thermal cycling that are not yet understood.$^{98}$ However, Naruse et al. report nine steady-state $c$-axis measurements of three Ca$_9$La$_5$Cu$_{24}$O$_{41}$ samples, none of which show such large variations. Further, for their highest quality sample (5N precursor purity, high-pressure oxygen anneal) they report a room temperature thermal conductivity consistent with the thick sample limit of the flash-diffusivity measurements of Ref.$^{91}$ as well as my own measurement (Fig. 4.1).

For the phonon thermal conductivity $\Lambda_p$, I use previously published steady-state measurements of the $a$-axis thermal conductivity of another Ca$_9$La$_5$Cu$_{24}$O$_{41}$ sample.$^{84}$ The $c$-axis and $a$-axis data sets come from different samples, but I expect a similar temperature dependence in the $c$-axis phonon component as is observed along the $a$-axis. As such, in my data analysis I scale down the $a$-axis data set by a factor of 0.94, so that the $a$- and $c$-axis phonon peaks near 20 K coincide, take that as $\Lambda_p$ along the $c$-axis, and derive $\Lambda_m$ from $\Lambda_m = \Lambda_c - \Lambda_p$. As I rely on steady-state data from samples other than my own, I conservatively estimate an uncertainty of 20% in both $\Lambda_p$ and $\Lambda_m$.

The magnon-magnon thermal conductance across the Al/substrate interface is zero because there are no magnon excitations in Al. Therefore, the two-temperature thermal model has two free parameters: the interface conductance $G$ that couples phonons in the Al transducer to the phonons in the spin-ladder, and the magnon-phonon coupling parameter $g$.

## 4.6 Data Analysis

I begin with TDTR ratio signals $r(t)$ at 1.6 MHz and 9.8 MHz over a range of temperatures. To quantify my ability to fit both $G$ and $g$ from my TDTR data, I calculate sensitivity parameters as described in Ref.$^{72}$. The sensitivity of $r(t)$ to a thermal parameter $\alpha$ is defined as $\partial \ln r / \partial \ln \alpha$. To be self-
consistent, sensitivities to the free parameters are computed relative to the values I report in Figs. 4.6, 4.7. I find that the TDTR signal is most sensitive to the areal heat capacity of the Al transducer. By fitting $g$ and $G$ to the $r(t)$ signals at one or both frequencies, I would retain systematic error in $C_{Al}$, magnifying the uncertainty in $g$. However, variations in $C_{Al}$ influence $r(t)$ similarly at both frequencies. As such, I find that I can reduce the sensitivity to $C_{Al}$ by half and improve the sensitivity to $g$ by fitting the two-temperature model to the ratio of the ratios: $R(t) \equiv r_{9.8}(t)/r_{1.6}(t)$. Sensitivities to this combined signal are computed from $S_\alpha \equiv \partial \ln R/\partial \ln \alpha$.

Fig. 4.5 plots the sensitivity of $R(t)$ to the two free parameters, $g$ and $G$, alongside sensitivities to other relevant thermal parameters, as a function of pump-probe time delay at low and high temperatures. The uncertainty in a free parameter due to another parameter is proportional to the ratio of their sensitivities, and if two sensitivities have distinct time-dependences, then the underlying parameters can be fitted independently. This is true for $G$ and $g$ at low temperature, but less so near room temperature. This is because I chose to fit the ratio of ratios $R(t)$, instead of the individual ratios $r(t)$, for which $g$ and $G$ remain separable. Near room temperature, I first fit $G$ and $g$ from 9.8 MHz data alone, as this data is more sensitive to $G$ than the 1.6 MHz data. I then fix $G$, and fit just $g$ to the combined signal $R(t)$. As reassurance that I have not gone astray in this process, note from Fig. 4.6 that the resulting $G(T)$ has the same temperature scaling as that of a simple phonon-mediated, metal-dielectric interface, exemplified by Al/SrTiO$_3$.

My error analysis follows the same protocol as described in Ref. 72. As shown in Fig. 4.5, the dominant source of uncertainty comes from uncertainty in the areal heat capacity of the aluminum transducer layer. I assume a 3% uncertainty in the volumetric Al heat capacity, and I measure the Al thickness by picosecond acoustics to within 4%. This error is magnified by the ratio of the TDTR sensitivities to $g$ and the Al areal heat capacity, a factor of $\approx 2 - 5$, depending on the temperature.

In estimating the uncertainty from $\Lambda_m$ and $\Lambda_p$, I consider the following. For $\Lambda_m$, the apparent TDTR values converges toward the steady-state data from Ref. 82 at room temperature. For $\Lambda_p$, I rescaled its magnitude to match the Ref. 82 data, and I do not expect much variability between samples in the temperature dependence, as the phonon conductivity of this cuprate is glass-like. Even so, I conservatively estimate a 20% uncertainty in both the
phonon and magnon thermal conductivities.

To compute the error bars in Figs. 4.6 and 4.7, however, I apply a brute-force technique incorporating uncertainties from all the relevant thermal parameters. The procedure I follow is to vary one fixed parameter by its uncertainty, replicate the original fit to $R(t)$ by modifying $g$ and $G$ in the two-temperature model, record the changes in the fit parameters, repeat for all fixed parameters, and sum the fit parameter changes in quadrature. Even a 100% assumed uncertainty in $C_m$ results in a maximum contribution of about 2% uncertainty in the fit for $g$ near room temperature, which is always dwarfed by other sources of uncertainty. Approximately three-fourths of the uncertainty in $G$ is due to the 20% uncertainty in $\Lambda_m$, and approximately one-third of the uncertainty in $g$ is due to the 20% uncertainty in both $\Lambda_m$ and $\Lambda_p$.

4.7 Results

The two-temperature model has six important material parameters: the magnon and phonon thermal conductivities, their heat capacities, the Al-cuprate interface conductance $G$, and the coupling strength $g$. The first four parameters were either previously measured or can be estimated as a function of temperature, as discussed in Section 4.5, such that the only free parameters are $G$ and $g$. I varied $G$ and $g$ according to Section 4.6 to obtain the best fit between the model and the data.

In Fig. 4.6 I compare my result for the thermal interface conductance $G$ of Al/Ca$_9$La$_5$Cu$_{24}$O$_{41}$ against a typical metal/dielectric interface conductance, that of Al/SrTiO$_3$. Both samples share approximately the same magnitude and trend with decreasing temperature, which indicates an ordinary phonon-mediated interface between the Al and my spin-ladder sample, as expected. This confirms my finding that $G$ and the magnon-phonon coupling parameter $g$ are separable in my measurement.

Fig. 4.7 shows $g$ obtained from 9.8 MHz modulation data using the two-temperature model. I took data to 600 K, but $g$ could not be measured above 300 K. Even if reference data for $\Lambda_m$ existed above 300 K, TDTR at 9.8 MHz has negligible sensitivity to $g$ above 300 K because $g$ becomes too large, such that $L_{mp} \ll L_{th}$. The decreasing $\Lambda_m$ at high temperature also reduces $L_{mp}$.
but not so strongly as the increasing $g$. The case of $\Lambda_m = \Lambda_p$ reduces $L_{mp}$ by only a factor of $\sqrt{2}$ from the $\Lambda_m \gg \Lambda_p$ limit, and $\Lambda_m \ll \Lambda_p$ is likely not reached before $\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}$ melts at around 1200-1300 K. 99

My value for $g$ at room temperature is many orders of magnitude larger than that reported recently using a comparison of steady-state measurements and measurements using the flash-fluorescence method (FFM) on msec timescales. 91 In the FFM measurements, I note that the spin-ladder and spin-chain compounds show nearly identical suppression of thermal conductivity as a function of the sample thickness: in both samples, at a sample thickness of 0.4 mm, the thermal conductivity is suppressed by $\approx 40\%$ relative to the thick sample limit. Since both materials have a similar thermal diffusivity, I believe it is likely that a significant part of the suppression in thermal conductivity reported in Ref. 91 is due to the finite-time resolution of the phosphor and is not due to decoupling of phonons and magnons. An analysis of the flash diffusivity experiments suggests that a 600 $\mu$s time-constant in the measurement is sufficient to explain the observed suppression of the thermal conductivity of thin samples. The lifetime of the EuTTA phosphor is typically reported as 350 $\mu$s; 100 i.e., less than a factor of two smaller than the time-constant needed to explain the thickness dependence reported in Ref. 91.

I can only speculate, however, as to why the steady-state measurements reported in Ref. 91 and Ref. 84 differ by a factor of $\approx 2$ from the thick sample limit of the FFM measurements, the steady-state data from Ref. 82 and my TDTR data near room temperature. I have used thermal conductivity mapping 48 to look for spatial variations in the thermal conductivity and have not observed significant inhomogeneity. I think it is possible that there exists a distinct and highly ballistic magnon channel that is suppressed in dynamic measurements and in some, but not all, steady-state measurements. Future experiments that systematically explore this issue using dynamic measurements on very long time-scales may provide some insight.

4.8 Magnon-phonon relaxation-time model

To gain physical insight on the magnitude and temperature dependence of $g(T)$, I calculate an upper bound on $g(T)$ constructed from the assumption
that all thermally resistive scattering events for magnons are thermalizing. For magnon energies $\hbar \omega$, I write $\tau^{-1}_s(\omega, T) = \tau_0^{-1}(1+s)(T)\omega^s$, where $s$ is a parameter that describes a power-law scattering rate for magnons as a function of frequency; $s = 0$ corresponds to the situation where all magnons have the same relaxation time. I use the measured magnon thermal conductivity $\Lambda_m$ to evaluate $\tau_0(T)$:

$$\Lambda_m(T) = \int c_m(\omega, T) \left[ \frac{d\omega}{dk} \right]^2 \tau_s(\omega, T)d\omega. \quad (4.4)$$

I evaluate all integrals in reduced wavenumber space $q = kc_L/2\pi \in [0,1]$, where $c_L = 0.393$ nm is the measured rung spacing of the two-leg ladder. Referring to the above discussion for the spectral heat capacity $C_m(\omega, T)$, I solve Eqn. (4.4) for $\tau_0(T)$. From that solution, I compute $g(T)$ in a similar manner from

$$g_s(T) = \int c_m(\omega, T) \frac{D_m(\omega)}{\tau_s(\omega, T)}d\omega \div \int D_m(\omega)d\omega. \quad (4.5)$$

In the constant relaxation time ($s = 0$) case, this can be expressed simply as $g_0(T) = C_m^2 \langle v_g^2 \rangle / \Lambda_m$. $\langle v_g^2 \rangle$ is the mean-square magnon group velocity weighted by the spectral heat capacity $c_m(\omega, T)$. The end results are plotted as lines in Fig. 4.7.

4.9 Discussion

In Section III, I explained why my TDTR measurement was sensitive to the magnon-phonon temperature equilibration length-scale $L_{mp}$, rather than the magnon-phonon relaxation time $\tau_{mp}$. As further confirmation, I can consider the spatially uniform limit of Eqns. (1–2), where $\partial T_{p,m}/\partial x = 0$. The solution becomes $(T_p - T_m) \propto \exp(-t/\tau_{mp})$, where $\tau_{mp}^{-1} = g(C_p + C_m)/(C_p C_m)$. From Figs. 4.7 and 5.2, my data indicates that $\tau_{mp} \approx C_m/g_{mp} < 0.1$ ns over the whole temperature range. Since $\tau_{mp} \ll \tau_{mod}$, the steady-state limit of Eqns. (1–2) is valid for small temperature gradients, and the $L_{mp}$ in Eqn. (4) is realistic.

The magnitude of the magnon-phonon coupling varies between $3 \times 10^{13}$
\(-5 \times 10^{15} \text{ W m}^{-3} \text{ K}^{-1}\) over the temperature range 70 – 300 K. Because of the \(\approx 28 \text{ meV}\) gap in the magnon spectrum of excitations,\(^{101,85}\) the magnon heat carriers are frozen out below 50 K, as observed by Ref.\(^{89}\). Hence in the 50–100 K range I can expect a rapid thermal activation of magnons and therefore \(g\).

The coupling parameter that I extract from the two-temperature model is an effective, volumetric rate of energy exchange between the magnon and phonon channels. I do not know the rate-limiting step in this process. I think it is likely that the phonon modes are well-coupled to other phonon modes, particularly since the phonon thermal conductivity of \(\text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41}\) is low, a signature of strong phonon-phonon scattering. Hess \textit{et al.}\(^{89}\) have interpreted the temperature dependence of the thermal conductivity in terms of scattering of magnons by the longitudinal optical phonon that corresponds to vibrations along the Cu-O legs of the spin ladders; i.e., Hess \textit{et al.} assumed that magnons interaction with a narrow spectrum of phonons. Alternately, magnons may be coupled to a broad spectrum of phonons, or only a narrow spectrum of magnons may couple to a broad spectrum of phonons. If the latter case is correct, \(g\) may be a measure of the interactions between the narrow spectrum of magnons that are strongly coupled to the phonons and the broader spectrum of magnons that contribute to heat-transport.

The temperature dependence of the model \(g_s(T)\) is qualitatively similar to that of the measured magnon-phonon \(g(T)\). This is true even though the model is not specific to magnon-phonon scattering. However, \(g_s(T)\) is \(\sim 10 \times\) larger in magnitude than \(g(T)\). In other words, the thermally resistive scattering rate for magnons is about \(10 \times\) the magnon-phonon relaxation rate. I do not know whether this resistive scattering rate includes a significant magnon-magnon interaction, or is mainly quasielastic scattering by phonons.

Finally, consider how the magnon-phonon \(g\) compares to typical electron-phonon coupling parameters \(g_{ep}\) in metals. Even in the most weakly coupled metal, Au, the coupling strength near room temperature is an order of magnitude greater, \(3 \times 10^{16} \text{ W m}^{-1} \text{ K}^{-1}\), and has relatively weak temperature dependence for \(T > 100 \text{ K}\).\(^{93}\) More typically,\(^{102}\) \(g_{ep}\) is on the order of \(3 \times 10^{17} \text{ W m}^{-1} \text{ K}^{-1}\), a factor of \(\sim 100\) larger than what I observe for magnon-phonon coupling in a spin ladder.
4.10 Conclusion

The MHz-scale heating frequency of time-domain thermoreflectance (TDTR) creates nanoscale temperature gradients in most materials, and these gradients can be used to probe nanoscale heat transport dynamics. Here I have used TDTR to make temperature-dependent measurements of the effective, volumetric magnon-phonon coupling rate in the spin-ladder cuprate \( \text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41} \). I have found this rate to be much larger than previously reported,\(^{91}\) but still two orders of magnitude weaker at room temperature than electron-phonon coupling in typical metals. The magnon-phonon coupling has a strong dependence on temperature.

The total resistive magnon scattering rate is estimated to be a factor of 10 greater than the magnon-phonon thermal relaxation rate. This suggests that inelastic magnon-phonon scattering, which determines the magnon-phonon thermal relaxation rate, is not the dominant resistive scattering process for magnons in \( \text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41} \).
Figure 4.1: The apparent thermal conductivity of Ca$_9$La$_5$Cu$_{24}$O$_{41}$ measured by TDTR at different modulation frequencies from 70 K to 600 K, as compared to steady-state a- and c-axis data from Refs. 84 and 82, respectively. Solid and open symbols refer to two different samples; the former is also represented in Fig. 4.2 and by red squares in Figs. 4.6 and 4.7.
Figure 4.2: Frequency dependence from 1-10 MHz of the apparent TDTR thermal conductivity at selected temperatures, from the spinladder sample marked by solid symbols in Fig. 4.1, and red squares in Figs. 4.6 and 4.7. The saturation at high temperature and low frequency indicates an approach to the fully coupled limit of the magnon and phonon heat channels.

Figure 4.3: Temperature amplitude profiles at the TDTR modulation frequency as a function of depth at low and high temperatures. The distance over which the temperatures converge is the two-temperature length $L_{mp}$. The profiles are computed from Eqns. (1-2) with thermal parameters as described in the text. The thermal penetration depth at both temperatures is about 0.6 microns, based on the heat capacity and the apparent, one-channel TDTR thermal conductivity of Ca$_9$La$_5$Cu$_{24}$O$_{41}$. Since the two length-scales are comparable, TDTR is sensitive to $L_{mp}$ and $g$. 
Figure 4.4: The Debye heat capacity for Ca$_9$La$_5$Cu$_{24}$O$_{41}$ (solid line) with a Debye temperature chosen to give a heat capacity comparable to measured values for other oxides (points). The calculated magnon heat capacity (dashed line) for the spin ladders is scaled up by a factor of 20 on this plot for visibility. Also plotted for comparison are the lattice and magnon heat capacities measured and calculated by Ref. 91.
Figure 4.5: Sensitivities to thermal parameters as a function of pump/probe delay time for the ratio of the TDTR ratio signals at 9.8 and 1.6 MHz. The different shapes of $S_G$ and $S_g$ indicate that these parameters can be fitted independently, and the uncertainty in $g$ is dominated by the larger sensitivity to $C_{Al}h_{Al}$. 

58
Figure 4.6: The thermal interface conductance $G$ of the Al/Ca$_9$La$_5$Cu$_{24}$O$_{41}$ interface of both samples (red squares, black circles), from data taken at 9.8 MHz pump modulation. $G$ and the magnon-phonon coupling $g$ are the two independent free parameters in the two-temperature TDTR model fit to the TDTR data. Approximately three-fourths of the uncertainty in $G$ is due to an assumed 20% systematic uncertainty in the magnon conductivity $\Lambda_m$. I also measured the interface thermal conductance of Al/SrTiO$_3$, which has no magnonic or electronic character and represents a typical phonon-mediated conductance.
Figure 4.7: Points: the magnon-phonon coupling parameters $g$ of two Ca$_9$La$_5$Cu$_{24}$O$_{41}$ samples as a function of temperature, as measured by TDTR in the two-temperature model, for two different samples (red squares, black circles). Lines: maximum $g_s(T)$ assuming all resistive scattering events are thermalizing with scattering rate $\tau^{-1} \propto \omega_s^s$, for $s = 0, 1, 2$. 
Chapter 5

THERMAL CONDUCTANCE OF METAL-DIAMOND INTERFACES AT HIGH PRESSURE

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5.1 Introduction

Interfaces play a key role in the science and engineering of materials and often determine the performance of engineering systems. Examples span the range from the mechanical properties of composites to the efficiency of photovoltaics to the corrosion of metals. Here, I am concerned with the exchange of thermal energy across an interface between two materials. This topic is of great current interest for the development of higher densities of information storage using thermally-mediated processes in phase change memories (PCM)103 and heat-assisted magnetic recording (HAMR).104 Precise control of heat input and spreading is necessary to minimize power demands and write to nanoscale bits of information without corrupting adjacent bits. As there are boundaries between the densely packed bits of memory, understanding thermal conductance across those interfaces is critical for the further development of PCM and HAMR.

Gaps in fundamental understanding of the thermal conductance of interfaces, although identified over 20 years ago,10 persist to this day.5,6 Thermal conductance is an integral property that convolutes contributions from a variety of heat carriers that have spectral distributions in their density, group velocity, and dominant scattering mechanisms. A typical experiment measures how much heat is transported across an interface, but not the spectral distribution of the heat current, or the governing mechanisms.

The interface between many metals and diamond, however, is a special case where elastic phonon processes clearly comprise only a fraction of the total
thermal conductance. The phonon radiation limit \(^{10,105}\) describes the maximum possible thermal conductance for elastic phonon transmission across an interface that is consistent with the respective phonon densities of states (DOS). This elastic limit lies a factor of 5-10 below the measured Au/diamond and Pb/diamond interface thermal conductances. \(^{10,70}\) Inelastic phonon scattering processes are probably significant at most material interfaces above cryogenic temperatures, but metal-diamond interfaces produce an extreme situation that enables the study of inelastic processes. In addition to advancing the thermal design of PCM, HAMR, and other nanoscale devices, understanding metal-diamond thermal conductance has direct relevance to the goal of using diamond as a substrate for high power RF devices \(^{106}\) and the thermal performance of diamond-metal composites. \(^{107,108}\)

Prior work at ambient pressure has implicated inelastic phonon scattering as the source of the excess metal-diamond conductance. Bi/diamond and Pb/diamond show a linear temperature dependence inconsistent with two-phonon elastic scattering models. \(^{70}\) In 2009, Hopkins described a model for diamond phonons absorbing or emitting 2-3 identical metal phonons \(^{109}\). Duda et al. \(^{110}\) subsequently generalized this model into the so-called anharmonic inelastic model (AIM). The AIM captures the magnitude and temperature dependence of the conductance of metal interfaces with diamond by considering \(n\)-phonon processes involving 1 diamond phonon emitting or absorbing \(n - 1\) metal phonons. A recent non-equilibrium molecular dynamics (MD) simulation by K. Sääskilahti et al., \(^{111}\) for an Ar:heavy-Ar interface suggests that frequency-doubling and -halving inelastic processes are favored. That is, the MD simulation suggests the importance of a mechanism where a diamond phonon splits into two equal frequency metal phonons, in support of the AIM model.

Aside from inelastic phonon processes, electron-phonon interactions may also play a significant role by either suppressing or enhancing the conductance. Given an adiabatic heat flux boundary condition on metal electrons at a metal-nonmetal interface, a two-temperature model predicts a thermal resistance of \(R_{ep} = 1/\sqrt{g\Lambda_e}\) in series with the phonon-phonon conductance channel. \(^{95}\) Here \(g\) is the volumetric electron-phonon coupling parameter and \(\Lambda_e\) is the lattice thermal conductivity of the metal.

Past theoretical work has argued that electron-phonon coupling may alternately increase the conductance, and that the thermal conductance of
Au-diamond may have a significant contribution from heat transfer between Au electrons and diamond phonons. These models describe an electron-phonon conductance in parallel with the phonon channels, as opposed to a resistance in series. However, these theories are apparently inconsistent with experiments that found that the thermal conductances of Bi and Pb interfaces with diamond are similar even though the electronic heat capacity of Pb is approximately 600 times that of Bi.

Another consideration is thermal conductance by electrons that are heated far out of equilibrium with the lattice. My experiments utilize metal-diamond cooling rates at the nanosecond time scale, well after the electrons have equilibrated with the lattice.

Thermal conductance at an interface can be complicated by surface chemistry and thin layers of interfacial material. To study intrinsic properties, these extrinsic factors should be minimized or controlled. This has motivated experiments on H-terminated diamond, metal-diamond conductances under a range of surface treatments, interfacial graphene, and self-assembled monolayers. Often, interfacial material produces weak bonding and limits the conductance, which is of interest in itself but obscures other conductance mechanisms involved in the transport of thermal energy across the interface. By applying 12 GPa of pressure to weak Al/SiC interfaces, Hsieh et al. showed that the influence of weak interfacial bonding on the thermal conductance can be reversibly removed.

In this chapter I report measurements of metal-diamond interface thermal conductance for Pb, Au$_{0.95}$Pd$_{0.05}$, Pt, and Al films deposited on Type 1A (nitrogen-rich) natural [100] and Type 2A (nitrogen-free) synthetic [110] diamond anvils up to 50 GPa in the diamond anvil cell. The thermal conductances increase weakly or saturate to similar values at high pressure in all cases. I expect three-phonon processes involving two metal phonons to have a strong pressure dependence, so the data suggests that such processes are not dominant, and that the important anharmonic process involves two phonons in diamond and one phonon in the metal.
5.2 Methods

5.2.1 thin film deposition

Thin metal films with thicknesses of \( \approx 100 \) nm were deposited on the culet of either a Type 1A or Type 2A diamond anvil. Multiple films of Pb, \( \text{Au}_{0.95}\text{Pd}_{0.05} \), Pt, and Al on diamond were measured by TDTR up to 30-50 GPa and back to ambient pressure.

