High Temperature And Pressure Resonant Ultrasound Spectroscopy Study Of Metal Hydride Systems

Rasheed Adebisi

University of Mississippi

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HIGH TEMPERATURE AND PRESSURE RESONANT ULTRASOUND SPECTROSCOPY STUDY OF METAL HYDRIDE SYSTEMS

by

Rasheed Adebisi

A Dissertation Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy
Department of Physics
University of Mississippi
University, MS 38677

December, 2011
ABSTRACT

The goal of this dissertation is to characterize the elastic properties of palladium hydride near the tri-critical point as a classic example of metal hydride systems using the resonant ultrasound spectroscopy. A high temperature and high pressure resonant ultrasound spectroscopy system which include the RUS cell and the direct contact transducer set-up was designed and constructed. The temperature and pressure dependent of elastic moduli of palladium hydride and palladium crystals were obtained at five isotherms near the critical temperature, 293°C and for pressure range of 250 – 500 psi. A strong softening of the shear modulus was observed at temperature and pressure points around the critical points, 293°C and 290 psi respectively. On the other hand, anomalous softening of the bulk modulus and the $C'$ was observed in the same temperature and pressure region. The investigations includes study of the equilibrium dynamics of hydrogen absorption/desorption in metal hydrides. A color map of the equilibrium dynamics pattern was developed and correlation between the color map and the palladium hydride phases was established.
ACKNOWLEDGMENTS

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Blank.
CHAPTER 1

INTRODUCTION

1.1 Importance of Elasticity Measurements

In the study of deformable materials, macroscopic approaches where the body is
treated as a solid continuous medium are employed. The elastic properties of solid materi-
als determine how the material deforms (strain) when it is subjected to an applied stress.
Within the limit of linear elastic theory, stress and strain are related by the elastic constants
of a solid material [1–5]. Elastic constants are tensor quantities that characterize the elastic
properties of solid materials. When a material is deformed, there is a change in the internal
energy and interatomic spacing between atoms of the material. Elastic constants are funda-
mentally a measure of the interatomic forces that bind the atoms of the material together.
Figure 1.1 shows a simple Lennard–Jones type plot of interatomic potential versus the in-
teratomic spacing. The elastic constant is related to the curvature of the potential around
the equilibrium spacing \( r_0 \). The sharper the curvature, the larger the elastic constants. The
measurement of elastic constants are therefore a useful tool for investigating the interatomic
potentials.

The response of materials to stress is of fundamental interest in engineering and
condensed matter physics. The elastic constants are second derivatives of the energy with
respect to strain. Elastic constants are important parameters in equations of state, lattice
Figure 1.1: Example of a simple interatomic potential. The equilibrium spacing is $r_0$ and the curvature at $r_0$ determines the elastic constants. The gradient of potential at $r$ is proportional to the restoring force toward the equilibrium spacing ($r_0$).

dynamics and phonon spectra. So, they are essential in the study of thermodynamics of a solid. Quantitative connections between thermodynamic properties of a solid such as specific heat capacity at constant volume, coefficient of thermal expansion and isothermal compressibility can be made if the elastic constants are known as functions of temperature and pressure. Elastic constants also manifest themselves in the macroscopic properties of materials such as the speed of sound in the material. They are of interest to engineers and materials scientists as well as to researchers in many areas of fundamental and applied physics.

Atoms in a solid always seek configurations (states) that yield minimum potential energy of the system. At such states the atoms will oscillate about equilibrium positions. When the temperature and (or) pressure on the material changes, the mean interatomic spacing will also change. Consequently, the interatomic potential potential curvature will
change and so do the elastic properties of the material. In crystals, temperature and (or) pressure change may induce structural, magnetic and electric phase transitions, as often indicated by small changes in the trends of elastic constant data or the elastic constants themselves. Elastic constants are sensitive probes for studying various phase transitions, particularly structural phase transitions. The temperature and (or) pressure trends of the elastic constant data can be obtained precisely by measuring elastic constants at various temperatures and pressures over a range of interest.

Several experimental techniques have been devised to measure the elastic properties of solid materials. Some of these methods are non-acoustic methods such as static loads with strain gauges, Brillouin scattering and inelastic neutron scattering. Others are acoustic methods such as surface acoustic waves, vibrating reed, torsional pendulum and ultrasonic techniques. The ultrasonic techniques have proved to be one of the most convenient and accurate methods for measuring elastic constants in isotropic and anisotropic materials. Ultrasonically, an elastic constant can be measured in two ways: one uses the theory of elasticity, which proved that elastic constants of a material can be determined by measuring the sound velocity in the material; the other uses the free-vibration frequencies, which depend on the sample’s dimensions, density and elastic constants. Hence, ultrasonic measurements are useful tools in condensed matter physics.

The pulse-echo method is the most commonly used method of measuring the speed of sound in isotropic and anisotropic materials. In the pulse-echo method, good acoustic coupling between the sample and transducer is required. To obtain all the elastic constants of a crystal, the same sample has to be repeatedly cut along different principal axes of
the crystal lattice and bonded to the transducer, or multiple samples are needed. This is labor intensive, especially for low-symmetry crystals. The lack of stable couplants prevents the pulse-echo method from being a suitable method for elastic constant measurements at high temperatures. The accuracy of pulse-echo ultrasonic method is not very high. This is because the process of measuring the time of flight of the ultrasonic pulse in the material is error prone, especially in small samples. The resonance ultrasound spectroscopy (RUS) is a resonance method that does not require the use of a coupling agent between transducer and sample. Unlike the pulse-echo method, RUS uses the free vibration natural frequencies of a sample to measure all the elastic constants in one measurement.

1.2 Resonant Ultrasound Spectroscopy

Resonant ultrasound spectroscopy is an experimental method that measures the mechanical resonances of solids and uses the resonance frequencies to extract the complete set of elastic constants of a solid material. An elastic body, under free-boundary conditions, when excited will resonate at its natural frequencies. The frequencies are called resonance frequencies and their values depend on the dimensions of the body, its density and its elastic constants.

The full elastic tensor and relative changes in acoustic attenuation of a material can be obtained in a single frequency sweep. In a RUS measurement a properly prepared sample, usually a regular parallelepiped, is placed between two transducers, where one drives the sample with a continuous sinusoidal stress which is generated with an acoustic synthesizer and the other picks up the response from the sample. The response is then transmitted
to a lock-in amplifier. The block diagram of a typical RUS set up is shown in Figure 1.2.

When the drive frequency equals a natural frequency of the sample, the sample’s surface
displacement amplitude increases, and the amount of increase depends on the quality factor
of the resonance. The quality factor \( Q = \frac{f_0}{\Delta f} \), where \( \Delta f \) is the frequency width at half
magnitude) is proportional to the inverse of the acoustic attenuation in the material.

Figure 1.2: The block diagram of RUS measurement

The sample peaks in the frequency domain are fit with a Lorentzian line shape to
extract the center frequencies and the quality factor. A complete measured vibrational
spectrum includes an ordered list of these center frequencies. The measured spectrum is then
used together with the sample’s measured density, dimensions and guessed initial values of
the elastic constants to do a fit with a nonlinear fitting scheme that compares the calculated spectrum, adjusted in a least square sense, to the measured spectrum. This is called the “inverse” problem; it is used to infer elastic constants from measured frequencies. The solution to the inverse problem relies on solving the “forward” problem first, which involve computing the normal modes of vibration and natural frequencies from known characteristics of an elastic body. The lack of exact solutions to the problem of the free vibrations of an elastic body of general shape and crystallographic symmetry limited the use of resonance technique to just few cases. The technique was largely confined to large–sized samples with regular geometrical shape such as spheres that has known analytical solutions of the forward problem [6, 7]. This is because the calculations involved in using approximation methods are tedious without computers. So, RUS only become a widely used method for elasticity measurements after modern powerful personal computers became very accessible and commonly owned devices.

Since the early 1990s, resonant ultrasound spectroscopy has stood out from the conventional ultrasonic methods due to efficiency, accuracy, and ability to handle mm-sized or even smaller samples [8] and low symmetry crystals well [9–12]. The RUS code treats a variety of sample geometries but rectangular parallelepipeds remain the most common and convenient geometry with which to work.

RUS has found applications in many fields. Materials scientists are interested in the mechanical properties of their newly developed and modified materials. When new kinds of materials are fabricated, their best grown crystals are often in small quantities and typical sizes of few hundred microns. RUS measures samples of such sizes easily [8, 13]. The use
of small samples of a material is more likely to guarantee the homogeneity of the material. In recent years, a great deal of attention has been placed on thin film materials and the knowledge of the elastic properties of such thin films is required in some applications. RUS has been used successfully to measure the elastic properties of thin film materials [13–15]. With a proper configuration a single measurement yields enough frequencies to determine all the elastic constants of the material. As many as 21 elastic constants of a triclinic crystal can be determined. However, the RUS code becomes unstable if the samples have more than 9 independent elastic constants. Practically, RUS is used to measure crystals of orthorhombic (9 independent elastic constants) or better symmetry. RUS is an extremely precise method of determining elastic constants of crystalline and non-crystalline materials. The results from RUS measurements can serve as references for other methods.

1.3 Metal Hydride Systems

The search for alternative sources of energy storage and distribution systems that will be environmentally friendly has been the moving force behind research into clean energy systems such as hydrogen gas, thus creating need for light and safe hydrogen storage media. One attractive possibility is the storage of hydrogen in low-density metal hydrides. Many of the rare–earth and transition metals readily absorb hydrogen, which occupies interstitial sites in the host lattice. The absorption of hydrogen is always associated with an expansion of the lattice and this will affect the elastic constants of the metals. Most desirable applications of metal hydrides require hydrogen storage to be reversible over many charging and discharging cycles. So understanding the absorption and desorption kinetics of hydrogen will help in the
design of hydrogen storage systems. In addition, the adsorption or desorption of hydrogen is a time consuming process [16]. The time scale may be reduced with the aid of an acoustic resonance of the sample.

Metal hydrides exhibit phases [17,18] which are classified based on the concentration and organization of hydrogen atoms in the metal. The fundamental thermodynamics of incorporating hydrogen atoms into a metallic lattice is also an interesting and active area of research that will help in understanding the phase behaviors of the material. The hydrogen gas molecule upon entering into the metal lattice dissociates into a pair of hydrogen atoms. Each hydrogen atom then can hop from site to site in the interstitial sites of the lattice. Phase diagrams play a very important role in materials science. They are “maps” of regions in which certain phases or phase mixtures exist. These diagrams represent fundamental thermodynamic characteristics of interacting particles. Beyond this, phase diagrams provide basic information that are essential for the preparation of samples, for applications of the material and for the correct interpretation of results of experiments on the material. Presently, the phase boundaries in the pressure–composition–isotherm phase diagrams are determined by taking the limiting values of the plateaus of each isotherm in temperature-composition plots with the pressure on a logarithmic scale. This is not very exact. Elastic constant data may provide more precise phase boundaries. Another common feature of metal hydride phase diagrams is the presence of hysteresis between the absorption and desorption parts of the cycle for each isotherm in the mixed phase regions [19].
1.4 Apparatus for High Temperature and High Pressure RUS Measurements

RUS has been used for room and low temperature measurements on a wide variety of materials. However, its applications in the high temperature regime have been limited [20,21], on one hand due to the weak resonance of the samples at high temperature and on the other hand due to design difficulties. Traditionally, high temperature RUS methods are made possible by separating the sample in the high temperature environment and the two transducers with buffer rods made of low acoustic attenuation materials with good thermal stability. In the buffer–rod system, the transmission of the acoustic signal through the buffer rods further reduces the signal. In addition to this, the buffer–rod resonances are likely to overlap the sample resonances in the frequency range, making the identification of sample resonances more difficult. Most of the high temperature applications are in geophysical studies of the earth. Geophysicists are interested in the elastic behavior of constituent phases in Earth’s mantle at temperatures beyond their Debye temperatures. The high temperature data of geophysically important minerals are needed for studying the thermal equation of state, the structure and composition in the Earth’s interior.

In order to improve the output signal strength and eliminate the unwanted buffer–rod resonances, a high temperature transducer system in which the sample is in direct contact with the two transducers has been developed. In this system, the resonances from piezoelectric element and transducer assembly are kept out of the range of interest. The system has been used to successfully perform RUS measurements up to 600°C. The measurement of elasticity of a solid as a function of temperature has been a useful technique for studying temperature–induced phase transitions. RUS is complementary to other conventional tech-
niques such as x–ray and neutron techniques for phase transition studies. The application of RUS as phase transition tools has been reported in the literature [14,22–25]. The addition of the pressure parameter as another “knob” that can be turned in a RUS system will extend the range of the technique to the studies of materials with phase transitions that can either be temperature–induced, pressure–induced or a combination of both.

The goals of my dissertation are to develop a high temperature and high pressure resonant ultrasound spectroscopy system and to use the system to study metal hydrides and other solids at high temperature and high pressure. The investigations include temperature and pressure dependent elastic constant measurements, and the equilibrium dynamics of hydrogen absorption/desorption in metal hydrides.

1.5 Outline of Dissertation

Chapter 2 presents some theoretical background of the RUS method. The chapter starts with the linear elasticity theory since the deformation of the samples is well within the linear elastic region. This is followed by a brief description of the RUS technique and its comparison with other techniques used to determine the elastic constants of materials. The processes involved in the RUS method are explained in detail; this includes (i) the “forward” and “inverse” problems, (ii) extraction of the resonance frequencies using the Lorentzian fitting scheme, (iii) estimation of the elastic constants using an iterative process to obtain the best match with calculated frequencies, (iv) error minimization done using the Levenberg–Marquardt (LM) method. Some issues in the inverse calculations are discussed as well.

In Chapter 3, the high temperature and high pressure RUS measurement set–up and
procedure is reported. The technical difficulties in a high temperature and high pressure RUS measurement were first discussed. This is followed by the design and fabrication (including the materials selection and the assembling) of the high temperature direct contact transducer system in which the piezoelectric elements are in direct contact with the sample. This eliminates the use of buffer-rod which is traditional in a high temperature RUS measurement but often accompanied by relatively poor signal to noise ratio. The next section describes the design and construction of the high temperature and high pressure RUS cell thoroughly. The rest of the chapter enumerates the experimental method starting with the sample preparation, experimental procedures, data acquisition and signal processing.

In Chapter 4, a brief background on metal hydride is discussed. The chapter starts with an introduction into metal hydride systems and the driving force behind the investigations of these materials. It then focuses on the palladium hydride system as a classic example of the metal hydride. A brief description of the historical development of the thermodynamics of metal hydrides is included. Lastly, the new model proposed by Schwarz and Khachaturyan is explained in some detail.

Chapter 5 presents the elastic constants of palladium hydride. The chapter starts with an introduction into the elastic properties of palladium and palladium hydride and sets the objectives of the current measurements. This is followed by a detailed description of the experimental runs and the adopted experimental procedures. The results and their discussion are presented, and close attention is paid to the anomalous softening of the elastic moduli of palladium hydride near the tri-critical point. Similar results are presented for the palladium crystal at high temperature. Finally, the observation of the equilibrium dynamics
of palladium hydride near the tri-critical point is discussed.
A brief review of some of the concepts of linear theory of elasticity will provide the necessary background for a discussion of the measurement of elastic properties. The theory has been treated in detail in many classical textbooks [1–5]. Imagine a stretched spring in which marked points are at \( x \) and subsequently at a separation of \( dx \), if the stretching force is a uniform force and let the mark on the spring be displaced according to some function \( \psi(x) \). The amount of stretching

\[
\frac{\psi(x + dx) - \psi(x)}{dx}
\]

can be estimated by considering the change in separation of any two neighboring points. The strain \( \varepsilon \) is defined as the fractional amount of stretch, hence

\[
\varepsilon \equiv \frac{\psi(x + dx) - \psi(x)}{dx} = \frac{d\psi}{dx}
\] (2.1)

Suppose instead of a spring, an elastic solid is deformed, using the indices \( i, j = 1, 2, 3 \) for the directions. The deformation \( \frac{d\psi}{dx_i} \) is a second-rank tensor that can be separated, uniquely,
into a symmetric and an antisymmetric component.

\[
\frac{d\psi_i}{dx_j} = \frac{1}{2} \left( \frac{\partial \psi_i}{\partial x_j} + \frac{\partial \psi_j}{\partial x_i} \right) + \frac{1}{2} \left( \frac{\partial \psi_i}{\partial x_j} - \frac{\partial \psi_j}{\partial x_i} \right) = \varepsilon_{ij} + \Theta_{ij} \tag{2.2}
\]

The antisymmetric tensor, \( \Theta_{ij} \), corresponds to the local rigid rotation of the medium and cannot produce a true internal deformation. So, \( \Theta_{ij} \) does not represent an elastic distortion. The true internal deformation of the elastic continuum thus arises only from the symmetric tensor \( \varepsilon_{ij} \) and we therefore define the elastic strain tensor as

\[
\varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial \psi_i}{\partial x_j} + \frac{\partial \psi_j}{\partial x_i} \right) \tag{2.4}
\]

It is assumed that the strains are small so that second–order terms may be neglected. The strain tensor defines the distortion produced in the body by the applied forces. Note that

\[
\varepsilon_{ij} = \varepsilon_{ji} \tag{2.5}
\]

The forces applied to any surface element of the solid can be written as

\[
f_i = \sum_{j=1}^{3} \sigma_{ij} dS_j \tag{2.6}
\]

Henceforth we will be using the Einstein notation where summation over repeated indices is understood. The stress tensor, \( \sigma_{ij} \), has units of force per unit area and is defined so
Figure 2.1: Components of stress tensor acting on a small element. For a stress component \( \sigma_{ij} \), the first index \( i \) indicates the plane that the stress acts on, and the second index \( j \) denotes the direction in which the stress acts.

that the first index indicates the plane on which it acts and the second index indicates its direction. \( dS_j \) is the element of surface area on which the force is applied. Figure 2.1 shows the components of the stress tensor acting on a small element of the solid. For a solid in static equilibrium, the net torque acting upon the body is zero, requiring the stress tensor to be symmetric, hence

\[
\sigma_{ij} = \sigma_{ji} \quad (2.7)
\]

For small deformations, the stress and the strain are related by Hooke’s law. So for a general solid, Hooke’s law becomes

\[
\sigma_{ij} = c_{ijkl} \varepsilon_{kl} \quad (2.8)
\]

where \( c_{ijkl} \) are components of the elastic stiffness tensor or elastic constants. The elastic constants \( c_{ijkl} \) are defined as the ratio of an applied stress on the \( i \)-plane along the \( j \)-direction over the resulting strain on the \( k \)-plane along the \( l \)-direction. The elastic stiffness tensor is an \( 3^4 \)-component tensor. Due to symmetries of the stress and the strain, there are only six
independent components of stress and six independent components of strain. This reduces
the number of independent components of $c_{ijkl}$ to 36. The requirement of positive potential
energy reduces the elastic stiffness tensor to 21 independent elements. It is common practice
to use the reduced index notation to write the $4^{th}$ rank tensor $c_{ijkl}$ as a $2^{nd}$ rank $6 \times 6$ matrix $c_{ij}$. In the literature, the elastic constants are often written in the reduced index form. Voigt
notation is the standard mapping for tensor indexes, $i, j$

$11 \rightarrow 1 \quad 23 \rightarrow 4$
$22 \rightarrow 2 \quad 13 \rightarrow 5$
$33 \rightarrow 3 \quad 12 \rightarrow 6$

For example $c_{1122} = c_{12}, c_{2323} = c_{44}$ With this simplified notation, the elasticity matrix can
be written as

$$c_{ijkl} \Rightarrow C_{ij} = \begin{bmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\
C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\
C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\
C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66}
\end{bmatrix}$$

Although $C_{ij}$ looks like a $2^{nd}$–rank tensor, it is indeed a $4^{th}$–rank tensor. As shown in
the matrix above there are at most 21 independent elements in matrix. With the application
of crystallographic symmetries the number can be reduced. For instance, a cubic crystal
has three independent constants while an orthorhombic crystal has nine. Table 2.1 lists the
arrays of reduced elastic constants for various crystal symmetries. The cubic system is one
of the simplest symmetries in crystals. The matrix below is the matrix representation for
Table 2.1: Independent elastic constants for various crystal symmetries

<table>
<thead>
<tr>
<th>Crystal class</th>
<th># of ( C_{ij} )</th>
<th>List of elastic constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>21</td>
<td>All possible combinations</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>13</td>
<td>( C_{11}; C_{12}; C_{13}; C_{16}; C_{22}; C_{23}; C_{26}; C_{33}; C_{36}; C_{44}; C_{45}; C_{55}; C_{66} )</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>9</td>
<td>( C_{11}; C_{12}; C_{13}; C_{22}; C_{23}; C_{33}; C_{44}; C_{55}; C_{66} )</td>
</tr>
<tr>
<td>Trigonal</td>
<td>6 or 7</td>
<td>( C_{11}; C_{33}; C_{44}; C_{12}; C_{14}; C_{25} )</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>6</td>
<td>( C_{11}; C_{33}; C_{44}; C_{13}; C_{12}; C_{66} )</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>5</td>
<td>( C_{11}; C_{33}; C_{44}; C_{12}; C_{14} )</td>
</tr>
<tr>
<td>Cubic</td>
<td>3</td>
<td>( C_{11}; C_{12}; C_{44} )</td>
</tr>
<tr>
<td>Isotropic</td>
<td>2</td>
<td>( C_{11}; C_{44} )</td>
</tr>
</tbody>
</table>

The anisotropic cubic crystal.

\[
C_{ij} = \begin{bmatrix}
C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{44}
\end{bmatrix}
\]

The three independent elastic constants are \( c_{11}, c_{12} \) and \( c_{44} \). For the cubic symmetry, one can easily obtain elastic properties such as bulk modulus \( B \), shear modulus \( G \), and \( C' \) where \( B = \frac{1}{3} (c_{11} + 2c_{12}) \), \( G = c_{44} \) and \( C' = \frac{1}{2} (c_{11} - c_{12}) \). Most materials are isotropic, where by definition, the material properties are equivalent in all directions. Such materials have only two independent elastic constants, \( c_{11} \) and \( c_{12} \), where \( c_{44} = 2 (c_{11} - c_{12}) \). Usually these two independent elastic constants are expressed as the 1st order elastic moduli: Young’s modulus \( (E) \) and the Poisson’s ratio \( (\nu) \). The alternative elastic constants that can be used are bulk modulus \( (B) \) and/or shear modulus \( (G) \).

### 2.2 Techniques for the Measurements of Elastic Constants

Elastic properties of solid materials can be determined via the full set of their elastic constants. Given the importance of elastic constants various innovative techniques have been
developed for their measurements. These techniques can be broadly classified into two (i) numerical and theoretical methods and (ii) experimental measurements.

In the numerical and theoretical methods, basic properties of solids such as equilibrium positions of atoms and free energy are used to determine the elastic constants of the solids [26–29]. At the atomic level, an elastic constant is a measure of interatomic forces that bind the atoms together. They are related to the curvature of the interatomic potential in the vicinity of equilibrium spacing. A sharper curvature near equilibrium position correspond to higher elastic constants, which means that the material is stiffer. If the form of the interatomic potential is known, the elastic constants can be calculated from first principles. Theoretical calculations such as \textit{ab initio} calculations of crystalline solids with known atomic structures and potentials have produced results that are in good agreement with experimental data. Although the theoretical methods yield good results for some materials, the experimental measurements are still more reliable. Also in some cases, such as complex materials and some non–crystalline materials experimental measurements will be the only technique that can be used.

Several experimental techniques [30–32] have been devised to measure the elastic properties of solid materials. Some of these methods are non–acoustic methods such as static loads with strain gauges, Brillouin scattering, inelastic neutron scattering and x–ray diffraction. In principle, elastic constants can be readily computed from stress and strain, which are related by $\sigma_{ij} = c_{ijkl}\varepsilon_{kl}$. For a given sample, the stress is related to the external force applied to the sample and the strain is related to the change of the sample shape or geometry. Therefore simple static mechanical tests may be used to evaluate the elastic
Table 2.2: Comparison of methods commonly used for elasticity evaluation [33]

<table>
<thead>
<tr>
<th>Main parameters measured/computed</th>
<th>Representative methods</th>
<th>Approximate accuracies (typical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical/numerical</td>
<td>Ab initio calculation</td>
<td>Fair (1 – 25 %)</td>
</tr>
<tr>
<td>Stress-strain</td>
<td>Static, quasi-static, indentation</td>
<td>Fair – good (1 – 10 %)</td>
</tr>
<tr>
<td>Speed of sound</td>
<td>Pulse-echo, continuous wave</td>
<td>Good – better (&lt; 1 %)</td>
</tr>
<tr>
<td>Frequencies</td>
<td>Resonance, RUS</td>
<td>Better – best (0.1 – 1 %)</td>
</tr>
<tr>
<td>Diffraction/Scattering</td>
<td>X-ray, neutron, Brillouin</td>
<td>Fair – good (1 – 5 %)</td>
</tr>
</tbody>
</table>

* Note: Accuracy of a method depends on elastic characteristic of the material, and note also that the accuracies (poor ~ best) are for the whole category and subjective in nature.

constants. Samples of relatively large sizes are either pulled, compressed, bent or twisted by known stresses, and the strains are measured by strain gauges. Static methods usually apply to large–sized, isotropic samples, and they are quick and convenient but lacking in accuracies and are limited in scope. The Brillouin scattering, inelastic neutron scattering and x–ray diffraction have also been used for elastic characterization of materials. X–ray and similar techniques are powerful tools for studying microstructures and mechanical properties of single crystalline and polycrystalline materials. These techniques have the abilities of measuring thin films, layered structures and inhomogeneous materials which traditional mechanical methods usually lack. The elastic constants measured by diffraction techniques are microstructure dependent and are correlated to the mechanical elastic constants which are of common interest to engineers. The diffraction patterns, with the help of diffraction elastic constants, are often used to calculate the localized residual stress in a material. In general, these elastic constant measurement techniques lack the accuracy that the ultrasonic methods have. Table 2.2, which was put together by Guangyan Li, shows these techniques categorized according to the measured parameters. The table also reflect the typical approximate accuracy levels for these techniques.

Other techniques are acoustic methods such as surface acoustic waves, vibrating reed,
torsional pendulum and ultrasonic techniques. The ultrasonic techniques have proved to be one of the most accurate methods for measuring elastic constants in isotropic and anisotropic materials. Ultrasonically, an elastic constant can be measured in two ways: one uses the theory of elasticity which proved that elastic constant of a material can be determined by measuring the sound velocity in the material; the other is by measuring the free-vibration frequencies, which depend on the sample’s dimensions, density and elastic constants.

Elastic constants can be determined from the ultrasonic wave velocities in various directions in a crystal [34]. In the linear regime, the general relationship between the speed of sound in a crystal, its density and its elastic constants is governed by the following equation

\[ V = \sqrt{\frac{C_{ij}}{\rho}} \]  

(2.9)

where \( V \) is the relevant speed of sound, \( C_{ij} \) is a component of the elastic constants, and \( \rho \) is the material density. The elastic constant can be computed using Equation 2.9 from the propagation velocities of ultrasonic waves in various directions along principle axes of the crystal. For instance, the shear modulus is related to the shear speed and the density of a material by \( V_s = \sqrt{\frac{C_{44}}{\rho}} \). In isotropic materials, only two speeds, longitudinal and shear speeds, are needed to compute the two elastic constants.

The pulse-echo [34–36] method is the most commonly used method of measuring the speed of sound in isotropic and anisotropic materials. In the pulse-echo method, good acoustic coupling or even bonding between the sample and transducer is required. To obtain all the elastic constants of a crystal, the sample has to be repeatedly cut along different
principal axes of the crystal lattice and bonded to the transducer, or multiple samples are needed. In the method, a generated pulse is transmitted through the transducer–sample interface into the sample. The polished surface of the sample reflected (echo) the pulse back to the transducer. The arrival times of the reflected pulses are then used to determine the time of flight of the pulse through the length of the material; this is then used to calculate the speed of sound in the material. The time of flight of the sound pulse, its crystallographic direction of travel, and the sample length along the sound path are all that is needed to extract three moduli in one direction: one longitudinal and two shear moduli. The uncertainty of the resulting velocity depends on the uncertainties of the time of flight and the thickness measurements. An overall uncertainty of better than 1% can be easily achieved in carefully performed pulse–echo measurements. For low symmetry crystals this technique is labor intensive. The lack of stable high temperature couplants prevents the pulse–echo method from being a suitable method for elastic constant measurements at high temperatures. The accuracy of pulse–echo ultrasonic method is apparently not very robust. The resonance ultrasound spectroscopy (RUS) is a resonance method that does not require the use of coupling agent between transducer and sample. Unlike the pulse–echo method, RUS uses the free–vibration frequency to measure all the elastic constants in one measurement.

Resonance frequencies are characteristic of the elastic properties, mass density and sample geometry. By measuring the resonance frequencies of a sample of a given geometry, the elastic properties of the sample can be deduced from the discrete resonance spectrum. The resonance method has existed for decades but analytical solutions for calculating normal
modes of elastic solids are available in few cases such as sphere and crystalline parallelepipeds. In addition, its demand in computing power has limited its applications.

Significant effort has been made in the literature [9, 31, 37, 38] to develop the RUS method, which is a convenient method for evaluating temperature/pressure–dependent elastic constants using single crystal samples. An accurate method is required for measuring the small variations in elastic constants associated with temperature/pressure changes. RUS provides extremely high accuracy (≤ 1%) compared to other routine experimental techniques for elastic constant evaluations. With the improvement in the algorithms and advances in computing power of modern personal computers, RUS has become a fast, accurate and powerful method for determining the elastic constants of solids. The next sections present an overview of the RUS technique.

2.3 Resonant Ultrasound Spectroscopy Method

RUS is based on the measurement of the resonance frequencies via vibrational eigen-modes of samples of well defined shapes (usually simple geometry such as spheres or parallelepipeds) by excitation and detection through, typically, piezoelectric transducers. Since the early 1990s, resonant ultrasound spectroscopy has stood out from the conventional ultrasonic methods due to its efficiency, accuracy, and ability to handle mm–sized small or smaller samples and low symmetry crystals well.

Researchers have attempted to use the Rayleigh–Ritz variational technique to calculate the natural vibration frequencies of a solid of given geometry, elastic constants and density. Using the variation principle, the Rayleigh–Ritz method predicted the normal modes
frequencies as

$$\omega^2 = \frac{\int c_{ijkl} \frac{\partial \psi_i}{\partial x_j} \frac{\partial \psi_k}{\partial x_l} dV}{\int \rho \tilde{\psi} \cdot \tilde{\psi} dV}$$

(2.10)

where $\tilde{\psi}$ is the displacement field, $x$ are the dimensions and $\rho$ is the density of the solid.

Analytical solutions for calculating normal modes of elastic solids have been in existence for decades but only for few special shapes such as cubes and spheres of isotropic, noncrystalline materials. The modern version of RUS evolved from the resonant sphere technique (RST) developed by Fraser and LeCraw for isotropic spheres [39]. The method was extended to cubic by Demarest, he also found numerical solutions for rectangular parallelepipeds of anisotropic, crystalline materials as well as for spheres of isotropic materials. Demarest’s method was later referred to as rectangular parallelepipeded resonance (RPR) method. Subsequently, other researchers refined and advanced the theory and applied it to the determination of elastic constants of solids. A careful examination of the history of modern RUS methods revealed that identification of efficient and suitable approximate solutions to the forward problems of many geometries is key to the development of RUS. The discovery of products of powers of the Cartesian coordinates as the basis functions for numerical solutions is an equally important milestone in RUS development. This set of basis functions can be applied to many geometries and general anisotropic materials with good accuracy and flexibility. Many applications of RUS have been reported in the literature, here are few references [9, 10, 22, 23, 40–47]. In addition to elasticity studies, RUS is also used in non-destructive testing (NDT), mechanical damping or internal friction studies [40,48,49], and many other engineering applications [50].

As mentioned earlier, two problems, a “forward” and an “inverse” problem, are involved in the computation of the elastic constants of a solid from the measured spectrum.
The forward problem computes the resonance frequencies from known parameters of the solid material. The inverse problem involves determining all independent elastic constants from the experimentally obtained spectrum. The forward problem is presented next.

2.3.1 Computation of Resonance Frequencies

An integral element of RUS is the comparison of measured and computed frequencies. Therefore, efficient calculation of the resonance frequencies of solids is the central requirement for the effective application of RUS. The calculation of vibration modes of elastic objects with free boundaries is a classic problem in mechanics. Unfortunately, exact solutions for a 3D object exist only in few cases such as an isotropic sphere and certain modes of a parallelepiped. An approximate solution is needed. In most cases, approximation methods such as the finite element method (FEM) or Rayleigh–Ritz method is used for estimating the eigenfrequencies of normal modes. The FEM relies on balancing all the forces on a differential volume element and calculating its responses. Hence, a complete knowledge of all the relevant forces acting on the volume element is required. FEM allows the determination of eigenfrequencies for arbitrary shape of sample made of heterogeneous, anisotropic materials such as layered composite materials. FEM is more general and usually requires more computing time. The Rayleigh–Ritz method is a widely used method for calculating the approximate natural vibration frequencies of a system. The theoretical development of RUS relies on this method. The Rayleigh–Ritz or any eigenvalue problem employs the energy minimization technique, the Hamilton’s principle of least action that the Lagrangian of a system is stationary with respect to small perturbations in the eigenfrequencies.
A normal mode is the motion in which all parts of the system move with the same frequency and are in phase. The normal mode frequencies of a system are its natural resonance frequencies. If a vibrating elastic solid is executing a normal mode, it still oscillates between extremes of maximum strain and zero velocity, where the potential energy is a maximum and kinetic energy is zero, and zero strain and maximum particle velocity, where the kinetic energy is a maximum and potential energy is zero. If the energy is conserved, these maximum quantities must be equal. The potential energy and the kinetic energy can be expressed in terms of the displacement field $\psi$. The potential energy density is

$$U = \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} = \frac{1}{2} c_{ijkl} \frac{\partial \psi_i}{\partial x_j} \frac{\partial \psi_k}{\partial x_l}$$  \hspace{1cm} (2.11)$$

and the kinetic energy density for a normal mode is

$$T = \frac{1}{2} \rho \omega^2 \psi_i \psi_i$$ \hspace{1cm} (2.12)$$

where an $\exp(i\omega t)$ time dependence has been assumed and first derivatives with respect to time have been performed ($v = \frac{d\psi}{dt}$). The Lagrangian is defined as $L = T - U$. Employing the Hamilton’s principle, the time integral of the Lagrangian is a constant of motion, hence

$$\delta \int_{t_1}^{t_2} \int_V (T - U) dV dt = 0$$ \hspace{1cm} (2.13)$$

The displacement field can be approximated by an expansion of some suitable set of basis...
functions:
\[
\psi_i(\vec{r}) \approx a_{i\lambda} \Phi_\lambda(\vec{r})
\]
(2.14)

where \(a_{i\lambda}\) are the expansion coefficients and \(\Phi_\lambda(\vec{r})\) are the basis functions. Substituting the expression above into the Lagrangian, we have
\[
L \approx \frac{1}{2} \left( a_{i\lambda} a_{i'\lambda'} \rho \omega^2 \right) \int_\mathcal{V} \delta_{ii'} \Phi_\lambda(\vec{r}) \Phi_{\lambda'}(\vec{r}) dV - \frac{1}{2} a_{i\lambda} a_{i'\lambda'} \int_\mathcal{V} c_{iij'j} \frac{\partial \Phi_\lambda(\vec{r})}{\partial x_j} \frac{\partial \Phi_{\lambda'}(\vec{r})}{\partial x_{j'}} dV
\]
(2.15)

The equation above can be written in matrix form as:
\[
L = \frac{1}{2} \omega^2 \vec{a}^T \vec{E} \vec{a} - \frac{1}{2} \vec{a}^T \vec{\Gamma} \vec{a}
\]
(2.16)

where \(\vec{a}\) is a matrix with elements \(a_i\) whose transpose is \(\vec{a}^T\) and where \(\vec{E}\) and \(\vec{\Gamma}\) are matrices with elements
\[
E_{\lambda\lambda'} = \delta_{\lambda\lambda'} \int_\mathcal{V} \Phi_\lambda \rho \Phi_{\lambda'} dV
\]
(2.17)
\[
\Gamma_{aia'j'} = c_{iij'j} \int_\mathcal{V} \frac{\partial \Phi_\lambda}{\partial x_j} \frac{\partial \Phi_{\lambda'}}{\partial x_{j'}} dV
\]
(2.18)

The requirement that the variations of the Lagrangian with respect to \(\vec{a}\) be zero (from the free boundary conditions), allows us to cast the problem in the matrix eigenvalue form:
\[
\omega^2 \vec{E} \vec{a} = \vec{\Gamma} \vec{a}
\]
(2.19)

The solutions of this eigenvalue equation give the free oscillation frequencies (the eigenvalues) of the solid and its physical displacements when oscillating (the eigenvectors) as shown in...
Figure 2.2. The maximum typical displacement in RUS measurement is few nanometers in magnitude [51]. The computed eigenvalues are used in the inverse problem to “correct” the set of input parameters so as to iterate towards a match between the computed and measured frequencies. There are standard computer routines for solving such eigenvalue problems.

Figure 2.2: Some magnified normal modes of vibration of the palladium crystal with an FCC crystal structure. The magnitude of typical maximum displacements is few nm

2.3.2 Choice of Basis Functions

The basis functions used to approximate the displacement field functions must be complete but not necessarily orthogonal. It is important that the basis functions chosen be integrable and differentiable over the volume of the sample. A properly chosen set of
basis functions can greatly increase the computing efficiency and minimize the errors. Sine functions and Legendre polynomials have been historically chosen as the basis functions because orthogonality simplifies matrices. W. M. Visscher et al [38] proposed using simple powers of the Cartesian coordinates

\[ \Phi_\lambda = x^p y^q z^r \]  

(2.20)

where \((p, q, r)\) are a set of positive integers with the maximum power set by \(N \leq p+q+r\). This is called XYZ algorithm, and is applicable to various irregular-shaped but mathematically definable and anisotropic materials. The high order polynomials are very flexible functions which can closely simulate a wide variety of geometries and displacement fields. A typical number of 10 or 12 for \(N\) can approximate the actual displacement adequately for modes of order \(\leq 50\). A comparison between the exact and the approximate solutions using the Visscher basis of \(N = 12\) for an isotropic sphere shows a nearly perfect agreement of 0.00001 \% up to 32 modes [52]. Larger values of \(N\) will yield basis functions that will simulate the actual displacement fields more accurately but not necessarily yield a better solution. On the contrary, the increased demand in computing power and the digital precision of the computer processors must be considered. Typically, \(N = 13\) is the limit for a 32-bit computer.

2.3.3 Estimation of Elastic Moduli

So far we have dealt with the forward problem, the computation of the resonance frequencies of a body given its density, dimensions, orientation angles, and elastic moduli.
The real power of RUS is in the ability to work backward and determine these parameters from a measurement of the resonance frequencies of the body. This is the inverse problem. The inverse problem is not a trivial computation. The forward calculations described above cannot be mathematically inverted. The forward calculation and the nonlinear fittings, with a little cleverness, is used to “invert” the problem. Given a set of measured resonance frequencies, dimensions and density, and a set of estimated elastic constants, a forward calculation is done to generate a set of resonance frequencies. The generated frequencies are compared to the measured frequencies iteratively and the parameters are adjusted during each iterations to minimize the error function. The error function is the sum of the squares of the differences between the calculated and measured frequencies, and is a measure of the closeness of the fit. This least-squares minimization procedure is repeated, up to some tolerance, over the space of all adjustable parameters.

The minimization of the error function is a nonlinear least-squares problem. The Levenberg-Marquart (LM) algorithm is an iterative technique that locates the minimum of a multivariate function that is expressed as the sum of squares of nonlinear real-valued functions, and it is an hybrid between Newtonian solution and the method of steepest descents. The LM algorithm is used in RUS to find the minimum of a non-linear function $F(x)$ that is a sum of squares of the difference between the calculated and measured frequencies

$$F(x) = \frac{1}{2} \sum_{i=1}^{M} w_i [f_i^{(calc)}(x) - f_i^{(meas)}(x)]^2 \quad (2.21)$$

where $f_i^{(calc)}(x)$ are the computed frequencies and $f_i^{(meas)}(x)$ are the measured ones. $w_i$
are the weights that reflect the confidence in the measured frequencies. These weights can have any values between 0 and 1 but they are usually all set to one. The minimization of the error function is performed by the gradient (LM) method with the assumption of a parabolic error surface near the minimum. In nonlinear fittings, appropriate starting values are important for the estimation of the model parameters. If either the initial set of the estimated elastic constants is off too much from the actual values or some modes are lost in RUS measurement, the fitting procedure may converge to a local, rather than the global, minimum in the parameter space. Therefore, it is advisable to try several starting points (elastic constants) when computing the elastic moduli from the frequencies.

The computer code developed by A. Migliori et al. handles the inverse problem in RUS well enough [31]. Unfortunately, good initial guesses of elastic moduli and identification of missing peaks are still important for obtaining good consistent results. The test sample is face-mounted (two transducers or buffer rods are in contact with two opposite flat surfaces of the sample) in our high-temperature and high pressure test. One or more resonance modes may be missed during measurement if the transducer touches the node of a mode, or if the transducer is insensitive to the direction a mode moves. A reasonable guess of the parameters usually gives an accurate density of modes per unit frequency. Therefore it is possible to establish a one-to-one mapping between calculated and measured frequencies. Using this mapping one can identify the missing modes in the measured frequencies. Errors after the missing mode tend to be the same sign, either positive or negative. Inserting a missing mode or a place-holder (zero in our code) in the input file may quickly reduce the error. RUS, just like all scientific methods, involves some judgment. Judgment is crucial to science!
Figure 2.3: A plot of resonance frequencies of palladium hydride at 290°C and 250.5 psi.

For a geometrically precise (errors in parallelism and perpendicularity of a few parts in $10^3$), high-Q (a few thousands or higher) sample, the overall RMS error between the calculated and measured frequencies for the elastic constants fits is typically in the range of 0.1-0.4%. This range of error is considered good in our high-temperature and high-pressure elasticity study of materials. Table 2.3 shows a typical “good fit” in the RUS calculation for a $PdH_x$ sample at 290°C and 250.5 psi.

Figure 2.3 shows a plot of the resonance peaks of the palladium hydride at 290°C and 250.5 psi. The plot shows the frequencies within the 400 – 460 kHz range of the typical scanned frequency range.
Table 2.3: Measured \( f^{\text{meas}} \) and calculated \( f^{\text{calc}} \) resonance frequencies after four iterations in RUS calculation for an palladium hydride (PdH) at 290°C and 250.5 psi. The average error magnitude of the included resonance frequencies is 0.2%.

<table>
<thead>
<tr>
<th>Mode</th>
<th>( f^{\text{meas}} ) (MHz)</th>
<th>( f^{\text{calc}} ) (MHz)</th>
<th>Difference (%)</th>
<th>INC/EXC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.236793</td>
<td>0.235370</td>
<td>0.604</td>
<td>EXC</td>
</tr>
<tr>
<td>2</td>
<td>0.257586</td>
<td>0.258931</td>
<td>-0.520</td>
<td>INC</td>
</tr>
<tr>
<td>3</td>
<td>0.269390</td>
<td>0.269633</td>
<td>-0.090</td>
<td>INC</td>
</tr>
<tr>
<td>4</td>
<td>0.282582</td>
<td>0.283511</td>
<td>-0.327</td>
<td>INC</td>
</tr>
<tr>
<td>5</td>
<td>0.287755</td>
<td>0.287713</td>
<td>0.015</td>
<td>INC</td>
</tr>
<tr>
<td>6</td>
<td>0.295460</td>
<td>0.295427</td>
<td>0.011</td>
<td>INC</td>
</tr>
<tr>
<td>7</td>
<td>0.315425</td>
<td>0.314854</td>
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<td>INC</td>
</tr>
<tr>
<td>8</td>
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<td>INC</td>
</tr>
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<td>INC</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
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<td>0.408087</td>
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<tr>
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<td>0.426634</td>
<td>0.480</td>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>24</td>
<td>0.508330</td>
<td>0.530334</td>
<td>-0.042</td>
<td>INC</td>
</tr>
</tbody>
</table>
CHAPTER 3

EXPERIMENTAL METHOD

3.1 Introduction

The use of RUS technique in the characterization of materials at room and low temperature has been widely reported in the literature. Its applications at elevated temperature have also been reported [20, 21, 24, 40–44, 53, 54]. These applications are relatively rare because of the technical difficulties that are involved in the design of high temperature applications RUS device. These include (i) samples of some materials and transducer probe components may suffer high-temperature corrosion such as oxidation in a highly oxidizing environment if they are not placed in a low oxygen environment therefore, creation of a low oxygen environment is necessary in a high-temperature measurements; (ii) sensitivity of most piezoelectric transducers decreases, if not rapidly, with increasing temperature, thus making them unstable above certain temperatures; (iii) strength of acoustic resonance of most materials become weaker at high temperatures than at room temperature, in addition, low quality factors (Qs) of samples caused by increased attenuation and internal friction in materials likely make it difficult, if not impossible, to separate sample modes; (iv) many other challenges posed by electrical connections, transducer bonding and other related issues need to be considered.