The \( \text{Au}_{0.95}\text{Pd}_{0.05} \), Pt, and Al films were deposited by DC magnetron sputtering. I use Au(Pd) instead of pure Au because Au(Pd) yields a clear picosecond acoustic signal from which I can extract the Au(Pd) film thickness in situ, unlike Au.\(^{123}\) I measured the Pd content by RBS on an Au(Pd)/Si reference.

For Al on Type 1A diamond and Pt on Type 2A diamond, the diamond surface was heated under vacuum prior to sputtering. The graphite stage, on which the tungsten carbide seat and diamond rested in the vacuum chamber, was resistively heated to \( \approx 650^\circ \) C for 10 minutes and left to cool for 30 minutes, at which point the Al or Pt was deposited. The standard epoxy fixing the diamond to the carbide seat is heat-sensitive, so a strong bond was maintained by sealing the epoxy under a ceramic adhesive.

The Pb films were thermally evaporated from a Mo boat using 99.999% Pb shot from Kurt Lesker Inc., in a separate chamber with a base pressure of at most \( 3 \times 10^{-7} \) torr. The evaporation chamber did not have stage-heating functionality as did the DC magnetron sputtering chamber, so instead I preheated the seat and diamond anvil assembly in an air furnace to 500\(^\circ\) C for 30 minutes, removed at 500\(^\circ\) C, and loaded it in the evaporation chamber within 10 minutes. Since Pb films rapidly roughen at room temperature within half an hour by de-wetting from diamond, the Pb deposition was done on a liquid nitrogen cooled stage. A Type K thermocouple was fed into the chamber to monitor the temperature of the carbide seat, on which the diamond was mounted with ceramic adhesive. During the Pb evaporation the seat temperature was at or above \(-90^\circ\) C, and at no point did the temperature of the seat fall below \(-110^\circ\) C, as that approaches the frost point of \( 3 \times 10^{-7} \) torr of water vapor.\(^{124}\) The Pb/diamond samples were kept in a vacuum desiccator placed in a standard freezer at \( T \approx -18^\circ\) C to halt oxidation and thermally-driven de-wetting of the Pb from the diamond until immediately prior to
anvil cell loading. At room temperature, such roughening and surface oxidation of a smooth Pb film on diamond becomes microscopically visible within 30 minutes, and intolerable for TDTR within days.

5.2.2 diamond anvil cell

I use a diamond anvil cell (DAC) to apply high pressure to the metal-diamond interfaces. The diamond anvils have 400 µm culets with bevels extending to 450 µm. The sample chamber is sealed by a rhenium gasket pre-indented to 50-100 microns with a 200 micron aperture. The pressure medium is 1 cSt viscosity silicone oil (octamethyltrisiloxane, molecular weight 237) from Alfa-Aesar or Sigma-Aldrich. Measurements on Au(Pd) and Pb on Type 1A diamond were done with the Alfa-Aesar silicone oil, all subsequent measurements with the Sigma-Aldrich silicone oil. The Alfa-Aesar silicone oil and argon are comparably hydrostatic up to 64 GPa, and I observed no significant difference in the performances of the two silicone oils.

Except for the Pt data series, where the same Pt film was measured for three DAC loadings, a new metal film was deposited on the same diamond anvil in the same DAC for each loading, and multiple loadings were done for each of the Al, Au$_{0.95}$Pd$_{0.05}$, and Pb data series. Between loadings, an ≈ 20 micron SiC microtool was used to scrape off press-fitted rhenium and the preceding metal film sample, followed by wiping with a cotton swab infused with acetone. This process was repeated until no features are visible on the culet through a stereomicroscope.

Two types of diamond anvils were used: Type 1A natural with [100] normal to the culet surface, and Type 2A synthetic with [110] orientation. For Type 1A the predominant defects are A- and B-type nitrogen centers, which are arrangements of nitrogen substitutions and vacancies in the diamond lattice. I measured the nitrogen defect content of one of my Type 1A anvils by FTIR and estimate approximately 1500 ppm A- and B-centers in total. This is consistent with the 700 W m$^{-1}$ K$^{-1}$ thermal conductivity I measured by TDTR from that Type 1A anvil. The thermal conductivities of the Type 1A anvils used in this project varied from 600 to 800 W m$^{-1}$ K$^{-1}$.

A Type 2A diamond has no nitrogen defects detectable by FTIR. At ambient pressure, multiple measurements with Al and Pt transducers yielded
Type 2A diamond conductivities between 2200 and 3400 W m\(^{-1}\) K\(^{-1}\). The lower end of this range is typical for low-nitrogen diamond with natural isotopic variation.\(^{127}\) The large scatter is due to a low out of phase signal (Section 5.5).

5.2.3 pressure calibration

One to three ruby spheres were included in the DAC sample chamber for pressure calibration by ruby fluorescence.\(^{51}\) The ruby fluorescence shift can be sensitive to non-hydrostatic behavior of the pressure medium, but the range of variations is small below 50 GPa.\(^{52}\) I estimate ±0.5 GPa uncertainty in the ruby pressure from spectrometer resolution and quasi-hydrostatic effects.\(^{128}\)

One of the Pt/diamond pressure runs (right-facing blue open triangles, Figs. 5.6(b) and 5.8) was done without ruby spheres. Instead I calibrated the pressure using an empirical fit \(f(P) = 13 \times P^{0.363}\) to the Brillouin frequency data I obtained from accumulated silicone-side TDTR measurements from other pressure runs (see Section 5.3 and Fig. 1). The Brillouin calibration measures the pressure precisely where the TDTR measurement is taken. The scatter in the \(f(P)\) data is larger than the statistical error of its points because the rubies are necessarily some distance away from the TDTR measurement point, and the quasi-hydrostatic medium supports small pressure gradients. I estimate ±2 GPa uncertainty in the Brillouin calibration at higher pressures, where my calibration data is sparse.

5.3 Brillouin spectroscopy

Time-domain thermoreflectance measurements taken through a transparent medium can carry a Brillouin signal on top of the thermal signal.\(^{129}\) This occurs because the probe beam interferes with its own partial reflection from a traveling strain pulse in the transparent pressure medium, which was launched by the pump pulse. For highly absorbing transducers (Pt, Pb) that launch large strain waves, a small Brillouin signal was also visible from the diamond side. For a laser wavelength \(\lambda\) and a pressure medium with index of refraction \(n\) and longitudinal speed of sound \(v\), the Brillouin frequency is \(f = nv/2\lambda\). Fig. 5.1 presents my measured Brillouin frequencies in diamond
and silicone oil under pressure.

I model the diamond-side Brillouin signal by direct calculation of 
\[ f = \frac{nv}{2\lambda} \]
using the known refractive index, equation of state, and individual flexible moduli of diamond at high pressures (Fig. 5.1, green and magenta dashed lines). The uncertainty in measured diamond Brillouin frequencies is 2%, smaller than the symbol size; the [100] diamond data is in agreement, and the [110] data above 30 GPa is about 4% higher than the model.

I use an empirical fit to the silicone-side Brillouin frequencies to estimate the silicone oil equation of state, and as an alternate pressure calibration for one of the Pt/diamond thermal conductance data sets (Methods). The Vinet EOS fit (Fig. 5.1, cyan dashed line) to \( f(P) \) for silicone oil was obtained in a self-consistent manner by relating \( n \) to the density through the Lorentz-Lorenz relation for isotropic transparent materials.

5.4 Pressure-dependent TDTR thermal parameters

Most materials will be appreciably compressed by pressures in the 1-50 GPa range, and their thermal properties will also change. Our experimental geometry implies bi-directional heat flow from the metal, into both the diamond and the pressure medium. The relevant thermal parameters are therefore the thermal conductivities \( \Lambda \) and volumetric heat capacities \( C \) of the pressure medium, metal film transducer, and diamond anvil, the thickness of the metal film, and the medium/metal and metal/diamond interface conductances.

The pressure medium and diamond are both thermally thick, so their only relevant thermal properties are their thermal conductivities \( \Lambda \) and heat capacities \( C \). This can be seen by considering the thermal penetration depth
\[ L_{th} = \sqrt{\frac{\Lambda}{\pi f C}}, \]
where \( \Lambda/C \) is the through-plane thermal diffusivity. For diamond with a \( f = 9.8 \) MHz pump modulation, \( L_{th} \) ranges from 3.5 to 6.3 microns, depending on the nitrogen defect content. The diamond anvil is over 1.5 mm thick, and the silicone oil pressure medium, which has a far lower \( \Lambda \) at all pressures, is at least 10 microns thick, as the presence of an approximately 10 micron diameter ruby sphere in the chamber precludes much further compression.

The metal film thermal conductivity \( \Lambda_m \) is only important during the initial
100-300 ps of my measurement, while heat is still diffusing through the metal film. I begin my fits after 100-300 ps such that I have no sensitivity to $\Lambda_m$, and I do not include any pressure dependence of the metal film thermal conductivities in my thermal model. Instead I fix the metal conductivities at their ambient values, derived from the Wiedemann-Franz Law from the electrical resistivity, measured by four-point probe and picosecond acoustics. These are 33, 79, 46, and 150 W m$^{-1}$ K$^{-1}$ for Pb, Au(Pd), Pt, and Al, respectively.

5.4.1 Silicone oil

In 1982, Sandberg and Sundqvist reported measurements of $\Lambda$ and $C$ for two Dow Corning 200 (DC-200) silicone oils at high pressures and low temperatures, with ambient viscosities of 1 and 5 cSt.\textsuperscript{134} For the 1 cSt oil, they reported a linear fit of $\Lambda(P) = 0.20(1 + 0.52P)$ W m$^{-1}$ K$^{-1}$ above the glass transition pressure, i.e. in the 1.5-2 GPa range. They do not report $C(P)$ for the 1 cSt oil, but for the 5 cSt oil they report a nearly constant $C(P)$ in the glass phase above 1 GPa, increasing linearly from $\approx 1.7$ J cm$^{-3}$ K$^{-1}$ by about 5% between 1-2 GPa.

However, this is a very restricted pressure range compared to the present measurement. More recently, Hsieh et al. found that the pressure scaling of $\Lambda$ for PMMA followed the minimum thermal conductivity model prediction $\Lambda_{\text{min}}(P) = \Lambda_0 n^{1/6} C_{11}^{1/2}$ up to 11 GPa.\textsuperscript{38} Here the model is taken in the high temperature limit and assumes that the ratio of compressive to shear moduli $C_{11}/C_{44}$ is constant, $N$ is the atomic number density, and $\Lambda_0$ is independent of pressure.

From my EOS fit to the measured Brillouin frequencies $f(P)$ of the silicone oil, I can extract $N$ and an isothermal bulk modulus $K_T$ and assume that $C_{11} \approx 3K_T/2$. I can also estimate the heat capacity scaling from $C(P) \propto \rho(P)$, where the mass density $\rho$ is derived from my EOS fit. Together with the low-pressure data by Sandberg and Sundqvist, this gives a rough estimate for the silicone oil properties: $\Lambda(P) \approx 1.86 \times 10^{-2} \rho^{1/6} (3K_T/2)^{1/2}$, $C(P) \approx 1.83 \times 10^3 \rho$ in SI units. Essentially, $\Lambda$ and $C$ increase by factors of 6 and 2, respectively, from starting values of 0.2 W m$^{-1}$ K$^{-1}$ and 1.5 J cm$^{-3}$K$^{-1}$. Near 50 GPa the thermal penetration depth at 9.8 MHz into the silicone oil
would be $\sqrt{\Lambda/\pi C_f} \approx 120$ nm, for an equivalent conductance of $\Lambda/L_{th} \approx 10$ MW m$^{-2}$ K$^{-1}$. The effusivity is so low that my sensitivity to the silicone oil thermal properties is negligible compared to that of diamond, and the low effective conductance implies that the TDTR model is also insensitive to the silicone-metal interface conductance, which I leave fixed at 100 MW/m$^2$K.

5.4.2 Metal film thicknesses

The ambient pressure film thicknesses were measured by picosecond acoustics prior to loading in the DAC. The longitudinal speeds of sound for [111] Pb, [111] Pt, and Al at ambient are 2.39, 5.05, and 6.42 nm/ps, respectively. By a combination of Rutherford backscattering (RBS), X-ray reflectivity (XRR), picosecond acoustic, and thermal measurements on reference samples, I determined the longitudinal speed of sound for [111]-textured Au(Pd) to be $3.3 \pm 0.1$ nm/ps, in contrast to the 3.42 nm/ps expected for pure [111]-textured Au. According to the rule of mixtures, the expected [111] longitudinal speed of sound for Au(Pd) with 5% Pd content is 3.49 nm/ps. This number was calculated using $C_{ij}$ for Au and Pd of (191, 162, 42.2) and (221, 171, 70.8) GPa for $(C_{11}, C_{12}, C_{44})$, respectively, and Au and Pd mass densities of 19.3 and 11.9 g/cm$^3$.

For all samples the speeds of sound were indirectly confirmed by TDTR measurement of reference 500 nm SiO$_2$/Si wafers coated with each of the metal film transducers. In all cases, the derived transducer thicknesses and TDTR data produced fits for $\Lambda_{SiO_2} = 1.3$ W m$^{-1}$ K$^{-1}$ to within 5%.

Under pressure, however, the speeds of sound are not known. The Al acoustic echo is suppressed after a few GPa of pressure, the Pb echoes are reversibly suppressed across its fcc-hcp phase transition above 13 GPa, and the Au echoes persist to relatively higher pressures. Pt and diamond have similar acoustic impedances, so the Pt acoustics are weak even at ambient.

Instead of direct pressure-dependent metal film thickness measurement, I take the volumetric compression of each metal film from its equation of state (EOS), and assert that this occurs by uniaxial compression facilitated by plastic deformation in the metal. This assumes that the metal film is well-adhered to the diamond culet, which forms a wall of the sample chamber and intuitively is under uniaxial pressure from the chamber interior. In reality
the diamond culet experiences a complicated combination of compressive and radial stress, but I assume that the radial strain in the diamond is negligible. In this picture the metal film compresses uniaxially, and relieves radial and shear stress by plastic deformation, so that the metal film is under hydrostatic pressure. Ultimately, it is the areal heat capacity \( h_m C_m \) of the metal film that is the relevant thermal property in my TDTR measurement.

5.4.3 Debye model for metal heat capacities

The volumetric heat capacity \( C \) of a crystalline material tends to increase with pressure due to a higher atomic density under compression, but the material also stiffens under pressure, which increases the Debye temperature \( T_{\text{Debye}} \) and tends to reduce \( C \). For a given crystalline material, I can estimate the pressure scaling of the heat capacity using the Debye model. This is done by calculating \( C_{\text{Debye}}(N,T_{\text{Debye}}) \), where now \( T_{\text{Debye}} \) and the atomic density \( N \) both depend on pressure. I assume that \( T_{\text{Debye}} \propto K_T^{1/2} N^{-1/6} \), where \( K_T \) is the isothermal bulk modulus, which can be derived from the pressure-volume equation of state from the definition 

\[
K_T(P) = -V \frac{dP}{dV}
\]

The pressure-volume equations of state (EOS) for diamond, Au, Pb, Pt, and Al have all been reported to pressures well above 50 GPa. Figure 5.2 plots the modeled \( C(P) \) for the metals and silicone oil. I expect the Debye extrapolation to be least accurate for Al at 50 GPa, which I estimate has a Debye temperature of \( \Theta \approx 700 \) K. The Al equation of state predicts a 75% increase in Debye temperature from 0 to 50 GPa, whereas a recent first principles calculation gives a 56% increase in the Al cutoff frequency from 0 to 50 GPa. The red point at 50 GPa on Fig. 5.2 is the Debye heat capacity of Al assuming \( \Theta \) scales with the first-principles Al cutoff frequency. This places an upper bound of 5% on the inaccuracy of the Debye extrapolation for these metals under pressure to 50 GPa. Thus I assume a 5% uncertainty in the extrapolated metal heat capacities. If I further assume 5% uncertainty in the assumed uniaxial compression of the metal film thicknesses \( h \) with pressure, I can expect a 7% uncertainty in \( hC \), which propagates to 15% uncertainty in the measured interface thermal conductances \( G \).

Of these materials, only Pb undergoes a phase transition below 50 GPa,
and the gradual Pb transition from fcc to hcp in the 13-20 GPa range does not appreciably impact the Pb EOS. Theoretical study of high pressure Pb indicates a small enthalpy change across the fcc-hcp transition,\textsuperscript{142} which implies minimal change in Pb stiffness across the transition, consistent with EOS measurements.

The Debye model is not accurate for high Debye temperature crystals with optic modes. For example, a Debye extrapolation for MgO predicts a 23% decrease in $C$ from 0 to 50 GPa, but from the literature I know that the volumetric $C_{\text{MgO}}$ is essentially constant to 50 GPa. Specifically, the per-atom $C_{\text{MgO}} = c_0 + c_1 P + c_2 P^2$, where $c_0 = 2.23 k_B$, $c_1 = -1.38 \times 10^{-2} k_B$ GPa$^{-1}$, $c_2 = 1.16 \times 10^{-4} k_B$ GPa$^{-2}$, and $P$ is in GPa.\textsuperscript{143-146} Likewise the Debye model predicts a 20% decline in the diamond heat capacity in this range, but is not applicable to diamond.

\subsection*{5.4.4 Fit parameters}

Considering the above, the remaining parameters in the TDTR model are just the metal/diamond interface conductance $G$, the diamond thermal conductivity $\Lambda_C$, and the diamond heat capacity $C_C$. Fortunately, TDTR measurements are generally sensitive to the substrate effusivity $\sqrt{\Lambda C}$, its diffusivity through $\sqrt{\Lambda / C}$, or somewhere in between, but not $\Lambda$ or $C$ independently. I am always in a regime where $G$ can be fitted independently of $\Lambda_C$ and $C_C$. Due to uncertainty in $C_C(P)$ and the low $V_{\text{out}}$ concern discussed in Section 5.5, I cannot confidently report $\Lambda_C(P)$.

\subsection*{5.5 Metal-diamond TDTR data analysis}

In order to fit the TDTR data to the metal-diamond interface conductance, the TDTR thermal model requires specification of thermal properties for the pressure medium, metal film, and diamond. Few of these have been measured at high pressure, but pressure-volume equation of state data is readily available. Section 5.4 details how we extrapolate thermal properties to high pressures using that data.

Measurements were taken with the laser beams incident on the diamond/metal interface. Below, I will refer to this interface as the "back interface" of the
metal film. The term "front interface" will refer to the interface between the silicone oil and the metal film.

As the film is pressed into the diamond culet, the back interface is guaranteed to remain as smooth as the culet, although the front may roughen from plastic deformation. The front surfaces of Al, Au(Pd), and Pb deformed plastically to varying extents under pressure, owing to tensile strain from the mismatch in compressibilities of the metals and diamond. Pt, with the highest bulk modulus, showed no front surface roughening at any pressure. Further, the optical properties of diamond are known and do not appreciably change up to 50 GPa, unlike those of silicone oil. Therefore most conductance data was taken from the back interface, although for verification or necessity some data was taken from the front.

The thermal diffusion time in the metal transducer is \( \tau_m = \frac{h^2}{C_m/\Lambda_m} \approx 100 \) ps. After the metal film has thermalized, the TDTR thermal model predicts identical ratio signals \( \phi(t) = -\frac{V_{in}(t)}{V_{out}(t)} \) for measurements from front and back. Front side measurements at the pressures indicated in Fig. 5.1 had equivalent \( \phi(t) \) to back side measurement at the same pressure, which verifies my expectation that the metal film thermoreflectance is the dominant contributor to \( \phi(t) \) at those pressures.

That verification is significant because the refractive index of diamond increases slightly with temperature, which could change the reflectance of the metal/diamond interface and invalidate my assumption that changes in reflectance are only due to changes in the metal film temperature. In practice this effect is generally negligible compared to the metal thermoreflectance signal. The effect should, however, be considered for the case of high pressure Al, as the Al thermoreflectance decreases and crosses zero near 35 GPa. I now proceed to calculate the relative magnitude of the effect in the worst-case scenario.

5.5.1 Quantifying the effect of temperature dependence in the diamond refractive index

In conventional TDTR, I assume that the dominant part of the change in reflectance of the metal transducer is directly proportional to the surface temperature rise. There is also a local temperature rise in the medium above
the transducer, which alters the medium’s index of refraction, which in turn affects the reflectance of the metal/medium interface. This is important because the per-pulse indirect heating of the diamond occurs over the same time scale as heat flow across the interface, so to the extent that I have spurious signal, it directly impacts the fitted interface thermal conductance.

To account for this, I can start from

$$R = \frac{(n_1 - n_0)^2 + k_1^2}{(n_1 + n_0)^2 + k_1^2},$$

where $R$ is the reflectance, $(n_1, k_1)$ is the complex index of the metal, and $n_0$ is the real index of the medium, assumed to be non-absorbing. The derivative with respect to temperature $T$ shows two terms:

$$\frac{dR}{dT} = \frac{\partial R}{\partial T}\bigg|_{n_0} + \alpha \frac{d\ln n_0}{dT},$$

where $\alpha \equiv \left(\frac{(n_1 - n_0)^2 + k_1^2}{(n_1 + n_0)^2 + k_1^2}\right)^{-1}2Rn_0 [(1 + R)n_0 - (1 - R)n_1].$ The first term is the thermoreflectance neglecting changes in $n_0$, and the second term is the contribution from $dn_0/dT \neq 0$. The actual signal, $\Delta R$, depends on the temperature rises $\Delta T_0$ and $\Delta T_1$ on either side of this interface, and in general $\Delta T_0 < \Delta T_1$:

$$\Delta R = \left(\frac{\partial R}{\partial T}\bigg|_{n_0} + \alpha \frac{1}{n_0} \frac{dn_0}{dT} \frac{\Delta T_0}{\Delta T_1}\right) \Delta T_1.$$

For simplicity I assume the worst case, high conductance limit $\Delta T_0 = \Delta T_1 \equiv \Delta T$. For diamond, $n_0 \approx 2.4$. Ruf et al.\textsuperscript{147} measured $n(T)$ for diamond in vacuum over a wide range of temperatures and found $d\ln n_0/dT = 3.2(7) \times 10^{-6} \text{ K}^{-1}$ at 300 K. High pressure increases the Debye temperature and is analogous to low temperature, where Ruf et al. observed lower $d\ln n/dT$, so I take the 300 K value as the upper bound. The thermoreflectance coefficients of various metal films at 785 nm in air are known and can be measured as part of a TDTR experiment.\textsuperscript{148,149} Under ordinary conditions the contribution from the metal film thermoreflectance dominates by orders of magnitude, but I took data with $dR/dT$ as low as $8 \times 10^{-6} \text{ K}^{-1}$ for Al near 30 GPa (Fig. 5.3). As for $\alpha$, the complex indices for the metals versus pressure are not known. If I assume that $n_1 \approx n_0$, $\alpha = 4R^2n^2/k_1^2$, and if I further fix $R = 0.87$ and $k_1 = 8.4$ from the ambient values for Al at 785 nm, I get $\alpha \approx 0.25$. All together, this means that for the lowest $dR/dT$ data point from Al near 30 GPa, the contribution to $\Delta R$ from changes in the refractive index of diamond is less than 10%. This is within the uncertainty in the
fitted $G$ for Al at high pressure. Pb at low pressure may have a similarly low $dR/dT$, but its very low $G \approx 30$ MW m$^{-2}$ K$^{-1}$ implies a much lower temperature rise in the diamond versus the metal, so the diamond refractive index part of $\Delta R$ is correspondingly smaller.