In the case of high temperature and high pressure applications, in addition to all the
concerns mentioned above, the type of materials that will be used in the construction of components that makes up the device is also a source of challenge and technical difficulties. The components of the set-up must be able to withstand the pressure range of the measurements in addition to the temperature. The RUS set-up is a combination of two major systems: (i) the high temperature direct contact transducer system; (ii) the high temperature and high pressure RUS cell. The rest of the chapter starts with the design and fabrication of the direct contact transducer system and a detailed description of the high temperature and high pressure RUS cell.

3.2 High Temperature Direct Contact Transducer System

3.2.1 Introduction

This section narrates the design and fabrication of the high temperature direct contact transducer system. In a direct contact system, the transducers are in direct contact with the sample. Several parameters are considered in the selection of the components that make up the transducer system. Unlike conventional ultrasonic transducers, resonance of the RUS transducer itself should be small compared to resonance of the sample. If possible, the resonance of the transducer should be kept out of the operating frequency range. In our case, the resonances of the transducers are in the range of 5–10 MHz, which is well above our operating frequency range.

Most of the regular ultrasonic transducers are not designed for applications in harsh environments such as elevated temperatures or high pressures. The upper limit of operating
temperatures of most piezoelectric transducer is determined by several factors: (i) most materials that exhibit good piezoelectric properties at room or low temperatures lose the piezoelectric effect quickly with increasing temperature; (ii) even those crystals with high Curie temperatures (theoretical temperatures at which their piezoelectric effects disappear), the operating temperatures are usually well below their Curie temperatures due to impurities in their crystalline structures, or the piezoelectric effect is too weak to be useful above certain temperatures; (iii) an upper temperature limit may be restricted by transducer components such as backing and supporting materials, bonding materials, and electrical connections.

The repeated heating and cooling cycles shortens the lifespan of the high temperature transducer probe. Therefore, it is desirable that the piezoelectric material be easy to acquire, the design should be simple, and the whole system can be assembled quickly. The whole design and fabrication process consists of several steps: identify and obtain the right materials, prepare the components, assemble the system, and finally, test the system.

3.2.2 Materials Selection

The lithium niobate (LiNbO$_3$) crystals exhibit good piezoelectric properties at high temperatures [55, 56]. The crystal has been used successfully in our laboratory at temperatures up to 650°C [57]. The high Curie temperature of LiNbO$_3$, which is above 1200°C, along with its wide availability from commercial suppliers, makes it a good candidate for high-temperature RUS applications [58]. Pure LiNbO$_3$ crystals with stoichiometric compositions exhibit remarkable piezoelectric properties even at 900°C [56]. However, in practice, the resonance signals picked up by LiNbO$_3$ at 650°C are very weak. Hence, we are limited
to 650°C. This temperature is far below the material’s Curie temperature but it agrees with the upper operating temperature reported in the literature [58,59]. One of the reasons responsible for the signal deterioration is the loss of oxygen at high temperature [59], this will be heightened by the low oxygen environment in which we are operating. Other factors that have been reported include impurities stoichiometry [55, 56]. LiNbO₃ with excellent optic and acoustic properties are readily available from commercial suppliers. The y/36°-cut chrome/gold plated lithium niobate single crystals, which are readily available from Boston Piezo-Optics Inc., were chosen as the piezoelectric elements for vibration excitation and detection. Given the average sample size, resonance peaks selected for RUS calculations are mostly in the frequency range of 200 kHz–1 MHz. The lithium niobate crystals are used in thickness mode and their intrinsic frequencies must be well above the resonance frequencies of the samples. The crystals used for the direct contact probes are 1–2 mm thick and frequencies of the compressional mode of the crystal are in the range of 5–10 MHz. This is well above the typical operating frequency range.

Next to the selection of piezoelectric material are the coaxial cables. Regular coaxial cable cannot withstand temperature of hundreds of degrees. Many so-called high temperature coaxial cables have upper temperature limits around 200°C. In coaxial cables, conductors made of metals are capable of withstanding high temperatures even in oxygen environment. The weak link, however, is the insulation between the conductor. The mineral insulated signal transmission cables can overcome the insulation problem at high temperatures and are thus our choice for high temperature applications. For the coaxial signal cable we used mineral insulated stainless steel cable from ThermoCoax® in France, the cable is
designed to withstand high temperature environments (above 1000°C). Both the outer and inner conductor are made of heat resistant Inconel™ metal alloys. Mineral insulated coaxial cables of 2 mm outer diameter are used in the direct contact system. The cable remain rigid at very high temperature thus it can provide structural support for the piezoelectric crystal of the probe.

The bonding between high temperature coaxial cables and the piezoelectric crystal is done using the silver filled conductive epoxy (Epo–Tek E2101). The epoxy serves as the electrical connections between the chrome/gold electrodes of the transducer and the mineral insulated stainless steel coaxial cable. The relative stiff structure of the cable body serves as the backing of the transducer. The resonances of the cable body are weak and below our normal operating frequency range.

The two transducer probes and temperature control element (thermocouple wire or resistance thermometry leads) need structural support. A cage consisting of steel disk baffles and steel bars was designed to provide the structural support. Steel was used because the set–up will be subjected to cycles of high temperatures and high pressures.

3.2.3 Assembling of Transducer Probe

With the transducer system components selected and acquired, the next step is to assemble them into a high temperature transducer probe. The frequencies of the LiNbO₃ elements are well above the operating frequency but when the piezoelectric element is bonded to a structural support, the characteristic resonance of the whole transducer probe shift lower. If the piezoelectric element is bonded to a rigid structure with high intrinsic reso-
nance frequencies, the resonances of the whole system can still be well above the intended working frequency range [50]. This design philosophy works for transducers used at ambient temperatures but may not for high temperature transducers. This is because the bonding material and rigid backing materials may become “softer” at high temperatures, resulting in lowered resonance frequencies or unpredictable resonance characteristics of the transducer system. Thus a transducer design in which the other components of the transducer probe are isolated as much as possible from the piezoelectric element is desired.

In our direct contact transducer probe, the piezoelectric element is directly bonded to the inner conductor of the mineral coaxial cable. A piece of about 25–35 cm–long coaxial cable is cut for making transducer probe. The outer conductor of about 0.5–1 cm long at both ends is stripped away. At one end of the exposed inner conductor the tip is bent into a ring which covers an area of about 2/3 of the piezoelectric disk. The plane of the ring is perpendicular to the cable body as shown in Figure 3.1. The area where epoxy is to be applied is carefully sanded and cleaned before applying epoxy. The two part epoxy is well mixed in equal parts at room temperature. The epoxy mixture is used to glue the piezoelectric disk to the ring (inner conductor of the coaxial cable). This is done with the mineral insulated coaxial cables installed in the steel cage as shown in Figure 3.2. The epoxy covers the whole electrode of the piezoelectric disk. The thickness of the epoxy mixture is kept in the range of 1–2 mm and thicker at the center. The thicker the epoxy spot on the disk, the heavier the load. Too much epoxy can significantly lower the free resonance frequencies of the piezoelectric element. The epoxy is cured by setting the epoxied parts (inner conductor and piezoelectric element) under electric lamp for 4 hours and covered by aluminum foil.
Figure 3.1: Direct contact transducer assembly showing the magnified portion of the inner conductor attached to the transducer by using the silvered epoxy.

The next step is the electrical connection between the outer conductor (electrical ground) and the front electrode of the piezoelectric crystal, a small piece of platinum wire is used to connect the electrode to the outer conductor of the cable. The epoxy spot on the front electrode of the crystal should be small and close to the edge so, much of the area can be used for holding the sample. The other end of the exposed inner conductor will be at the upper cooler part of the transducer probe.

Two transducer probes are constructed for the direct contact transducer system. After the construction, they are examined under microscope for bonding defects. Any hidden electrical connection problem can be identified by measuring electrical resistance and check-
ing for continuity between different parts of the probes. The resistance across the length of the high temperature cable is in the range of 0.3–0.5 Ohms. The resistance between the two electrodes of the piezoelectric element should be at least several mega Ohms or above; the resistance may drop to hundreds of kilo Ohms, which is considered acceptable, due to ‘impurity’ accumulation on the sides of the piezoelectric element after several cycles of high temperatures and high pressures. A much lower resistance usually warrants a cleanup or replacement of the piezoelectric element.

At the completion of assembling the direct contact transducer system, the excitation probe is fixed at a position with the piezoelectric element facing up and near the center of the cage, the detection probe is left to move freely at the top, the test sample is mounted between these two vertically aligned transducers, the weight of the upper transducer system hold the sample in place. The transducers are put in a set of steel baffles to provide rigid structure and to serve the purpose of reducing the effect of gas convection so as to maintain a stable temperature in the cell especially around the test sample. Flexible regular coaxial cables are used at the cooler upper part of the cell to connect the free ends of the mineral insulated coaxial cables using male–female coaxial connectors. The other ends of the flexible coaxial cables are connected to the coaxial feed-through at the top of the cell. The figure below shows a section of the high temperature direct contact transducer. The schematic diagram and the photo of the actual direct contact transducer system is given in Figure 3.2.
3.3 High Temperature and High Pressure RUS Cell

3.3.1 Introduction

The major considerations in the design of the high temperature and high pressure (HT&P) RUS cell are: (i) the material that can hold pressure at the upper temperature range of the experiment (550°C); (ii) the upper part of the cell should be cold enough at all times during experimental runs to prevent the flexible coaxial cables and the electrical
connections at the upper part from melting, it will also keep the pressure seal gasket at the
top of the cell stable; (iii) the cell must have feed-through for coaxial cables and temperature
control element leads as well as gas inlet and outlet terminals.

3.3.2 Cell Design and Construction

The cell is made of stainless steel tube and a removable top portion also made of
stainless steel. The top portion includes the gas inlet, the pressure meter, coaxial and
temperature control feed-through. The stainless tube has an outside diameter of about
1.4 inches with wall thickness of about 0.2 inches from TW Metals. The upper part of the
tube is encased with copper “cold–finger” through which we run tap water to cool the upper
part of the cell. Welded to the steel tube at the other end is the gas outlet line. The inlet
gas line is connected to two gas tanks; an ultra–pure argon tank and a hydrogen tank. Gas
regulators are attached to the tanks and thus enable a controlled release of gas into the
HT&P RUS system. Gas lines are made of stainless to be of 0.25 inches outside diameter
and rated for 10000 psi. Needle valves of working pressure 5000 psi and ball valves of working
pressure 3000 psi were used to regulate the rate at which gas is let into and out of the cell.
The outlet gas line is connected to a vacuum pump. VCR fittings obtained from Swagelok
were used to connect that gas lines and the valves to the stainless steel tube and the vacuum
pump. All the specifications of the set up were at least 2000 psi. Figure 3.3 shows the
schematic diagram of the HT&P RUS system set-up while Figure 3.4 shows the schematic
diagram of the RUS cell and the photograph of the whole set-up.
3.3.3 Pressure and Temperature Control

The pressure meter used in the set-up is DXD Series–Precision Digital Pressure Transducer from Heise, the range of the meter is from 0–2000 psia (absolute pressure) and the precision is 0.01 psia. The pressure of the system is increased by letting gas into the cell while the outlet is shut off and by letting gas out at a controlled rate from the outlet, the pressure can be decreased. The RUS cell is lowered into the furnace such that the center of the cell is approximately at the center of the furnace. The cold finger is about 1.0–1.5 cm above the top of the furnace.
Figure 3.4: The RUS cell (a) Schematic diagram of the RUS cell showing the sample and transducers. (b) Photograph of the HT&P RUS system during an experimental run, it is enclosed by a protective Plexiglas cage. It also show the cold tap water line, in and out of the “cold–finger”.

The furnace temperature is controlled by a temperature controller (Eurotherm Model 2408CP), which is manually adjusted. The temperature of the sample inside the cell is different from the set temperature of the furnace. This is due to the following factors; (i) the cold finger at the upper part of the stainless tube cell and the hydrogen/argon gas in it create temperature gradient between the upper part and the center of the tube where the sample is located, (ii) the heat required to raise temperature of the stainless steel tube cell across its thickness causes a temperature gradient between inside and outside the tube and (iii) the temperature monitoring sensor of the furnace is in the wall of the furnace and not
inside the cell. The sample temperature is then monitored by type N thermocouples. In the thermocouple set-up, the hot junction is mounted within a radial distance of 1–2 mm of the sample surface. The cold junction is submerged in a well–mixed ice and water bath. A Keithley multimeter (Model 2000) reads the voltage and a computer code was written to convert the voltage to the temperature.

During the first run of the experiment, the temperature reading obtained was not stable enough to meet the isothermal requirement. The fluctuation of the temperature over a 60 hours period is up to 6°C. We suspected few things that might lead to the temperature instability. Firstly, it could be due to partial contact of the thermocouple wires at another part of the set-up. Secondly, the cold finger could be so effective that the temperature gradient between the upper part of the rig and the center is large and thus causing convection current that reduces the temperature resulting in the temperature instability as detected by the thermocouple. Lastly, the elements of the thermocouple might be reacting with hydrogen gas.

The temperature monitoring set-up was changed from thermocouple to a platinum resistance thermometry detector (RTD) as one of the measures to solve the temperature instability problem, at least eliminate the possibility of partial contact. In the RTD set-up we do not have to employ an ice–water bath as required when using a thermocouple. The RTD is platinum based and platinum, being a noble metal, is stable, easily workable and has a high melting point. It resists corrosion and chemical attack and it is not readily oxidized. The flow rate of cold water through the cold finger was also reduced and monitored to reduce the effect of convection to minimum. The reduction of the cold water flow rate from
an average of 8.6 ml/sec to 5.6 ml/sec worked well. The temperature variation was initially ±3 degree Celsius in a time period of 60 hours as shown in Figure 3.5. After water flow rate reduction and with the RTD, the temperature variation was ±0.3 degree Celsius over the same time period. It is important to state here that the large variation is largely due to the fluctuation in the actual temperature which results from the cooling effect of the “cold finger” and less on the fluctuations in our temperature sensing devices.

The RTD element uses a four point probe connections. Figure 3.6 shows the photographs of the connections at the top of the RUS cell and the RTD element in place close to the transducers (position of test samples). The figure also shows a schematic diagram of the RTD circuit, an accurate external current source and two power resistors (a 10 Ohms and a 100 Ohms) are used in the circuit. The power resistors are very ohmic in nature. Unlike regular resistors, resistance of a power resistor does not change as the heat is dissipated due to current increases. The output potential difference is read by a digital voltmeter (in this case we use the Keithley multimeter). Computer code was written to accept the output voltage from the digital voltmeter and convert it to the temperature of the sample.

3.4 Sample Preparation

The RUS code has evolved over the years to deal with samples in a variety of regular geometric shapes such as rectangular parallelepipeds, spheres, ellipsoids, hemispheres, cylinders and many other analytic shapes. A rectangular parallelepiped is a convenient regular geometry that can be cut from a raw material of any shape. Therefore, sample preparation involves the making of a geometrically perfect sample with well polished surfaces. In most
Figure 3.5: The plots of temperature readings showing variations in the measurements from thermocouple and RTD with cold water flow rates of 8.6 ml/sec and 5.6 ml/sec, respectively, in the “cold–finger”.
cases the original test material that we receive comes in various sizes and shapes. So the first step is sample preparation.

The RUS code can compute the crystal orientations in addition to elastic constants, but such calculations takes a longer time and may increase instability in the non-linear fittings. A sample with known crystal orientation is always preferred for the RUS calculation. Suppliers often provide crystal orientation information along with the crystals. If crystal orientations are not provided, the Laue x–ray diffraction method is a useful and popular
technique for determining the orientations in crystals. Once the crystal axes are obtained they must be carefully tracked throughout the whole sample preparation process. So crystal axes and geometric axes are always known during the sample preparation.

For isotropic or polycrystalline materials that can be treated as isotropic materials for RUS there are no orientation concerns in the cutting and polishing processes. For those expensive or rare materials that are often available in small sizes, they are simply cut in such a way that maximum sample yield can be achieved. The cutting and polishing procedures described in the following sections are applicable to polycrystalline materials that can be treated as “isotropic” if crystallites are randomly oriented and small compared to the sample size.

3.4.1 Cutting

A low–speed diamond saw (South Bay Technology Model 660) with a cutting fluid is used to cut the bulk samples into smaller rectangular parallelepiped test samples. The bulk sample is mounted on a cutting board using low temperature mounting wax (QuickStick Mounting Wax, South Bay Technology) to secure the sample and prevent its edge from breaking apart or cracking. The low speed cutting and use of the cutting fluid ensures that there will be minimum mechanical and thermal impact on the samples and prevent the samples, especially fragile and brittle samples, from breaking apart. Residual wax is removed by submerging the sample into acetone in a glass container.

In the case of an anisotropic sample, for instance, an irregular shaped piece of material with unknown lattice orientation, the sample cutting is preceded by a crystal orientation.
The sample can be mounted on a goniometer that allows free rotation in two planes and then the Laue method of x-ray diffraction can be used to set the crystal orientation by aligning the sample with a known axis. The next step is to cut a regularly shaped piece from the sample. Once again, a cleaner sample cut is achieved by encasing the sample within a blob of low-temperature wax, and the residual wax is removed by dissolving it in acetone.

The dimensions of fresh cut parallelepipeds are typically in the range of 2 to 5 mm. The three dimensions of the sample should be different to avoid frequency degeneracy. This is especially critical in temperature/pressure induced phase transition studies. After the sample temperature and (or) pressure is changed, two adjacent peaks may shift in opposite directions. The correct order of these two peaks is easily mistaken, resulting in tracking the wrong peak after the transition temperatures and pressures. A worst case scenario is to track the wrong peak after the transition temperature and (or) pressure and an incorrect conclusion is consequently drawn. In most cases, one or more dimensions may be restrained by the sizes of the original bulk samples. If one dimension is significantly larger than the other two, sample resonances will be unevenly dominated by bending modes. As a general rule of thumb, the length of the largest dimension is kept within twice the length of the smallest dimension.

3.4.2 Polishing and Cleaning

A lapping and polishing machine (South Bay Technology Model 920) is then used to polish the sample to produce high quality surfaces. Aluminum oxide (Al₂O₃) abrasive film disks of different grit sizes from 30 to 0.5 μm are used to get the desired surface quality. All
six surfaces of the rectangular parallelepiped sample will be polished. The polishing starts with one face of the sample glued to the flat surface of a stainless steel mounting disk by Duco cement thinned out with acetone. The mounting disk is then placed on a hot plate heated to about 60 – 70°C, and some pieces of the low-temperature wax are placed on top and around the sample. Once the wax has melted and completely covered the sample, the mounting disk is removed from the hot plate and allowed to cool at room temperature. The cooling process may be accelerated by placing the disk on a heat sink. The hardened wax that encases the sample will provide a protective support for the sample during polishing. The disk is then attached to the polishing jig using a shaft. Sandpaper is used with distilled water as lubricant to quickly wear down the wax covering. The polished wax surface is checked frequently so that one can stop as soon as a flat surface, good corners and edges of the sample are obtained.

Once the sample surface is exposed, it is transferred to the lapping machine and the abrasive films are used to complete the job. Usually, starting with 15 µm grit size and then to 8, then 5, 3 and perhaps 1 µm to get a smooth, shiny surface. Distilled water is used as lubricant and the sample surface is carefully examined, regularly throughout the polishing process, under microscope to be free of major defects. The mounting disk is detached from the polishing jig and it is put in a beaker. Enough acetone is put in the beaker to just cover the disk and the sample; this will dissolve all the wax. Eventually, the sample will detach from the mounting disk and it is removed and cleaned with acetone and methanol. The polished side is then glued to the mounting disk so that the opposite side may be polished parallel to it.
After the first two opposite faces are finished, two rectangular blocks are needed to mount the sample so faces that are 90° with respect to the first two polished faces can be obtained. Figure 3.7 shows how the sample mounted using two right angle stainless steel blocks. This makes the remaining two pairs of opposite parallel faces perpendicular to each other and to the two originally polished faces. When all the six faces are done, the samples are carefully examined under the microscope to be free of major defects such as large scratches, holes on the surface, damaged edges or corners. The sample is ultrasonically cleaned in methanol before testing. Figure 3.7 shows the stages of polishing procedure with the use of rectangular (right angle) blocks.

The mass and dimensions of the polished samples are measured before the sample is mounted for RUS measurement. Dimensions are measured using a micrometer (Mitutoyo Series 293) with a resolution of 0.001 mm. Each dimension is taken at three different spots on the surface and the average is used for the RUS calculation. The dimensions are usually fixed during the RUS calculation because the measured dimensions are very close to their actual values. A digital micro–balance (Mettler AE50) with resolution of 0.0001 g is used for the mass measurement. The dimensions and mass are then used to calculated density of the test sample.
Figure 3.7: Polishing parallelepiped sample using the right angle blocks (a) the sample is mounted and glued to the block with thinned duco cement (b) a blob of wax used to encase the sample to protect the corners and edges of the sample (c) polished surface and the residual wax will be removed by dissolving it in acetone

3.5 Experimental Procedures

3.5.1 Introduction

The experimental procedures are similar to those of regular RUS measurements; they involve mounting the sample between two transducers, driving one with vibrational energy and using the other to detect sample resonances, except that the emphasis in our experiments is on high temperature and high pressure regimes. High temperature and high pressure measurement is a prolonged process, and the duration of a typical run being 2-3 weeks.
A complete experimental run consists of many RUS measurements at various temperatures and pressures. For each isotherm, data are taken as pressure increases and as pressure decreases to check for hysteresis at the isotherms. The ranges of temperature and pressure were chosen based on the available phase diagram. The intervals at which measurements were taken are based on the desired resolution. The interval and range may be adjusted based on observations as the measurements are being taken or in the previous run of the experiment. For instance an abrupt change in the elastic constants trend may require a higher resolution in the next run.

The strength of the acoustic resonances usually deteriorates with an increase in temperature and pressure; the rate of deterioration depending on the material. In addition the sensitivity of piezoelectric transducers decreases with an increase in temperature. The room temperature spectrum can be used to determine how good the data will be at much higher temperature because the quality of the signal typically will decrease with an increase in temperature, so it is very important to have a good acoustic signal at room temperature. A series of room temperature scans of the sample, that usually starts with a very broad scan, is done to determine several experimental parameters: (i) the mounting style of the sample between the two transducers that will yield the best acoustic signal; (ii) suitable frequency range(s) for sweeping, either one or a whole frequency range or several ones according to the way the resonance peaks are spaced; (iii) the lowest frequency mode; (iv) use the resonance spectrum obtained with the measured density and initial guesses of the elastic constants to obtain a good room temperature fit of the elastic constants.
3.5.2 Sample Mounting

In RUS measurements, the sample must be mounted such that it is held as lightly as possible between the two transducers. Plastic tweezers are used to load the samples to avoid damages and scratches on the surface of the samples. Soft and very small samples can be mounted by vacuum tweezers. Samples are commonly mounted in two different ways as shown in Figure 3.8. In the “corner mount”, the two diagonal corners of the sample are in contact with the two transducer faces. The advantage of corner mount is that, theoretically all the vibration modes can be detected. However, the corner mount has its own drawbacks. It is a very tedious mounting style. In a set–up such as ours, once sealed, the sample is unreachable and if the sample dropped in the midst of a run, the measurement will be terminated. Lastly, if the samples have been well prepared, they will have sharp edges and corners which can damage the surface of the transducers especially at high temperatures and pressures. Hence, corner mount is not suitable for high temperature and high pressure RUS measurements.

Practically, “face mount” is adopted throughout all the high temperature and high pressure measurements. In face mount, the sample is usually in good contact with the lower transducer. Though the transducer system is constructed such that the opposing faces of the two transducers are parallel, the upper transducer may likely touch the edge or corner of the sample’s face. Some resonance frequencies may not register signals on the upper pick up transducer when the sample if face mounted. A 90° rotation or a lateral shift of the sample can change the relative strengths of peaks, and the missing peaks may reappear. An overlay of several resonance spectra with sample mounted differently usually show a
complete resonance spectrum. An optimum mount is determined to be the one that has least number of missing peaks and the most peaks that are stronger. The relative strength of each peak may also vary with changing temperatures. The first mode is almost always one of the weakest modes with the face mount but strongest in a corner mount.

Figure 3.8: The two common ways of mounting a sample between the transducers in a RUS measurement (a) Corner mount: transducers sit on the two diagonal sharp corners of the sample. (b) Face mount: transducers sit on the two opposite faces of the sample.

After the sample is mounted between the two transducers, the whole cage including the sample and the transducers is lowered into the center of the stainless steel tube of the RUS cell. During the lowering process, the sample may shift or even drop. So, prior to sealing the whole system, a quick frequency sweep is done to ensure that sample is still
3.6 Data Acquisition and Signal Processing

3.6.1 Data Acquisition Electronics

The basic electronics for RUS measurement consists of a function generator, a lock-in amplifier and possibly a pre-amplifier. The function generator DS345 (Stanford Research Systems Inc.) is used to generate sinusoidal waveforms from around 100 kHz to 1 or 2 MHz for sample excitations. The driving transducer is connected to the function generator, thereby making it the excitation transducer. The function generator’s output voltage is usually set at 1–10 V (Vpp) range for most measurements.

Lock-in amplifiers are designed to detect and measure very small sinusoidal voltages; all the way down to a few nanovolts. Accurate measurements can be made even when the small signal is enveloped by noise sources many thousands times larger. These capabilities make the lock-in amplifier particularly suitable for resonance measurement in RUS. Unlike regular voltmeters, the lock-in amplifier use a technique known as phase sensitive detection to single out the component of the signal at a specific reference frequency and phase. Noise signals at frequencies other than the reference are rejected and do not affect measurement. Hence, lock-in amplifier needs a reference input to “find” the right (frequency) signal to be measured. In our RUS measurement, the output from the function generator is split into two parts: one is used to drive the excitation transducer, the other is used as reference signal for the lock-in amplifier. Suppose the reference signal is \( V_R \sin(\omega_R t + \theta_R) \), and the response
signal from the pickup transducer is $V_I \sin(\omega_R t + \theta_I)$. The lock-in amplifier multiplies the signals using an internal mixer. The mixer generates the product of its two inputs as

$$V_{\text{MIX}} = V_R \sin(\omega_R t + \theta_R) V_I \sin(\omega_R t + \theta_I) =$$

$$\frac{1}{2} V_R V_I \cos(\theta_R - \theta_I) + \frac{1}{2} V_R V_I \sin(2\omega_R t + \theta_R + \theta_I)$$

(3.1)

The first term is the DC component since both the input and reference signals are at exactly the same frequency. The second term is at a frequency that is twice the reference frequency and can be readily removed using a low-pass filter. After filtering, the output becomes

$$V_{\text{MIX+FILT}} = \frac{1}{2} V_R V_I \cos(\theta_R - \theta_I)$$

(3.2)

which is proportional to the cosine of the phase difference between the input and the reference. The SR844 (Stanford Research System Inc.), employ two mixers to determine the amplitude of the input signal. One of the mixers use a 90° out-of-phase reference input. Therefore, both the in-phase and quadrature (90° out-of-phase) components of the sample resonance can be detected. The amplitude and phase of the input signal can be determined from the output of the two mixers. In the RUS measurements, the pickup transducer feeds the signal directly to a lock-in amplifier SR844 (a pre-amp can be used if the signal is weak).
3.6.2 High Temperature and High Pressure Measurement Procedures of Metal Hydrides

A set of room temperature measurements are carried out to ensure that good fit for the elastic constants are obtained. The whole system is sealed off and flushed with an inert gas for few minutes. In most cases metal hydrides exist in phases and there may be need to avoid mixed phase regions. This is achieved by heating up the system to a temperature (isotherm) that is outside the mixed phase region before exposing the sample to hydrogen gas. After the system is sealed off, the inert gas/air mixture in it is evacuated using a vacuum pump. It is then back filled with inert gas up to atmospheric pressure and the furnace is turned on. The inert gas enhanced heat transfer in the system and because of thickness of the stainless steel tube cell, the difference between furnace temperature and temperature reading by RTD near the sample is large. For instance, at 300 psi oven temperature of $362^\circ\text{C}$ gives a sample temperature of $306^\circ\text{C}$. The furnace temperature is controlled by a Eurotherm 2408CP temperature controller which is adjusted manually, usually in a series of step increases until the desired temperature is reached. At the same time the tap water ("cold") that runs through the cold finger is turned on at a controlled rate. The rate is measured and monitored at regular interval throughout the experimental run and it is approximately 5.6 ml/sec. It is measured by collecting the water in a large beaker and using a stop clock to calculate the flow rate. When the temperature stabilized, the inert gas is evacuated again using vacuum pump, at this point hydrogen gas will be introduced into the system in a controlled and gradual manner. The pressure is attained by introducing gas into the cell, gradually, through the inlet while the outlet is closed. The pressure level is
monitored by a Heise pressure gauge.

The temperature and pressure are displayed on the computer screen for instant monitoring. A computer code (written in Python) is used to read out the temperature and pressure values, and to determine if the sample's temperature and pressure have stabilized. The hydrogen atoms are expected to get absorbed into the metal lattice and the process will require a period of time before reaching equilibrium. A small range scan is set up to run every 90 seconds to monitor the shift in the frequency of a selected frequency range, known to have a well defined sample's resonance peak. The idea is, when the system is at equilibrium the resonance peak will cease to shift. This is done to ensure that equilibrium state has been reached before taking a complete scan.

The data acquisition process, apart from the temperature and pressure controls, in a single temperature and pressure run is automated and controlled via GPIB bus by a custom developed batch scan module in RUSTOOLS_HP_HEISE_RTD (see Appendix C.1) running on a personal computer. During the data acquisition the sample temperature and pressure are recorded at every tenth interval of the data collection. The averages are used as sample's temperature and pressure. To obtain the sample resonances, the input frequency to the synthesizer is incrementally swept through a small step frequency (for instance 20 Hz). The drive frequency along with the in-phase and quadrature components of sample response detected by the lock-in amplifier are recorded into a data file.

An input text file, named “rusin.txt”, is used to set the parameters for the frequency scans. In this text file, any line with leading character ‘#’ is considered as a comment line. The first non-comment line at the top of the input file sets global parameters for the
synthesizer: output voltage (in volts) from the synthesizer, wait time (in seconds) after each
frequency increment and wait time after a change of frequency range, and the number of
averaging of signals at a particular frequency; the second line and the rest of the file sets
the frequency ranges (in MHz) to be scanned, the number of data points, and the names
of data file. A frequency range line with minus sign as the leading character implies that
frequency range will be skipped during the scan. This handy feature is useful when one or
more frequency ranges are to be skipped during a rescan. A typical input file looks like:

```
# Rusin file for the PdH data acquisition
5.0, 0.02, 3, 1
-0.39, 0.42, 1500, tmp.dat
0.20, 0.60, 20000, s1_hp_cell.dat
0.28, 0.35, 3500,s2_hp_cell.dat
```

In the file, output of the function generator is set to 5 volts (Vpp). The lock-in
amplifier waits 0.02 seconds after each frequency increment. If the wait time is too short,
the amplifier may not be able to detect the frequency change of the sample resonance and
achieve the 'lock', the result of short wait time will be an incorrect (out-of-sync) reading in
voltage. When the synthesizer jumps from one frequency range to another, a longer wait time
of 3 seconds is used. The number, 1, at the end of the line indicated that there is no averaging
in the data acquisition. The third line is skipped during the scan because of 'minus' sign.
The fourth line describes a frequency range for scanning, starting from 0.2 MHz to 0.6 MHz,
a total of 20000 data points are recorded into the data file named “s1_hp_cell.dat”. The last
line describes another frequency range that will be scan. In most cases, a single frequency
range is used during high temperature and high pressure RUS measurement because the
resonance peaks will shift. Thus breaking the frequency range into series of ranges might
result into missed resonance peaks at high temperature and pressure. The use of input file provides a flexible and convenient means to control the measurement. While the scans are in progress, the detected resonance signals are displayed on the computer screen for instant monitoring. Figure 3.9 shows a typical screen shot of the data collection. The scans can be terminated right after a problem is spotted, without waiting for the current scan to finish. A rescan will be initiated immediately after the problem is resolved, if needed the input file can be adjusted.

3.6.3 Frequency Extraction

The detected resonance signals in the frequency domain have both magnitude and phase information. The response is separated into in-phase and quadrature components. The resonance modes are computed from the in-phase component. In the phase-sensitive system, the phase information helps identify the resonance response peaks correctly. Each single mode is assumed to have Lorentzian lineshape with some arbitrary phase shift. Mathematically, the Lorentzian lineshape can be expressed as

\[
L(\omega) = a_0 + a_1\omega + a_2\omega^2 + a_3\omega^3 + \cdots + A\left(\frac{\omega}{\omega_0}\right) \cos \phi + \frac{\left(1 - \left(\frac{\omega}{\omega_0}\right)^2\right) Q \sin \phi}{\left(\frac{\omega}{\omega_0}\right)^2 + \left(1 - \left(\frac{\omega}{\omega_0}\right)^2\right)^2 Q^2} \tag{3.3}
\]

where \(A\) is a dimensionless constant, \(\omega_0\) is the resonance frequency, \(\omega\) is the reference frequency, \(Q\) is the quality factor and \(\phi\) is the phase angle of the resonance signal with respect to the reference. The first part of the function represents the background due to crosstalk of the transducers, and the last term is the peak. This model is used in the present work.
Figure 3.9: Typical screen shot of the data collection of the high temperature and pressure RUS experiment.
to fit the resonances, and a Scilab script is written using this model as our fitting code. Multiple
overlapping modes are considered to be a superposition of Lorentzians. Figure 3.10 shows a
typical Lorentzian lineshape fit of the resonance frequencies. In the figure the fitted
frequencies are 407433 Hz, 408586 Hz, 415353 Hz, 420134 Hz and 428231 Hz, the respective
quality factors are 1266, 1456, 1180, 1475 and 584.

With high SNR and well-separated modes, the fitting code can automatically extract
the center frequency and quality factor for each single mode. But in most cases, one has to
manually fit several modes at once due to degeneracy and the overlapping modes. The Scilab
script was specially written to handle multiple peak fitting process. Instead of working with
one peak at a time, a group of peaks is fitted at once. After the resonance data file is loaded
and plotted on the computer screen, one need to left click and right click on the plot to set
the lower and upper frequency boundaries, then click where you think each peak is located.
The fitting program will automatically extract the center frequencies and quality factors for
all the peaks over the frequency range just selected.

The fitting procedure works well when the peaks are well separated from each other.
In the case of closely located peaks, one should use some judgment to determine the number
of peaks and properly select the lower and upper frequency boundaries throwing part of a
peak outside of the frequency range. When one strong peak (in amplitude) dominates a
neighboring small peak, the small one appears to be a tiny “bump” over the “hill” of the
large one. If the small peak is not properly identified, the computer code may mistakenly
treat it as noise. The relative strengths of most peaks will change when the sample is
mounted differently. An overlay of resonance responses from several scans helps determine
Figure 3.10: Sample of a typical Lorentzian lineshape fit. In this sample five resonance frequencies are fitted from the datafile: C:/PdH2010/PdMTK07/T290/P250/s1.dat. The fitted resonance frequencies and their corresponding quality factors are listed at the top of the graph.
the exact number and positions of peaks, especially weak ones. It is not uncommon that two overlapping peaks appear to be one. Care should be taken not to fit them with just one peak. Whenever the error in fitting a single peak is high, it is wise to check if this single peak is actually two overlapping peaks.

There is sometimes no definitive way to know the exact number of peaks without actually fitting the measured spectrum to the computed one. Some guesswork is then needed in RUS calculation. It is a good practice to start fitting the first few peaks (make sure to include the lowest mode), and add more peaks to the fit process in each trial. The missed peaks may be eventually revealed in this “trial-and-error” method. In high temperature and high pressure RUS, the known resonance spectrum at one temperature and pressure point can be used as reference for identifying the peaks at the next higher/lower temperature and pressure point.

After the spectra for all the temperature and pressure points have been acquired, they are batch processed by the specially written Python script to compute elastic constants (see Appendix C.2). The measured spectra along with temperature and values are organized in a text file named “allfreqs.dat” as shown in Table 3.1. The first row is temperature value in °C, this is same value for all columns since it is an isotherm. The second row contain the pressure values in psi. The rest are frequencies in MHz. The zero (0.000000) serves as a place holder for a mode that cannot be detected or identified. The batch processing script reads the temperature value once from the file. Next, it reads in the pressure point with its corresponding spectrum (column one) and compute the elastic constants. These computed elastic constants are used as the initial guess values for the next pressure point (column
two) calculation. The dimensions and density are adjusted using the coefficient of thermal expansion and the temperature. If one mode cannot be detected at one pressure point, it must be ignored in all other pressure points in the RUS calculation. The rows that start with ‘-’ are ignored. This will ensure that the same modes are used in the RUS calculations. The batch process continues until the last pressure data is processed. The output including the elastic constants and RMS errors is written to a text file named “alldata.dat”. Typical RMS errors are between 0.1–0.3%, tending toward the higher end at the higher pressures due reduction of the quality factors and also and increase of noise in the data.
Table 3.1: A sample allfreqs.dat file used in the computation of elastic constants for an isotherm and all pressure points. The first row is the temperature value (the isotherm) in °C. The second row are the pressure values in psi. The rest are frequencies in MHz. The zero (0.000000) serves as a place holder when a mode cannot be detected or identified. The rows starts with ‘-’ are not used in the calculations. (Note that a section of the frequency data is used here full pressure range is from 250 psi–500 psi)

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CHAPTER 4

METAL HYDRIDE

4.1 Introduction

The search for alternative sources of energy storage and distribution systems that will be environmentally friendly has been the moving force behind research into “clean” energy systems such as hydrogen gas. The abundant availability of hydrogen with its desirable properties such as light weight, low density, high energy density and non-polluting nature makes it attractive to many researchers as an ideal alternative source of energy. Hence, there is need for creating light, efficient and safe hydrogen storage media. One possibility is the storage of hydrogen in low–density metal hydrides where the hydrogen can be stored as solid-state at moderate temperatures and pressures [60]. Metal hydrides are made up of metal atoms as the host lattice for the hydrogen. When a hydrogen molecule interact with the metal surface, the molecule dissociates into a pair of hydrogen atoms. The atoms then diffuse into the bulk metal and move in between the interstitial sites of the metal lattice to form the hydride phase. These H–atoms sit on the tetrahedral interstitial sites in metals with BCC lattices (such as niobium, tantalum and vanadium) and on the octahedral interstitial sites in metals with FCC lattices (such as palladium). Figure 4.1 shows the schematic diagram of an hydrogen atom at an octahedral interstitial site of a FCC unit cell.

The hydriding mechanism involves two stages; the physisorption and the chemisorp-
Figure 4.1: Schematic diagram of the hydrogen atom residing at the octahedral interstitial of a FCC unit cell.

The physisorption of hydrogen molecule on the metal surface is the first step in which the molecule sticks on to the surface physically usually by either van der Waals or electrostatic attractive forces (the same kind of forces that are responsible for the imperfection of real gases and the condensation of vapors) without forming any chemical bonds. Physisorption is a reversible process which depends on the temperature and pressure. If the temperature and pressure are high enough, the physisorbed hydrogen molecules dissociate into atoms and become chemisorbed. Chemisorption of hydrogen is the combination of hydrogen atoms with metal (the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds) to form a new compound and both
parties change chemically. During this process hydrogen atoms penetrate the surface and diffuse into the sub-layers of the metal.

Absorption/desorption of hydrogen by metal structure is a slow exothermic/endothermic process. When metal hydrides absorb hydrogen heat is released as shown in Figure 4.2. On the other hand, heat is required to release hydrogen atoms from the metal lattice. Figure 4.2 shows the schematic diagram of the absorption and desorption processes. The upper part of the diagram shows the absorption process where hydrogen molecules are attached to the metal surface and dissociate into hydrogen atoms. Metal hydrides are formed when the hydrogen atoms penetrate into metal structure. The lower part of the diagram shows the desorption process where hydrogen atoms leave the metal structure and combine to form hydrogen molecules. A consequence of the heat exchange between the metal hydride and the surrounding gas will be a change in the temperature. In order to maintain an isothermal process, hydrogen gas pressure change must be done very slowly.

Many of the rare-earth and transition metals readily absorb hydrogen, which occupies interstitial sites in the host lattice. The absorption of hydrogen is always associated with an expansion of the lattice. This is another reason why hydrogen gas must be introduced slowly since sudden large expansion might “crack” the metal. The expansion will affect the elastic constants of the metals. Most desirable applications of metal hydrides require hydrogen storage to be reversible over many charging and discharging cycles. So understanding the absorption and/or desorption kinetics of hydrogen will help in the design of hydrogen storage systems. In addition, the absorption or desorption of hydrogen is a time consuming process [16]. The time scale may be reduced with the aid of an acoustic resonance of the
Metal hydrides exhibit phases which are classified based on (i) the crystal structure of the metal atoms, (ii) the site(s) that H-atoms occupy and (iii) whether the H-atoms are ordered or disordered. A change in any of these parameters is usually denoted as a new phase. The fundamental thermodynamics of incorporating hydrogen atoms into metallic lattice is an interesting and active area of research [17,62–66] that will help in understanding the phase behaviors of the material. Phase diagrams play a very important role in materials science. They are “maps” of regions in which certain phases or phase mixtures exist. These diagrams represent fundamental thermodynamics characteristics of interacting particles.

Figure 4.2: Schematic diagram of the hydrogen absorption and desorption processes in metal hydrides.
For metal hydride systems, the thermodynamic criterion for equilibrium between the solid and gaseous phases is the equality of the hydrogen atom chemical potentials. The chemical potential is a function of temperature and pressure, $\mu(T,p)$, so the temperature and pressure of the hydrogen gas surrounding the metal are significant thermodynamic variables in the determination of the phase boundaries. Beyond this, phase diagrams provide basic information that are essential for the preparation of samples, for applications of the material and for correct interpretation of experimental results. A common feature of the metal hydride phase diagrams is the presence of hysteresis between the absorption and desorption cycle for each isotherm in the mixed phase region. The hysteresis as shown in Figure 4.3 indicates that the absorption plateau is higher than desorption plateau. The reaction of hydrogen with metal can be expressed as a reversible reaction:

$$M + \frac{x}{2}H_2 \leftrightarrow MH_x + \text{Heat}$$

4.2 Palladium Hydride

The palladium hydrogen system is a metal hydride system that has been extensively studied over many years [16,67–71] and can be considered as a classic metal hydride system. The reason for this is because it is the system in which reliable experimental data can easily be obtained. Pure bulk samples of palladium can be obtained with negligibly small interstitial defects and no surface treatments are needed to achieve equilibrium between the
Figure 4.3: Schematic diagram of isothermal pressure hysteresis in metal hydride during the absorption and desorption processes.

gaseous and solid phases.

Palladium has FCC structure so H-atoms sit in the octahedral interstitial sites of its lattices. At room temperature, the lattice parameter of palladium is 0.3890 nm, upon hydrogen absorption the lattice undergoes an isotropic expansion while maintaining the FCC structure. In the dilute α-phase ($PdH_{x=0.02}$), where the H-atoms are randomly dispersed in the metal lattice, as shown in Figure 4.4(a), the lattice parameter slightly increased to 0.3894 nm [19]. Above this concentration and up to $PdH_{x=0.6}$ the high concentration, ordered β-phase appears resulting in a mixed phase region and the lattice parameter becomes substantially greater than that of a pure palladium for instance at $x = 0.7$, the lattice
parameter is 0.4040 nm [19]. When $x > 0.6$ the $\alpha$-phase disappears, Figure 4.4(b) shows the schematic diagram of the ordered $\beta$-phase. These phases combine to form a single phase region [72] above the critical point (temperature, pressure and composition). Figure 4.5 shows the pressure-temperature-composition phase diagram of $PdH_x$ including the critical point indicated as $\ast$. For $T > T_c$ (critical temperature) the isotherm never passes through the two-phase region irrespective of the hydrogen gas pressure. The measured value of the tricritical point in palladium hydride system is: $T_c = 293^\circ$C, $P_c = 290$ psi and $(\frac{H}{T}) X_c = 0.26$.

The boundary of the mixed phase region was traced out by taking an average of the
limiting values for the isotherm plateaus of the each $T - X$ plots determined by several investigations [73–80]. Due to the presence of hysteresis between the absorption and desorption cycles it is possible to have two different sets of boundaries for the mixed phase region at each isotherm, Figure 4.5 was derived from the desorption isotherms. The limiting $T - X$ values for the isotherm plateau are used with 4th order polynomial fit to determine the critical temperature, $T_c$, the critical pressure, $P_c$ and the critical hydrogen concentration, $X_c$. 