5.5.2 Fitting to the in-phase TDTR signal

As Type 2A diamond has a very high thermal conductivity of $\Lambda_c \approx 2400$ W m$^{-1}$ K$^{-1}$, I have $V_{out}(t) \ll V_{in}(t)$. Hence the ratio $\phi(t)$ becomes very large and sensitive to noise and spurious sub-$\mu$V offsets in $V_{out}(t)$ that can come from the pump modulation reference signal generator. At higher pressures, the signal in some cases decreased to the point where $V_{out}(t)$ was of order 1 $\mu$V, such that $V_{out}(t)$ and $\phi(t)$ become unreliable for data analysis. Fortunately, I can use $V_{in}(t)$ to determine the interface conductance. For consistency, instead of fitting $\phi(t)$ and $V_{in}(t)$ at low and high pressures, I fit $V_{in}(t)$ at all pressures for all samples on Type 2A anvils.

The TDTR thermal model does not output an absolute $V_{in}(t)$, so I scale the data and model for $V_{in}(t)$ at a particular delay time $t_0$ to perform the fit. I chose $t_0$ at early delay times to maximize sensitivity to $G$, which is largest at later delay times. Generally $t_0 = 100$ ps. For the Pb on Type 2A diamond data I chose to fit $V_{in}(t)$ at all pressures and set $t_0 = 500$ ps and 200 ps for the low- and high-pressure fcc and hcp phases of Pb, respectively, since the thermalization time and picosecond acoustic echoes in my fcc Pb films both extended out to 500 ps. Fitting to $V_{in}(t)$ instead of $\phi(t)$ removes most of my sensitivity to the diamond thermal conductivity $\Lambda_c$, but measuring $\Lambda_c$ is not the purpose of this study. For the data where $\phi(t)$ was reliable, fitting to $V_{in}(t)$ or $\phi(t)$ yielded similar $G$. When $\phi(t)$ was unreliable, the $G$ from $V_{in}(t)$ typically differed from that of $\phi(t)$ by only about 10%. The spurious signal in $V_{out}(t)$ greatly changes the magnitude but not the decay rate of $\phi(t)$, which is controlled by the decay rate of $V_{in}(t)$ and determines $G$ for reasonably high values of $G$.

When fitting $V_{in}(t)$ I lose the normalization advantage in $\phi(t)$. Specifically, the pump beam has some divergence in free space, such that its focused diameter on the sample varies with delay time as the pump optical path length changes. Changes in spot size over delay time are cancelled out to
first order in the ratio signal, but not \( V_m(t) \). The scaled \( V_m(t) \) is nominally insensitive to spot size, but an increasing spot size over delay time means less of a temperature rise per unit area, which leads to a decreasing trend in \( V_m(t) \) and an overestimated conductance if not accounted for.

I refined the beam shaping optics in the TDTR system (TDTR-1) to place the pump beam waist at the back-focal plane of the objective lens at the mid-scan delay stage position. The free space waist is 3\% smaller than the free space beam at either end of the scan, so from start to finish the net change in free space pump spot size is less than 1\%. However, in this TDTR system the pump beam intensity has a \( 1/e^2 \) radius of 0.9 mm entering the 1.35 mm radius aperture of the electro-optic modulator (EOM), so that its electric field is partly clipped.\(^{50,150}\) Because of this I observed a non-Gaussian component to the free space beam shape at a short distance from the EOM, which corresponds to longer delay times on the TDTR system. This affects the diffraction-limited spot size on the sample. I measured the pump-probe correlation spot size on an 80 nm Al/500 nm SiO\(_2\)/Si reference sample by x- and y-axis beam offset scans as a function of delay time.\(^{34}\) From an initial \( 1/e^2 \) radius of 11.7 microns, much larger than the lateral heat spreading in this reference sample over delay time, the correlated spot size linearly increased by 9.5\%, implying a 19\% increase in pump spot size across delay time. This increase could not be explained by changes in the free space beam radius as the pump optical path length changed with delay time; see Chapter 2, Figure 2 of this thesis for details. By introducing this into the thermal model, I obtained identical fits to \( G \) from both ratio and \( V_m(t) \) signals from a high conductance Al/Si reference sample.

My error analysis follows the same protocol as described in Ref.\(^{72}\). Uncertainties in the heat capacity of the diamond, thermal conductivity of the metal film, or thermal properties of the silicone oil do not appreciably impact the fitted \( G \), especially when fitting by \( V_m(t) \). I estimate roughly 15\% systematic uncertainty in \( G \) due to uncertainty in my high pressure extrapolation of the areal heat capacity \( h_m C_m \) of the metal films, as discussed in Section 5.4. For the high pressure Al data where the thermoreflectance signal is low, I include error bars in the main paper conductance figure, representing an additional 10-20\% random uncertainty in the fits to \( G \).
5.6 Reflectance and thermoreflectance

Each TDTR measurement also contains information about the diamond-metal reflectance $R$ and thermoreflectance $dR/dT$ of the metal film. It is important to stress that TDTR data analysis never depends on the exact values of $R$ and $dR/dT$. They are only important because they determine signal-to-noise and the relative significance of possible artifacts in the probe signal, such as a refractive index change with temperature of the adjacent transparent medium (e.g. air, diamond), or strain-dependent diffuse light scattering at the sample surface.\(^6\)

$R$ is obtained by comparing the incident probe power to the time-averaged voltage measured by a photodiode detector. This is not an absolute measurement, but is relative to the diamond-side measurement at 0 GPa, before the DAC is assembled. The reflectances shown in Fig. 5.3 are normalized to the expected diamond-metal reflectance at 0 GPa, based on the known complex refractive indices and the Fresnel equation for normal incidence:

$$R = \frac{(n_1 - n_2)^2 + k_1^2}{(n_1 + n_2)^2 + k_1^2}.$$  

The diamond anvil is 1.5 mm thick, so I do not expect coherent interference between the diamond/metal and air/diamond reflections. The distance in vacuum between the 80 MHz laser pulses is 3.75 meters, so let’s consider individual pulses in the diamond. If we take the coherence length to be $L = c/(n\Delta f)$, where $c$ is the speed of light, $n$ is the diamond refractive index, and $\Delta f$ is the bandwidth of the pulse, and suppose that we have a Gaussian pulse at 785 nm with FWHM of 10-30 nm, the coherence length is on the order of 10 microns. 1.5 mm of diamond corresponds to roughly 100 coherence lengths or nearly 2000 vacuum wavelengths, hence my assumption of no coherent interference in the diamond.

The thermoreflectance coefficient $dR/dT$ is then derived from\(^{148,149}\)

$$\frac{dR}{dT} = \left(\sqrt{2}GQ\right) \left[\frac{V(t)}{V_0(t)}\right] \left[\frac{R}{\Delta T(t)}\right],$$  \hspace{1cm} (5.1)

where $G = 5$ is the preamplifier gain, $Q \approx 11$ is the Q-factor of the resonant circuit in the TDTR system, $V(t)$ is the in-phase signal at time delay $t$, $V_0(t)$ is the DC voltage recorded by the photodiode at each time delay, and $\Delta T(t)$ is the temperature rise calculated from the TDTR thermal model at time delay $t$. This temperature rise scales with the absorbed pump power $A = 2(1-R)P_0/\pi$, where $P_0$ is the time-averaged pump power incident
on the metal film. As the diamond culet is optically smooth, I assume the diamond/metal interface has specular reflectance $R$ and absorption $1 - R$. I correct for first-order reflections from the air/diamond interface by dividing $V_0(t)$ through by $[T^2 + (1 - T)/R]$, where $T$ is the air/diamond transmission coefficient.

I omit $R$ and $dR/dT$ for Au(Pd) because the reflectance was very high, around 95% at 785 nm, such that $1 - R$ and $dR/dT$ were too poorly constrained for the data to be meaningful. I stopped measuring Al on diamond by 30-35 GPa because the TDTR signal became very small near a second, shallow zero-crossing in $dR/dT$.

My data for $R$ and $dR/dT$ is shown in Fig. 5.3. For Al, light-edged symbols in the 6-30 GPa range represent $dR/dT < 0$, and heavy-edged symbols outside of this range represent $dR/dT > 0$. There are discrepancies between initial (red) and post-decompression (magenta) Al $dR/dT$, and between the three Pt $dR/dT$ sets. Given the number of parameters that enter into $dR/dT$, I believe these discrepancies are artifacts due to systematic uncertainty in recorded laser power, reflectivity, and other parameters that can vary from session to session of TDTR measurement. That would indicate uncertainty in $dR/dT$ of 25-100%, although the trends within individual data sets versus pressure seem robust.

The unusual behavior in the Al $dR/dT$ versus pressure has been observed previously\textsuperscript{123}, and is related to the interband transition energy that passes through the 785 nm operating wavelength at high pressures.\textsuperscript{151} The Pt thermoreflectance shows a factor of 2 decline across 50 GPa, and that of Pb also decreases with pressure in its high pressure hcp phase. The Pt and Pb reflectances $R$, on the other hand, remain constant or increase slightly with pressure, and that of Al closely follows the data from Tups and Syassen.\textsuperscript{151} Again, my use of the TDTR thermal model to extract thermal properties never depends on the exact values of $R$ or $dR/dT$, although the extracted $dR/dT$ depends on the thermal model through $\Delta T(t)$.

5.7 Electron-phonon resistance

Given an adiabatic heat flux boundary condition on metal electrons at a metal-nonmetal interface, a two-temperature model predicts a thermal re-
istance of $R_{ep} = 1/\sqrt{g\Lambda_L}$ in series with the phonon-phonon conductance channel. Here $g$ is the volumetric electron-phonon coupling parameter and $\Lambda_L$ is the lattice thermal conductivity of the metal. This expression for $R_{ep}$ assumes steady-state heat flow and that the thermal conductivity of the metal is dominated by its electronic component. The electron-phonon coupling time scales are all of order 1 ps or less, so for my purposes the steady-state assumption is valid. In this section I explore the implications of electron-phonon resistance on the measured interface conductances $G$.

According to pump-probe data, the zero-pressure $g$ for Al, Pt, Au, and Pb are 2.45, 10.9, 0.22, and $1.3 \times 10^{17}$ W m$^{-3}$ K$^{-1}$. There is a relatively large spread in experimental results for $g$ of Au, from $0.22 \rightarrow 0.4 \times 10^{17}$ W m$^{-3}$ K$^{-1}$. I can use the Leibfried-Schlömann (LS) equation to estimate $\Lambda_L$:

$$\Lambda_{LS} = \frac{24}{20} \frac{4^{1/3}}{\gamma^2} \frac{k_B^3}{(2\pi)^3 h^3} MV^{1/3} \Theta^2 \frac{\Theta}{T}$$

Here $k_B$ is Boltzmann’s constant, $\gamma$ is the Gruneisen parameter, $M$ is the atomic mass, $V$ is the atomic volume, $\Theta$ is the Debye temperature, and $T$ is the temperature. The room temperature $\Theta$ for Al, Pt, Au, and Pb are 390 K, 225 K, 178 K, and 87 K, respectively. According to Gschneidner’s review of experimental Gruneisen parameters, $\gamma$ for Al, Pt, Au, and Pb are 2.14, 2.69, 3.06, and 2.74, respectively. With these parameters the LS equation predicts lattice thermal conductivities for Al, Pt, Au, and Pb as 8.5, 7.2, 2.9, and 0.54 W m$^{-1}$ K$^{-1}$, respectively. For comparison, consider that the first-principles lattice thermal conductivity of nickel was reported to be 15 W m$^{-1}$ K$^{-1}$. By my calculation with the LS equation, using $\gamma = 1.83$ and $\Theta = 345$ K for nickel, I obtain a very similar $\Lambda_{LS} \approx 15.2$ W m$^{-1}$ K$^{-1}$, not considering significant figures in the input parameters for the LS equation. Furthermore, the extrapolation of low temperature Au alloy data, where lattice conductivity is dominant, to room temperature yields an Au lattice thermal conductivity of about 3 W m$^{-1}$ K$^{-1}$, which the LS equation replicates.

Therefore the ambient electron-phonon conductances $G_{ep} \approx \sqrt{g\Lambda_L}$ are approximately 1440, 2800, 250, and 260 MW m$^{-2}$ K$^{-1}$ for Al, Pt, Au, and Pb, respectively. These $G_{ep}$ act as resistors in series with the phonon-phonon conductances $G_{pp}$, such that the measured $G$ are suppressed from $G_{pp}$ by
a factor of $1 - G/G_{ep}$. On decompression, I found that the stiffened interface conductances for Al, Pt, Au(Pd), and Pb were approximately 220, 155, 70, and 60 MW m$^{-2}$ K$^{-1}$, for electron-phonon suppressions of approximately 15%, 5%, 30%, and 20%, respectively.

5.7.1 Pressure extrapolation

Since these anticipated suppressions are significant for Au(Pd) and Pb, I attempted a rough extrapolation of $G_{ep}$ to consider its influence on $G$ at higher pressures. To do so I extrapolated $\gamma$, $\Theta$, $V$, and $g$. I got $\Theta$ and $V$ from the pressure-volume equations of state as described in Section 5.4, but $\gamma$ and $g$ are more uncertain.

The Slater Gruneisen parameter$^{157}$ assumes a volume-independent Poisson ratio and is given by $\gamma = (1/2)dB/dP - 1/6$, where $B$ is the isothermal bulk modulus. Based on their high pressure equations of state (EOS), the zero-pressure Slater Gruneisens for Al, Pt, Au, and Pb are 1.9, 2.18, 2.58, and 2.70. More recently Burakovsky and Preston$^{158}$ suggested a generalization of the Slater, Dugdale-MacDonald, and Vashchenko-Zubarev forms Gruneisen parameters, with parameters fitted to melting temperature data; they obtained 2.5, 2.67, 3.32, and 2.77, respectively. In 1980 Bohler and Ramakrishnan reviewed Gruneisen parameter measurements on some metals to 3.5 GPa,$^{159}$ obtaining $\gamma_{Al} = 2.14(V/V_0)$ and $\gamma_{Pb} = 2.63(V/V_0)^{1.2}$, where $V/V_0$ is the fractional compression given by the EOS. Neither the Slater nor Burakovsky-Preston models are especially consistent with the experimental values reviewed by Gschneidner or Bohler and Ramakrishnan. For simplicity, and since the literature EOS data is extensive, I chose the Slater Gruneisen to monitor the pressure scaling of $G_{ep}$. A more careful investigation would simply calculate the ab initio $\Lambda_L$ versus pressure, as was done at 0 GPa for nickel.

In the low electron temperature limit of the Eliashberg theory, the electron-phonon coupling parameter $g$ can be written as $g = (\pi k_B/\hbar) \times \lambda\langle \omega^2 \rangle \times D(\epsilon_F)$.$^{102,160,161,12}$ Here $D(\epsilon_F)$ is the electronic density of states at the Fermi energy $\epsilon_F$, and $\lambda\langle \omega^2 \rangle$ is McMillan’s second moment of the Eliashberg function $\alpha^2 F(\omega)$.
\[ \lambda \langle \omega^2 \rangle = 2 \int_0^\infty h \omega \alpha^2 F(\omega) d(\hbar \omega). \quad (5.3) \]

Here \( F(\omega) \) is the phonon density of states. \( \lambda \langle \omega^2 \rangle \) has units of energy squared in this definition, although \( \lambda \) is dimensionless. Although one can approximate \( \langle \omega^2 \rangle \) as \( \Theta^2/2 \), due to the integral convolution Eqn. (3) is not equivalent to calculating \( \lambda = 2 \int_0^\infty d(\omega) \omega^{-1} \alpha^2 F(\omega) \) separately from \( \langle \omega^2 \rangle \), which by itself is the second moment of the phonon spectrum, as defined by McMillan.\(^\text{162}\)

The Eliashberg function is usually calculated by ab initio DFT,\(^\text{163;160;161}\) which is beyond the scope of this project. However, I do know that \( \lambda \) tends to decrease with pressure, while \( \langle \omega^2 \rangle \) increases as the lattice stiffens.\(^\text{163}\) There exists low pressure data on \( \lambda \) for Al, Au, and Pb, which I can extrapolate as a function of compression \( V/V_0 \).\(^\text{164}\) With this and the \( \Theta^2/2 \) approximation for \( \langle \omega^2 \rangle \), I can estimate a pressure scaling from the known zero-pressure \( g \) for Al, Au, and Pb.

Figure 5.4 shows the estimated pressure dependence of the electron-phonon coupling parameters \( g \), LS equation lattice conductivities \( \Lambda_{LS} \), and electron-phonon conductance \( G_{ep} \) for Al, Au, and Pb. The scaling of \( g \) for the high pressure hcp-Pb (above 13-20 GPa) is more uncertain, as the same \( d\lambda/dV \) is used for both fcc- and hcp-Pb. Comparing Fig. 5.4 to my conductance data, I estimate that the suppression factor \( 1 - G/G_{ep} \) for Al decreases with pressure, and for Au(Pd) and Pb it is insensitive to pressure.

If electron-phonon coupling resistance is present, then the underlying \( G_{pp} \) for Au(Pd) and Pt are even more similar than the \( G \) that I measure, which at high pressure are \( G \approx 140 \) MW m\(^{-2}\) K\(^{-1}\) and \( G \approx 230 \) MW m\(^{-2}\) K\(^{-1}\) for Au(Pd) and Pt, respectively. Given the similarity to within a factor of 2, it seems difficult to reconcile my data with an electron-phonon conductance channel that depends strongly on the electronic structure of the metal, since Au(Pd) and Pt are very different.
5.8 Irreversible interfacial stiffening and intermediate phases

Pressure can stiffen weak bonds at an interface, increasing the thermal conductance to values equivalent to that of a clean interface. My metal-diamond TDTR data show irreversible stiffening of the Al/diamond and Pb/diamond bonds, unlike the reversible stiffening observed previously. For my thesis I have included an additional figure, Fig. 5.9, that isolates the irreversible stiffening effect that I observed from my Al / Type 1A diamond, Al / Type 2A diamond, and Pb / Type 1A diamond samples.

The available evidence indicates that no intermediate phases were formed between the metals and diamond under pressure. I am not aware of any literature indicating carbide formation or other reactions between Al, Pt, Au, or Pb with diamond in the diamond anvil cell at room temperature in this pressure range. The geophysical literature contains detailed pressure-volume equation of state studies, for which these metals were loaded in a helium pressure medium and necessarily in contact with one of the diamond anvil faces; they did not observe reactions between the metals and diamond. The optical reflectivity of Al on diamond does not show any abnormality either.

An intermediate layer at the interface would alter the picosecond acoustic signal from strain waves through the layers. A carbide in particular should qualitatively alter the electron-phonon thermalization in the first few picoseconds after the pump impulse, as well as abruptly impact the reflectivity at the pressure at which it forms. It is not obvious that such a reaction would maintain a polished surface, or stop before consuming the entire film. None of these signs were observed in any of my measurements.

Of the metals in this study, only Pb has a structural phase transition in or near the 0-50 GPa range. Were a transparent, non-metallic, acoustic impedance-matched interlayer to form, there is experimental evidence that it would only reduce the measured thermal conductance. Thus, irreversible stiffening of weak interfacial bonds is the simplest and most viable interpretation for the permanent enhancement of thermal conductance that I observe after compression for certain metal-diamond samples.
5.9 Results

5.9.1 Experiment

Figure 5.5 illustrates my experiment and the underlying concepts. At pressures in the tens of GPa, comparable to the bulk modulus of many metals, the phonon DOS extends to significantly higher frequencies. By measuring different metal films on diamond as a function of pressure, one can explore a wide range of characteristic phonon frequencies in the metals, for a relatively unchanged diamond DOS.

Time-domain thermoreflectance (TDTR) is a well-established optical pump-probe technique for measuring thermal transport properties. The TDTR system that I use has a Ti:sapphire ultrafast pulsed laser with a 785 nm center wavelength, so the diamond anvils serve as transparent windows to the metal films for my experiment, which I deposited on the diamond anvil culets directly. The pressure is measured using ruby calibrants and the silicone oil Brillouin frequency; see Methods, Section 5.3, and Fig. 1 for details. The TDTR measurement and data analysis proceeds normally, except bidirectional heat flow into both the pressure medium and diamond anvil must be taken into account.

I obtain the metal-diamond interface thermal conductances by fitting the bidirectional TDTR thermal model to the measured TDTR data. The important thermal parameters, such as the metal film areal heat capacity, are extrapolated to high pressure using known pressure-volume equations of state (see Section 5.4).

For the TDTR measurement to have sensitivity to the thermal conductance $G$ between a thin metal film and substrate, the rate at which the metal film surface cools should be limited by the interface decay time $\tau_G = hC/G$, not the thermal diffusion time $\tau_{\text{diff}} = h^2C/\Lambda$ in the metal film. Here $h$, $C$, and $\Lambda$ are the film thickness, volumetric heat capacity, and thermal conductivity. The condition $\tau_G > \tau_{\text{diff}}$ is non-trivial for thick (> 100 nm) films of low thermal conductivity metals such as Pt and Pb. To obtain $\Lambda$, I applied the Wiedemann-Franz Law from four-point probe electrical resistivity measurements at ambient, and found $\Lambda = 33, 79, 46,$ and $150 \text{ W m}^{-1} \text{ K}^{-1}$ for my Pb, Au(Pd), Pt, and Al films, respectively. $\tau_{\text{diff}}$ can be nearly 500 ps for the case of 100 nm Pb at zero pressure, since $C = 1.47 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$. However,
the raw TDTR data shows progressive shortening of $\tau_{\text{diff}}$ with pressure, and I do not observe $\tau_G$ shorter than 1 ns for the Pt and Pb data sets, where $\tau_{\text{diff}}$ is longest due to the lower $\Lambda$.

I do not report diamond thermal conductivity data as a function of pressure due to low signal-to-noise, as discussed in Section 5.5. At ambient pressure, the conductivity of one of my Al-coated Type 1A diamond anvils was approximately 550 W m$^{-1}$ K$^{-1}$, due to nitrogen defects. Multiple measurements with Al and Pt transducers on the Type 2A diamond anvil yielded conductivities between 2200 and 3400 W m$^{-1}$ K$^{-1}$. The corresponding apparent Type 1A and 2A diamond thermal conductivities with an Au(Pd) transducer were approximately 400 and 1100-1500 W m$^{-1}$ K$^{-1}$ at ambient pressure. These fitted values for the Type 2A diamond, and the difference between Al, Pt, and Au(Pd) values, should not be taken as quantitative measurements of the thermal conductivity of Type 2A diamond. The measurement sensitivity and signal-to-noise for this parameter is low, the high reflectivity of Au(Pd) exacerbates the low signal-to-noise, and the bulk thermal conductivity of diamond does not decrease because Au(Pd) is coating its surface instead of Al. With the Pb transducer, the interface conductance at 0 GPa was too low for appreciable sensitivity to the diamond thermal conductivities. Regardless, the thermal conductivity measured by TDTR occurs in the bulk of the diamond at the time scale of the 9.8 MHz pump modulation frequency. Thermal transport at that time scale is not relevant to conductance across the metal-diamond interface, which occurs in the sub-10 ns regime.