Figure 4.5: Pressure-Temperature-Composition phase diagram of $PdH_x$. [17]
4.3 Thermodynamics of Metal Hydride

The incorporation of hydrogen atoms in the metal lattice is accompanied by the distortion of the host metal lattice; this will cause a structural change and affect the thermodynamics of the system. Several attempts [19, 81, 82] have been made to find the correct theoretical explanation for the phase diagram and the thermodynamic properties that results from incorporating H-atoms into metals. The usual procedure is to develop a microscopic model of hydrogen in metal with some set of assumptions on the nature of the interactions between the atoms and then obtain the phase diagram and the thermodynamic properties using statistical mechanics. The microscopic model is usually the lattice-gas model in which particles are restricted to sites but can jump from one site to another. Only one particle is allowed per site and the interactions between particle are a function of the distances between the sites on which the H-atoms sit [83, 84]. The simplest model with this procedure is to assume a very dilute solution where hydrogen atoms are far enough apart that their mutual interaction can be taken as zero. The grand partition function of the model is then calculated and from this, the chemical potential of the system and the equation of state will be derived. Using this approach, Hall [18] showed that it could only predict correctly the behavior of the metal hydride system in the dilute limit. The model was modified by Lacher [85] to include attractive interactions between nearest neighbor hydrogen atoms. Speiser and Spretnak [86] have also considered a model with repulsive interactions between nearest hydrogen atoms. In 1962, Libowitz [82] considered metal hydride deviation from stoichiometry due to hydrogen vacancies or excess metal interstitials. The equation of state derived by Libowitz showed a behavior similar to the phase diagram obtained from experimental result. Especially at tem-
peratures greater than the critical temperatures which in turn is a function of the interaction energy between vacancies. The equation of state is

\[
\ln(p) = K'(T) + 2\ln\left(\frac{n}{s-n}\right) + \frac{2}{k_o T} \left[\frac{D_o}{2} - E_\nu + z \left(1 - \frac{n}{s}\right) E_{\nu\nu}\right]
\] (4.1)

where \(K'(T)\) is a temperature dependent constant containing the mass, nuclear spin weight and moment of inertia

\(p\) is pressure of hydrogen gas

\(D_o\) is dissociation energy of hydrogen

\(n\) is ratio of hydrogen atoms to metal atoms

\(s\) is maximum hydrogen to metal ratio

\(z\) is number of nearest neighbor hydrogen sites around each hydrogen site

\(E_\nu\) is energy of creating a hydrogen vacancy

\(E_{\nu\nu}\) is interaction energy of a pair of hydrogen vacancies

The critical temperature is set to

\[
T_c = \frac{zE_{\nu\nu}}{4k_o}
\] (4.2)

Gillespie and Galstaun [73] estimated this critical temperature for palladium hydride as 295.3 °C.

Figure 4.6 is similar to the plot of van der Waal's equation of state. When the temperature is above the critical temperature \(T_c\), each values of \(\log(p)\) correspond to different
values of \( n/s \). Below the critical the critical temperature and for pressures \( p_1 < p < p_2 \), there are three values of \( n/s \) for each \( \log(p) \). In this region the curve has two positive slopes corresponding to the single phases \( \alpha \) and \( \beta \). However for \( 0.2 < n/s < 0.5 \), the \( \alpha \)-phase will be more stable and at \( 0.5 < n/s < 0.8 \), the \( \beta \)-phase becomes more stable.

The presence of hysteresis in metal hydride systems in the absorption and desorption cycles of hydrogen atoms has been attributed, by the early models, to the plastic deformation that accompanied the volume change during the absorption and desorption processes. In 2006, Schwarz and Khachaturyan [62] proposed a model which showed that the hysteresis is an intrinsic thermodynamic phenomenon caused by coherency strains between the metal
phase and the transformed hydride phase. Coherency strain is the strain required to maintain a perfect lattice matching at the interface between two phases due to a slight difference in lattice parameter and orientation. The distortions associated with coherency strain lead to local increase in the internal energy of the lattice. They derived an equation for the elastic strain energy generated by each of the solute (H) atoms as

\[ E_{el} = 2N\nu_oG\frac{1+\sigma}{1-\sigma}\bar{\varepsilon}_o^2\bar{c}(1-\bar{c}) \]  

Equation 4.3 predicts the dependence of the elastic strain energy on the shear modulus of the metallic hydride system for a given composition. Schwarz and Khachaturyan explained that the coherency strain generates a macroscopic thermodynamic barrier that opposes both the forward and reverse isostructural hydriding transformations, and this causes a thermodynamic hysteresis on the isothermal pressure-composition curves for the cyclic absorp-
tion/desorption of hydrogen. Figure 4.7 was used to illustrate the transformation between α and β phases and the hysteresis involved in the transformation. Consider a reservoir that can exchange interstitials (H-atoms) with a solid placed in it and let the chemical potential of the interstitials in the reservoir be $\mu_r$. Thermodynamic equilibrium in the system can be established under the condition of a fixed chemical potential. Starting with the α-phase, the value of $\mu_r$ is increased monotonically and as long as $\mu_r < \mu_\alpha (c_\alpha^s)$, the solid can exist in the single α-phase. For $\mu_\beta (c_\beta^s) \leq \mu_r \leq \mu_\alpha (c_\alpha^s)$, the solid can exist in either the α or the β-phase but since the system was originally in the α-phase, and no phase transition can occur as long as $\mu_r < \mu_\alpha (c_\alpha^s)$, the system will remain in the α-phase. When $\mu_r$ equals $\mu_\alpha (c_\alpha^s)$, the α-phase becomes unstable and the $\alpha \rightarrow \beta$ commences. The solid absorbs interstitials until it transforms entirely to the β-phase of composition $c_\beta^{end}$. Hence the starting point for $\alpha \rightarrow \beta$ is

$$\mu_r^{\alpha \rightarrow \beta} = \mu_\alpha (c_\alpha^s)$$

(4.6)

where $\mu_\alpha (c_\alpha^s)$ is a material constant at a given $T$ and $P$. The saturation composition, $c_\beta^{end}$, is determined by the equilibrium equation,

$$\mu_r^{\alpha \rightarrow \beta} = \mu_\alpha (c_\alpha^s) = \mu_\beta (c_\beta^{end})$$

(4.7)

Similarly, starting with the single β-phase and decreasing the value of $\mu_r$, the desorption process for the reverse $\beta \rightarrow \alpha$ transformation is also blocked by a macroscopic energy barrier. The onset of the reverse transformation requires the chemical potential of interstitial atoms in the reservoir to decrease below the critical value $\mu_\beta (c_\beta^s)$. Therefore the starting point of
Figure 4.7: Schematic chemical potential for the coherent two-phase solid. The arrows indicate the transformation paths when the solid is in equilibrium with a source of interstitials of constant chemical potential [62].

the desorption is determined by the condition,

\[ \mu_r^{\beta \rightarrow \alpha} = \mu_\beta (c_\beta^*) = \mu_\alpha (c_{\alpha}^{\text{end}}) \]  \hspace{1cm} (4.8)

In metal-hydrogen systems hysteresis is usually expressed in terms of the difference in gas pressures \( p_g^{\alpha \rightarrow \beta} \) and \( p_g^{\beta \rightarrow \alpha} \) corresponding to respective chemical potentials needed to generate the \( \alpha \rightarrow \beta \) and \( \beta \rightarrow \alpha \) transformations. The chemical potential of the atomic gas
formed by a dissociation of its diatomic gas is

$$\mu_g (p_g, T) = \mu_g^0 + \frac{1}{2} kT \ln \left( \frac{p_o}{p_g} \right)$$  \hspace{1cm} (4.9)

A simple equation for the thermodynamic hysteresis expressed as the ratio of the diatomic gas pressures that trigger the forward and reverse transformations was derived by Schwarz and Khachaturyan as

$$\ln \left( \frac{p_{\alpha \to \beta}}{p_{\beta \to \alpha}} \right) = \frac{8 \nu_o G_1^0 + \sigma (c^*_{\beta} - c^*_{\alpha})}{kT}$$  \hspace{1cm} (4.10)

This proposed model predicts a softening of the shear modulus near the tri-critical point of $PdH_x$ system. The generated strain energy due to the coherent strain vanishes for single phase cases. As the system approaches the tri-critical point, $p_{\beta \to \alpha}$ approaches $p_{\alpha \to \beta}$, so the left hand side of Equation 4.10 decreases and on the right hand side the strain energy component of the equation will also decrease. The combination of this pressure difference effect and the vanishing strain energy implies that the shear modulus must also decrease near the tri-critical point.

To verify this assertion, Schwarz and Khachaturyan performed a partial $\alpha \to \beta \to \alpha$ transformation, on palladium powder in hydrogen environment up to maximum H/M interstitial concentration of about 0.3. The measured value of $c^*_{\beta} - c^*_{\alpha} = 0.52$ at 340 K temperature. This measured value was used with theoretical values of $\sigma$, $G_s$, $\nu_o$ and $\varepsilon_o$ in the Equation 4.10 to obtain $\ln \left( \frac{p_{\alpha \to \beta}}{p_{\beta \to \alpha}} \right) = 3.3$. However the measured equilibrium pressure values yielded $\ln \left( \frac{p_{\alpha \to \beta}}{p_{\beta \to \alpha}} \right) = 0.8$. From this observation, the parameters on the right hand side of the equation that can vary are the $G$ and $\frac{1+\sigma}{1-\sigma}$. 

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CHAPTER 5

ELASTIC CONSTANTS OF PALLADIUM HYDRIDE

5.1 Introduction

The elastic properties of palladium and palladium hydride have been the subject of several investigations [68, 71, 87–89]. However most of these studies are limited to low temperature regime. Yoshihara et al [88] studied the elastic properties of palladium crystal at high temperature. Elastic properties such as bulk modulus are essential for the calculation of many thermodynamic quantities. In this study, the elastic properties of palladium crystals at high temperature in an inert environment and those at high temperature and high pressure near the tri-critical point in hydrogen environment are measured. The purpose of measuring the elastic constants near the critical point is to look for thermodynamic instabilities which will reflect in the values of the elastic constants. Critical behavior is normally manifested by large spatial temporal fluctuations in mechanical and physical properties. A good example is the density fluctuations in water near the critical point.

5.2 Experimental Procedure

5.2.1 Sample Preparation and Test Layout

In this study single crystals of palladium were received from our collaborator, the crystals have been cut into good parallelepipeds and are in good conditions. Two \{001\}
plane FCC crystals, \textit{PdMTK}06 and \textit{PdMTK}07 are used. \textit{PdMTK}07 has been used at high temperature and high pressure in a hydrogen environment. The \textit{PdMTK}06 was tested at high temperature in an inert atmosphere up to 600 °C.

The mass and dimensions measurements were done and the results were used to calculate the densities of both samples. The information is given in Table 5.1, the dimensions and densities are the room temperature values only. They are adjusted accordingly at higher temperatures using thermal expansion coefficient of \(11.2 \times 10^{-6}/^\circ\text{C}\).

Table 5.1: Dimensions and densities of two sample of palladium single crystal with \{001\} plane

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dimension(cm)</th>
<th>Mass(g)</th>
<th>Density(g/cm(^3))</th>
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<tr>
<td>PdMTK06</td>
<td>0.2739 × 0.3519 × 0.3290</td>
<td>0.3757</td>
<td>11.8491</td>
</tr>
<tr>
<td>PdMTK07</td>
<td>0.2633 × 0.3509 × 0.3203</td>
<td>0.3525</td>
<td>11.9116</td>
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5.2.2 Room-temperature Test

Prior to the high temperature and high pressure RUS measurements, a series of room temperature tests were performed on the samples as part of the standard practice. The crystals are cubic so the elastic constants fits are done with a cubic computational model for extracting elastic constants from the measured resonance spectrum. Three independent elastic moduli are required to fully characterize the crystal. The three elastic constants obtained from the fits are \(C_{11}\), \(C_{12}\) and \(C_{44}\) from which three elastic moduli of interest can be calculated. These elastic moduli are shear modulus (G), bulk modulus (B) and Cprime (\(C'\)).
Another parameter that is of interest is the Poisson’s ratio ($\sigma$)

\[ G = C_{44} \]  

(5.1)

\[ B = \frac{1}{3} (C_{11} + 2C_{12}) \]  

(5.2)

\[ C' = \frac{1}{2} (C_{11} - C_{12}) \]  

(5.3)

\[ \sigma = \frac{C_{12}}{C_{11} + C_{12}} \]  

(5.4)

The result of the room temperature test are recorded in detail in Table 5.2. A total number of 28 sample peaks were used in the fits and the average RMS errors as < 0.2%. One of the two sample was reported to have been annealed. From our result we can conclude that PdMTK06 is the annealed crystal since its values are generally greater as shown in Table 5.2.

Table 5.2: Elastic properties of palladium crystal samples at room temperature

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<th>Property</th>
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<th>PdMTK07</th>
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<td>$C_{11}$ (GPa)</td>
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<tr>
<td>$C_{12}$ (GPa)</td>
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<td>$G, C_{44}$ (GPa)</td>
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<td>B (GPa)</td>
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<td>$C'$ (GPa)</td>
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<td>Error (%)</td>
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</tbody>
</table>

5.2.3 High Temperature and High Pressure Test

In the high temperature and high pressure test our focused region on the pressure-temperature-composition phase diagram is around the tri-critical point, where the single-
phase Pd-H alloy decomposes into $\alpha$- and $\beta$-phases. We carefully approached the critical point from above $T_c$ in a manner that avoided the mixed-region. The rate of introduction of hydrogen gas into the chamber needs to be very low. This is because when the pressure-concentration plot of isotherms flattens out, a small increase in pressure results in large increase in hydrogen concentration. The associated strain that comes with this increase will result in copious formation of dislocations and there will be generation of incoherent phase boundaries between the $\alpha$- and $\beta$-phases. Both can severely degrade the acoustic properties of the sample.

The high temperature and high pressure measurement was done according to the detailed procedure given in Chapter 3. Here the pressure range of interest is 250 psi - 500 psi, pressure intervals of 20, 10 and 5 psi are used, and all pressure measurements are absolute pressure. Data was acquired for 22 pressure points and 5 isotherms; 310°C, 300°C, 297°C, 294°C and 290°C. In order to avoid the mixed phase region, the following specific procedure was adopted for this experimental run:

1. Pump out chamber and back fill it with argon gas.

2. Heat the chamber filled with argon up to 310°C, the desired starting temperature, then evacuate through the outlet that is connected to a vacuum pump. A liquid nitrogen cold trap is setup along the connection between the outlet and vacuum pump to prevent oil deposition on the surface of the palladium crystal.

3. Then back fill the chamber with hydrogen gas up to 250 psi. Start the peak-tracking python script to monitor the equilibrium dynamics of the metal hydride system. A
complete RUS scan is done after equilibrium has been established.

4. Slowly increase the pressure up to 500 psi repeating step 3 at each predetermined pressure points. The total time spent on each pressure point is about 2-3 hours; this includes time taking to establish equilibrium and the time taking to do a RUS scan. Typical RUS scan takes about 20 minutes.

5. Repeat the process during pressure release (from 500 psi to 250 psi) checking for hysteresis.

6. Lower the temperature to the next isotherm then repeat steps 3 and 4.

The final temperature and pressure point of this procedure is 290 °C and 250 psi in hydrogen gas environment. In order to avoid the mixed phase region still, we need to increase the temperature. So, the temperature was increased to 313 °C and peak-tracking script was run to monitor the equilibrium of the system. After equilibrium has been established, a complete RUS scan was taken for the 313 °C, 250 psi temperature and pressure point. The hydrogen gas was then bled off gradually down to atmospheric pressure. Argon gas was used to flush the cell at 20 psi for 10 minutes. The temperature stabilized at 310 °C and a complete RUS scan was done for the 310 °C, 20 psi temperature and pressure point in argon (inert) environment. Lastly, the temperature was reduced to room temperature and another complete RUS scan was taken for the 22 °C, 14 psi temperature and pressure point, again, in argon environment. This run of experiment is a continuous process and it was done in 18 days without break. This run of the experiment was done with the sample *PdMTK07*. 
5.2.4 High Temperature Test

The second crystal (PdMTK06) was used in the high temperature test in an inert gas environment at atmospheric pressure. Ideally, temperature range of interest will be to get as high as possible close to the melting temperature of the crystal but the highest temperature possible is limited by the direct contact transducer system which is 650°C. The test was done in steps of 50°C. RUS measurements are taken after the temperature stabilizes. Typically, after the temperature has reached the set temperature and stabilizes, a wait time of about 5-10 minutes is needed for the sample to temperature to reach equilibrium. When equilibrium has been established a complete RUS scan of the palladium crystal is taken and the measurement takes about 20 minutes. Measurements were taken for both an increase and decrease in temperature. The high temperature RUS system was continuously flushed with low flow of argon gas, and an oxygen analyzer was used to monitor the oxygen content in the system. The upper limit of the measured oxygen content was 10 ppm.

5.3 Results and Discussion

The resonance frequencies were extracted using the Lorentzian lineshape fitting scheme for each isotherm and all pressure points. The file named “allfreqs.dat” was developed as described in Chapter 3. Files of the resonance spectrum containing the resonance frequencies of each temperature and pressure point were developed. These files were used in a batch process of the elastic constant fitting scheme for cubic crystal. The moduli; shear modulus, bulk modulus and $C'$ were calculated from the the elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ for each temperature and pressure points. Plots of the three elastic moduli as a function of
pressure for each isotherm were obtained and a detailed explanation of the plot are given below. Similarly, resonance spectrum file was developed for the high temperature test and using the fitting scheme in a batch process the elastic constants were obtained. These are, again, used to determine the elastic moduli of interest. Plots of the elastic moduli as a function of temperature were obtained as well.

5.3.1 Shear Modulus of Palladium Hydride at High Temperature and High Pressure

The shear modulus of palladium hydride as a function of the temperature and pressure near the tri-critical point is discussed in this section. Figure 5.1 shows the shear modulus of the palladium hydride as a function of pressure for the five isotherms near the tri-critical point. Open symbols are used for moduli measured during pressure increase and the filled symbols are moduli measured during the pressure decrease part of the experiment. The symbol represent the shear modulus at the end of the experiment at 312.81°C, 251.02 psi temperature and pressure point. The value of the shear modulus at this point is 64.6 GPa. In comparison to the value at the starting point, 310.36°C, 249.80 psi, which is 67.2 GPa. Generally, the trend of the shear modulus for all the isotherms are similar. The shear modulus decreases with increase in pressure almost nearly up to a pressure point and then the values drop off quickly after which it flattens upon reaching the lowest value for each isotherm. The softening of the shear modulus increases with decrease in temperature from 310°C to 290°C. As mentioned at the end of Chapter 4, the other possible variable term in the hysteresis equation will be $\frac{1+\sigma}{1-\sigma}$. So plots of $\frac{1+\sigma}{1-\sigma}$ ("Poisson’s ratio effect") versus
pressure for each isotherm was obtained as shown in Figure 5.2. This Poisson’s ratio effect increases with increase in pressure and decrease in temperature before the tri-critical point and it decreases almost linearly with pressure beyond the critical pressure. The percentage change in the values of shear modulus and \( \frac{1 + \sigma}{1 - \sigma} \) over the pressure ranges of 280 - 310 psi and 280 - 325 psi for 290°C and 294°C isotherms respectively were calculated. The percentage increment in \( \frac{1 + \sigma}{1 - \sigma} \) is 2% while the percentage decrease in the shear modulus is 8% for both isotherms.
Figure 5.2: Poisson’s ratio effect \(\frac{1+\sigma}{1-\sigma}\) versus pressure for the five isotherms. Open symbols are used for the pressure increase and filled symbols are used for pressure decrease.

5.3.2 Bulk Modulus of Palladium Hydride at High Temperature and High Pressure

Figure 5.3 show plots of the bulk modulus of the palladium hydride versus pressure for the five isotherms near the tri-critical point. Similarly to the plot of shear modulus, the open symbols are for the bulk modulus values during the pressure increase and filled symbols are the values during the pressure decrease part of the experimental run. The ★ is the equivalent value of the bulk modulus for the “end point” as described in Figure 5.1 and it is 169.5 GPa. The corresponding “start point” value is 169.8 GPa. The pressure trends of
Figure 5.3: Bulk modulus of the palladium hydride versus pressure for the five isotherms. Open symbols are used for the pressure increase and filled symbols are used for pressure decrease.

The bulk modulus in Figure 5.3 is quite different from those of the shear modulus in Figure 5.1. The bulk modulus values increase almost linearly with pressure after the initial decrease unlike the in the shear modulus plots where the values are almost constant after the initial decrease for each isotherm. Again, the values of the bulk modulus are smaller with decrease in temperature but after the turning points in the plots, at the higher end of the pressure, the values are larger with decrease in temperature.
5.3.3 $C'$ of Palladium Hydride at High Temperature and High Pressure

The plots of the $C'$ values in the region of interest are shown in Figure 5.4. The open symbols are for the $C'$ values during the pressure increase and filled symbols are the values during the pressure decrease part of the experimental run. The trends of the values are similar to those in the bulk modulus plots, the only difference is the actual values of the modulus. The $*$ is the value of the $C'$ for the “end point” and it is 20.3 GPa. The corresponding “start point” value is 20.7 GPa. It is important to state here that Figures

![Figure 5.4: $C'$ of the palladium hydride versus pressure for the five isotherms. Open symbols are used for the pressure increase and filled symbols are used for pressure decrease.](image)

5.1 - 5.4 did not show hysteresis between the plots of the increasing pressure (for instance T310P) and the decreasing pressure (for instance T310DP). Also note that the same set
of resonances was used to compute $C_{ij}$ (where $i, j = 1, 2, 3$) for all pressure points of each isotherm and very similar sets are use for all isotherms.