5.9.2 Interface thermal conductance

Figures 5.6(a-b) shows all of the high pressure metal-diamond thermal conductance data. The results for Al and Pb, and for Pt and Au(Pd), are split into separate figures for clarity. The data is color-coded by the metal transducer: red hues belong to Al, blue to Pt, black to Au(Pd), and green to Pb. The data is further identified by symbol, as listed in the legend. Magenta symbols, downward filled cyan triangles, filled grey circles, and left/down-facing bright green triangles, are decompression data for Al, Pt, Au(Pd), and Pb, respectively.

Decompression (decreasing pressure) is distinguished from compression
(increasing pressure) because of hysteresis, where the decompression conductances are generally higher but limited by the maximum conductance reached. The red/magenta and filled brown squares represent two different Al films on the same Type 1A diamond anvil, and similarly for the right/left and up/down triangle pairs for Pb on Type 1A diamond. The compression runs on separate Au(Pd) films are not distinguished. The Pt on Type 2A data is from three separate pressure runs on the same Pt film; it was decompressed twice.

The error bars on selected Al points represent random uncertainty in the fitted conductance due to low signal levels from Al at high pressure (see Section 5.6 and Fig. 3). Not shown is the roughly ±15% systematic uncertainty propagated from my high pressure extrapolations of relevant TDTR thermal model parameters (see Section 5.5).

5.9.3 One-phonon radiation limit

The dashed lines in Figs. 5.6(a-b) are one-phonon radiation limits for the respective metals on diamond.\textsuperscript{10} The one-phonon radiation limit is the maximum thermal conductance achievable in a two-phonon process, i.e., the interaction of one phonon in diamond with one phonon in the metal layer. It assumes that all diamond phonons with \( \omega < \omega_c \) that impinge on the interface transmit, where \( \omega_c \) is the maximum (cutoff) phonon frequency in the metal.

For low cutoff frequency metals such as Au(Pd) and Pb in contact with diamond, the high temperature Debye approximation \( G_{1R} = \pi k_B \omega_c^3 / v_d^2 \) is valid. Here \( v_d \) is the diamond Debye velocity: \( 3v_d^{-2} = v_l^{-2} + 2v_t^{-2} \), where \( v_l \) and \( v_t \) are the longitudinal and transverse sound velocities in diamond. This simplification is not well satisfied for higher cutoff frequency metals Pt and Al, particularly at high pressure, so I instead apply a finite temperature radiation limit, starting from Eqn (16) of Ref.\textsuperscript{10}:

\[
G_{1R} = \frac{\partial}{\partial T} \sum_j B \int_0^{\omega_c} n(\omega_j, T) \frac{d\omega_j}{dk} t(\omega_j) D(\omega_j) d\omega_j \tag{5.4}
\]

Here the sum over \( j \) is over the diamond phonon modes, the superscript \( B \) indicates the sum is over phonons moving toward the interface, \( n(\omega, T) \) is the thermal occupation, \( d\omega_j/dk \) is the diamond group velocity, \( D(\omega) \) is
the phonon density of states, and $t(\omega)$ is the transmission coefficient, which is assumed in the radiation limit model to be unity for $\omega \leq \omega_c$ and zero otherwise.

To approximate the diamond group velocities and density of states (DOS) as a function of pressure, I assume an isotropic quadratic dispersion in the longitudinal and transverse acoustic modes, as opposed to the linear Debye model. The pressure dependence of the acoustic mode parameters are taken by linear interpolation between best isotropic fits to the diamond dispersions at 0 and 50 GPa.\textsuperscript{167} These dispersion relations are then used to compute the group velocities and density of states. The diamond optical modes are irrelevant, since they are always above the metal cutoff frequencies. In the end, using a quadratic rather than linear dispersion only increases the radiation limit slightly. The quadratic dispersion contains opposing corrections: higher densities of states and lower group velocities in the acoustic modes near the Brillouin zone edge.

The $\omega_c$ for the metals are assumed to scale linearly with the Debye temperature of the metal, which increases with pressure according to $T_D = T_{D,0} \left[ K_T/K_{T,0} \right]^{1/2} \left[ V/V_0 \right]^{1/6}$. Here $K_T = -VdP/dV$ and $V/V_0$ come from the respective pressure-volume equations of state (EOS) for Au,\textsuperscript{136} Pb,\textsuperscript{137,138} Pt,\textsuperscript{139} and Al.\textsuperscript{140}

Figure 5.7 shows the resulting $\omega_c$ and compares them to more sophisticated theoretical and first-principles calculations for Al,\textsuperscript{141} Pt,\textsuperscript{168} and Au.\textsuperscript{169} At 50 GPa my Debye extrapolation deviates from the theoretical $\omega_c$ of Al, Pt, and Au +11%, -6%, and -8%, respectively. Since the radiation limit scales strongly with $\omega_c$, my $G_{1R}$ at 50 GPa differ by +32%, -16%, and -21% from radiation limits calculated with the theoretical $\omega_c$. I expect comparable error in my extrapolated Pb $\omega_c$ at the highest pressures.

The quantity $G - G_{1R}$ (Fig. 5.8), when positive, represents the minimum value of the thermal conductance that is not due to elastic phonon processes, within the uncertainty in my extrapolation of $G_{1R}$ to high pressure. Negative values for $G - G_{1R}$ imply that anharmonic phonon processes are not necessary to describe the total conductance. If I posit electron-phonon resistance (Section 5.7, Fig. 4), the "phonon-only" $G_{pp} - G_{1R}$ for Au(Pd) and Pb may be roughly 20-30% higher, closer to the Pt values.

The green line represents $(G_{2R} - G_{1R})_{Pb}$, which is the amount by which the Pb/diamond two-phonon radiation limit exceeds the one-phonon radiation limit.
limit. Analogous to $G_{1R}$, $G_{2R}$ is the upper limit on conductance for three-phonon processes involving one diamond phonon, which I discuss in the next section. It is included for comparison because 4th- and higher-order phonon processes have been considered for the Pb/diamond interface in the past. The two-phonon radiation limits for Au(Pd) and Pt have much higher values, starting above 150 MW m$^{-2}$ K$^{-1}$ at ambient and increasing rapidly with pressure.

While the radiation limit is just an upper bound on the elastic conductance, I have reason to believe it is a good approximation to the elastic conductance across highly mismatched interfaces. In such cases, the diffuse mismatch model (DMM) and radiation limit predictions are very similar, since the DMM transmission coefficient into the low frequency material is already near unity. Prior work found that the thermal conductance of Pb/Si and Bi/Si interfaces scale with their radiation limits at low temperature to within a factor of 2. In another work, the thermal conductance between Fe-doped rhodium and sapphire was found to converge to its radiation limit below 50 K. At low temperatures the phonons above the cutoff of the lower frequency material are partly frozen out, which reduces the inelastic contribution to the thermal conductance and tends to reveal the elastic channel.

5.9.4 Three-phonon scattering models

The two-phonon radiation limit is an extension of the one-phonon radiation limit that allows diamond phonons up to twice the metal cutoff frequency to participate. In the high temperature Debye model, the two-phonon radiation limit is simply $G_{2R} = 8G_{1R}$. Both radiation limits have a strong pressure dependence because the number of diamond phonons that can participate is determined by the metal cutoff frequency. But the two-phonon radiation limit is restricted to three-phonon processes involving two metal phonons, so now I consider the pressure dependence of three-phonon processes involving just one metal phonon.

In the radiation limit, incident diamond phonons with energies $E > \hbar \omega_c$ are elastically reflected from the interface. I propose that some of these high energy diamond phonons inelastically scatter at the interface, emitting or absorbing a metal phonon in what I refer to as a partial transmission (PT)
process. Since any diamond phonon can participate in PT, this category of phonon interactions at the interface has a large phase space. I write the PT thermal conductance as

$$G_{PT} = \frac{1}{4} \sum_j \int_0^{\omega_{d,j}} \langle E_m \rangle \frac{\partial n(\omega_j, T)}{\partial T} v(\omega_j) D_d(\omega_j) d\omega_j.$$  (5.5)

Here $\omega_{d,j}$ is the cutoff frequency for the $j$th diamond branch, and $\langle E_m \rangle \equiv \int_0^{\omega_c} P(\omega' | \omega_j) \hbar \omega' d\omega'$ is the average energy emitted into the metal by a reflecting diamond phonon. In other words, $P(\omega' | \omega_j)$ represents the probability that an incident diamond phonon of energy $\omega_j$ emits a metal phonon of energy $\omega'$. The lower bound of the $\omega_j$ integrals are set by the metal cutoff frequency for consistency with the one-phonon radiation limit. I do not know the form of $P(\omega' | \omega_j)$; I expect that its derivation would require knowledge of bond anharmonicity at the interface. However, a reasonable assumption is that the pressure dependence of $\langle E_m \rangle$ will scale with the average energy of a phonon in the metal, which in the Debye model is $(3/4)\hbar \omega_c$. By this assumption

$$G_{PT} \approx \left[ \frac{3}{4} \frac{\hbar \omega_c}{k_BT} \right] k_B \left( \frac{k_B T}{\hbar} \right)^3 \frac{1}{8\pi^2} \sum_j v_{a,j}^{-2} \int_{\hbar \omega_c/k_BT}^{\hbar \omega_{d,j}/k_BT} \frac{x^3 e^x}{(e^x - 1)^2} dx. \quad (5.6)$$

This expression should be an upper bound on the pressure dependence for PT because I expect the factors that I neglected in $P(\omega' | \omega)$, the diamond density of states (DOS) and interface anharmonicity that drives 3-phonon processes, to both decrease with pressure. In the high temperature limit, for $(\omega_c/\omega_d)^2 \ll 1$, $G_{PT} \propto \omega_c^3/\omega_d^3$, in contrast to the two-phonon radiation limit $G_{2R} \propto \omega_c^3/\omega_d^2$. The weak pressure dependence of $G_{PT}$ versus $G_{2R}$ is due to the fact that diamond phonons contributing to $G_{PT}$ are independent of the metal cutoff frequency, and $\omega_d$ is relatively insensitive to pressure.

To take a specific example, let us assume that PT completely accounts for the extra conductance that I observe in my experimental data for Pt on diamond (Fig. 5.8). If I assume that all incident diamond phonons above the metal cutoff frequency participate in PT, then I can solve for $\langle E_m \rangle$ in Eqn. (2) by setting $G_{PT} \approx 100 \text{ MW m}^{-2} \text{ K}^{-1}$. The result is $\langle E_m \rangle = 2.4 \text{ meV}$, which is only 13% of the average energy $\langle E_m \rangle = (3/4)\hbar \omega_c$ that I assumed.
earlier.

I can remove the Debye energy assumption by instead taking $\langle E_m \rangle$ as the first moment of the Pt phonon energy DOS. For ambient Pt, Feldman and Horton\textsuperscript{172} measured $\hbar\langle\omega^1\rangle = (3/4)k_B\Theta$, where $\Theta \approx 245 \pm 5$ K. So $\langle E_m \rangle \approx 15.8$ meV at zero pressure.

In other words, the extra conductance can be fully explained if all incident diamond phonons participate with an average emitted energy of 2.4 meV, or alternately if 15% of incident diamond phonons above the metal cutoff frequency participate with an average emitted energy given by the first moment of the Pt phonon DOS. Similar participation rates on the order of 10% can account for the extra Pt, Au(Pd), and Pb conductances at high pressure as well.

To check that PT processes can realistically represent the extra conductance in Fig. 5.8, I reformulate $G_{PT}$ in terms of a relaxation time model. The energy flux across the interface is driven by diamond phonons that are out of equilibrium with the metal reservoir. From the relaxation time approximation to the Boltzmann transport equation, I write $dE/dt = (\hbar\omega/\tau)[n' - n(T)]$. For a small deviation from equilibrium, $n' = n(T) + (\partial n/\partial T)\Delta T$, so $dE/dt \approx (\hbar\omega/\tau)(\partial n/\partial T)\Delta T$. This defines a volumetric energy transfer rate $\dot{Q} \equiv (\hbar\omega/\tau)(\partial n/\partial T)$ and relaxation time $\tau$ for conductance by PT processes.

Integrating $g$ over an interfacial thickness $a_0$, I obtain a conductance:

$$G_{PT} = \frac{1}{2V} \sum_j \int_0^{\omega_{d,j}} \dot{Q} a_0 D_d(\omega_j) d\omega_j.$$  \hspace{1cm} \text{(5.7)}

I now assume that $\tau$ is an average value, so that $\tau$ and $a_0$ can be moved out of the integral, leaving an integral over the diamond heat capacity. Then, $G_{PT} = a_0 C/(2\tau)$, where $C = 1.81$ J m$^{-3}$ K$^{-1}$ at ambient. For an interface region of one metal lattice spacing thick, $a_0 \approx 0.4$ nm, and $G_{PT} \approx 100$ MW m$^{-2}$ K$^{-1}$, it follows that the average relaxation time is $\tau \approx 4$ ps.

The simple expression $\Lambda = (1/3)Cv^2\tau$ implies, for diamond with $\Lambda = 2400$ W m$^{-1}$ K$^{-1}$ and Debye velocity $v \approx 1.4 \times 10^4$ m s$^{-1}$, that the bulk average anharmonic scattering time in diamond is 20 ps. In other words, the magnitude of the measured Pt/diamond conductance is consistent with a three-phonon scattering rate near the interface that is only five times higher than in the bulk. The difference may be largely due to anharmonicity of the interfacial bonds and relaxed selection rules for scattering at the interface.\textsuperscript{171}
5.10 Discussion

While Hsieh et al. observed reversible stiffening of their Al/SiC interfaces up to 12 GPa, I observe that the Al/diamond and Pb/diamond conductances return to significantly higher zero pressure conductances after decompression. The Type 1A diamond was heat cleaned in vacuum before Al deposition, the Type 2A surface was not, but both returned to the same conductance on decompression. I deposited Al on the Type 2A surface after heat cleaning and measured a 240 MW m\(^{-2}\) K\(^{-1}\) interface conductance, equivalent to the conductances for decompressed Al on diamond. Evidently, by applying over 30 GPa of pressure, I have irreversibly changed the interfacial bonding. This is consistent with studies showing that organic materials, such as may be present as contaminants at a weak interface, undergo chemical reactions and polymerization in the 1-30 GPa range.

I believe that the decompressed conductances measured in this study are near the intrinsic zero pressure metal-diamond conductances, in the sense that weak bonding is absent. Thus for a well-bonded Pb/diamond interface, I may expect a thermal conductance near 60 MW m\(^{-2}\) K\(^{-1}\) at room temperature, twice the value for thermally evaporated Pb/H/diamond\(^{70}\) and comparable to Au(Pd) on diamond. See Section 5.8 for further discussion.

As discussed in the introduction, a two-temperature model predicts a thermal resistance of \(G_{\text{ep}}^{-1} \approx 1/\sqrt{g\Lambda_L}\) in series with the phonon-phonon conductance channel.\(^{95}\) Here \(g\) is the volumetric electron-phonon coupling parameter and \(\Lambda_L\) is the lattice thermal conductivity of the metal. These \(G_{\text{ep}}\) would act as resistors in series with the phonon-phonon conductances \(G_{\text{pp}}\), such that the measured \(G\) would be suppressed from \(G_{\text{pp}}\) by a factor of \(\approx 1 - G/G_{\text{ep}}\).

I calculate (Section 5.7) that the ambient electron-phonon conductances \(G_{\text{ep}} = \sqrt{g\Lambda_L}\) are approximately 1440, 2800, 250, and 260 MW m\(^{-2}\) K\(^{-1}\) for Al, Pt, Au, and Pb, respectively (Section 5.7). On decompression, I found that the stiffened interface conductances for Al, Pt, Au(Pd), and Pb were approximately 220, 155, 70, and 60 MW m\(^{-2}\) K\(^{-1}\), yielding electron-phonon suppression factors of approximately 15%, 5%, 30%, and 20%, respectively.

I also estimate the pressure scaling of \(G_{\text{ep}}\) (Fig. 4), and estimate that the suppression factor for Al decreases with pressure, and for Au(Pd) and Pb it is insensitive to pressure. If electron-phonon coupling resistance is present, then the underlying \(G_{\text{pp}}\) for Au(Pd) and Pt are even more similar than the
Regardless, the conductances that I measure for Au(Pd) and Pt (Fig. 5.6(b)) are similar to within a factor of 2. Pt and Au(Pd) have very different band structures, and Pt has an order of magnitude larger electronic density of states near the Fermi energy. It seems difficult to reconcile my data with models of added conductance that depend on electronic properties of the metal.

In prior work to which I contributed, Rich Wilson et al. posited that a significant portion of the interfacial thermal resistance measured in a TDTR experiment can be due to a spatial mismatch in the spectral distribution of the heat-current. If the majority of the heat carried across the interface is carried by different phonons than the phonons that carry heat in the solid, the measured interfacial conductance will include an additional nonequilibrium thermal resistance, $G^{-1}_{\text{NE}}$. $G^{-1}_{\text{NE}}$ quantifies the resistance between the phonons that carry the heat across the interface and the phonons that carry the heat in the solid, and is analogous to the interfacial electron-phonon resistance.

If $G^{-1}_{\text{NE}}$ is an important contributor to the interface conductance values I measure between Al/Pt/Au/Pb and diamond then changing the spectral distribution of the diamond thermal conductivity should alter the measured interface conductance. Recent work by Katcho et al. used an ab initio Green’s function approach to calculate the effect of nitrogen defects on the thermal conductivity of diamond. They found that nitrogen defects strongly scatter a broader range of phonons than previously thought, from high frequencies to as low as 5 THz.

If the transmission spectrum for heat entering diamond were elastic, much of the heat from Au(Pd), and Pb would enter below 5 THz, and the details of defect scattering above 5 THz would not impede transport away from the interface. Since the thermal conductances of Pt, Au(Pd), and Pb on diamond greatly exceed their respective phonon radiation limits, I know the transmission spectrum cannot be mainly elastic for these metals. For Al/diamond, even if the conductance were elastic, the high Al cutoff frequency is within the nitrogen scattering regime in diamond. Ultimately, for non-equilibrium resistance it does not matter how heat enters the diamond, so much as in which diamond modes the heat enters.

Hence, phonons from the metal may be in different degrees of non-equilibrium with heat-carrying diamond phonons near the interface, depending on the
presence or absence of nitrogen defect scattering. To check this, I measured metal-diamond thermal conductances on both Type 1A (1500 ppm nitrogen; see Methods) and Type 2A (nitrogen-free) diamond anvils. At pressures high enough to stiffen weak interfacial bonding, I cannot resolve a difference in the interface conductance for the two types of diamond (Figs. 5.6(a-b)). This suggests that $G_{NE}^{-1}$ is not an important contributor to the interface conductance.

If electron-phonon interactions and non-equilibrium resistance do not control the Al, Pt, Au(Pd), and Pb thermal conductances on diamond, and two-phonon processes cannot produce the observed Pt, Au(Pd), and Pb conductances, then we are left with higher order phonon processes to explain the measured conductances. Three-phonon processes involving two metal phonons should depend strongly on the metal phonon density of states, because only diamond phonons below twice the metal cutoff can participate. However, the Al, Pt, Au(Pd), and Pb densities of states encompass a wide range from 0-50 GPa, and I do not observe strong pressure or metal cutoff frequency dependence in the conductances, beyond what can be expected from two-phonon processes.

This observation at first appears inconsistent with the recent non-equilibrium molecular dynamics work by K. Sääskilahti et al., but I believe this is because we are studying different systems from different perspectives. K. Sääskilahti et al. categorized "evanescent dissipation" as part of the elastic thermal conductance in their calculations, whereas I consider it effectively a three-phonon process. This is important because their evanescent component is comparable to their inelastic category, which they calculate is dominated by frequency-doubling or -halving, essentially diamond phonons splitting into multiple equal metal phonons.

The other key difference is that K. Sääskilahti et al. simulated a Ar:heavy-Ar interface with cutoff frequencies of 2 THz and 1 THz, respectively. I am studying diamond:metal interfaces with cutoff frequency mismatches much greater than 2:1. By analogy I have "light-Ar" : heavy-Ar, with >2 THz phonons that cannot participate in frequency-halving transmission into the 1 THz material. Such phonons can, however, have evanescent dissipation into the metal. Since the diamond:metal mismatch is several times larger than Ar:heavy-Ar, the phase space for evanescent or partial transmission processes is much larger. Thus it is not surprising that they dominate over
multiple-metal-phonon processes in the metal-diamond system.

The emphasis of my research is experimental; my models are admittedly approximate and are intended to provide context for the experimental results and physical insight on important thermal conductance mechanisms. The essence of my three-phonon conductance models lie in their pressure dependence. Regardless of the details of the model, for processes involving two metal phonons and one diamond phonon, the conductance must be sensitive to the metal cutoff frequency. This demands a strong pressure dependence that I do not observe. For processes involving two diamond phonons, the pressure dependence is weak because diamond phonons above the metal cutoff frequency can participate. The upper frequency limit to the thermally excited phonons in diamond is $3k_B T/h$, and that frequency is independent of pressure.

My null result for non-equilibrium resistance is also consistent with dominant partial transmission. I expect that most diamond phonons gain or lose only a small amount of energy to the metal phonon, so the diamond phonons near the interface should maintain a thermal distribution. In addition, I estimated (Eqn. 4) that the effective anharmonic scattering rate is about five times larger near the interface than in bulk diamond. A faster scattering rate implies stronger coupling between diamond modes near the interface. Thermal equilibrium, plus enhanced coupling, would tend to suppress any non-equilibrium behavior in the near-interface region.