### 5.3.4 Anomalous Softening of the Elastic Moduli

The abnormal softening of the bulk modulus and the $C'$ plots did not show up in the shear modulus. The normalized frequency plots revealed that this difference could not have been a fitting problem. Similar difference in trends was also noticed between the plots of strongly shear modulus dependent frequency modes and those that are less dependent on the shear modulus as shown in the Figure 5.5. Another evidence for this behavior is the spectrum of the resonance frequencies shown in Figure 5.6. The frequency shifts downward for the pressure range 290 psi to 310 psi as the pressure is increased. However, beyond 310 psi the frequencies shift upward with increase increase in pressure. The frequency for each pressure point used was selected to illustrate the three modes of interest. Lastly, there is need to verify that this behavior is not due to the pressure effect. The $PdMTK06$, which has not been expose to hydrogen was used in a high pressure experiment at room temperature. This was done in inert argon gas and the pressure range is from 9 – 1000 psia. As shown in Figure 5.7 variation in the bulk modulus between this pressure range is about 0.07 GPa. This is very small compared to about 1.5 GPa change in the stiffening of the bulk modulus as shown in Figure 5.3 despite being over a smaller pressure range (300 – 500 psia). The comparison of the $C'$ plots resulted in the same conclusion that the abnormal stiffening is not due to the effect of hydrogen pressure on the palladium hydride but rather it is due to the absorption and desorption of hydrogen.
5.3.5 Elastic Moduli of Palladium Crystal at High Temperature

The temperature trends of the elastic moduli of palladium crystal are shown in Figures 5.8, 5.9 and 5.10. The open symbols are used for the moduli with “ramp-up” in temperature and the filled symbols for decrease in temperature. The bulk modulus and the \( C' \) decreases with increase in temperature, the trend is not linear, probably a quadratic function can be use to fit the trend. There is an upward shift in the trend of the moduli (bulk and \( C' \)) during the temperature decrease portion of the plot. Hence, it can be concluded that there is stiffening of these moduli as the temperature is decrease from 600°C to room temperature as evident in Figures 5.9 and 5.10. The temperature trends of the shear modulus is different...
Figure 5.6: Spectrum of resonance frequencies showing upward shift in the frequency with increase in pressure.

from those of the bulk and $C'$. Figure 5.8 shows that there is an anomalous stiffening of the shear modulus. Shear modulus increase with increase temperature from room temperature up to about 300°C where it is at the maximum value and it decreases afterwards. Also unlike the bulk modulus and the $C'$, the values of shear modulus during the temperature decrease is very similar to the values during the temperature increase part of the experimental run. The data for the high temperature experimental run was compared to that of Leisure and Hsu [68]. The publication have the value of shear modulus as 71.25 GPa at 300 K and our value for the shear modulus is 71.13 GPa at 295 K with an average error of 0.17%. Our values of shear modulus and $C'$ at high temperatures are also in good agreement with data
Figure 5.7: Bulk modulus of the palladium versus pressure in argon at room temperature. The bulk modulus values only show the difference relative to 193.78 GPa of Yoshihara et al [88].

5.4 Equilibrium Dynamics of Palladium Hydride Near the Tri-Critical Point

As mentioned in the procedure the equilibrium of the metal hydride system was monitored and we only did full RUS scan when the equilibrium has been established. This was done by using Python script. “Track_peak” to run scan over a selected frequency range, known to include a well defined sample resonance frequency, every 1.5 minutes. The idea is, when the system is at equilibrium the resonance frequency will cease to shift. The data of the shift in the resonance frequency was fitted to exponential function, $A_o \left(1 - e^{\frac{-t}{\tau}}\right) + offset$
Figure 5.8: Shear modulus of palladium crystal versus temperature at 1 atmosphere of pressure in argon gas. The open symbol is for the increase in temperature and filled symbol for decrease in temperature.

where the offset is some starting frequency. Some temperature and pressure resonance shift data fitted perfectly well to the exponential function as shown in Figures 5.11 and 5.12. Some other ones behaved non-monotonically as in Figure 5.13 while the rest are almost stable, shifting just about 200 Hz as shown in Figure 5.14. All the figures are from data during the pressure decrease and at 290°C. However, Figures 5.11 and 5.12 show opposite trends. This is because one is at 280 psi; before the critical pressure and the other at 410 psi; after the critical pressure. This reverse of trends is another indicator that supports the abnormal softening of the bulk modulus and $C'$.  

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Figure 5.9: Bulk modulus of palladium crystal versus temperature. The open symbol is for the increase in temperature and filled symbol for decrease in temperature.

The four categories of plots are shown with color code that is used to generate the colored map in Figure 5.15. The upper map is for increasing pressure from 250 psi to 500 psi, while the lower map is that of the decreasing in pressure from 500 psi to 250 psi. A clear correlation that can be easily deducted from the color map is that the flat portion of the shear modulus plots of palladium hydride corresponds to the “red” and mostly “yellow” portion of the color map. A possible explanation for the non-monotonic sections of the color map is that at those pressure points there might be merging of phases which resulted in slow dynamics in the $\alpha$ and/or $\beta$ phases. Also the range of frequency on the “quasi-stable state” graph is small. Possibly, in those pressure points the phase of the hydride might not
Figure 5.10: $C'$ of palladium crystal versus temperature. The open symbol is for the increase in temperature and filled symbol for decrease in temperature.

be changing and the system comes to equilibrium quickly that we were unable to observe it.

The color map can be used as probe to understand what happened in the palladium hydride system during the absorption and desorption processes. A good starting point is to state the sequence through which the color map was acquired. For each isotherm, the absorption (pressure increase) cycle was immediately followed by the desorption (pressure decrease) cycle. The color map for each isotherm during the absorption cycle is different from those obtained during the desorption cycle, this can be an indication for the presence of the thermodynamic hysteresis proposed by Schwarz and Khachaturyan [62]. This hysteresis was
Figure 5.11: A very good exponential fit of the equilibrium dynamics data of palladium hydride taking during the pressure decrease at 280 psia

not observed in the elastic moduli plots of the palladium hydride in Figures 5.1 - 5.4. A clear example of this is the clustering of the “red” at the end point of the pressure increase part of the color map but during the pressure decrease this portion are mostly “yellow” especially near the critical temperature. Secondly, the behavior of the palladium hydride around the critical point (293 °C and 290 psi) is mostly “green” on the color map of both pressure cycles. This represent a large change in the resonance frequencies and hence corresponding changes in the elastic moduli.
Figure 5.12: A good exponential fit of the equilibrium dynamics data of palladium hydride but the frequency shift occur over a small range. The data was taken during the pressure decrease at 410 psia.
Figure 5.13: Non-monotonic fit of the equilibrium dynamics data of palladium hydride taking during the pressure decrease at 440 psia.
Figure 5.14: Quasi-stable state fit of the equilibrium dynamics data of palladium hydride taking during the pressure decrease at 320 psia.
Figure 5.15: The colored map of the equilibrium dynamics behavior of palladium hydride. Showing the map for both pressure increase and pressure decrease parts of the experiment.
CHAPTER 6

CONCLUSION

The goal of this dissertation was to develop a high temperature and high pressure resonant ultrasound spectroscopy (HT&P RUS) system and to use the system to study metal hydrides and other solids at high temperature and high pressure. The investigations include temperature and pressure dependent elastic constant measurements, verification of the presence of hysteresis between the hydriding and de-hydriding processes of the metal, and the equilibrium dynamics of hydrogen absorption/desorption in metal hydrides. These goals have been successfully met. A direct-contact transducer system that can withstand the temperature and pressure range of interest was designed and constructed. A high pressure RUS cell that can hold pressure up to 2000 psi was also designed and constructed. The elastic constants of palladium crystal were evaluated at high temperature, 23 – 600 °C and those of the palladium hydride were evaluated near the tri-critical point (temperature $T_c = 293$ °C, pressure $P_c = 290$ psi and atomic ratio $\left( \frac{H}{Pd} \right) X_c = 0.26$). Successful measurements at elevated temperatures and high pressures demonstrate that RUS can be used as characterization tools for materials under extreme conditions.

Elastic properties are such fundamental properties of a solid that the measurement of elastic constants plays an important role in materials characterization. RUS is an acoustic method that is very precise, efficient, and capable of handling sub-mm sized samples and low symmetry crystals. The technique has been extensively used for room- and low-
temperature measurements. For applications in extreme conditions (under high temperatures and pressures) many hindrances need to be overcome. One of the major obstacles is that the transducer system must be able to produce effective acoustic resonance measurements under these conditions. The resonance frequencies of the transducers used in the transducer system are not within the frequency range of interest of all the measurements. As a result of these conditions, a custom designed transducer system, “direct contact transducer system” was made. Secondly, the RUS set-up must remain stable as the temperatures and pressures are being ramp up and down for many cycles. A low-oxygen environment is also required to protect test samples and the transducer system from being oxidized at high temperatures.

The elastic constant studies of the palladium hydride were done to verify the proposed model by Schwarz and Khachaturyan which claim that strong softening of shear modulus occur near the tri-critical point. This claim has been successfully verified, the plots of the shear modulus shows a drastic softening of the shear modulus near the tri-critical point. The plots of the result also indicate the absence of hysteresis in the elastic moduli. The RUS set-up was also used to measure the elastic properties of palladium crystal at high temperature but inert environment and the elastic moduli are comparable to those available in the literature. Another feature that was present in the elastic moduli trends with increase in pressure at temperatures near the critical temperature is the abnormal stiffening of the bulk modulus and the $C'$ at pressure points above critical pressure, $P_c$. This feature is absent in the shear modulus plots. Equilibrium dynamics of the hydrogen absorption and desorption by the palladium crystal was also studied and a color map was developed. Correlation between the color map and the phases of the palladium hydride was also established. Unlike
the elastic moduli plots, there are differences in the color map of absorption and desorption cycles. This is an indication of the presence of hysteresis, probably supporting the claim that the hysteresis is an intrinsic thermodynamic phenomenon.

This dissertation can be used as foundation for future work in this field. The limitations that were encountered include a direct connection between the onset of hysteresis and the softening of the shear modulus. This is because the required data to show this connection were not available. Hence, for future work; $\alpha \rightarrow \beta \rightarrow \alpha$ transformation experiments can be performed at temperature close to the critical temperature, $T_c$. Measured values of $c^*_{\beta}, c^*_{\alpha}$, $p_g^{\alpha \rightarrow \beta}$ and $p_g^{\beta \rightarrow \alpha}$ can be obtained. These values can then be used with our measured shear modulus, $G$ and Poisson’s ratio, $\sigma$ values to establish a direct connection.

Secondly, an extensive study of the equilibrium dynamics can be performed to check for the reproducibility of the “color map” and the pattern. A non-monotonic fitting scheme can be developed as well for the non-monotonic behavior of the hydrogen absorption/desorption. This study will enhance a complete understanding of the kinetics of the hydrogen absorption and desorption in the palladium hydride, and it can be extended to other metal hydrides.

Finally, one of the measured parameters in the equilibrium dynamics experiment was how long it takes the palladium hydride system to attain equilibrium. The time constants can be obtained for each pressure and temperature points with different driving transducer amplitudes. A plot of time constants as functions of the driving amplitudes can be used to determine how a change in amplitude affects how fast the equilibrium state is reached in the system. This study can be used to determine if resonance can assist in hydrogen absorption in metal hydrides.
Bibliography.
Bibliography


List of Appendices.
APPENDIX A
ELASTICITY MEASUREMENTS OF SOME THERMOELECTRIC MATERIALS AT HIGH TEMPERATURE

A.1 Introduction

The flow of electrons in solids creates electric current. In the presence of temperature gradient, electrons can flow from the hot side to the cold side to cause electric current. This direct conversion of temperature differences to electric voltage and vice-versa is called the thermoelectric effect. The two predominant thermoelectric effects are the Seebeck effect and the Peltier effect [90].

The Seebeck effect [91] is the conversion of temperature difference into electricity (named after the German scientist that discovered it in the 19th century). The induced voltage \( V \) is directly proportional to the applied temperature difference \( \Delta T \) and it is expressed as equation A.1 where \( S \) is the Seebeck coefficient.

\[
V = S \Delta T \tag{A.1}
\]

The Peltier effect is the absorption or emission of heat at an electrified junction made from two different conducting materials. The amount of heat \( Q \) absorbed or emitted at the junction due to the applied current \( I \) can be expressed as equation A.2 where \( \Pi \) is the Peltier coefficient.

\[
Q = \Pi I \tag{A.2}
\]

Seebeck coefficient of a material measure the magnitude of an induced thermoelectric voltage in response to a temperature difference across that material and the entropy per
charge carrier in the material. An applied temperature difference will cause charge carriers such as electrons in the material to diffuse from one end to the other. The hot carriers with a higher density at the hot end will diffuse to the cold end while the cold carriers will diffuse in opposite direction. In a system where both ends of the material are kept at a constant temperature difference, there is a constant diffusion of the carriers. If the rates of diffusion of the hot and cold carriers are equal, there is no net charge across the hot and cold ends. However, the diffusing charges are scattered by impurities, imperfections and lattice vibrations (phonons). If the scattering is energy dependent, the hot and the cold carriers will diffuse at different rates, creating a higher density of carriers at one end of the material [92]. The accumulation of charge carriers at one end sets up an electric field across the material and consequently an electrostatic voltage. This implies that the Seebeck coefficient of a material will depend on impurities, imperfections, and structural changes that vary with temperature and electric field. Therefore the Seebeck coefficient of a material is a function of collection of many different effects.

A thermoelectric device creates a voltage when there is a different temperature on each side. On the other hand, when a voltage is applied to it, it creates a temperature difference. Thermoelectric materials are therefore used to convert thermal energy into electricity using the Seebeck effect. The efficiency of thermoelectric devices, as defined in Equation A.4, primarily depends on a material’s figure-of-merit, which is defined as shown in Equation A.3

$$Z = \frac{S^2 \sigma}{\kappa}$$

(A.3)

where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity and $\kappa$ is the total thermal conductivity of the material ($\kappa = \kappa_L + \kappa_E$; the lattice and the electronic contributions, respectively). The larger $Z$ is, the larger the conversion efficiency is. The dimensionless figure-of-merit $ZT$ is formed by multiplying $Z$ with the average absolute temperature because $Z$ varies with temperature. $ZT$ is therefore a method for comparing the potential efficiency
of devices using different thermoelectric materials and it is connected to the thermoelectric efficiency ($\eta$) [93] of a material as

$$\eta = \frac{T_H - T_C}{T_H} \sqrt{1 + ZT} - \frac{1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}}$$

(A.4)

where $T_C$ is the temperature at cold end and $T_H$ is the temperature at the hot end.

Various types of materials including metal alloys, oxides, semiconductors, nanostructured materials, and so on, have been investigated as thermoelectric materials—-. Typically, metals have small Seebeck coefficient and they are usually not good thermoelectric material. This is because their half-filled bands caused by equal negative and positive charges cancels each other’s contributions to the induced thermoelectric voltage. Secondly, according to the Weidemann-Franz law, the ratio of the electronic contribution to the thermal conductivity ($\kappa$) and the electrical conductivity ($\sigma$) of a metal is proportional to the temperature ($T$). On the other hand, semiconductors can be heavily doped with electrons or holes resulting in a higher magnitude Seebeck coefficient with moderately low thermal conductivity and electrical resistivity. In practical use, couples are combined in a module as shown in Figure A.1 where they are connected thermally in parallel, and electrically in series.

Conventional thermoelectric materials include bismuth chalcogenides (commercial thermoelectric devices are dominated by (Bi, Sb)$_2$, (Te, Se)$_3$-based alloys, metal oxides, skutterudites, Zintl phases, SiGe and so on. Recently many more thermoelectric devices are made from alternating p-type and n-type semiconductor elements. The efficiency of a thermoelectric device is directly related to the $ZT$ of the thermoelectric materials used in the device. For decades, the efficiency of thermoelectric materials, measured by the $ZT$ value, stayed relatively low. A values of $ZT \approx 1$ has been a practical upper limit for decades. New materials with enhanced thermoelectric material properties and low cost are required for developing practical thermoelectric devices.

Recent research and development in thermoelectricity has been focused on synthe-
Figure A.1: Thermoelectric module consisting of n-type and p-type thermoelectric materials connected thermally in parallel and electrically in series.

sizing and identifying novel thermoelectric materials of high performance, and improving existing thermoelectric materials. One of the methods employed to achieve this is through the use of nanostructured materials, the intention is to reduced the total thermal conductivity. The thermoelectric properties of nanostructured materials differ significantly from those of macrostructured ones because of classical and quantum size effects. The nano-scaled technologies have been explored for fabricating nanostructured thermoelectric materials such as superlattices for which theoretical studies predict significant enhancement in $ZT$ [94–97]. In addition, fast theoretical modeling of thermoelectric materials has also resulted in a more rapid evaluation of new materials. So far, the best reported values of $ZT$ are in the 2-3 range. However, $ZT$ values of 3-4 range are essential for thermoelectric to compete with mechanical devices in efficiency [98–100]. Due to relatively low $ZT$ of materials thermoelectric genera-
tors cannot compete with the traditional energy sources in large electrical power generation but they play a huge role in energy savings by increasing energy efficiency. Thermoelectric devices have demonstrated potentials for harvesting waste heat energy from power plants, industrial waste heat, in automobiles as automotive thermoelectric generators (ATGs) for increasing fuel efficiency and in deep space probes as radioisotope thermoelectric generators (RTGs) [92, 101–103]. Thermoelectric power generators are preferred to other energy conversion devices in applications requiring high reliability, long life, and the ability to survive harsh environments.

A good thermoelectric materials requires a low thermal conductivity, so most of the studies on the thermal conductivities of thermoelectric materials have been focused on ways of reducing the thermal conductivities without having any adverse effect on the material’s electrical power factor, $S^2\sigma$. The problem with this is that heavily doped semiconductors have significant contributions of thermal conductivities from the electrons and holes. Another requirement is a fairly large band gap to minimize the effect of minority carriers, however, materials with large band gaps possess large lattice thermal conductivity. Any attempt to reduce lattice thermal conductivity with reasonably little adverse effect on the band gap and electric power factor will lead to a better choice of thermoelectric material. Mechanisms such as alloy disorder (deliberate introduction of point defects, solid solutions) and grain size boundaries manipulation are used to effectively scatter phonons. Phonon scattering at grain boundaries, interfaces and defects reduces the phononic part of the thermal conductivity while the electrical properties stay constant and enhance the electrical to thermal conductivity ratio in thermoelectric materials [104–106].

A.2 High-temperature Thermoelectric Materials

The objectives of thermoelectric materials research and development are to identify materials with high figure-of-merit and enhance the figure-of-merit in these materials. As
shown in Equation A.4, $T_H - T_C$ is the temperature difference between the hot and the cold ends, so the larger the temperature difference the higher the efficiency of the thermoelectric device. In addition, at higher temperature ($T_H$) a larger value of $ZT$, which is the key to the development of thermoelectric power generators, can be achieved. In the past several decades the Jet Propulsion Laboratory (JPL) has shown particular interest in the application of thermoelectric materials at high temperatures as power generation devices in the deep-space probes.

Thermoelectric devices are known for their contributions in the powering of spacecrafts for decades. The RTG has been used in many NASA missions, and it is probably the only possible power source for the on-board electronics where solar energy is unavailable for deep-space probes. The need for higher efficiency from thermoelectric devices has propel NASA into the search for materials that will be used in the next generation of RTGs. Researchers at Jet Propulsion Laboratory (JPL) are currently using nanotechnology to improve the $ZT$ of nanostructured n-type and p-type thermoelectric materials. The thermoelectric properties of these materials are usually first studied and well characterized. However, there is need to also characterized their mechanical properties such as elastic moduli as well. Especially at high temperatures required for engineering applications. Hence the purpose of this study is characterize the temperature dependent elastic moduli of these thermoelectric materials.

A.3 High Temperature RUS Set-up

The high temperature (HT) RUS set-up is similar in principle to the high temperature and high pressure (HT&P) RUS set-up. However, there are differences in the materials used in constructing the components. The steel disks baffles and steel rods used to construct the support cage in the HT&P set-up are replaced by alumina disks and rods in the HT RUS set-up. Secondly, the gas inlet and outlet are used in the HT&P set-up to control
the pressure levels in the system but they are used for continuous inert gas flushing in the
HT set-up. This is used to keep the oxygen content at a very minimized level and prevent
oxidation of the sample at high temperatures. Also the steel RUS cell in the HT&P set-
up is replaced with a quartz tube in the HT set-up. Lastly, a second transducer system, “the buffer-rod transducer system” is needed in the HT RUS set-up. This is necessary for measurements beyond 650°C, the upper limit of the operating temperature of “the direct contact transducer system” described in Chapter 3. A detailed description of the buffer-rod transducer system is given in the next section.

A.3.1 Buffer-Rod Transducer System

Acoustic buffer-rods have long been for making high-temperature ultrasonic measurements including elasticity measurement. The conventional buffer-rod system makes RUS measurements possible at extremely high temperatures and such applications have been reported in the literature [20, 44, 53]. The buffer rods, usually made out of materials of low acoustic loss such as ceramics or fused quartz, serve as waveguides for sound transmission. In the buffer rods system, piezoelectric elements are permanently glued to one end of the thin, cylindrical buffer rod while the other end of the rod is in direct contact with the test material. The piezoelectric elements are in the cool part of the set-up while the test material is in the high temperature environment. Figure A.2 shows the buffer rod transducer system.

Unfortunately, the buffer-rod system suffer some drawbacks, the acoustic signal transmitted through the long buffer rod loses some strength as compared to the direct contact system. This is particularly harmful to high temperature RUS measurement, which is often involved with weak resonance signals because the strength and quality factor of many materials decreases with increase in temperature. Secondly, the lower radial modes of the buffer rods can be excited and mixed with the sample resonances. Separation of the sample resonance peaks from buffer-rod resonance peaks is very difficult, time consuming and error
Figure A.2: The buffer rod transducer system. (a) Photo of the buffer rod system with the buffer rods in place in a cage made of ceramic rods and disks as support also shown in the photo are the piezoelectric elements (drive and pickup transducer) (b) Schematic diagram of the buffer rod transducer system.

prone. These added difficulties brought by the buffer-rod system motivated the design and fabrication of the direct contact transducer system for RUS measurement at high tempera-
ture (up to 650°C). Figure A.3 shows the direct contact transducer system with a sample in place as well as the thermocouple in a position close to the test sample.

Figure A.3: The direct contact transducer system. (a) Photo of the direct contact transducer probes placed in the cage made of ceramic rods and disks as support. (b) An enlarged portion of the photo showing the drive and pickup transducer elements, the test sample and the thermocouple.
A.3.2 High Temperature Measurement Procedure

The test samples are usually prepared as described in Chapter 3. After the dimensioning and the determination of the densities, series of room temperature RUS measurements are done to ensure that “good” elastic constants are obtained. The test sample is then loaded into the high temperature RUS set-up and the whole set-up is sealed off. The inert gas flushing is done at very low flow for at least 10-30 minutes before the furnace is turned on. The furnace temperature is adjusted manually and monitored through the thermocouple placed near the test sample in the transducer system. The sample temperature is always lower (a slight difference) than the furnace temperature. The adjustment of the furnace temperature is done in a “multi-step” approach especially during the ramp-up in temperature. This is because there is an initial large jump in the furnace temperature before it settles down to the set temperature. In order to avoid exposing the sample to a temperature higher than the set temperature, the furnace temperature will be increased by a few degrees such that the initial jump will take the temperature closer to the desired temperature. Then with one or two adjustments the target temperature will be reached. At higher temperatures above 200 °C, this initial jump reduces to about 3 degrees so the multi-step adjustment will not be needed. On the other hand, at higher temperatures the difference between the sample temperature and the oven temperature increases, so it is certain that the sample temperature will not go beyond the set temperature on the furnace.