To summarize, I experimentally show that the metal-diamond interface conductances for Al, Pt, Au(Pd), and Pb increase weakly or saturate at high pressures, that the conductances of Pt, Au(Pd), and Pb on diamond are all of similar magnitude at high pressure, and that there is no resolvable distinction in the high pressure conductances for Type 1A [100] versus Type 2A [110] diamond. I find that compression above 30 GPa irreversibly stiffens weak interfacial bonding, such that the decompressed metal-diamond conductances are near their corresponding "clean interface" zero-pressure values, $\approx 60$ MW m$^{-2}$ K for Pb/diamond. The similarity in thermal conductances for Pt and Au(Pd) to high pressure, despite the major differences in their electronic band structures, is difficult to reconcile with existing models of electron-phonon conductance across metal-dielectric interfaces, i.e., a contribution to the conductance generated by the coupling of electrons in the metal with phonons in diamond that enhances thermal transport across the
For metals with low phonon cutoff frequencies, the extra conductance above the one-phonon radiation limit is likely controlled by partial transmission three-phonon processes, where reflecting diamond phonons emit or absorb a fraction of their energy as a metal phonon. My calculations indicate that the extra conductance can be accounted for by partial transmission processes with a diamond phonon participation rate near 10%, or alternately, with an interfacial scattering rate about five times faster than the three-phonon scattering rate in bulk diamond at ambient pressure.
5.11 Figures

Figure 5.1: **Stimulated Brillouin backscattering frequency data.** Brillouin frequencies were collected from TDTR measurements done on the diamond and silicone oil pressure medium sides of various metal transducers. The dashed lines for [100] and [110] diamond are solutions to \( f = \frac{nv}{2\lambda} \) from the known diamond refractive index \( n \) and speeds of sound \( v \) at high pressure.\textsuperscript{130–133} The dashed line for silicone oil was estimated using the Vinet EOS and Lorentz-Lorenz relation (see Section 5.4). The solid line is an empirical power law fit used as a pressure calibration for one of the Pt/diamond data sets (Methods).
Figure 5.2: **Volumetric heat capacities extrapolated to high pressure.** The metals are extrapolated by assuming that they scale according to the Debye model. The Debye scaling depends on the atomic number density and Debye temperature, both of which are obtained from the pressure-volume equations of state (EOS). The color-coded labels and dashed lines indicate the resulting heat capacities versus pressure. The red point at 50 GPa is the Debye heat capacity assuming the Debye temperature scales not from the Al EOS, but the Al cutoff frequency at 50 GPa from a recent first-principles study. The equation of state for silicone oil is estimated from the Brillouin data, and the silicone heat capacity is scaled by its density.
Figure 5.3: Reflectance and thermoreflectance data. (a) Reflectance and (b) thermoreflectance data from the TDTR measurements on Al, Pt, and Pb. The reflectance values are not absolute measurements: they are normalized to the expected value for the diamond/metal interface at 0 GPa based on the known refractive indices. The thermoreflectance $dR/dT$ data are not normalized. The inconsistency between $dR/dT$ from different data sets (different symbol shapes and colors) are artifacts due to systematic errors, although the trends within data sets are robust.
Figure 5.4: **Electron-phonon resistance.** Estimated pressure scalings of the electron-phonon coupling strength $g$ (dot-dashed lines), the Leibfried-Schlomann equation lattice thermal conductivities $\Lambda_{LS}$ (dashed lines), and the proposed electron-phonon interface thermal conductance $G_{ep} = \sqrt{g\Lambda_{LS}}$ (solid lines) for each metal. Red, black, and green lines correspond to Al, Au, and Pb. The scaling of $g$ for the high pressure hcp-Pb (above 13-20 GPa) is more uncertain, as the same $d\lambda/dV$ is used for both fcc- and hcp-Pb.
Figure 5.5: **Experimental concept.** (a) shows the experimental system, where I use time domain thermoreflectance (TDTR) to measure the thermal conductance of metal-diamond interfaces at high pressure in a diamond anvil cell. (b) illustrates how high pressure stiffens the metal, increasing its maximum phonon frequency and its overlap with the diamond density of states. Panel (c) depicts elastic phonon transmission across the interface and two-phonon radiation into the metal. Panel (d) depicts a partial transmission three-phonon process. My results provide strong evidence that partial transmission processes control the inelastic conductance across interfaces between materials with low overlap in their phonon densities of states.
Figure 5.6: **Metal-diamond interface thermal conductances.** The thermal conductances of Al, Pt, Au(Pd), and Pb on Type 1A [100] and Type 2A [110] oriented diamond anvils were measured as a function of pressure in the DAC by TDTR. The results are separated into panels (a) and (b) for ease of viewing. The data and radiation limits (dashed lines) are color-coded: red hues for Al, blue for Pt, black for Au(Pd), and green for Pb. The dot-dashed lines are alternative radiation limits using theoretical phonon cutoff frequencies from the literature (Fig. 5.7). Magenta symbols, downward filled cyan triangles, filled grey circles, and left/down-facing bright green triangles, are decompression data for Al, Pt, Au(Pd), and Pb, respectively. The kink in the Pb radiation limit from 13-20 GPa is from an interpolation across the broad phase transition between fcc and hcp Pb in that pressure range (Section 5.4). The error bars on certain high pressure Al points represent random uncertainty in the TDTR thermal model fits, owing to a reduced thermoreflectance signal from Al at high pressure (Fig. 3). Not shown is $\approx \pm 15\%$ systematic uncertainty due to uncertainty in the extrapolation of the metal film areal heat capacity (Section 5.5).
Figure 5.7: **High pressure cutoff frequencies.** I extrapolate the maximum or cutoff frequencies $\omega_c$ for Al, Pt, Au, and Pb phonons based on a linear scaling with the Debye temperature, itself derived from the pressure-volume equations of state of the metals (Section 5.4). This extrapolation is in fair agreement with prior theoretical results for Al, Pt, and Au (points and dot-dash lines). At 50 GPa my Debye extrapolation deviates from the theoretical $\omega_c$ of Al, Pt, and Au by +11%, -6%, and -8%, respectively.
Figure 5.8: Excess thermal conductance. The remainder $G - G_{1R}$ represents the minimum value of the thermal conductance that is not due to elastic phonon processes. $G_{1R}$ is calculated from my Debye extrapolated cutoff frequencies, not the theoretical cutoff frequencies from the literature (Fig. 5.7). I only include data from Figs. 5.6(a-b) that represent the intrinsic thermal conductance in the absence of weak interfacial bonding. The open blue triangles for Pt include all the Pt data, the red squares are for Al on compression ("Al up"), and the rest are Pb, Au(Pd), and Al decompression data. The dark green dashed line is $G_{2R} - G_{1R} \approx 7 \times G_{1R}$ for Pb. It shows that for Pb, $G(P)$ is comparable to its two-phonon radiation limit $G_{2R}$. This is not the case for Pt or Au(Pd).
Figure 5.9: **Irreversible interfacial stiffening.** This figure isolates data from Fig. 5.6 that demonstrates irreversible interfacial stiffening by the fact that the interface thermal conductances did not return to their initial ambient pressure values after pressurization above 10 GPa. The red X’s are data from a single Al / Type 2A diamond sample, the red squares are from a single Al / Type 1A sample, and the magenta X’s and squares are decompression data from those two samples. The dark green right- and up-facing triangles are for two different Pb / Type 1A diamond samples, and the bright green left- and down-facing triangles are decompression data from those two samples. The return value of the Al / Type 2A conductance (magenta X’s) is noteworthy for being equal to the highest interface thermal conductance obtained by TDTR measurement from a clean Al / Type 2A diamond interface without pressure treatment.
Chapter 6

THERMAL TRANSPORT ACROSS HIGH PRESSURE SEMICONDUCTOR-METAL TRANSITION IN Si & Si$_{0.991}$Ge$_{0.009}$

Parts of this Chapter were submitted to Phys. Rev. B by Gregory T. Hohensee, Michael R. Fellinger, Dallas R. Trinkle, and David G. Cahill. It is in press at the time of this writing.

6.1 Introduction

High pressure thermal transport measurements can provide information and reveal physics that is not otherwise clear from ambient pressure experiments. Geophysical models of planetary heat flow, notably near the Earth’s core-mantle boundary where the pressure reaches 130 GPa, rely on knowledge of the thermal conductivity of minerals at high temperatures and pressures.\textsuperscript{14,15} Experimental data on the pressure scaling of thermal transport in amorphous\textsuperscript{38} and crystalline materials\textsuperscript{15,19-21,39,31,30,40} helps build a basis for extrapolation to more extreme pressure-temperature conditions.

Similarly, high pressure electrical transport experiments have been invaluable in the study of the physics of superconductors, as they enable monitoring of superconductivity as a function of atomic spacing and phase transitions under compression.\textsuperscript{175,176} The broad interest in carbon materials also extends to electrical transport measurements at high pressure,\textsuperscript{177} and metal-insulator transitions under pressure in silicon,\textsuperscript{178} CS$_2$,\textsuperscript{179,180} MoS$_2$,\textsuperscript{181,182} and VO$_2$-related materials,\textsuperscript{183,184} among others,\textsuperscript{185} have received a great deal of attention recently.

Silicon is an extensively studied material, as a template for other materials and in its own right for its nanoscale thermal transport dynamics.\textsuperscript{186–190} Silicon also has several phase transitions at moderately high pressures: from diamond cubic to $\beta$-Sn above 11 GPa, to primitive hexagonal near 15 GPa, and to hcp through an intermediate Cmca phase around 36-42 GPa.\textsuperscript{191–193}
In 1962 Minomura and Drickamer observed an abrupt, five to six orders of magnitude drop in two-point electrical resistance in silicon above 20 GPa, concluding that it had entered a metallic phase.\textsuperscript{194} Since then, experiments have used the resistance drop to map out the semiconductor-metallic phase transition, either as a function of temperature,\textsuperscript{195} or as a function of uniaxial pressure by local indentation of silicon along different crystalline axes.\textsuperscript{196} The superconducting phase transition for metallic Si under pressure has also been mapped out as a function of pressure by electrical transport measurements.\textsuperscript{197} Si also shows a pronounced change in optical reflectivity into the metallic phase.\textsuperscript{198} Despite this attention, I am not aware of any absolute electrical resistivity or thermal conductivity reports for metallic silicon.

While there are a variety of techniques sensitive to the onset of a metallic phase under pressure, absolute thermal and electrical transport measurements often rely on physical contact with the sample, such as the Angstrom method\textsuperscript{19} or four-point probe. The requisite metal leads must be simultaneously protected from the high pressure environment, electrically insulated from the gasket, and in good contact with the sample. Stress gradients can build under pressure to damage or deform the metal leads, and the sample geometry will also change under compression or across phase transitions.\textsuperscript{22} For experiments in the highest pressure ranges where the diamond anvil cell (DAC) is necessary,\textsuperscript{16} researchers have developed designer diamond anvils with embedded metal leads to perform electrical measurements in the DAC.\textsuperscript{23,24}

Recently, all-optical techniques have been developed for thermal transport measurements at high pressure in the DAC. Optical techniques are less demanding in that the diamond anvils double as optical windows. For simultaneous high pressure, high temperature measurements in particular, high speed spectroradiometry is used to sample blackbody radiation from intensely laser-heated DAC samples. The resulting 2D temperature map is then fitted for thermal conductivity.\textsuperscript{25–27} Optical laser flash diffusivity experiments have also measured the thermal diffusivity of a variety of materials under pressure, including MgO, MgSiO\textsubscript{3}, and Fe-doped variants.\textsuperscript{31,30,15}

My approach has been to leverage time-domain thermoreflectance (TDTR), an established ultrafast pump-probe technique for measuring thermal transport properties.\textsuperscript{32,5,6} Over the past few years high pressure TDTR experiments have provided new insight into the role of weak interface bonding
in suppressing the thermal conductance of an interface between two materials,\textsuperscript{36} as well as information about the mechanisms behind the enhanced heat conduction at interfaces between dissimilar materials.\textsuperscript{37} TDTR has also verified theoretical predictions of the thermal conductivity in amorphous and crystalline solids at high pressure.\textsuperscript{38–40}

In this chapter, I present thermal conductivity measurements of [001] Si and the mixed crystal \( \text{Si}_{0.991}\text{Ge}_{0.009} \) up to 45 GPa. This spans multiple phase transitions, in particular the semiconductor-metal transition which abruptly alters the thermal transport. I then apply the Wiedemann-Franz law to derive the anisotropic electrical resistivity of the metallic phase.

### 6.2 Experimental method

For measurements of thermal conductivity by TDTR, the sample is typically coated with an approximately 80 nm metal transducer film, the pump pulses heat the surface, and the probe pulses monitor the change in reflectance over time due to the temperature rise and subsequent cooling. A thermal model for the TDTR signal is generated from a solution to the heat diffusion equation for a multi-layered sample, where each layer is assigned a thickness, heat capacity, and thermal conductivity.\textsuperscript{32} The thermal model is fitted to the TDTR signal by varying one or two unknown thermal parameters, for example the thermal conductivity \( \Lambda \) of a bulk isotropic substrate, and the interface thermal conductance \( G \) between the metal transducer and the sample.

I performed TDTR measurements on Al-coated and Au(Pd)-coated commercial undoped Si and Si(Ge) wafers, where the Pd and Ge contents were established by Rutherford backscattering spectroscopy to be 5\% and 0.9\%, respectively. The Al and Au(Pd) thin films were deposited by DC magnetron sputtering, with thicknesses of approximately 80 nm confirmed by picosecond acoustics.\textsuperscript{61} I also performed TDTR measurements on bare metallic Si and Si(Ge) in the primitive hexagonal phase at high pressures, and supplemented these measurements with beam-offset TDTR as well.

For a sample coated with a metal transducer layer, the sensitivity of the TDTR measurement to the cross-plane thermal conductivity \( \Lambda_z \) comes from the out-of-phase temperature response of the transducer surface relative to the pump heating at the pump modulation frequency \( f \). This phase lag
depends on the areal heat capacity of the transducer relative to the volumetric heat capacity $C$ of the substrate integrated over the thermal penetration depth $L_{th} = \sqrt{\Lambda_z/(\pi C f)}$. Hence conventional TDTR with a transducer layer is sensitive to the thermal effusivity, since $L_{th} C \propto \sqrt{\Lambda_z C}$.

If TDTR is used to measure a bulk metallic sample without a transducer layer, the measurement loses almost all sensitivity to the $\Lambda_z$ of the substrate. However, with or without a transducer, for sufficiently small pump and probe laser spot sizes on the sample, the heat transport is no longer in the one-dimensional limit and the TDTR measurement gains sensitivity to thermal diffusion in the plane of the sample. For an uncoated bulk metallic substrate, TDTR mainly probes the in-plane thermal diffusion length relative to the pump and probe laser spot sizes. As such, for sufficiently low pump modulation frequency and small pump and probe spot sizes, TDTR is sensitive to the in-plane thermal diffusivity of a bulk metallic sample. In fact, since the areal heat capacity of a metal transducer layer is a major source of systematic uncertainty in conventional TDTR, measurements on an uncoated bulk metal can be even more precise, assuming the laser spot size is also measured precisely.

My TDTR thermal model for metallic samples assumes that heat is initially deposited in the electrons within an optical penetration depth, that the electrons and phonons equilibrate over some electron-phonon thermalization length, and that the thermal penetration depth at the pump modulation frequency is much longer than either of these lengths. I can calculate the optical penetration depth in metallic Si because Hanfland et al.\textsuperscript{198} have measured the diamond/silicon reflectance $R$ and calculated the imaginary part of the silicon permittivity $\epsilon_2$ at high pressures. At center wavelength of 785 nm used for TDTR, they report $R \approx 0.7$ and $\epsilon_2 \approx 15$ at 30 GPa. Since the optical properties of diamond are comparatively insensitive to pressure, this gives me enough information to back out the refractive index $n$ and absorption coefficient $\kappa$ for metallic silicon. I find that $n \approx 1.4$ and $\kappa \approx 5.5$ at this wavelength and pressure, for an optical penetration depth of $\alpha^{-1} \approx 11$ nm.

The electron-phonon thermalization length in metals is typically 10-100 nm, depending on electron-phonon coupling strength. I estimate the relevance of electron-phonon dynamics for TDTR measurement of bare metallic Si by specifying in the model that energy deposition is uniform and immediate in the top $L_{eq}$ nanometers of the sample. As for any other model
parameter, I calculate the sensitivity of the TDTR signal to $L_{ep}$ as a function of delay time. Taking an extreme case where $L_{ep} \approx 100$ nm as in Au, and using representative model parameters for metallic Si, I computed sensitivities and found that the TDTR signal is five times less sensitive to $L_{ep}$ than to the thermal conductivity $\Lambda$ at 500 ps, and ten times less at 1 ns delay time. From my experimental data, the thermal penetration depth in metallic Si is already $\approx 270$ nm or longer after 1 ns. By this reasoning I found that I can fit the TDTR signal for $\Lambda$ starting from 1 ns delay time, without quantitative knowledge of the electron-phonon coupling in the material.

I paired each TDTR measurement on bare metallic Si and Si(Ge) with a beam-offset TDTR measurement at the same position on the sample. Beam-offset TDTR is a variation of TDTR where the pump beam spot is scanned across the probe spot at a fixed delay time, typically along the two lateral axes in the plane of the sample surface.\textsuperscript{34} Taken at short positive delay time, the $V$(in) signal of beam-offset TDTR provides a precise measure of the correlated pump and probe spot sizes, before heat has time to spread in the sample. I then took two perpendicular beam offset scans in the plane of the sample at short negative time delay, obtaining two $V$(out) profiles. The width of each $V$(out) beam offset profile is determined by the initial spot size and the thermal penetration depth along that direction in the plane of the sample.

Because the TDTR pump modulation is in the MHz frequency range, even high thermal conductivity samples thin enough for DAC loading are essentially bulk or semi-infinite for the thermal model. At 1 MHz, a sample with a thermal conductivity of 200 W m$^{-1}$ K$^{-1}$ and a heat capacity on the order of 2 J cm$^{-3}$ K$^{-1}$ has a thermal penetration depth $L_{th} = \sqrt{\Lambda/(\pi C_f)} \approx 5.6\mu$m, much less than the 10-15 $\mu$m thickness of typical DAC samples. In my experiments on Si and Si$_{0.991}$Ge$_{0.009}$, the lowest modulation frequency was 3.35 MHz, $L_{th}$ was always less than 4 $\mu$m, and the sample thicknesses between 8-16 $\mu$m. Therefore, because I measured the side of the sample facing the silicone oil pressure medium, the exact thickness of the sample and the thermal properties of the diamond anvil are irrelevant to my measurement.

For the bare metallic Si and Si(Ge) data sets, I used a 3.35 MHz pump modulation frequency and a laser spot size of approximately 3 $\mu$m $1/e^2$ radius, which I measured at each pressure point. The resulting signal-to-noise and significant lateral diffusion length relative to the spot size permitted beam-
offset TDTR fits to the thermal diffusivity to within 10%. The only other relevant parameter in the thermal model is the thermal effusivity of the silicone oil pressure medium in the DAC, which is comparatively negligible. For conventional TDTR on Al- or Au(Pd)-coated Si and Si(Ge), systematic uncertainty in the transducer areal heat capacity yields the usual 5-10% uncertainty in the fitted thermal conductivities for a given Si heat capacity.

Since TDTR has previously been used to measure the dynamic heat capacity across the metal-insulator transition (MIT) in vanadium dioxide (VO$_2$),\textsuperscript{199} it is worthwhile to consider whether my high pressure silicon TDTR experiment is sensitive to the dynamic heat capacity across the various high pressure silicon phase transitions at room temperature. Deb et al.\textsuperscript{200} studied pressure-induced amorphization of porous silicon, and also provided a calculated pressure-temperature phase diagram for crystalline Si. In their Figure 3a, they portray the diamond cubic to beta-Sn phase boundary as having a slope of $10^3$ Kelvin per GPa, extending up to a melting temperature above 900 K. The few-Kelvin temperature excursions in my experiment does not create significant thermal pressure or cross a phase boundary in temperature.

In TDTR, one can obtain sensitivity to the dynamic heat capacity of a phase transition if the transition rate exceeds the time scale of the TDTR pump modulation frequency. In my experiment, the pump modulation time scale is $\tau \approx (2\pi f)^{-1} \approx 16$ ns. The TDTR study of the MIT of VO$_2$\textsuperscript{199} had sensitivity because the VO$_2$ transition is sub-picosecond, which is what makes it interesting for ultrafast optical switching.\textsuperscript{201} In silicon, all the pressure transitions at room temperature involve changes in symmetry and atomic bonding; it is not obvious that they would have nanosecond transition rates, even if the sample was near a temperature phase boundary.

Experimentally, the DAC pressure gradient that I describe in Section III allowed me to avoid taking measurements on Si within 1 GPa of any phase transition. The small pressure gradient across my samples meant that I could observe the wavefront of a phase transition between higher and lower pressure regions of the samples. These could be seen in visible light by increased optical reflectivity in the metallic phases, as well as volume collapse across the transitions. I always applied an $\approx 1$ GPa pressure increment after observing such a wavefront, so that the measurement was not taken near a phase boundary.
6.3 DAC sample preparation and pressure calibration

I used commercial [001] Si (P-type (Boron), 3-50 Ω cm resistivity) and Si$_{0.991}$Ge$_{0.009}$ wafers for my experiment. For the samples measured with a metal film transducer, the Al and Au$_{0.95}$Pd$_{0.05}$ films were deposited by DC magnetron sputtering. The Si and Si(Ge) substrates were heated to approximately 600°C for 30 minutes in vacuum and allowed to cool immediately before Al and Au(Pd) deposition in the same chamber, without exposure to air. I deposited Au(Pd) instead of pure Au because Au(Pd) yields a clear picosecond acoustic signal from which I can extract the Au(Pd) film thickness in situ, unlike Au. After sputtering, the Si and Si(Ge) samples were backpolished to 8-16 micron thickness, and squares approximately 100 µm x 100 µm in size were cleaved and loaded into the DAC with a low viscosity silicone oil (1 cSt octamethyltrisiloxane, molecular weight 237) as the pressure-transmitting medium. The bare Si and Si(Ge) samples were back-polished and loaded into the DAC without heating or sputter deposition.

One to three ruby spheres were included in the DAC sample chamber for pressure calibration by ruby fluorescence. The ruby fluorescence shift can be sensitive to non-hydrostatic behavior of the pressure medium, but the range of variations is small below 50 GPa. I estimate ±0.5 GPa uncertainty in the ruby pressure from spectrometer resolution.

An important aspect of using ruby as a pressure calibrant is that the pressure experienced by the ruby is not necessarily the pressure at the region of the sample measured by TDTR. For a quasi-hydrostatic medium like silicone oil, pressure gradients on the order of 10% can develop across the sample chamber. It is difficult to ensure that the spatial separation between ruby and sample is small after loading a fluid medium, and the gasket hole that forms the sample chamber can also drift with increasing pressure. As a result the ruby can be at lower pressure near the edge of the diamond culet, while the sample remains at the culet center under slightly higher pressure.

Because TDTR also provides an in situ Brillouin frequency measurement of the pressure medium, it is possible to calibrate the medium’s Brillouin frequency versus pressure, and later compare the measured Brillouin frequency against the pressure reading from a distant ruby. I did this for silicone oil in my metal-diamond project, and in Fig. 6.1 I make that comparison for DAC loadings with the bare Si and Si(Ge) samples. Above 15 GPa the press-
sure at the sample deviated from the ruby pressure by approximately 15% (Fig. 6.1, dashed green line), plus or minus 1 GPa (solid green lines). I extracted the raw Brillouin frequencies from the TDTR signals to within 2%, but systematic error in my frequency-to-pressure calibration is expected to be somewhat larger, between 5 to 10%. More data points from adjacent ruby and TDTR measurements under pressure are needed for a more precise silicone oil Brillouin frequency calibration, but even so I was able to correct for systematic differences between ruby and sample pressures in this manner.

To judge whether this observed gradient is realistic, I examined literature data for the ruby R1 linewidth as a function of pressure in silicone oil pressure media. Increases in R1 linewidth with pressure correlate with decreased hydrostaticity in the pressure medium. Previous work with silicone oil pressure media indicate a that a 10% standard deviation or gradient in pressure across a DAC sample chamber is not unusual above 20 GPa.\textsuperscript{53,125} The maximum deviation from center to edge of a sample chamber that has drifted under pressure, then, is likely to be comparable to the 15% that I report in Fig. 6.1 for some of my DAC loadings.

### 6.4 Pressure-dependent thermal modeling

As in most TDTR experiments the thermal model is simply an analytic solution to the heat diffusion equation through a multilayer, as laid out for coaligned pump and probe beams by Cahill in 2004.\textsuperscript{32} All high-pressure TDTR experiments must additionally consider bidirectional heat flow from the heated sample surface:\textsuperscript{166} both into the sample, and into the pressure medium, which is in this case silicone oil. Since very few thermal properties have been experimentally measured at high pressure, I calculate most of these properties as accurately as possible, leaving the most complex properties such as thermal conductivity to be fitted by my experimental data.

I model the pressure-dependent thermal properties of the metal transducer films of Al and Au(Pd) in the same manner as in my metal-diamond project.\textsuperscript{37} Since I can only measure the thermal diffusivity or effusivity of silicon, all of my reported silicon thermal conductivity data is necessarily dependent on how certain I am of the silicon heat capacity under pressure. Since the thermal model includes heat transport into the silicone oil pressure
medium, I also consider how sensitive the measurement is to that heat transfer pathway, and provide an adequate estimation for the silicone oil thermal conductivity and heat capacity under pressure.

For the silicon heat capacity in the different high pressure phases, Mike Fellinger and Dallas Trinkle performed *ab initio* lattice dynamics calculations for Si in the diamond cubic, primitive hexagonal, and hcp phases at high pressure due to the absence of experimental heat capacity data. Density functional theory (DFT) computes forces on displaced atoms for input to the direct force-constant approach to phonon thermodynamics. The DFT calculations utilize the plane-wave basis program VASP. The Perdew-Burke-Ernzerhof generalized gradient approximation functional accounts for electron exchange and correlation, and a projector augmented wave potential with electronic configuration [Ne]3s²3p⁶ generated by Kresse and Joubert represents the Si nuclei and core electrons. Forces on atoms displaced from their ideal lattice sites by 0.02 Å determine the force constants for Si in the diamond cubic phase at 11 GPa (DFT lattice parameter \(a = 5.289\) Å), the primitive hexagonal phase at 15, 27, and 38 GPa (DFT lattice parameters \(a = 2.549\) Å and \(c = 2.402\) Å, \(a = 2.494\) Å and \(c = 2.360\) Å, and \(a = 2.452\) Å and \(c = 2.239\) Å, respectively), and the hcp phase at 42 GPa (DFT lattice parameters \(a = 2.467\) Å and \(c = 4.182\) Å). The diamond cubic and primitive hexagonal calculations require a plane-wave energy cut-off of 400 eV, and the energy cutoff for the hcp calculation requires 450 eV. Force calculations are carried out in a \(4 \times 4 \times 4\) supercell for diamond cubic (128 atoms), \(5 \times 5 \times 5\) supercells for primitive hexagonal (125 atoms), and a \(5 \times 5 \times 3\) supercell for hcp (150 atoms). The corresponding \(k\)-point meshes for each supercell are \(4 \times 4 \times 4, 6 \times 6 \times 6,\) and \(6 \times 6 \times 6\). For the insulating diamond cubic phase at 11 GPa Mike Fellinger used the linear tetrahedron method with Blöchl corrections for the Brillouin zone integration; while for the metallic primitive hexagonal and hcp phases, he used order-one Methfessel-Paxton smearing with energy smearing widths of 0.6 eV (hexagonal) and 0.5 eV (hcp). These settings ensure energy convergence of less than 1 meV/atom for each phase. Figure 6.2 shows the computed phonon density of states (DOS) for the primitive hexagonal phase at 15, 27, and 38 GPa.

Figure 6.3 plots the calculated \(C(P)\) for Si and the silicone oil pressure medium. The *ab initio* Si heat capacity was calculated at six pressures.
(magenta points), and for the thermal model I simply used a linear interpolation between these points (magenta line) for the Si heat capacity at all pressures. As can be seen by comparing the *ab initio* curve against the classical (high temperature) $C = 3Nk_B$ limit (black lines), the jumps in heat capacity across the phase transitions are largely density-driven. My use of interpolation rather than direct calculation for the $\beta$-Sn heat capacity may underestimate the heat capacity in that phase, following the behavior of the classical limit. This would mean I overestimated the cross-plane $\Lambda_z$ from my transducer-coated samples in the $\beta$-Sn phase.

For silicone oil, I extrapolated $C(P)$ assuming that the silicone oil heat capacity per molecule is constant with pressure, and that the volumetric heat capacity is solely a function of density. I derived the change in density with pressure in my metal-diamond project from the Lorentz-Lorenz relation and a pressure-volume equation of state (EOS) fit to my own Brillouin frequency vs. pressure data.$^{37}$

In my metal-diamond project I extrapolated the silicone oil thermal conductivity $\Lambda(P)$ from low pressure literature data$^{134}$ using the minimum thermal conductivity model, with the assumption that the ratio of the longitudinal and transverse speeds of sound is constant with pressure.$^{37}$ This assumption has been previously used to successfully replicate the pressure dependence of PMMA.$^{38}$

For conventional TDTR, the sensitivity to the silicone oil relative to the Si and Si(Ge) samples is approximately the ratio of their thermal effusivities $\sqrt{\Lambda C}$. My calculations in Ref.$^{37}$ showed that the silicone oil thermal conductivity remains of order $1 \text{ W m}^{-1} \text{ K}$ to 50 GPa. Since the thermal conductivity of both Si and Si(Ge) are 1-2 orders of magnitude larger than that of silicone oil, and the Si and Si(Ge) heat capacities are larger than that of silicone oil, my measurements are 10 to 100x more sensitive to the Si and Si(Ge) effusivity than to the silicone oil effusivity. The same argument holds for the bare Si and Si(Ge) measurements, for which the measured parameter is thermal diffusivity rather than effusivity.
6.5 Interface thermal conductance

Figure 6.4 shows the measured interface thermal conductances between the Al and Au(Pd) transducers and their Si and Si(Ge) substrates. Blue symbols represent data for Al / Si interfaces, while open and closed brown symbols are for Au(Pd) / Si and Au(Pd) / Si(Ge) interfaces, respectively. It is important to note that all of the Si and Si(Ge) samples have a native oxide of 2-3 nm on their surface, so the Al/Si, Au(Pd)/Si, and Au(Pd)/Si(Ge) interface conductances all include the thermal resistance of the native oxide. I measured the native oxide thicknesses on untreated Si and Si(Ge) wafers by ellipsometry, obtaining approximately 2.2 and 3.1 nm, respectively.

The difference in initial thermal conductances between Au(Pd)/Si and Au(Pd)/Si(Ge) is likely due to weak interfacial bonding in the latter sample, although both were heated to approximately 600°C in vacuum prior to Au(Pd) deposition. The difference is suppressed by 10 GPa, as expected from prior work on weakly bonded Al/SiC interfaces under pressure. Meanwhile the Al/Si sample conductance is high and reversible up to 13 GPa (open and filled blue triangles), just before the β-Sn to primitive hexagonal phase transition. The initial Al / native oxide / Si conductance is high and typical of a clean interface on Si with native oxide, so I expect the pressure dependence is intrinsic to Al / native oxide / Si interfaces with ≈ 2 nm of native SiO₂. The Al / native oxide / Si thermal conductance increases from 260 to 380 MW m⁻² K between 0 and 10 GPa, a nearly 50% increase.

I used the radiation limit for Al to estimate the maximum possible increase in thermal conductance due to elastic phonon processes. In the radiation limit picture, the ≈20% increase in Al phonon cutoff frequency with pressure would suggest an ≈75% increase in thermal conductance. As this limit is larger than the observed increase, elastic processes can explain the increase in Al / native oxide / Si interface conductance that I observe under pressure. This is consistent with recent theoretical work.

I also compared the observed increase in interface conductance to the change in the theoretical maximum conductance $G_{\text{max}}$ for Al, which is defined as the interface conductance assuming 100% transmission of all Al phonon modes incident on the interface. Figure 4 of Ref. plots $G_{\text{max}}$ for Al as a function of pressure up to 60 GPa, and predicts an ≈ 6% increase in $G_{\text{max}}$ for Al between 0 and 10 GPa, much smaller than the nearly 50% increase in $G$.
that I observe for Al / native oxide / Si. The authors of Ref.\textsuperscript{11} made a similar observation when comparing $G_{\text{max}}$ for Al against the $G$ of an Al / MgO interface between 0 and 10 GPa. I make the same inference as they made: that interfacial stiffness is an influential parameter for interfacial conductance, even when the interface is relatively clean.

I did not remove the Si and Si(Ge) native oxides prior to Al or Au(Pd) deposition because I was interested in how the thermal conductance of phonons might change across the semiconductor-metal transition starting near 15 GPa. I observed the following changes in the Al / native oxide / Si interface thermal conductance as I increased the pressure into the metallic Si phase. First, the hot-electron peak in the picosecond acoustics disappeared when Si became metallic, and returned on decompression back to non-metallic Si.\textsuperscript{61} Hot electrons from a pump pulse cause a hot-electron peak in the TDTR signal by generating a stress discontinuity at the interface between the transducer and an electrically insulating surface, such as an oxide layer or a non-metallic substrate. Second, the decay rate of the in-phase TDTR signal, which determines the apparent interface thermal conductance, increased sharply after Si became metallic. Fits to the interface conductance $G$ yielded values of 1-3 GW m\textsuperscript{-2} K\textsuperscript{-1}, at the upper limit of the TDTR measurement sensitivity to $G$. These values are 10% of what is typical for electronic thermal transport between two metals at ambient pressure. The fitted $G$ was also not reversible on decompression to ambient pressure. An Al / native oxide / Si sample compressed to just below the metallic transition returned to about 260 MW m\textsuperscript{-2} K\textsuperscript{-1} conductance, whereas decompression from the metallic phase yielded 500 MW m\textsuperscript{-2} K\textsuperscript{-1} at ambient, similar to the interface conductance between Al and a Si wafer that was HF-dipped to remove the native oxide. These results are suggestive of direct metal-metal contact between Al and Si after Si becomes metallic. I do not know how this comes about. One possibility may be the mechanics of the phase transition, another may be chemistry between the Al and native oxide.

I have chosen not to include the Al / Si TDTR results for metallic Si for two reasons. First, the TDTR measurement lacks significant sensitivity to interface conductances on the order of a GW m\textsuperscript{-2} K\textsuperscript{-1}. Second, my thermal model predicted thermal conductivities for metallic Si from the Al / Si data that were far in excess of the values I obtained from my Au(Pd) / Si and bare metallic Si data, which were consistent with one another. An assumption of
my thermal model is that heat is initially deposited only in the transducer layer; if there is appreciable direct metal-metal contact at the interface, energy from hot electrons may deposit directly in the substrate, which violates that assumption. Conversely, I do include the Au(Pd) / Si and Au(Pd) / Si(Ge) results because the interface thermal conductances were measurable, and the obtained thermal conductivities were consistent with the results from the bare metallic Si TDTR data, for which interfacial transport is a non-issue. We I not know why the Au(Pd) results were consistent with bare metallic Si and the Al results were not. It could possibly have to do with differences in the mechanical properties or chemical reactivities of Al versus Au(Pd) at high pressures.

After the semiconductor-metal transition, the thermal conductances for Au(Pd) on Si and Si(Ge) have average values of 750 and 470 MW m\(^{-2}\) K\(^{-1}\), respectively. The ratios of the oxide thicknesses and interfacial thermal resistances were both approximately 1.6. The interfacial conductances were equivalent to the thermal resistance of oxides with a thermal conductivity of approximately \(\approx 1.5\) W m\(^{-1}\) K\(^{-1}\) and initial thicknesses given in Fig. 6.4. Note that the interface conductances between Au(Pd) and metallic Si and Si(Ge) are of a similar magnitude to the electron-phonon conductance for Au that I extrapolated to high pressure in my previous work,\textsuperscript{37} which would act as a limiting interface conductance if the Au electrons cannot propagate or deposit energy into the substrate.\textsuperscript{114,37}

### 6.6 Thermal conductivity - semiconducting

Figure 6.5(a) shows the measured thermal conductivities for the Al- and Au(Pd)-coated Si and Si(Ge) samples, by conventional TDTR. Blue squares and triangles are Al/Si data, open and closed brown circles are Au(Pd) on Si and Si(Ge), respectively. The filled blue square and triangle at 0 GPa are the thermal conductivities of the recovered Al/Si sample after decompression from the $\beta$-Sn and primitive hexagonal phases near 13 and 16 GPa, respectively. Vertical lines mark phase transition pressures.\textsuperscript{191–193}

The thermal conductivity of amorphous\textsuperscript{38} and crystalline materials\textsuperscript{40} will generally increase with pressure due to bond stiffening. In a crystal the pressure scaling is stronger due to the reduction in the phonon density of
states and associated reduction in the rate of three-phonon scattering. The thermal conductivity is expected to scale with powers of the bulk modulus $K_T$, specifically $K_T^{1/2}$, $K_T^{3/2}$, and $K_T$ for amorphous, crystalline, and mixed crystalline materials. The Si(Ge) data in the diamond cubic phase is not inconsistent with this expectation, although it is also consistent with no pressure scaling. The diamond cubic Si thermal conductivity, however, is lower than its zero pressure value and constant in the diamond cubic phase.

At ambient pressure, the diamond cubic phase of Si is known to exhibit non-Fourier thermal transport when heated at sufficiently small length scales. In particular, Wilson and Cahill measured an approximately 15% reduction in the apparent thermal conductivity of bulk Si by conventional TDTR as the laser spot size is decreased from 10 to 3 microns $e^{-2}$ radius due to non-diffusive transport. I performed spot-size dependent measurements down to 3 microns spot size on Al/Si samples across the entire diamond cubic high-pressure phase. I obtained an expected 146 W/m-K at 0 GPa for the largest spot size, but above 1 GPa, I measured conductivities of 115-130 W m$^{-1}$ K$^{-1}$ for all spot sizes with no discernable pressure or spot size dependence. As such I distinguished symbols (blue open triangles and squares, Fig.6.4(a)) for different samples, but not different spot sizes. The scatter in my current high-pressure data is comparable to the spot size dependence in ambient Si down to a 3 micron spot size. It is conceivable that a more precise series of measurements down to a 1 micron spot size could resolve a trend.

The lack of pressure dependence that I observe in the thermal conductivity of the diamond-cubic phase of Si is unusual: more typical behavior can be seen in diamond, which has the same crystal structure and is predicted to have an increasing trend in its thermal conductivity under pressure. A recent first principles calculation by Parrish et al. for Si up to ±3% strain (equivalent to $\approx$ 4 GPa for Si) reports a similar lack of pressure dependence in the thermal conductivity of compressed Si. Parrish et al. observed that Si atoms had shorter phonon lifetimes and were allowed greater root-mean-square (RMS) displacement under compression. Along the same lines, Soma and Shen et al. have produced theoretical and experimental work indicating that the transverse acoustic modes in diamond cubic Si soften as the pressure approaches the beta-Sn phase transition. This is in contrast to the behavior of diamond, as Broido et al. calculated no significant alteration.
in the transverse acoustic modes of diamond up to 400 GPa.\textsuperscript{213} Softening of the transverse phonons in silicon increases their occupation number and increases their Umklapp scattering rates. The softening also reduces the transverse mode group velocities, which further suppresses the thermal conductivity. Apparently, these factors act to cancel out the factors that would otherwise increase the thermal conductivity, as predicted for diamond and observed for ice\textsuperscript{39} and MgO.\textsuperscript{40}

I measured a thermal conductivity of 34 W m\textsuperscript{-1} K\textsuperscript{-1} from an Al / Si sample decompressed from the primitive hexagonal Si-V phase near 16 GPa (Fig. 6.5(a), filled blue square). Decompression of Si-V is known to yield polycrystalline metastable Si-III (BC8 structure).\textsuperscript{217} The measured Si-III thermal conductivity is comparable to that of my Si(Ge) with 0.9\% Ge. Decompression from the $\beta$-Sn Si-II phase is also known to yield Si-III,\textsuperscript{217} but I measure a somewhat higher thermal conductivity of 72 W m\textsuperscript{-1} K\textsuperscript{-1} on recovery of Al-coated Si-II to ambient pressure (Fig. 6.5(a), filled blue triangle).\textsuperscript{218} This may be because decompressing from Si-II avoids the additional grain and defect formation that occurs when entering Si-V.

It is interesting to compare these Si-III thermal conductivities against those obtained in recent uniaxial high pressure torsion experiments by Harish \textit{et al.}\textsuperscript{219} In their experiment, two opposing anvils applied 24 GPa of pressure on single crystalline Si wafers, and explored the resulting thermal conductivity as a function of torsion under pressure, before and after annealing at 600°C. My 72 W m\textsuperscript{-1} K\textsuperscript{-1} sample decompressed from Si-II has a similar thermal conductivity to that of samples by Harish \textit{et al.} obtained from their zero torsion, post-anneal experiment. The 34 W m\textsuperscript{-1} K\textsuperscript{-1} sample released from 16 GPa Si-V likewise has a similar thermal conductivity to those of Harish \textit{et al.}'s post-anneal samples after 10 revolutions of torsion at 24 uniaxial GPa. Evidently, entry into the Si-V phase by hydrostatic pressure reduces the thermal conductivity of recovered Si-III by a factor comparable to the effect of high pressure torsion on Si post-anneal. For Harish \textit{et al.}, the higher post-anneal thermal conductivities were attributed to three factors: thermal relaxation to Si-I, increased grain sizes, and reduced lattice defects. Since my samples were maintained at room temperature, it seems likely that the reduced thermal conductivity of my Si-III recovered from Si-V was due to grain and defect formation across the Si-II to Si-V phase transition.
6.7 Thermal conductivity - metallic

There was no visible roughening or grain formation across the diamond cubic to $\beta$-Sn transition. According to Shen et al.,\textsuperscript{216} the diamond cubic to $\beta$-Sn transition occurs by fast lattice fluctuations rather than static nucleation. However, the transition to primitive hexagonal Si is marked by simultaneous surface roughening and an abrupt increase in optical reflectivity. As shown in Fig. 6.5(a), between the diamond cubic and primitive hexagonal phases the Si and Si(Ge) thermal conductivities both increase sharply to similar values as the materials become metallic. Also, it is in the primitive hexagonal phase that I observe discrepancies between the thermal conductivities measured along orthogonal in-plane directions and in the [001] cross-plane direction of my samples, by beam offset and conventional TDTR, respectively.

My beam offset data on bare metallic Si and Si(Ge) were taken along two perpendicular axes in the plane of the sample, so at each pressure point I have two beam offset data points, representing the in-plane thermal conductivities along two orthogonal axes. These are the diamond symbols in Fig. 6.5(b). The cyan and brown triangles are TDTR measurements on bare metallic Si and Si(Ge), respectively. I should emphasize that TDTR on metallic samples without a transducer is not sensitive to the cross-plane thermal transport, but rather the in-plane thermal diffusivity, and then only if the lateral thermal penetration depth is a significant fraction of the laser spot size. Upward and rightward triangles are for increasing pressure, downward triangles for decreasing pressure. Overall the thermal conductivities for metallic Si and Si(Ge), including those using the Au(Pd) transducer, are consistently scattered within a band that increases with pressure up to the next phase transition near 36 GPa. The equivalence in Si and Si(Ge) metallic thermal conductivities within this band indicate that the phonon thermal conductivity, which should be strongly affected by the Ge defects in Si(Ge), is negligible compared to the electronic thermal conductivity in the metallic phase. This electronic dominance is typical for high thermal conductivity metals.

I was unable to measure bare Si or Si(Ge) above the Cmca/hcp transition, or to measure Au(Pd)-coated Si(Ge) on decompression from the hcp phase, because of excessive sample surface roughness. The large volume changes and grain nucleation across different Si phase transitions causes surface rough-
ening that compounds with each transition. Excessive roughness prevents reliable TDTR measurement due to an excess of diffuse light scattering and thermoacoustic effects that distort the TDTR signal from the sample surface.\textsuperscript{6} My data for Au(Pd)-coated Si(Ge) above 36 GPa indicate a sharp loss in thermal conductivity in the mixed intermediate Cmca/hcp phase, followed by a rapid recovery into the hcp phase. My measurements above 36 GPa for bare Si and Si(Ge) are suggestive of similar behavior, but are not reliable enough to report.

To properly understand the scattered band of thermal conductivities that I measure in the primitive hexagonal phase, I revisited the geometry of the beam offset measurement and the symmetries involved in the semiconducting to metallic structural phase transitions in silicon. A conventional TDTR measurement, with or without a transducer, measures the temperature response of a sample due to radially symmetric heating at one point. Defining the plane of the sample as the xy-plane, such a measurement can only sample the geometric mean thermal transport along the x- and y- in-plane axes.

Beam offset TDTR, however, breaks radial symmetry by displacing the probe beam relative to the pump. In beam offset the signal is the temperature profile along a line crossing the center of pump heat source. Over the time scale of the pump modulation frequency, an elliptical Gaussian temperature profile develops from the circular Gaussian pump heat source, due to the in-plane anisotropy of the sample. If the crystalline axes are known, two perpendicular beam offset line scans are sufficient to obtain the major and minor in-plane thermal conductivities.\textsuperscript{220}

Recall that the crystalline orientations of the diamond cubic, \(\beta\)-Sn, and primitive hexagonal phases are related to one another in a specific manner. The \(\beta\)-Sn tetragonal phase occurs as a 45-degree rotation about one of the cubic symmetry axes, for a threefold degeneracy in the orientations \(\beta\)-Sn can take relative to the polished [001] Si face of my sample.\textsuperscript{216} Either the \(\beta\)-Sn [001] is perpendicular to the polished surface, or the \(\beta\)-Sn [001] and [110] axes are parallel to that surface.

Next, the c-axis of the primitive hexagonal phase forms along either the [100] or [010] axis of the \(\beta\)-Sn phase by a 90 degree rotation about the [010] or [100] axis, respectively.\textsuperscript{221,222} Relating this back to my polished [001] diamond cubic surface, there are two scenarios. In the first scenario where the \(\beta\)-Sn c-axis forms perpendicular to the sample surface, the primitive hexagonal
c-axis lies 45 degrees out of the plane, along [011] and [011], or [011] and [001]. Alternately, the hexagonal c-axis lies in the sample plane, along [110], [110], [101], or [101]. In each scenario, the hexagonal ab-plane cuts across one of the lateral or diagonal in-plane directions, respectively.

Due to how Si wafers cleave along the cubic symmetry axes, I know which orthogonal in-plane axes I measured by beam-offset TDTR. For bare Si and Si(Ge), I measured along the diagonal ([110], [110]) and lateral ([100], [010]) in-plane axes of the diamond cubic phase, respectively. Finally, the conventional TDTR measurements in Fig. 6.5(a) on Au(Pd)-coated metallic Si and Si(Ge) were sensitive to the cross-plane thermal conductivity.

Since the primitive hexagonal phase has so much degeneracy in its choice of c-axis, it is no surprise that the sample surface roughens on entering this phase. The samples become polycrystalline, and the scattered thermal conductivities imply significant anisotropy between the hexagonal ab-plane and c-axis thermal transport. However there is no clear trend to distinguish the beam offset and conventional data sets from bare Si and Si(Ge), so I do not know if one or another set of orientations is preferred.

Regardless, I can say that the in-plane measurements had access to grain orientations varying from the hexagonal c-axis to one of the planar hexagonal axes. The cross-plane data in Fig. 6.5(a), meanwhile, could conceivably probe orientations ranging from the c-axis to 45 degrees off the c-axis. These ranges would be continuous for grain sizes smaller than the 3 micron $1/e^2$ radius laser spot for the bare Si, Si(Ge) measurements, or the 6 micron $e^{-2}$ radius laser spot used on the Au(Pd)-coated samples.

If the c-axis thermal conductivity is higher than the in-plane thermal conductivity, as is typical for hexagonal metals, this may partly explain how the conventional TDTR measurements on Au(Pd)-coated Si and Si(Ge) (Fig. 6.5(a)) yielded above-average thermal conductivities within the range presented in the bare Si, Si(Ge) data (Fig. 6.5(b)). That said, since the data sets in Figs. 6.5(a-b) have different sensitivities to the Si heat capacity $C$, that slight difference could just originate in a small systematic error in the calculated $C$.