The data acquisition and processing is the same as described in Chapter 3. However, the full temperature range measurements are done in two stages. During the first stage measurements are done using the direct contact transducer system up to 600 °C, data are taking on both heating and cooling cycles. The sample is then transferred into the buffer rod transducer system for the second stage of the measurement. At this stage data are taking up to 1000 °C
A.4 Temperature Dependent Elastic Moduli Measurements

In this study, elastic moduli of five different nanostructured, polycrystalline thermoelectric materials were measured at high temperatures. Four of these materials are lanthanum telluride (LaTe) and an N-type lead telluride (PbTe). The measurements of the LaTe were done in the temperature range of room–1000°C so the two stage measurements (the direct contact and the buffer rod systems) was employed. In the PbTe measurement only the direct contact system was used because the temperature range of interest in this case is from room–600°C.

A.4.1 Sample Preparation

Bulk samples of the thermoelectric materials were prepared by our collaborators at JPL and sent to our lab at the National Center for Physical Acoustics (NCPA) as cylindrical bars. The samples were labeled as Late1, LaTe2, Late3a, LaTe3b and N-type PbTe. The low-speed diamond saw was used to cut small parallelepipeds out of the cylindrical bars and then each of the parallelepipeds were polished. The cutting and the polishing procedures has been thoroughly described in Chapter3. The mass and dimensions were measured and used to calculated the density. The detailed information of the five test samples that were prepared are given in Table A.1. The values of the dimensions and the densities given in Table A.1 were for room temperature only. These values were adjusted at higher temperatures using the thermal expansion coefficients. \(19.4 \times 10^{-6}/^\circ\text{C}\) was used as the thermal expansion coefficient for all four samples of LaTe at high temperatures while \(5.4 \times 10^{-6}/^\circ\text{C}\) was used for the PbTe.

A.4.2 Room Temperature Measurements

As part of our standard practice a series of room temperature measurements were taken before the high temperature measurements. This series of room temperature measure-
Table A.1: Dimensions and densities of the five properly prepared thermoelectric samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dopant type</th>
<th>Dimension(mm)</th>
<th>Mass(g)</th>
<th>Density(g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaTe1</td>
<td>-</td>
<td>2.882 × 4.032 × 3.635</td>
<td>0.2664</td>
<td>6.309</td>
</tr>
<tr>
<td>LaTe2</td>
<td>-</td>
<td>3.162 × 4.013 × 4.043</td>
<td>0.3051</td>
<td>5.946</td>
</tr>
<tr>
<td>LaTe3a</td>
<td>-</td>
<td>3.705 × 3.885 × 3.953</td>
<td>0.3803</td>
<td>6.684</td>
</tr>
<tr>
<td>LaTe3b</td>
<td>-</td>
<td>2.959 × 4.074 × 4.912</td>
<td>0.3747</td>
<td>6.328</td>
</tr>
<tr>
<td>N-PbTe</td>
<td>N</td>
<td>1.824 × 2.589 × 2.985</td>
<td>0.1150</td>
<td>8.156</td>
</tr>
</tbody>
</table>

The crystallites in the polycrystalline materials are small enough and are randomly-oriented, the material can be treated as an isotropic material at the macroscopic level. The elastic properties of such materials can be fully characterized by two independent elastic moduli, for example Young’s modulus (E) and shear modulus (G). These two independent elastic moduli can be derived from the three elastic constants: $C_{11}$, $C_{12}$ and $C_{44}$ that are obtained from the fits. Equations A.5 and A.6 show the relationship between the elastic constants and the elastic moduli

$$E = \frac{(C_{11} - C_{12}) (2C_{12} + C_{11})}{C_{11} + C_{12}} \quad (A.5)$$

$$G = C_{44} \quad (A.6)$$

In RUS measurements of isotropic materials the lower modes are dominated by the shear modes. To obtain values of longitudinal moduli that are reasonable, at least the first dozen modes should be used. In this case, at least the first 25 modes are used for each of the sample to compute the elastic moduli at room temperature and the average RMS errors are < 0.3%. The room temperature moduli measurements of the five samples including their average RMS errors are listed in Table A.2

A.4.3 High Temperature Measurements

The full range of high temperature measurements is done in a “two-stage step” as mentioned in A.3.2. The direct contact transducer system is first used to take data from
Table A.2: Elastic moduli of the five properly prepared thermoelectric samples at room temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s modulus (GPa)</th>
<th>Shear modulus (GPa)</th>
<th>Error (%)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaTe1</td>
<td>65.92</td>
<td>25.99</td>
<td>0.11</td>
<td>19.3</td>
</tr>
<tr>
<td>LaTe2</td>
<td>59.26</td>
<td>23.37</td>
<td>0.19</td>
<td>23.2</td>
</tr>
<tr>
<td>LaTe3a</td>
<td>64.85</td>
<td>25.64</td>
<td>0.20</td>
<td>22.7</td>
</tr>
<tr>
<td>LaTe3b</td>
<td>65.77</td>
<td>25.54</td>
<td>0.26</td>
<td>22.3</td>
</tr>
<tr>
<td>N-PbTe</td>
<td>55.93</td>
<td>22.19</td>
<td>0.23</td>
<td>23.8</td>
</tr>
</tbody>
</table>

room temperature to 600°C in increments of 50°C. The sample is then cooled back to room temperature with data taken at every 100°C decrease in temperature as well as at room temperature after cooling. The sample is then removed and remounted on the buffer–rod transducer system for measurements at temperatures up to 1000°C. In the buffer–rod system data is taken in increments of 100°C up to 600°C to check for consistency between the two systems, loading effects and to aid in the rejection of peaks that are due to buffer–rod. Above 600°C, temperature increments of 50°C. The sample is again cooled back to room temperature taking data at every 100°C decrease in temperature as well as at room temperature after cooling. The average time duration for a complete frequency scan at each temperature including the time required for the temperature to stabilized is 40 minutes. A typical direct contact full temperature range measurement requires about 12 hours while the buffer–rod measurements takes about 16 hours.

A.5 Results and Discussion

The resonance frequencies were extracted and compiled into files named “allfreqs.dat”. These files were used in batch process of the elastic constant fitting scheme for isotropic materials. The elastic moduli were calculated from the elastic constants obtained from the fits. This section reports the temperature dependent trends of the elastic moduli of all the thermoelectric samples tested.
A.5.1 Lanthanum Telluride (LaTe)

A.5.1.1 Young’s Modulus

The temperature dependent trends of the Young’s modulus of the four LaTe samples are discussed here. Figure A.4 shows the Young’s moduli of the direct contact run of the four samples. The plots revealed that LaTe2 is clearly “softer” than the other three samples. A common feature in all the samples is the subtle “shoulder” around 300 °C. This feature is more pronounced in the LaTe1 plot. Similar trends are observed from the results obtained from the buffer-rod transducer system where the temperature range was extended to 1000 °C from room temperature. This is shown in Figure A.5. Open symbols are moduli measured by the direct contact transducer system and the filled symbols are moduli measured by the
buffer-rod system. The overall trend of the Young’s modulus is almost linearly decreasing with temperature for all the samples. The plots were divided into two portions (temperature ranges of < 300°C and > 300°C) due to the subtle “shoulder” around 300°C. Each portion was then fitted to a linear model \( y = aT + b \). This was done for all measurements from both transducer systems as shown in Figure A.6. The fitted parameter \( a \) and \( b \) are listed in Tables A.3 and A.4 for the < 300°C and > 300°C temperature respectively. In the tables the transducer systems are represented by DC for direct contact and BF for buffer-rod system. As it is reflected in the plots, the fitted parameters also the disparity between LaTe2 and rest. Generally, samples LaTe1, LaTe3a and LaTe3b have similar values of the Young’s modulus as well as the fitted parameters. The difference in the corresponding values of Tables A.3
Figure A.6: Linear model of fits of the Young’s modulus of all the LaTe samples. The results from direct contact transducer system are represented with open symbols and those of the buffer-rod system are represented with filled symbols.

and A.4 justifies the subtle “bump” in the plots.

Table A.3: Fitted parameters of the Young’s modulus of the LaTe samples for temperatures < 300°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Transducer system</th>
<th>a (GPa/°C)</th>
<th>b (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaTe1</td>
<td>DC</td>
<td>−1.749x10⁻²</td>
<td>66.18</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>−2.029x10⁻²</td>
<td>66.90</td>
</tr>
<tr>
<td>LaTe2</td>
<td>DC</td>
<td>−1.554x10⁻²</td>
<td>59.63</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>−1.702x10⁻²</td>
<td>58.96</td>
</tr>
<tr>
<td>LaTe3a</td>
<td>DC</td>
<td>−1.841x10⁻²</td>
<td>65.26</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>−1.901x10⁻²</td>
<td>66.63</td>
</tr>
<tr>
<td>LaTe3b</td>
<td>DC</td>
<td>−1.866x10⁻²</td>
<td>66.15</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>−1.999x10⁻²</td>
<td>66.84</td>
</tr>
</tbody>
</table>
Table A.4: Fitted parameters of the Young’s modulus of the LaTe samples for temperatures > 300°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Transducer system</th>
<th>a (GPa/°C)</th>
<th>b (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaTe1</td>
<td>DC</td>
<td>-2.068x10^{-2}</td>
<td>67.33</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>-1.973x10^{-2}</td>
<td>66.75</td>
</tr>
<tr>
<td>LaTe2</td>
<td>DC</td>
<td>-1.777x10^{-2}</td>
<td>60.20</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>-1.803x10^{-2}</td>
<td>59.29</td>
</tr>
<tr>
<td>LaTe3a</td>
<td>DC</td>
<td>-2.132x10^{-2}</td>
<td>66.31</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>-2.043x10^{-2}</td>
<td>66.93</td>
</tr>
<tr>
<td>LaTe3b</td>
<td>DC</td>
<td>-1.990x10^{-2}</td>
<td>66.58</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>-2.035x10^{-2}</td>
<td>66.89</td>
</tr>
</tbody>
</table>

A.5.1.2 Shear Modulus

The focus of this section is on the temperature dependent trends of the shear modulus of the four LaTe samples. The general trend of the plots of shear modulus versus temperature is similar to that of the Young’s modulus. Figure A.7 shows the plots of measurements via the direct contact transducer system and Figure A.8 shows the results of both transducer systems. The open symbols, again, are used for the plot of results from direct contact system and the filled symbols for the buffer-rod transducer system. The shear modulus plots were also fitted with linear model (Figure A.9) as well. The parameters from the fits are recorded in Tables A.5 and A.6 for the < 300 °C and > 300 °C temperature regimes.

Table A.5: Fitted parameters of the shear modulus of the LaTe samples for temperatures < 300°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Transducer system</th>
<th>a (GPa/°C)</th>
<th>b (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaTe1</td>
<td>DC</td>
<td>-7.457x10^{-3}</td>
<td>26.11</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>-8.338x10^{-3}</td>
<td>26.37</td>
</tr>
<tr>
<td>LaTe2</td>
<td>DC</td>
<td>-6.467x10^{-3}</td>
<td>23.52</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>-6.850x10^{-3}</td>
<td>23.46</td>
</tr>
<tr>
<td>LaTe3a</td>
<td>DC</td>
<td>-7.594x10^{-3}</td>
<td>25.80</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>-7.424x10^{-3}</td>
<td>25.87</td>
</tr>
<tr>
<td>LaTe3b</td>
<td>DC</td>
<td>-7.158x10^{-3}</td>
<td>25.68</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>-7.979x10^{-3}</td>
<td>25.67</td>
</tr>
</tbody>
</table>
A.5.2 N-Type Lead Telluride

A.5.2.1 Elastic Moduli

The fifth thermoelectric materials that was measured at high temperature is the N-type lead telluride (PbTe). The temperature range in this case is up to 600°C from room temperature. Figures A.10 and A.11 show the plots of the Young’s modulus and the shear modulus versus temperature respectively. The elastic moduli decreased linearly with increase in temperature up to 500°C. So the data were fitted to a linear model \( y = aT + b \). There is a deviation from the linearity beyond this temperature, so the last two points were excluded from the linear fitting of the data. The fitted parameters, \( a \) and \( b \) are \(-2.605 \times 10^{-2}\) (GPa/°C) and 56.52 (GPa) for the Young’s modulus. The shear modulus fitted parameters are...
A.6 Conclusion

The high temperature elasticity studies of the five thermoelectric materials has been done successfully. The elastic moduli plots of the measurements of four samples of LaTe supplied by JPL show that three of the samples have similar values while one (LaTe2) is clearly different from the rest. Generally, all the samples have similar linear trends; they all decrease with increase in temperatures. There is a subtle break in the slope of the plots near 300 °C. Linear fit models were used to get the slope of the plots with a break at 300 °C.
Figure A.9: Linear model of fits of the shear modulus of all the LaTe samples. The results from direct contact transducer system are represented with open symbols and those of the buffer-rod system are represented with filled symbols.

Table A.6: Fitted parameters of the shear modulus of the LaTe samples for temperatures > 300°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Transducer system</th>
<th>a (GPa/°C)</th>
<th>b (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaTe1</td>
<td>DC</td>
<td>$-8.582 \times 10^{-3}$</td>
<td>26.51</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>$-8.178 \times 10^{-3}$</td>
<td>26.34</td>
</tr>
<tr>
<td>LaTe2</td>
<td>DC</td>
<td>$-7.228 \times 10^{-3}$</td>
<td>23.72</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>$-6.556 \times 10^{-3}$</td>
<td>23.27</td>
</tr>
<tr>
<td>LaTe3a</td>
<td>DC</td>
<td>$-8.273 \times 10^{-3}$</td>
<td>26.07</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>$-7.869 \times 10^{-2}$</td>
<td>25.93</td>
</tr>
<tr>
<td>LaTe3b</td>
<td>DC</td>
<td>$-7.936 \times 10^{-3}$</td>
<td>25.96</td>
</tr>
<tr>
<td></td>
<td>BF</td>
<td>$-8.126 \times 10^{-3}$</td>
<td>25.79</td>
</tr>
</tbody>
</table>
These subtle deviations from linearity were reflected by the values of the slopes of all plots at $< 300 \, ^\circ\text{C}$ and $> 300 \, ^\circ\text{C}$.

The elastic moduli trend of N-PbTe was also measured and determined. The values obtained were comparable with the available literature [107]. Similar to the LaTe plots, the trend of the PbTe was also very linear. These plots were also fitted to linear model.
Figure A.11: Shear modulus temperature trend of the N-type PbTe sample using the direct contact transducer system.
APPENDIX B

CONSTRUCTION OF HIGH TEMPERATURE AND HIGH PRESSURE TRANSDUCER SYSTEM

B.1 Direct Contact Transducer System

The direct contact transducer system consist of (i) the transducer cage, (ii) the direct contact transducer probes and (iii) the temperature monitoring system.

B.1.1 The Transducer Cage

The transducer cage provides structural support for the transducer probes and temperature control element. The cage is made using steel disk baffles and steel bars. Steel was used because the set-up will be subjected to cycles of high temperatures and high pressures. Four steel disks with holes drilled through them as shown in Figure B.1 were used. The transducer probes and the temperature control element are placed in the cage through these holes. The steel bars are used to hold the steel disks together. The disks are 0.0625" thick and 0.963" diameter. The steel bars are 0.265" in diameter. The cage length is 4.5", the space between the second and third disk is about 2.5" and a spacing of 1.0" between the top two and the bottom two disks respectively. The top two disks have additional hole for the temperature monitoring element. The holes for coaxial cables and temperature monitoring element are 0.141" in diameter. Similarly the holes for the steel bars are made to fit the bars tightly. Lastly, a thin steel wire, which is bent into a “U” shape is used to hang the steel cage to the top part of the RUS cell.
Figure B.1: Schematic diagram of materials used in the construction of the steel cage that provide structural support for the transducers and the temperature monitoring element.

B.1.2 Direct Contact Transducer

The materials required to construct the direct contact transducers are show in Figure B.2. The list include (i) high temperature coaxial cable, a mineral insulated coaxial cable with both outer and inner conductors made of heat resistant Inconel™ metal alloys obtained from ThermoCoax® in France. (ii) steel tube with outer diameter of 0.125". (iii) lithium niobate piezoelectric element; a y/36°-cut chrome/gold plated lithium niobate single crystals disk, which are readily available from Boston Piezo-Optics Inc. (iv) a very thin platinum wire used to connect the outer conductor of the coaxial cable to the piezoelectric element. (v) silver filled conductive epoxy (Epo–Tek E2101) part A and B, the epoxy serves as the electrical connections between the chrome/gold electrodes of the piezoelectric element and
the mineral insulated Inconel\textsuperscript{TM} metal alloys coaxial cable.

Two high temperature direct contact transducer probes are used. The dimensions of the two high temperature coaxial cables are about 11" and 18". The longer is used for the bottom probe and the shorter for the upper probe. Two rectangular blocks are cut out of the piezoelectric element disks, the dimensions are about 3 – 4 \textit{mm}. The steel tube is used as support for the coaxial cable to hold it in place in the cage. Two steel tubes of about 3" are prepared, one for each of the transducer probes.

Figure B.2: Schematic diagram of materials used in the construction of the direct contact transducers.
B.1.3 Assembling Direct Contact Transducer System

In the direct contact transducer probe, the piezoelectric element is directly bonded to the inner conductor of the mineral coaxial cable. The coaxial cables are cut and the outer conductor of about 0.5–1 cm long at both ends is stripped away as shown in Figure B.2. At one end of the exposed inner conductor the tip is bent into a ring which covers an area of about 2/3 of the piezoelectric disk. This is done using a long nose plier. The plane of the ring is made to be perpendicular to the cable’s body as shown in Figure B.2. The area where epoxy is to be applied is carefully sanded and cleaned before applying epoxy. The two part epoxy is well mixed in equal parts at room temperature. The epoxy mixture is used to glue the piezoelectric disk to the ring (inner conductor of the coaxial cable). This is done with the mineral insulated coaxial cables installed in the steel cage as shown in Figure B.3. The epoxy covers the whole electrode of the piezoelectric disk. The thickness of the epoxy mixture is kept in the range of 1–2 mm and thicker at the center. The thicker the epoxy spot on the disk, the heavier the load and we need to reduce the loading effect as much as possible. The epoxy is cured by setting the epoxied parts (inner conductor and piezoelectric element) under electric lamp for 4 hours and covered by aluminum foil. The next step is the electrical connection between the outer conductor (electrical ground) and the front electrode of the piezoelectric crystal, a small piece of platinum wire is used to connect the electrode to the outer conductor of the cable. The epoxy spot on the front electrode of the crystal should be small and close to the edge so, much of the area can be used for holding the sample. The other end of the exposed inner conductor will be at the upper cooler part of the transducer probe.

Two transducer probes are constructed for the direct contact transducer system. After the construction, they are examined under microscope for bonding defects. Any hidden electrical connection problem can be identified by measuring electrical resistance and checking for continuity between different parts of the probes. The resistance across the length
of the high temperature cable is in the range of 1–2 Ohms. The resistance between the two electrodes of the piezoelectric element should be at least several mega Ohms or above; the resistance may drop to hundreds of kilo Ohms, which is considered acceptable, due to ‘impurity’ accumulation on the sides of the piezoelectric element after several cycles of high temperatures and high pressures. A much lower resistance usually warrants a cleanup or replacement of the piezoelectric element. Often times, the continuity problem might be due to the epoxy running across the edge and bridging the center conductor and the ground. In such cases, one can use a sharp tip of objects like blade or tweezers, to scrape off the dried epoxy from the edge to break the electrical continuity. Another possible connection problem is when the platinum wire used for connecting the outer conductor touches the epoxy that is used for the center conductor.

At the completion of assembling the direct contact transducer system, the excitation probe is fixed at a position with the piezoelectric element facing up and near the center of the cage, the detection probe is left to move freely at the top, the test sample is mounted between these two vertically aligned transducers, the weight of the upper transducer system hold the sample in place. The transducers are put in a set of steel baffles to provide rigid structure and to serve the purpose of reducing the effect of gas convection so as to maintain a stable temperature in the cell especially around the test sample. Flexible regular coaxial cables are used at the cooler upper part of the cell to connect the free ends of the mineral insulated coaxial cables using male–female sub miniature coaxial connectors (SSMC). The center conductors of other ends of the flexible coaxial cables are connected to the coaxial feed-through at the top of the cell. The outer conductors are all connected to the wall of the stainless steel lid of the RUS cell for common ground. The figure below shows a section of the high temperature direct contact transducer. The schematic diagram and the photo of the actual direct contact transducer system is given in Figure B.3.

Therefore the transducer system for high-temperature measurement consists of two transducer probes, a resistance thermometry detector element, and the steel cage which pro-
B.1.4 Temperature Monitoring System

This section describes all the components of the resistance thermometry detection system used for temperature monitoring. The main component of the temperature detection system is the Platinum Resistance Temperature Detector (RTD), 2PT100KN3026CLA, obtained from Omega® as shown in Figure B.4. A 12" long ceramic rod with four holes drilled...
Figure B.4: Schematic representation of the temperature monitoring system showing the platinum resistance temperature detector element, the ceramic rod that support and insulates the platinum leads, and circuit representation of the set-up.

In it was also purchased from Omega®, four pieces of platinum wires are pass through the rod holes and connected to the four leads of the RTD at one end of the rod. The wires at the other end of the rod are soldered to the leads that come from the temperature feedthrough. The bare platinum wires between the RTD element and the ceramic rod are separately coated with a high temperature non-conducting putty to insulate the wires and avoid electrical contact. As shown in the circuit representation power resistor is connected in series to the current source and the RTD element to ensure that the current remains the same throughout the temperature range. The power resistor is a very ohmic resistor, the resistance does not change with increase in temperature. On the other hand the resistance of the Platinum RTD element changes with increase in temperature just like a variable resis-
tor. It has a resistance of 100 Ω at 0°C and has a temperature coefficient of 0.000385 Ω per
Ω · degree. So the resistance of the RTD at the boiling point of water is 138.50 Ω (that is
\[ \frac{0.000385 \text{Ω}}{\text{degree}} \times 100 \text{Ω} \cdot 100 \text{ degree} + 100 \text{ Ω} \]).