I cannot simply take pairs of TDTR measurements with and without transducers in order to fit for $C$ because the hexagonal metallic silicon is thermally anisotropic. Conventional TDTR with a transducer measures cross-plane thermal conductivity, TDTR without a transducer measures mean in-plane
thermal conductivity, and beam offset TDTR measures two orthogonal in-plane thermal conductivities. All of these are different if the material is anisotropic. At best, I can only note the overlap in the thermal conductivity bands from the Au(Pd)-coated and bare metallic Si samples, and state that Mike Fellinger and Dallas Trinkle’s *ab initio* silicon heat capacity is accurate to within the thermal anisotropy of the polycrystalline hexagonal metallic Si. But I cannot claim that it is experimentally verified to within less than the anisotropy of the sample.

### 6.8 Electrical resistivity

If I assume that the phonon contribution to the thermal conductivity of metallic Si and Si(Ge) is negligible, then I can take my analysis a step further by converting the electronic thermal conductivity $\Lambda$ to an electrical resistivity $\rho$ using the Wiedemann-Franz law, $\rho = L_0 T/\Lambda$, where $T \approx 300$ K is the temperature and $L_0$ is the Sommerfeld value of the Lorenz number $L_0 = 2.44 \times 10^{-8}$ W Ω K$^{-2}$. The result is shown in Fig. 6.6 for metallic Si and Si(Ge), in comparison to the ambient electrical resistivities of pure Al, Au, Zn, Cd, and Be.\textsuperscript{223,224} The electrical resistivity in metallic Si and Si(Ge) is comparable to highly conductive metals such as Al and Au, with an electrical anisotropy of approximately 1.4, very similar to that of ambient hcp Be.

I compared simple Wiedemann-Franz conversion to a more sophisticated electronic transport model to better understand the pressure dependence. In pure metals at room temperature, electron-phonon scattering controls the electrical resistivity. The Bloch-Grüneisen law gives the electrical resistivity due to electron-phonon scattering, with several assumptions. The assumptions include a spherical Fermi surface, no resistivity from Umklapp processes, and a Debye model for the phonon spectrum.\textsuperscript{225} Because of the spherical Fermi surface, there are no normal electron-phonon processes for transverse phonons, leaving only N-processes involving longitudinal acoustic phonons. None of these assumptions are strictly valid for Si, which becomes a tetravalent hexagonal metal under pressure. Umklapp processes in particular are known to be significant for other tetravalent metals, Sn and Pb.\textsuperscript{226}

Even so, I am encouraged by the work of Hanfland *et al.*, who measured the optical reflectivity of primitive hexagonal Si as a function of pressure,
calculated the electronic band structure, and found their results consistent with Si being a nearly free electron metal in this phase. Therefore I proceed with the Bloch-Grüneisen equation for the electrical resistivity:

\[
\rho_{BG} = \frac{K}{\Theta} \left( \frac{T}{\Theta} \right)^5 \int_0^{\Theta/T} \frac{z^5 e^z dz}{(e^z - 1)^2}
\]

Here \( K \) represents the combined factors relating to the Fermi surface geometry and electron-phonon scattering matrix elements, but which are assumed to be independent of temperature. The pressure dependence of \( K = K_0 (V/V_0)^\beta \), where \( \beta \equiv d \ln K / d \ln V \), is generally not important unless the volume change causes the Fermi energy to cross an unpopulated band, which is not evident from Hanfland et al.’s band structure calculations. The main part of the pressure dependence of the resistivity is expected to come from the lattice through the Debye temperature parameter \( \Theta \). To calculate the pressure dependence of the Bloch-Grüneisen resistivity, I first formally differentiate Eqn. (1):

\[
\frac{d \ln \rho_{BG}}{d \ln V} = \beta + 2 \gamma
\]

Note that \( \gamma \equiv \frac{d \ln \Theta}{d \ln V} \) is the Grüneisen parameter. I then use the Wiedemann-Franz electrical resistivities to fit \( K_0 \) and \( \beta \), and derive \( \Theta \equiv \langle E \rangle / k_B \) from the first moment \( \langle E \rangle \) of the same phonon densities of states that I calculated for the Si heat capacity. The frequencies corresponding to \( \langle E \rangle \) across the primitive hexagonal phase are shown by vertical lines in Fig. 6.2. The resulting \( \Theta \) varies from 505 to 607 K between 15 and 38 GPa, and \( \gamma \) is calculated from \( \Theta \) and the Si equation of state.

Two Bloch-Grüneisen models are plotted in Fig. 6.6; the red line is for \( \beta = 0 \), and the black dot-dash line is for \( \beta = 1 \). Much of the pressure dependence in my Wiedemann-Franz \( \rho \) can be explained by the pressure dependence of \( \gamma \). Meanwhile I fit \( K_0 \) by the magnitudes of the upper and lower bounds of the measured \( \rho \) band near 15 GPa: \( K_0 = 2.1 \times 10^4 \) and \( 1.4 \times 10^4 \) K µ\( \Omega \) cm, respectively. I notice that \( \beta \approx 1 \) is consistent with the observed pressure dependence, and that it is similar in magnitude to the \( \beta \) values of 0.87 and 0.78 for the other tetravalent metals, Pb and Sn.
6.9 Conclusion

I have used conventional and beam-offset TDTR to establish the thermal conductivities of [001] Si and Si_{0.991}Ge_{0.009} across the semiconductor-metal phase transition and up to 45 GPa. I performed measurements sensitive to alternately the thermal effusivity \( \Lambda C \) and the thermal diffusivity \( \Lambda / C \), and obtained consistent fits for \( \Lambda \) with the same \( C \) that I derived from Mike Fellinger’s \textit{ab initio} phonon densities of states. The polycrystallinity of the primitive hexagonal Si phase, combined with the beam-offset TDTR technique, allowed me to measure the anisotropy in the thermal transport for hexagonal Si. I found that the metallic Si and Si(Ge) thermal conductivities are predominantly electronic in origin. Thus I applied the Wiedemann-Franz law to derive the associated electrical resistivity, and found it consistent with the Bloch-Grüneisen model.
6.10 Figures

Figure 6.1: **Observed pressure differential between ruby and samples.** The TDTR signals contain normal incidence Brillouin frequency data from the pressure medium, and in my metal-diamond project I calibrated these frequencies in 1 cSt silicone oil against the ruby pressure standard.\(^{37}\) We observed that when the ruby is displaced relatively far from the Si or Si(Ge) sample, the pressure gradient in the quasi-hydrostatic pressure medium caused the ruby and sample pressures to differ significantly. The black solid line is for 1:1 agreement between ruby pressure and the pressure at the sample. The green dashed line marks sample pressures that are 15% higher than the pressure at the ruby, and the green solid lines are ±1 GPa above and below the +15% line. The inset photo shows a view into the DAC sample chamber, when this bare Si piece was on the cusp of the beta-Sn transition. The sample was centered on the 400 micron diameter anvil culet, and the pressures at the sample were consistently ≈ 15% higher than the ruby pressure.
Figure 6.2: **Phonon density of states (DOS) for primitive hexagonal Si at high pressure.** Density functional theory computes the phonon DOS at 15, 27, and 38 GPa. The DOS broadens with pressure, causing an increase in the Debye frequency which is computed from the first frequency moment of the DOS.\(^{172}\) The Debye frequencies shown as vertical lines determine Debye temperatures \(\Theta\) for the Bloch-Grüneisen model of electrical resistivity.
Figure 6.3: **Computed Si and silicone oil heat capacities.** The Si heat capacity (magenta points and interpolation line) used to extract the thermal conductivity $\Lambda$ from my TDTR data is computed using the phonon densities of states from density functional theory (Fig. 6.2). The point at 38 GPa in the mixed-phase (Cmca + hcp) region is computed for the primitive hexagonal structure. By comparing the classical limit $C = 3Nk_B$ for Si (blue lines) to Mike Fellinger’s computation, one sees that most of the change in heat capacity is driven by the change in density. The heat capacity for silicone oil (dashed brown line) is extrapolated on the assumption that the heat capacity per molecule is constant, so that the only pressure dependence is from changes in density.
Figure 6.4: **Si and Si(Ge) interface thermal conductances.** Blue symbols represent data for interfaces between Al and Si with \( \approx 2.2 \text{ nm} \) native oxide, determined by ellipsometry. Open and closed brown symbols are for Au(Pd) / Si and Au(Pd) / Si(Ge) interfaces with \( \approx 2.2 \) and \( \approx 3.1 \text{ nm} \) native oxide, respectively. The Al / Si data showed signs of hot electron transport into the metallic Si substrate, indicating direct metal-metal contact over some fraction of the interfacial surface area. This invalidated my thermal model, so my Al / Si data stops as Si becomes metallic.
Figure 6.5: **Si and Si(Ge) thermal conductivities** $\Lambda$. Panel (a) shows $\Lambda$ extracted from the thermal effusivity versus pressure measured by TDTR on Al- and Au(Pd)-coated samples, and panel (b) shows $\Lambda$ from conventional and beam-offset TDTR on uncoated metallic Si and Si(Ge) samples. In panel (a), the blue squares and triangles are from Al-coated Si, and the brown open and filled circles are from Au(Pd)-coated Si and Si(Ge), respectively. The vertical lines denote phase transition pressures. In panel (b), the cyan and orange triangles are TDTR measurements on bare metallic Si and Si(Ge), respectively. The corresponding pairs of beam-offset measurements for each TDTR point are represented by cyan and orange diamonds. Blue symbols are decompression (decreasing pressure) data from the bare metallic Si sample. The equivalence between Si and Si(Ge) $\Lambda$ in the metallic primitive hexagonal phase suggests that the phonon contribution to $\Lambda$, which I expect to be different in Si versus Si(Ge), is negligible. All of the metallic Si and Si(Ge) thermal conductivities are confined to a band of values, indicating that this hexagonal phase is both polycrystalline and anisotropic in its thermal transport.
Figure 6.6: Wiedemann-Franz derived electrical resistivities. The Wiedemann-Franz law relates the electron-mediated thermal conductivity \( \Lambda_e \) to the electrical resistivity \( \rho \) of a metal according to \( \Lambda_e = L_0 T / \rho \). Here \( T \) is the temperature and \( L_0 \) is the Sommerfeld value of the Lorenz number. I assume that the metallic thermal conductivities presented in Fig. 6.5(b) are equal to \( \Lambda_e \). The resulting electrical resistivity for primitive hexagonal Si is comparable to that of highly conductive metals such as Al and Au, and very similar in magnitude and anisotropy (upper and lower bounds in data) to ambient Be, which is also a hexagonal metal. The symbols are the same as those in Figs. 6.5(b). The magneta dashed lines are upper and lower bound Bloch-Grüneisen models assuming purely anharmonicity-driven pressure dependence \( (d \ln K / d \ln V \equiv \beta = 0) \), and the black solid lines are the same, except \( \beta = 1 \) (Eqns. (1-2)).
Chapter 7

MAGNETIC VERSUS NON-MAGNETIC
POINT DEFECTS IN MIXED CRYSTALS

Some of the experimental data shown in this Chapter were published in two papers, namely:


The first two figures of this Chapter are borrowed from work in the literature, by J. Y. Wong229 and by Speziale et al.,230 respectively.

7.1 Introduction

So far, DAC-TDTR measurements have verified the accuracies of the Liebfried-Schlomann (LS) equation231 for the pressure scaling of the thermal conductivity $\Lambda$ of crystalline water39 and MgO,40 and the minimum thermal conductivity model232 for amorphous PMMA.38 The LS equation and minimum thermal conductivity model predict $\Lambda \propto P^{3/2}$ for crystals and $\Lambda \propto P^{1/2}$ for amorphous solids, respectively. The Klemens model, in the limit of strong point defect scattering, predicts $\Lambda \propto P^1$ for such mixed crystals.233;234 The Debye-Callaway model, which operates on the relaxation time approximation, also predicts a suppressed pressure dependence in $\Lambda$ due to defect scattering.40

Measuring the pressure dependence of a crystal with point defects is as much a test of the assumed form for the point defect relaxation rate $\tau_d^{-1} \propto \Gamma \omega^4$ as it is a test of models that incorporate $\tau_d^{-1}$. The defect scattering strength $\Gamma$ is a function of the differences in mass, bond lengths, and bond
strengths of the defects relative to the atoms they replace. Of these only mass is guaranteed to be independent of pressure.

To study the effect of point defects on the thermal conductivity of crystals, I chose the MgO basis because MgO is well characterized under pressure, and the thermal conductivity of MgO to 60 GPa is known. Also, among crystals with point defects, a system of particular geophysical interest is Mg$_{1-y}$Fe$_y$O ferropericlase. Mg$_{1-y}$Fe$_y$O is expected to exist in significant quantities near the core-mantle boundary of Earth, and its thermal properties under those high pressure and high temperature conditions are important for planetary heat flow models of the Earth. However, the iron atoms present an additional complication: not only can they scatter phonons by mass and bond scattering, but the electronic structure of the iron atoms in the MgO lattice contain an energy level that can resonantly scatter with thermal phonons. This additional complication to the physics makes it desirable to first study a control material without resonant electronic scattering at high pressure, and compare the results to the thermal transport of Fe-doped MgO at high pressure.

The control material that I chose was Zn-doped MgO, and I have been working with Daniel Shoemaker’s group at UIUC to prepare a sample of it. At the present time we are close to having a well-characterized Zn-doped MgO sample for TDTR measurement. Zn is a suitable non-resonant defect because it has high solubility in MgO and a large mass difference relative to Mg. Although ZnO forms a wurtzite (hexagonal) structure instead of the rocksalt (cubic) MgO structure, a pure cubic solution of Zn in MgO can be formed with up to 40% Zn. The lattice parameter of Mg$_{0.6}$Zn$_{0.4}$O in that case was 4.230 angstroms, versus 4.208 for MgO. The differences between Zn-O and Mg-O bonding should be negligible compared to the 270% mass difference. For contrast, while Ca is isoelectronic with Mg, it is only 67% more massive, its ionic radius is 14% larger, and its solubility in MgO is low.

7.2 Resonant scattering in Mg$_{1-y}$Fe$_y$O

Mg$_{1-y}$Fe$_y$O ferropericlase is a crystalline material with substitutional point defects. In addition to phonon-defect scattering by mass, bond length, and bond strength differences between Fe and Mg in the MgO lattice, the Fe
atoms contain electronic energy levels that can resonantly scatter thermal phonons.

The energy levels and spin states of the Fe$^{2+}$ atoms in the MgO lattice are represented in Figs. 7.1 and 7.2. Each Fe$^{2+}$ experiences an octahedral crystal field that splits the valence d-orbitals into two $e_g$ orbitals, oriented toward the oxygen ligands, and three lower energy $t_{2g}$ orbitals, representing the $d_{xy}, d_{yz}, d_{xz}$ orbitals between the Fe-O axes. At low pressure the six d-electrons in Fe$^{2+}$ form a high-spin state according to Hund’s rule, with two unpaired electrons in $e_g$. The fourth electron in the $t_{2g}$ orbitals is free to rotate between them, which causes a weak tetragonal distortion that defines a $z$-axis, also known as spin-orbit coupling or the weak Jahn-Teller effect. The $e_g$ degeneracy is lifted, and the $t_{2g}$ levels also split into $\Gamma_{5g}, \Gamma_{4g}, \Gamma_{3g}$ levels. The $\Gamma_{4g}$ and $\Gamma_{3g}$ levels are nearly degenerate, about 105 cm$^{-1}$ above the $\Gamma_{5g}$ level.\(^{229}\) The thermal conductivity versus temperature of dilute Mg$_{1-y}$Fe$_y$O shows a pronounced suppression in $\Lambda(T)$ near 80 K.\(^{237}\) This was explained as due to resonant scattering of phonons driving the $\Gamma_{5g} \rightarrow \Gamma_{4g}, \Gamma_{3g}$ transitions.

With increasing pressure, the energy scale of the crystal field splitting and spin-orbit coupling will increase (Fig. 7.2). Initially the $\Gamma_{5g} \rightarrow \Gamma_{4g}, \Gamma_{3g}$ energy gap increases, so that it couples to higher frequency phonons. Since higher frequency phonons are less effective heat carriers due to Umklapp and ordinary defect scattering, pressure will reduce the impact of the resonance on the total heat current. Therefore the thermal conductivity of Mg$_{1-x}$Fe$_x$O should increase rapidly with pressure and approach that of Zn-doped MgO, given comparable (non-resonant) defect scattering strengths $\Gamma$.

At sufficiently high pressure, the crystal field splitting of the $e_g$ and $t_{2g}$ levels is high enough to overcome Hund’s rule, and the Fe$^{2+}$ atoms transition to a low spin state with all six electrons paired in the $t_{2g}$ orbitals.\(^{230}\) The transition pressure decreases with decreasing iron content, and begins around 40 GPa for 20% or less Fe.\(^{238}\) Without pairing degeneracy the Jahn-Teller effect is absent, as is the gap between $t_{2g}$ levels that had allowed resonant scattering. In the high pressure low-spin state, the Fe$^{2+}$ is essentially a non-resonant Zn$^{2+}$ that has lost its $e_g$ electrons. The crystal field $t_{2g} \rightarrow e_g$ energy gap is of order 1 eV, far above thermally conductive phonon energies. Mg$_{1-y}$Fe$_y$O in the low-spin state should only exhibit ordinary point-defect scattering.

The expectation for the thermal conductivity of Mg$_{1-y}$Fe$_y$O as a function
of pressure, then, is the following. At low pressure, Mg$_{1-y}$Fe$_y$O should have a lower thermal conductivity than Mg$_{1-x}$Zn$_x$O with a comparable degree of conventional phonon-defect scattering. In some pressure range before the Fe atoms fully transition to their high pressure low-spin state, the thermal conductivity of Mg$_{1-y}$Fe$_y$O should increase more rapidly than expected for a crystal with point defects. In the high pressure limit, the value and pressure scaling of the thermal conductivity of Mg$_{1-y}$Fe$_y$O should be similar to that of a comparable Mg$_{1-x}$Zn$_x$O material.

7.3 Sample preparation

I obtain my [Mg,Fe]O samples from Professor Jung-Fu "Afu" Lin and his student Jill Yang at UT Austin. Professor Lin’s group prepares the samples with 8% Fe by solid state diffusion, and has recently measured the individual elastic moduli of similar samples to high pressures (unpublished as of this writing). Jill Yang provides the samples already polished to about 10-15 microns thickness, I deposit the TDTR transducer, and return the samples to UT Austin for loading in a DAC capable of reaching 70-90 GPa pressures.

For transducer deposition, I use DC magnetron sputtering in a vacuum chamber designed with a graphite heating stage for in-vacuum heat treatment prior to deposition. The graphite stage is heated resistively using a voltage/current source, and the graphite stage temperature is monitored with a pyrometer through a window of the vacuum chamber. The pyrometer collects blackbody radiation, and is inoperative for graphite stage temperatures below about 600°C. The MgO sample in the TDTR study of the thermal conductivity of Al-coated MgO to 60 GPa was heated in this chamber to $\approx 1200$ K, allowed to cool to near room temperature, and sputtered with an Al transducer. This was done to eliminate organic residue and hydroxide on the surface of the MgO, which forms in the presence of water or water vapor and tends to reduce the transducer-MgO interface thermal conductance. In my case, Jung-Fu Lin specified that the [Mg,Fe]O piece was not to be heated near the anneal temperature of MgO, for concern that the Fe$^{2+}$ ions may react or change oxidation states. Instead I heated my [Mg,Fe]O samples to about 300-400°C, estimated from the power output of the voltage/current source that heats the graphite stage. This helped reduce organic residue
from epoxy used in transporting the [Mg,Fe]O samples from UT Austin, but
would probably not have reduced a hydroxide layer. The resulting ambient
interface conductances that I measured for Nb and Pt transducers were in
the range of 150-250 MW m\(^{-2}\) K\(^{-1}\), versus the \(\approx 500\) MW m\(^{-2}\) K\(^{-1}\) interface
conductance achievable from a clean Al / MgO interface.\(^{11}\)

I have experimented with a variety of metal film transducers for this
project. The thermoreflectance coefficient of aluminum decreases rapidly
with pressure,\(^{37}\) so aluminum is not ideal. I tested niobium for its similar
compressibility to that of MgO, but observed irreversible changes in the short
time delay TDTR signal suggestive of a chemical reaction between the nio-
bium and its environment. As such my latest work uses Pt as the transducer,
since it is unreactive and provides a relatively stable thermoreflectance co-
efficient to at least 50 GPa.\(^{37}\) For the first successful experimental run, I
deposited approximately 55 nm of Pt, thinner than the usual 80-100 nm
in order to maximize sensitivity to the interface thermal conductance. The
[Mg,Fe]O sample itself was 14 microns thick, and loaded in the DAC with
mineral oil and ruby spheres for pressure calibration.

7.4 Data collection and analysis: transient
absorption, coherence, and reflectance

In a recent work where I contributed Debye-Callaway-Morelli calculations
for the expected thermal conductivities versus pressure of MgO and MgO
with point defects, the experimental procedure for measuring the thermal
conductivity of MgO to 60 GPa was comparatively straightforward.\(^{40}\) Since
the diamond anvil cell (DAC) has two opposing optical windows (the diamond
anvils), it is possible to pump and probe a sample for a TDTR measurement
from either the front or the back side of the metal film transducer, provided
the sample is transparent. This is true for MgO, and in the preceding study,
the MgO sample was coated with an aluminum transducer and probed from
the back side, at the transducer/MgO interface rather than the pressure
medium / transducer interface. After the metal transducer has thermalized,
usually on the order of 100 ps of time delay, the TDTR signal is typically the
same for front and back side measurements, and the TDTR data analysis is
straightforward.
[Mg,Fe]O ferropericlase is more complex because the Fe atoms have a broad absorption band in the near-IR, overlapping with the wavelength of the Ti:sapphire laser cavity used in our TDTR system.\textsuperscript{239} The absorption band has some temperature dependence, which means that the periodic heating in TDTR would generate not only a thermoreflectance signal from the transducer / [Mg,Fe]O interface, but a transient absorption signal if the TDTR experiment is done through the [Mg,Fe]O. I am not aware of literature data on the temperature dependence of the absorption coefficient of ferropericlase, so I used existing data on a similar mineral, olivine,\textsuperscript{240,241} to estimate that it may be of order $10^{-6} \mu m^{-1} K^{-1}$. For comparison the thermoreflectance coefficients of transducers suitable for TDTR vary from about $5 \times 10^{-4}$ to $10^{-5} K^{-1}$ at ambient pressure.\textsuperscript{148,149} In my experiments on metal-diamond thermal conductance to 50 GPa, I also found that the thermoreflectance of various transducers generally decreased with pressure.

I originally attempted to avoid transient absorption in the [Mg,Fe]O by measuring from the pressure medium side of the DAC-loaded sample. This has the disadvantage of sending the pump and probe beams through multiple high-reflectance interfaces between diamond and air, and diamond and the pressure medium. The reflectance coefficient for a diamond/air interface is about 17%, which suggests that roughly one third of the incident pump and probe light are reflected before reaching the sample, and another third of the TDTR signal is lost on the return trip. Since the [Mg,Fe]O thermal conductivity is of order $10^3 W m^{-1} K^{-1}$, the pump and probe laser powers cannot be arbitrarily raised to increase the signal, or else steady state heating\textsuperscript{32} of the sample will rise above an acceptable range of 0-10% of the ambient temperature.

Although pressure medium side measurements were viable for the Si and Si(Ge) samples of my project on metallic silicon, I found them infeasible for [Mg,Fe]O. Above 10 GPa the TDTR signal decreased rapidly, the $V_{\text{out}}$ component approached zero, and the ratio signal predicted unphysically large thermal conductivities as a result. I am not certain of the cause, but whatever false signal component is entering the TDTR data is probably worse for the fact that the TDTR signal itself was necessarily small. Candidate effects include the temperature derivative of the refractive index of the pressure medium, $dn/dT$, which is large for organic fluids such as the mineral oil pressure medium that I used for my most recent [Mg,Fe]O measurements,
but should be suppressed after the mineral oil solidifies under a few GPa of pressure. Another relates to the microscale geometry of DAC sample chambers under pressure, where the thickness of the pressure medium between a diamond anvil and the Pt-coated sample surface can be less than 5 microns at the highest pressures. That said, I saw no difference in the collected signal when varying the full width half max of the wavelength spectrum of the Ti:sapphire laser output from 30 to 60 nm, so laser coherence near the sample surface does not seem to be important.

Measurements from the back side, however, yielded plausible TDTR data, and so I investigated the contribution of transient absorption (TA) to the total signal I was collecting. Figure 7.3 shows the most prominent signature of TA signal in the collected data as compared to regular TDTR data, which is an enhanced peak near zero time delay in the V(in) signal. I confirmed that this effect was due to TA by directly measuring the TA of an uncoated piece of [Mg,Fe]O of the same Fe concentration and thickness. This was done by loading the sample in a DAC and mounting it for a transmission mode pump-probe measurement in our system, with the same optical layout as for transient absorption from gold nanorods.242 The transient absorption data from a 14 micron thick, 8% Fe piece of [Mg,Fe]O near ambient pressure is shown in Fig. 7.4. By comparing the TDTR and TA data for similar pump and probe laser powers and spot sizes, I reached two conclusions: first, that the V(out) contribution from TA would significantly affect the TDTR + TA total signal that I obtained from Pt-coated [Mg,Fe]O measured from the backside, and second, that the V(in) contribution from TA becomes increasingly negligible relative to the TDTR component after about 100 ps.

Fortunately, TDTR sensitivity calculations versus time delay6 show that, because the interface thermal conductance of my Pt/[Mg,Fe]O sample was sufficiently high, the normalized V(in) signal component had independent sensitivities to both the Pt/[Mg,Fe]O thermal conductance G and the thermal conductivity Λ. I also obtained identical fits to G and Λ at low pressures by fitting either the ratio or V(in) signal components from both front and back sides of the sample. The results of these fits to 70 GPa are presented in the Results section below.
7.5 Transient absorption revisited

For my [Mg,Fe]O samples with 8% Fe, I found that the transient absorption (TA) signal was significant at short time delays and in the V(out) signal component. It is possible to model the TA signal with the TDTR thermal model by considering how an uncoated [Mg,Fe]O sample is heated and cools. The coaligned pump and probe beams pass through and heat the sample with a weak gradient in the beam propagation (cross-plane) direction, due to attenuation by absorption. Over time, the heat diffuses radially around the laser-heated region. According to the literature, the absorption coefficient of [Mg,Fe]O with 12% Fe is $\alpha = (0.75/40)$ microns$^{-1}$ at 785 nm, so for a 15 micron thick sample, $1 - e^{-\alpha \times 15} \approx 25\%$ of the pump and probe light is absorbed by the sample. For a suitably small pump and probe spot size of 2.7 microns, the radial temperature gradient and heat diffusion should dominate.

At this focused spot size, the Rayleigh length is $Z_R = \pi w_0^2 / \lambda \approx 29$ microns, a 15 micron sample is half the Rayleigh length, so the pump and probe spot sizes can be expected to vary by up to 11% through the sample, which can be accounted for. To a first approximation, I can ignore the cross-plane temperature gradient and Rayleigh length, and consider the TA thermal modeling problem as equivalent to that of TDTR modeling for a uniformly heated, thermally thin material where the heat flow is dominated by radial diffusion. The thermal model parameters would then consist of a single, 10 nm layer of [Mg,Fe]O with thermal conductivity $\Lambda = 10$ W m$^{-1}$ K$^{-1}$ and heat capacity $C = 3.37$ J cm$^{-3}$ K$^{-1}$.

One possible problem with this analysis that may require further study is how the adjacent diamond anvil may affect the thermal model. Type 1A diamond anvils typically have thermal conductivities ranging from 500 to 800 W m$^{-1}$ K$^{-1}$, while Type 2A diamonds reach 2400 W m$^{-1}$ K$^{-1}$. The TA signal at negative delay time may be sensitive to heat flow into the diamond on the time scale of the pump modulation frequency. However, there is a counteracting inaccuracy in applying the TDTR thermal model here, which is that the TA signal measures the average temperature rise throughout the 15 microns of sample, rather than the surface temperature that is generated in a conventional TDTR thermal model.

Disregarding these complications for now, Figure 7.5 shows the parametric sensitivity calculation for the TA ratio signal at 12 ns delay time from an
isolated, uniformly heated [Mg,Fe]O layer, as a function of pump modulation frequency. The parametric sensitivity calculation shows a peak sensitivity to $\Lambda$ (actually $\Lambda/C$) for the sample near 1 MHz, which is readily accessible to our TDTR system. Ignoring additional factors in the heat flow, this calculation, along with the adequate signal strength I observed in my preliminary TA measurement, demonstrates that a properly designed TA experiment could measure the thermal transport in [Mg,Fe]O to high pressures in the DAC.

If heat flow into the diamond anvil turns out to be a major concern, it can be suppressed by loading the uncoated [Mg,Fe]O sample with a standard solid pressure medium such as NaCl or KBr, as that would put microns of thermal insulation between the sample and diamond. Even though NaCl and KBr, as crystalline solids, may be expected to have similar thermal conductivities to that of [Mg,Fe]O, the reduction by a factor of 10-100 relative to the thermal conductivity of diamond should improve the relative sensitivity to [Mg,Fe]O. Otherwise, solid amorphous pressure media loading can be investigated, or an attempt can be made to accurately predict the thermal properties of a pressure medium to high pressure, so that the [Mg,Fe]O thermal conductivity can be fitted from the TA data.

7.6 Discussion of preliminary results

The experimental design for measuring the thermal conductivity of [Mg,Fe]O to high pressures using transient absorption from an uncoated sample in transmission mode is still under development. At this time, my results consist of TDTR data to 70 GPa, analyzed as I discussed in Section 7.4 above. The thermal conductivity results are summarized in Fig. 7.6, and the corresponding interface thermal conductances between the Pt transducer and [Mg,Fe]O sample are presented in Fig. 7.7.

In Fig. 7.6, I include for reference some recent high pressure results from thermal diffusivity measurements on 5% and 20% Fe [Mg,Fe]O samples by Manthilake and Koker (filled circles).\textsuperscript{15} I also include (open and filled triangles) thermal conductivity fits to TDTR data that I collected by frontside measurements of Al-coated 10% Fe samples in collaboration with Goncharov at the Carnegie Institute in Washington.\textsuperscript{228} For the 10% Fe samples, we switched from an argon to a 1 cSt silicone oil pressure medium because the
argon thermal conductivity is comparable to that of $[\text{Mg,Fe}]\text{O}$, which introduces systematic error in the thermal modeling. Both of the 10% Fe samples were measured from the pressure medium side, on an Al transducer whose thermoreflectance coefficient approached zero near 30 GPa. Due to this and the vanishing TDTR signal under pressure for frontside measurements from my current Pt-coated, 8% Fe samples, the accuracy of the 10% Fe data is not certain.

My more recent thermal conductivity data from an 8% Fe sample (pluses and crosses in Fig. 7.6), using a mineral oil pressure medium, is still preliminary for a number of reasons. The jump in thermal conductivity near 20 GPa is suspect because it occurred at the finish and start of two TDTR measurement sessions, and I do not have a strong theory for why it should have that trend at low pressure. One possibility is that the frequency of the Fe spin state resonance with thermal phonons moves away from that of the dominant heat carrying phonons near this pressure. At higher pressures, I do see a greater pressure dependence from 40-60 GPa than in the 60-70 GPa range, consistent with my expectations for the high- to low-spin state transition of the Fe atoms. Future measurements of $[\text{Mg,Fe}]\text{O}$ samples, controlling for factors such as the Pt transducer thickness and $[\text{Mg,Fe}]\text{O}$ thickness, are desirable to check the validity of the data against concerns about the Pt reflectance being affected by the pressure medium and transient absorption, respectively.

The thermal conductance data starts lower than might be expected for an ideal Pt/$[\text{Mg,Fe}]\text{O}$ interface because I did not heat the $[\text{Mg,Fe}]\text{O}$ sample to a very high temperature before depositing Pt, as the oxidation state of the Fe impurities may be sensitive to temperature. The theoretical maximum conductance $G(\text{max})^{11}$ is a quantity that provides a heuristic for the "ideal", stiffly bonded interfacial thermal conductance of Pt. In short, the conductance of a clean Pt interface should be roughly 1/2 to 2/3 of $G(\text{max})$. Using literature calculations for Pt material properties$^{168}$, one can estimate that $G(\text{max})$ varies from 900 to 1300 MW m$^{-2}$ K$^{-1}$ from 0 to 60 GPa, so the Pt/$[\text{Mg,Fe}]\text{O}$ conductance could reasonably have an upper limit of 600-800 MW m$^{-2}$ K$^{-1}$ from ambient to high pressures. This is consistent with the results in Fig. 7.7.

I collected data for decreasing pressure from my Pt/$[\text{Mg,Fe}]\text{O}$ sample starting at 45 GPa; above 45 GPa, I was unable to get an accurate pressure reading.
from the rubies, all of which had been bridged and uniaxially stressed by the diamond anvils at the maximum recorded pressure. However, for reasons yet to be determined, the thermal conductivity was not entirely reversible in this range. The interface thermal conductance was also not reversible, returning to a value near \(300 \text{ MW m}^{-2} \text{ K}^{-1}\), but this was to be expected given the less than ideally clean surface condition of the [Mg,Fe]O sample prior to Pt sputtering, and the results of my metal-diamond project. I have chosen not to include the decompression data in this thesis because of the questionable nature of the non-reversible apparent thermal conductivity, however. More TDTR and transient absorption measurements are needed to confirm my preliminary results described here.

7.7 Figures
Figure 7.1: Cubic crystal field and spin-orbit splittings of the Fe\textsuperscript{2+} orbitals in [Mg,Fe]O. This figure, taken from a 1968 experimental study,\textsuperscript{229} sketches the electronic energy states for the Fe\textsuperscript{2+} atom in the MgO crystal structure. The free ion d-orbitals (5d) are altered by the cubic crystal field of the lattice (\(5T_2\)), and split by the Jahn-Teller effect due to 4 electrons occupying the 3 t2g states (see Fig. 7.2). Second-order spin-orbit coupling further defines the \(\Gamma_{4g}\), \(\Gamma_{3g}\), and \(\Gamma_{5g}\) states. In this figure the 200 cm\(^{-1}\) energy spacing is marked with a question mark because this work established, by far-infrared spectroscopy, that the spacing was actually 105 cm\(^{-1}\), or about 3.3 THz. It is this transition that provides a resonant scattering mechanism for heat-carrying phonons in [Mg,Fe]O.
Figure 7.2: **High-spin to low-spin electronic transition in [Mg,Fe]O at high pressure.** This figure is taken from Speziale et al.’s 2005 work, studying the iron spin transition in Earth’s mantle. At low pressure, two electrons occupy the $e_g$ orbitals of the Fe$^{2+}$ ion in the [Mg,Fe]O lattice because unpaired electronic states are energetically favorable (Hunds rule). With increasing pressure the $e_g$ orbital energy levels increase until their occupancy is no longer favorable, at which point the two electrons collapse to fill the $t_{2g}$ orbitals with paired electronic states. This eliminates the degeneracy that gave rise to the Jahn-Teller spin-orbit splitting of the $t_{2g}$ levels in Fig. 7.1, which removes the resonant scattering mechanism for heat-carrying phonons in [Mg,Fe]O.
Figure 7.3: Influence of transient absorption component on TDTR signal for backside TDTR measurement of Pt / Mg\textsubscript{0.92}Fe\textsubscript{0.08}O. The y-axis represents signal magnitude normalized by the pump power and photodiode voltage on the detection circuit; the latter quantity accounts for optical losses of the probe beam through the experimental system. Green square data is a (scaled to 1) reference diamond / Pt TDTR V(in) signal from my metal-diamond project at a similar pressure and a different laser spot size. Subtracting half the scaled TA signal from the TDTR signal (red circles) is enough for the Pt / Mg\textsubscript{0.92}Fe\textsubscript{0.08}O V(in) signal to qualitatively match the diamond / Pt reference V(in) signal. The V(out) component (blue circles) is from Pt / Mg\textsubscript{0.92}Fe\textsubscript{0.08}O measurement, with red offsetting lines showing the effect of adding or subtracting 1/2 the V(out) component of the normalized TA signal.
Figure 7.4: **Comparison of raw V(in) signals for transient absorption and backside TDTR on Mg$_{0.92}$Fe$_{0.08}$O samples.** The transient absorption (TA) signal was taken from an uncoated, 14 micron thick piece of Mg$_{0.92}$Fe$_{0.08}$O loaded in my DAC at low pressure, and the TDTR signal was collected at a similar pressure from the Pt / Mg$_{0.92}$Fe$_{0.08}$O backside interface of the Pt-coated sample in another DAC. Both measurements were taken at the same pump modulation frequency and laser spot size, on the same system, with similar pump and probe powers, although the TA signal was collected in transmission mode and the other in reflection mode. Because the TA V(in) signal decreases more rapidly over time delay, accounting for a TA component in the TDTR signal as in Fig. 7.3 has a negligible effect on the TDTR V(in) signal.
Figure 7.5: Sensitivities versus pump modulation frequency for simplified [Mg,Fe]O transient absorption thermal model. The simplified transient absorption (TA) thermal model is generated from the TDTR thermal model for a 10 nm thick, isolated [Mg,Fe]O model layer with adiabatic cross-plane boundary conditions. The thermal conductivity is $10 \text{ W m}^{-1} \text{ K}^{-1}$, the heat capacity is $3.37 \text{ J cm}^{-3} \text{ K}^{-1}$, and the laser spot size is 2.7 microns. The sensitivity of the ratio signal at 12 ns delay time (equivalent to negative delay time) to variations in the [Mg,Fe]O thermal conductivity (L1) and spot size (w0) is maximal near 1 MHz modulation frequency, which corresponds to a radial thermal penetration depth of approximately 1 micron.
Figure 7.6: Preliminary TDTR thermal conductivities for Pt-coated Mg$_{0.92}$Fe$_{0.08}$O to 70 GPa. For reference, I include some recent high pressure results from thermal diffusivity measurements on 5% and 20% Fe [Mg,Fe]O samples by Manthilake and Koker (filled circles). I also include (open and filled triangles) thermal conductivity fits to TDTR data that I collected by frontside measurements of Al-coated 10% Fe samples in collaboration with Goncharov at the Carnegie Institute in Washington. The crosses and pluses represent ratio and in-phase TDTR fits to my most recent TDTR data from Pt-coated, 8% Fe samples, respectively. The colors of the crosses and pluses indicate different TDTR measurement sessions spaced over a few weeks, on the same sample without decompression. The ratio-fitted data points above 60 GPa (pink X’s) are not valid, and are included to demonstrate how fitting by V(in) (the corresponding dark green plus symbols) avoids signal contamination from transient absorption at high pressures where the Pt thermoreflectance coefficient is lower. 9.1 MHz refers to the TDTR pump modulation frequency of the 8% Fe measurements.
Figure 7.7: Preliminary TDTR interface thermal conductances between Pt and Mg$_{0.92}$Fe$_{0.08}$O to 70 GPa. For reference, my conductance data is compared against the Al / MgO interface conductances previously obtained by TDTR on our group’s system. The sensitivity of the TDTR measurement to the Pt / Mg$_{0.92}$Fe$_{0.08}$O thermal conductance is low at high pressures because the conductances were large. The low starting value and steeper rate of increase in conductance with pressure for Pt / Mg$_{0.92}$Fe$_{0.08}$O versus Al / MgO is most likely due to weaker initial interfacial bonding, as the Mg$_{0.92}$Fe$_{0.08}$O surface could not be heat-cleaned at as high a temperature as the MgO sample prior to transducer sputtering.
8.1 Summary

The MHz-scale heating frequency of time-domain thermoreflectance (TDTR) creates nanoscale temperature gradients in most materials, and these gradients can be used to probe nanoscale heat transport dynamics. I used TDTR to make temperature-dependent measurements of the effective, volumetric magnon-phonon coupling rate in the spin-ladder cuprate \( \text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41} \). I have found this rate to be much larger than previously reported,\(^9\) but still two orders of magnitude weaker at room temperature than electron-phonon coupling in typical metals. The magnon-phonon coupling has a strong dependence on temperature, owing to the fact that a band gap separates the triplet magnon states from the singlet ground state, so the magnons are frozen out below about 50 K. The total resistive magnon scattering rate is estimated to be a factor of 10 greater than the magnon-phonon thermal relaxation rate. This suggests that inelastic magnon-phonon scattering, which determines the magnon-phonon thermal relaxation rate, is not the dominant resistive scattering process for magnons in \( \text{Ca}_9\text{La}_5\text{Cu}_{24}\text{O}_{41} \).

I began my high pressure research program by studying metal-diamond interface thermal conductances as a function of pressure to 50 GPa. I experimentally showed that the metal-diamond interface conductances for Al, Pt, Au(Pd), and Pb increase weakly or saturate at high pressures, that the conductances of Pt, Au(Pd), and Pb on diamond are all of similar magnitude at high pressure, and that there is no resolvable distinction in the high pressure conductances for Type 1A [100] versus Type 2A [110] diamond. I found that compression above 30 GPa irreversibly stiffens weak interfacial bonding, such that the decompressed metal-diamond conductances are near their corresponding "clean interface" zero-pressure values, \( \approx 60 \text{ MW m}^{-2} \text{ K} \).
for Pb/diamond. The similarity in thermal conductances for Pt and Au(Pd) to high pressure, despite the major differences in their electronic band structures, is difficult to reconcile with existing models of electron-phonon conductance across metal-dielectric interfaces, i.e., a contribution to the conductance generated by the coupling of electrons in the metal with phonons in diamond that enhances thermal transport across the interface. For metals with low phonon cutoff frequencies, the extra conductance above the one-phonon radiation limit is likely controlled by partial transmission three-phonon processes, where reflecting diamond phonons emit or absorb a fraction of their energy as a metal phonon. My calculations indicate that the extra conductance can be accounted for by partial transmission processes with a diamond phonon participation rate near 10%, or alternately, with an interfacial scattering rate about five times faster than the three-phonon scattering rate in bulk diamond at ambient pressure.

My next project dealt with metallic silicon at high pressure. I performed regular and beam-offset TDTR to establish the thermal conductivities of Si and Si$_{0.991}$Ge$_{0.009}$ across the semiconductor-metal phase transition and up to 45 GPa. The thermal conductivities of metallic Si and Si(Ge) are comparable to aluminum and indicative of predominantly electronic heat carriers. Metallic Si and Si(Ge) have an anisotropy of approximately 1.4, similar to that of beryllium, due to the primitive hexagonal crystal structure. I used the Wiedemann-Franz law to derive the associated electrical resistivity, and found it consistent with the Bloch-Grüneisen model.

My fourth major project seeks out new information about how point defects scatter phonons in crystals by measuring of the thermal conductivity of mixed crystals as a function of pressure, rather than temperature. Not all crystalline point defects are alike in how they scatter phonons, however. Heat-carrying phonons in iron (Fe) doped MgO, or [Mg,Fe]O ferropericlase, are known to be resonantly scattered by interaction with a 3.3 THz electronic transition in the high-spin state of the Fe impurities. At sufficiently high pressures, the Fe atoms transition from a high-spin to a low-spin state, which eliminates the resonant interaction and reduces the Fe atoms to simpler point defect phonon scatterers. To study the behavior of phonon-defect scattering with and without this resonant scattering process, I measured the thermal conductivity of Mg$_{0.92}$Fe$_{0.08}$O ferropericlase up to and above the 40-60 GPa spin transition. Fe-doped MgO (ferropericlase) is also a model
system relevant to geophysical modeling of the Earth’s core-mantle boundary, so data on its thermal transport under pressure is valuable in itself.

8.2 Next steps

The two-temperature model that I used to study magnon-phonon coupling in Ca$_9$La$_5$Cu$_{24}$O$_{41}$ is applicable to a variety of other cuprate materials with significant heat transport by magnetic excitations. Ongoing research in the Cahill group is exploring magnetic heat transport and in materials with different magnetic geometries, including transport in materials with 2-dimensional Cu-O crystalline planes and 1-dimensional spin chain structures.

One aspect of my metal-diamond project for which I do not have a satisfying explanation is the details of interface thermal conductance when the two materials are not so dissimilar in their phonon densities of states, specifically Al on diamond at high pressure. I can say that the Al / diamond thermal conductance is not larger than its radiation limit at high pressure, indicating that predominantly elastic phonon transport can in theory explain the conductance. However, the consistency with which the more dissimilar interfaces have an $\approx 100$ MW m$^{-2}$ K$^{-1}$ component above their radiation limits, despite some variation in their maximum phonon frequencies, suggests to me that this inelastic channel may also contribute to the Al / diamond case, if only to a lesser degree. But I do not have an explanation for why, specifically, the Al / diamond interface conductance appears to saturate at high pressures, and the small thermoreflectance of Al at these pressures makes extending this data set to higher pressure problematic. It may be informative to measure a similarly high phonon frequency metal such as molybdenum on diamond, which may retain its thermoreflectance signal to higher pressures. It would also be interesting to study a wider variety of interfaces under pressure, with varying degrees of similarity in the materials’ phonon densities of states.

Along that vein, the original intent of the metallic silicon project was not so much to measure the thermal transport of a metal under pressure, but to determine what happens to interfacial heat transport by phonons when the substrate becomes metallic, but there is still no direct metal-metal contact between the transducer and substrate. An outstanding curiosity of thermal transport physics is the narrow range within which phonon-mediate interface
thermal conductance values fall; one can almost blindly predict, for any two materials, a value of $\approx 100 \text{ MW m}^{-2} \text{ K}^{-1}$ for a modestly well-bonded interface and be correct to within a factor of two. For clean interfaces, a factor of $1/3$ to $1/2$ reduction from the theoretical maximum interface conductance of the lower phonon frequency material, $G(\text{max})$,\textsuperscript{11} appears to be a fairly accurate heuristic, but the mechanisms that lead to this are far from understood. A high pressure study of interface thermal conductance across a simple non-metal to metallic phase transition, without the interfacial complication of a large volume change as in silicon, should provide new information on this front.

The high pressure study of point defects with and without Fe$^{2+}$ spin state scattering is ongoing, and promises to strengthen the thermal physics foundation on which the geophysical community builds its planetary heat transport models for deep Earth, high pressure / high temperature conditions. The control experiment with Zn-doped MgO is still in preparation, and the idea of measuring heat transport by transient absorption in Fe-bearing minerals, if viable, is promising as a simpler, more practical way to study heat transport at simultaneous high pressure, high temperature conditions than TDTR may be, considering that transient absorption does not rely on a potentially reactive metal film transducer for its signal. More work needs to be done on the thermal modeling, experimental design, and proof of concept for this technique.
Chapter 9

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