A table of RTD temperature versus resistance was supplied by Omega\textsuperscript{®} with the
RTD element. After the installation of the RTD, we need to calibrate it and write a script
that will read the temperature values from the voltages read off the Keithley multimeter
(Model 2000). In order to convert the voltage to temperature we need a fitting equation,
so the data supplied by the table fitted perfectly well to a fifth order polynomial as shown
in Figure B.5, the data set is the blue dots and the fitted line is the black line. The fitted
equation is temperature as a function of resistance,

\[
T = -6.617 \times 10^{-12} R^5 + 7.658 \times 10^{-9} R^4 - 2.428 \times 10^{-6} R^3 \\
+ 1.334 \times 10^{-3} R^2 + 2.293 R - 240.9 \tag{B.1}
\]

Since the value of current is known, it is combined with the voltage that is read off the
voltmeter to determine the resistance. The resistance is then used in the fitted equation to
calculate the temperature. It was tested for various known temperatures by hand-held digital
thermocouple (for example mixed ice-water, boiling water and various points in-between).
Both the RTD reading on the computer screen and the thermocouple reading were similar
and very close at all points. The next section describes the design and construction of the
RUS cell.

B.2 RUS Cell

The RUS cell consists of two parts both made of stainless steel; (i) the top portion
which also serves as the lid, houses the gas inlet, the pressure meter and, the coaxial and
temperature monitoring control feedthroughs. (ii) the steel tube which houses the direct
Figure B.5: Plot of temperature versus resistance of the Platinum RTD fitted to a fifth order polynomial. The fitting equation is used in the computer script that convert voltage readings to temperature values.

contact transducer system including the steel RUS cage.

B.2.1 Lid (Top Part)

Figure B.6 shows the photo of the top part of the RUS cell and the schematic diagram of the cross-section of both coaxial and temperature monitoring control feedthroughs. The coaxial feedthrough was custom made in our laboratory while a component of the temperature feedthrough was purchased from Pave Technologies®. As shown in Figure B.6(b), the temperature feedthrough consist of $\frac{1}{8}"$ NPT type screw plug from Pave Technologies and a $\frac{1}{8}" - \frac{1}{4}"$ female NPT adapter purchased from Swagelok®. The NPT plug contain four conductors and was filled with "PAVE seal epoxy black" to act as seal and hold pressure
up to 2000 psi. The four conductors were soldered to the four platinum wire leads from the RTD as shown in Figure B.6(a). The four platinum leads are separated and held in place by passing them through a four hole ceramic rod purchased from Omega.

The coaxial feedthrough was custom made in our lab, it is made from a regular 1/4" screw plug. Two holes were drilled into the plug, the holes were tapped, conductors were soldered to the center conductor of two male sub-miniature connectors (SSMC) purchased from East Coast Microwave. The holes were filled with JB weld and the SSMC’s were screwed into the tapped holes as shown in Figure B.6(c). The set-up was allowed to set. The outer conductor was connected to the body of the steel lid to act as common ground for the whole set-up. The plug was tested and it was stable up to 1000 psi for over 24 hours.

B.2.2 Steel Tube

The steel tube was constructed at the machine shop of the National Center for Physical Acoustics (NCPA). Steel pipe of 1.375" in diameter and 0.188" in thickness was purchased from TW Metals. 20" of the pipe was used, a flange was constructed and welded to one end of the pipe. The other end of the pipe was welded to a nut through which the gas outlet line was connected to the pipe. Figure B.7(a) shows photo of the steel tube and Figure B.7(b) shows the schematic of cross section diagram of the steel tube.

Figure B.7(c) shows the “cold finger” made of copper. A copper cylindrical block of 3" in diameter and thickness was obtained from Omega, a hole big enough to contain the pipe was bored out of the copper block and a slice of cut out of the wall of the cylinder so that the cold finger can be compressed to fit tightly on the steel pipe. A thin layer was cut out from the top of the resulting “pipe-like” copper. Then groove was made in the copper pipe formed, then the thin layer cut out was replaced as the lid to the groove and sealed. Figure B.7(d) & (e) shows the groove and with the lid in place respectively. It is important to state that cold water from the tap is introduced into the “cold finger” from bottom and
Figure B.6: Top portion of the RUS cell. (a) Photo of the lid showing both feedthroughs, the gas inlet and, the electrical connections of the signal and four point probe RTD cables. (b) Schematic diagram of the cross-section of temperature control cables feedthrough. (c) Schematic diagram of the custom made coaxial signal cables feedthrough.

allowed to flow out from the top.
Figure B.7: Steel tube of the RUS cell. (a) Photo of the steel tube showing the tube, the cold finger and the gas outlet. (b) Schematic diagram of the cross-section of the steel tube showing the groove and the water inlet and outlet of the cold finger as well as the gas outlet. (c) Photo of the steel tube with focus on the copper cold finger. (d) Schematic of the cross section of the top view of cold finger, here the groove is shown. (e) Schematic of the cross section of the top view of cold finger with the groove lid in place.
APPENDIX C

COMPUTER CODES FOR DATA ACQUISITION AND PROCESSING

C.1 RUSTOOLS-HP-HEISE-RTD

# RUSTOOLS-HP-HEISE-RTD
#
#
# Rustools v1.1, 8/2007
# Author: Josh Gladden, Univ. of Mississippi
# Rustools is set of useful tools written in python for acquiring and manipulating
# RUS data. The functions rely heavily on the Pylab (matplotlib) module, so it must
# be installed first. Data acquisition relies on the PyVISA module.
#
# Version 1.1 uses the Visual.graph module for realtime plotting since it seems to
# be much more stable as data accumulates. Once data is complete however,
# the final graph is produced with matplotlib.
#
# Assumed GPIB addresses (these can be adjusted at the top of the rustools.py module):
#   Keithley 2000 DMM: 16
#   SRS DS345 Synthesizer: 19
#   SRS SR844 Lock-in: 8
# Connect to Heise DXD pressure transducer through serial port

Supplied functions:
(1) catdata(list_of_files) -> concatenates a list of data files, stripping
   off the header line of each.

(2) track_peak() -> accepts parameters and use them to run over a frequency
   range for a specified time interval repeatedly. It is interrupted with CTRL+C key.

(3) monitor_t_p() -> reads and prints the temperature and the pressure.
   The temperature monitoring system consist of an N-type thermocouple or a four
   point probe platinum resistance thermometry detector connected to a
   Keithley 2000 DMM. The pressure monitoring is done using a Heise DXD
   pressure transducer. It optionally plots the data in real time and dumps
   the data to a file.

(4) plot_rus(list_of_files) -> simply plots a list of resonance data files,
   either in-phase (channel=1) or out of phase (channel=2).

(5) single_scan(start_freq,end_freq,num_points) -> performs a single frequency
   sweep using a SRS DS345 synthesizer and SRS SR844 lock-in amplifier. There are
many other optional arguments, see the docstring for more details.

(6) batch_scan() - reads a list of scan parameters from "rusin.txt"
    and performs them sequentially.

(7) batch_scan_temp(): Same as batch_scan(), but monitors and
    records temperature data during the scan.

# Define GPIB addresses:
DMM_GPIB=16
DS345_GPIB=19
SR844_GPIB=8
VERS="1.2"

__all__=['catdata()','single_scan()','batch_scan()','batch_scan_temp()','
    plot_rus()','monitor_temp()','batch_scan_temp()','plot_init()','
    plot_update()']

try: from visual.graph import *
except:
    print "The module visual is required for these tools. Stopping loading \n    of rustools."

try: from pylab import *
except:
    print "The module Pylab is required for these tools. Stopping loading \n    of rustools."

try: import visa
except:
    print "This function requires the PyVISA module. Install this first. \n    Data acquisition disabled .."

import time as t

print
print 'Welcome to the Python based RUS data acquisition and processing system.
This is version %s.
Required modules are: PyVISA, Pylab (matplotlib), and visual.
Supplied modules are:
    %s
print
print __all__
print
# Connect to Keithley 2000 DMM
dmm = visa.instrument("GPIB::%i"%DMM_GPIB)

# Connect to Heise DXD pressure transducer through serial port
dxd = visa.instrument('ASRL1::INSTR')
dxd.parity = 2
dxd.baud_rate = 19200
dxd.data_bits = 7

print "Hello"

############################
# Initialize realtime plots
############################

def plot_init(linecolor=color.blue, ttext='Acquiring Data ...',
               xtext='Time (sec)', ytext='Temp (C)', lowx=0., lowy=0.):
    close('all')
    graph = gdisplay(title=ttext, xtitle=xtext, ytitle=ytext,
                     background=color.white, foreground=color.black,
                     xmin=lowx, ymin=lowy)
    line = gcurve(color=linecolor, width=4)
    return line, graph

############################
# Update plots
############################

def plot_update(x, y, curv):
    try: curv.plot(pos=(x, y))
    except:
        print "Error updating curve: ", curv, "/n Has it been initialized?"
        return False
    return True

############################
# smooth() data smoothing algorithm
############################

def smooth(x, y, level=2):
    for j in range(level):
        xp = zeros(len(x)-1, dtype='float')
        yp = zeros(len(y)-1, dtype='float')
        for i in range(len(xp)):
            xp[i] = (x[i] + x[i+1]) / 2.0
            yp[i] = (y[i] + y[i+1]) / 2.0
        x = xp
        y = yp
return xp, yp

def catdata(files,ofile="all_data.dat"):  
    Purpose: Take a list of data files and concatenate them into a single RUS data file. The header line is stripped off. Usage: rustools.catdata(list_of_files,[ofile="alldata.dat"])) where list_of_files is a list of file names (strings) to be concatenated. Output: write concatenated files to "all_data.dat" by default.
    
alldata=[]
    for file in files:
        data=load(file)
        data=data[1:]
        alldata=alldata+data.tolist()
    alldata=array(alldata)
    save(ofile,alldata,fmt='%.16e',delimiter='\t')
    print "List of %i data files written to file: %s " %(len(files),ofile)
    return

# Thermocouple calibration (N-type)
def tc_poly(x):
    a0=0.000000000
    a1=3.8783277E-2
    a2=-1.1612344E-6
    a3=6.9525655E-11
    a4=-3.0090077E-15
    a5=8.8311584E-20
    a6=-1.6213839E-24
    a7=1.6693362E-29
    a8=-7.3117540E-35
    return a0+a1*x+a2*x**2+a3*x**3+a4*x**4+a5*x**5+a6*x**6+a7*x**7+a8*x**8

# RTD calibration (four point probe)
def r_poly(r):
    a0 = -240.9
    a1 = 2.293
a2 = 0.001334
a3 = -2.428E-6
a4 = 7.657E-9
a5 = -6.617E-12
return a0+a1*r+a2*r**2+a3*r**3+a4*r**4+a5*r**5

####################
#GetT_P
####################
def getTP(navg=1.0,curr=0.001):
  
  #close('all')
t.sleep(1)

  data=[]
  vtsum=0
  psum=0
  for i in range(navg):
    press=dxd.ask_for_values("'#01PS[CR]"")[0]
    vt=dmm.ask_for_values(":meas:volt:dc?"))[0]
    t.sleep(0.2)
    psum+=float(press)
    vtsum+=float(vt)
  press=(psum/navg)
  rt=(vtsum/navg)/curr
  #print "V1 = %.3f V" % vp
  #print "V2 = %.3f V" % vt
  temp=tc_poly(vt) #use for thermocouple
  temp=r_poly(rt)
  return (temp,press)

########################
# Track_peak
########################
def track_peak(startF,stopF,numfreqs,time_step=300,MAXSCANS=200,plotIt=True):
  t0=time()
  maxfreques=[]
  times=[]
  pointCounter=0
  #outfile='peaktrack.dat'
  #of=open(outfile,'w')
  print
  print '====== Starting Peak Tracking (CTRL-C to stop)======='
Start Freq: %4.3f  
Stop Freq: %4.3f  
Time step: %2.2f min  
=============================================
Time 	 	 Temp 	 	 Press 		 Approx. Freq
----------------------------------------------------------
#of.write('Time 	 	 Temp 	 	 Press 		 Approx. Freq')
#of.write('----------------------------------------------------------')
if plotIt:
    f=figure(1,figsize=(12,9))
for scan in range(int(MAXSCANS)):
    tf=t.time()-t0
    T,P=getTP()
    currentfile='peaktrack_t%3.2fmin_T%3.1f_P%3.1f.dat'%(tf/60.,T,P)
    data=single_scan(startF,stopF,numfreqs,ofile=currentfile,Output=False)
    f=data[:,0]
    amp1=data[:,1]
    amp2=data[:,2]
    baseline=amp1[5]
    amp=sqrt((amp1-baseline)**2 + amp2**2)
    f,amp=smooth(f,amp,level=10)
    maxfreq=f[argmax(amp)]/1000
    baseline=amp[5]
    if max(amp)-baseline < 10*(average(amp[:50])-baseline):
        print 'WARNING: Peak seems weak or out of range!'
    maxfreqs.append(maxfreq)
    times.append(tf/60)
if plotIt:
    ion()
    subplot(211)
    plot(f,amp,'-',label='t=%2.1f'%(tf/60.))
    xlabel('Freq (kHz)')
    legend()
    subplot(212)
    plot(array(times),array(maxfreqs),'-o')
    if pointCounter==0: Fplot,=plot(array(times),array(maxfreqs),'-o')
    else:
        Fplot.set_data(array(times),array(maxfreqs))
    Fplot.autoscale()
    draw()
    ylabel('Freq (kHz)')
    #ioff()
outstring= '%3.1f 	 	 %3.1f 	 	 %3.1f 	 %3.3f'

% (tf/60, T, P, maxfreq)

print outstring
#of.write(outstring)
tff=t.time()-t0
pointCounter+=1
t.sleep(time_step-(tff-tf))

#################################
#Monitor_temp
#################################
def monitor_t_p(plotit=False,MAXPOINTS=10000,time_step=12,curr=0.001, 
ofile = 'TP_ramp.dat',tavg=2):
   
   Purpose: Realtime monitoring of the Temperature and Pressure
   with optional plotting. Assumes type-N thermocouple with ice bath or a four point
   probe platinum resistance thermometry detector and Heise DXD pressure transducer.
   UNITS: Temp (C) and Pressure (psi)
   IMPORTANT: Pressure is CH1 and Temp is CH2
   Usage: monitor_temp([plotit=True,MAXPOINTS=10000,time_step=12, 
                           ofile='t_p_ramp.dat',tavg=2])

   Returns: Tdata array [times,temps]
   Output: Writes data to "temp_ramp.dat"
   
   close('all')
t.sleep(2)
temp_thresh=1
print "=#15
print "Monitoring Temp and Pressure \nMaximum time is %.2f minutes. \nCTRL-C to quit." %((MAXPOINTS*time_step)/60.)
print "=#15

if plotit:
   curvT,figureT=plot_init(ttext="Monitoring Temperature")
   curvP,figureP=plot_init(ttext="Monitoring Pressure")

data=[]
stime=t.time()
print "Temp (C) \t Pressure(psi) \t Pressure(Pa) \t Log(P[Pa])"
print "=#60
while 1:
   if len(data)>MAXPOINTS:
      print " Maximum data points exceed! Stopping monitor ..."
      break

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t.sleep(time_step)
temp, press = getTP(navg=tavg)
time = t.time() - stime
if plotit:
    plot_update(ctime, temp, curvT)
    plot_update(ctime, press, curvP)
data.append([ctime / 60., press, temp])
print "%.2f \t %3.2f \t %3.3e \t %3.2f"
    % (temp, press, press*6895, log10(press*6895))
odata = array(data)
x = odata[:, 0]
y1 = odata[:, 1]
y2 = odata[:, 2]
save(ofile, odata, fmt='%.2f', delimiter='\t')
if plotit:
    figureT.display.visible = 0
    figureP.display.visible = 0
PTdata = array(data)
times = data[:, 0]
temps = data[:, 1]
press = data[:, 2]

figure(1, figsize=(11, 8))
subplot(211)
plot(times, temps)
xlabel("Time (sec)")
ylabel("Temp (C)")
subplot(212)
plot(times, press)
xlabel("Times (sec)")
ylabel("Pressure (psi")
show()
return Tdata

# plot_rus

# Purpose: Plot sets of RUS data.
# Inputs: List of filenames containing data to be plotted.
# Channel to plot: 1 -> In phase (default),
# 2 -> out of phase
# 3 -> Magnitude
# Usage: plot_rus(("b0.dat","b1.dat"),(channel=2))
# Returns: Nothing
if type(files) != type(()): files=files,        #convert to tuple
close()

for file in files:
    data=load(file,comments='#')
data=data[1:]
f=data[:,0]
    if channel <3: y=data[:,channel]
    if channel ==3: y=sqrt(data[:,1]**2+data[:,2]**2)
    if smoothing:       
        fs,ys=smooth(f,y,level=10)
        plot(fs,ys,label='smoothed')
        plot(f,y,label=file[:-4])
    legend()
    show()
return

###############################################################################
# Datacq: single scan
###############################################################################

def single_scan(start_freq,end_freq,num_freq,plotit=False,amp=9.0,
df_time=0.05,num_avg=1,ofile='tmp_data.dat',
dump=True,Output=True):
    
    try: import visa
    except:
        print "This function requires the PyVISA module. Install this first. \nStopping run .."
return 1
import time as t
dumpfile='dump.dat'
start_freq=start_freq*1e6
end_freq=end_freq*1e6
step=(end_freq-start_freq)/float(num_freq)
if Output: print 'Frequency step is: ',step

#Connect to and initialize equipment

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ds345 = visa.instrument("GPIB::%i" % DS345_GPIB)
sr844 = visa.instrument("GPIB::%i" % SR844_GPIB)
t.sleep(0.1)

cmd = "AMPL %.2fVP" % amp
ds345.write(cmd)
t.sleep(0.1)
ds345.write("FREQ %f" % start_freq)
t.sleep(0.5)
sr844.write("APHS")

if plotit:
    curv, figure = plot_init(xtext="Freq (Hz)", ytext="Signal (mV)", ttext="F0=%s" % start_freq)
    # t.sleep(10)
    data = []
    for i in range(0, num_freq+1):
        f = start_freq+i*step
        ds345.write("FREQ %f" % f)
        t.sleep(df_time)
        sumy = sumy90 = 0.
        for j in range(0, num_avg):
            response = sr844.ask_for_values("SNAP?1,2")
            sumy += response[0]
            sumy90 += response[1]
            t.sleep(0.01)

        avgy = sumy / float(num_avg)
        avgy90 = sumy90 / float(num_avg)
        data.append([f, avgy, avgy90])
        pc_done = (float(i) / float(num_freq) * 100)
        if pc_done % 10 == 0:
            if Output:
                print "%.1f % done"
                if dump:
                    dumpdata = array(data)
                    save(dumpfile, dumpdata, fmt='%1.6e', delimiter='	')
        if plotit:
            if i == 0:
                curv, figure = plot_init(f, avgy, xtext="Freq (Hz)", ytext="Signal (mV)")
            plot_update(((f-start_freq)/1e6, avgy, curv)

# ioff()
if plotit:
    figure.display.visible = 0

    adata = array(data)
    if Output:
        f = adata[:, 0]
        y = adata[:, 1]
y90 = adata[:, 2]
plot(f, y/1000.)
xlabel("Freq (kHz)"), ylabel("Signal (mV)"
show()

data.insert(0, [start_freq, end_freq, step])
save(ofile, data, fmt='%1.6e', delimiter='\t')
return adata

#batch_scan_temp()
#batch_scan_temp()
def batch_scan_TP(bfile="rusin.txt", tempfile="temps.dat", plotit=False,
tavg=1, dump=True):

Perform a batch scan and monitors temperature and pressure during
the scan.
Usage: batch_scan_temp([bfile="rusin.txt", tempfile="TP.dat",
plotit=False, tavg=2])
Output: frequency data files and temperature vs time data file
Returns: nothing

global Tfigure, Ffigure
try: import visa
except:
    print 'a'*3
    print "This function requires the PyVISA module. Install this first. \nStopping run .."
    return 1
import time as t
ion()

#Real time plotting flag and make sure all existing plots are closed
close('all')
t.sleep(2)  # let threads release
start_time = t.time()
dumpfile = "dump.dat"

#Read and parse scan parameters and initialize equipment
#(freqs are in MHz, times in seconds, and amplitude in volts P to P)
#rusin.dat format:
#    amplitude, time b/t freq. steps, time b/t scans, number of averages
#    start_freq, end_freq, num steps, data file name
#       ........

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def initialize():
    ''' Initialize equipment settings:
    amplitude, phase'''
    
    ifile=open(bfile,'r')
    lines=ifile.readlines()
    amp=float(lines[0].split(',')[0])
    df_time=float(lines[0].split(',') [1])
    ds_time=float(lines[0].split(',') [2])
    num_avg=int(lines[0].split(',') [3])
    ifile.close()
    time.sleep(0.5)
    cmd="AMPL %.2fVP" % amp
    time.sleep(0.5)
    ds345.write(cmd)
    print '''
    ==============
    Beginning Batch scan:
    Amplitude = %.2f
    Number of scans = %i
    Number of averages = %i
    Temperature (C) = %.2f
    Pressure (psi) = %.2f
    ==============
    ''' % (amp,len(lines)-1,num_avg,T,P)

    return df_time,ds_time, num_avg,lines[1:]

###
#Connect to equipment
###
ds345=visa.instrument("GPIB::%i"%DS345_GPIB)
sr844=visa.instrument("GPIB::%i"%SR844_GPIB)
dmm=visa.instrument("GPIB::%i"%DMM_GPIB)

tdata=[]
t0=t.time()
T,P=getTP(navg=tavg)
tdata.append((0.0,T,P))

df_time,ds_time,num_avg,scans=initialize()

# if plotit: Tcurv,Tfigure=plot_init(ttext="Monitoring Temperature")
global Tfigure
for scan in range(0,len(scans)):
    params=scans[scan].split(',',',')
    start_freq=float(params[0])*1e6
    if start_freq < 0:
        print '===============
NOTICE: Skipping a scan.
==============,'
        continue
    end_freq=float(params[1])*1e6
    num_freq=int(params[2])
ofile=params[3].strip()
    if len(params)==5:
        num_avg=int(params[4])
        print "Changing number of averages for this scan to: ",num_avg
    step=(end_freq-start_freq)/float(num_freq)
    fmid=(end_freq-start_freq)/2.+start_freq
    data=[]
    if plotit:
        Fcurv,Ffigure=plot_init(ttext="Resonance Data",xtext="Freq (Hz)",
ytext="Signal (mV)")
global Ffigure
    print "Beginning scan %i of %i: %6.0f to %6.0f with step size %4.0f ...
    % (scan+1,len(scans),start_freq,end_freq,step)
ds345.write("FREQ %f" % start_freq)
t.sleep(0.5)
sr844.write("APHS")
print "="*40
print "% Done \t Temp(C) \t Press(psi)"
print "="*40
for i in range(0,num_freq+1):
    f=start_freq+i*step
    ds345.write("FREQ %f" % f)
    if i == 0: t.sleep(ds_time)
    sumy=sumy90=0.
    for j in range(0,num_avg):
        t.sleep(df_time)
        response=sr844.ask_for_values("SNAP?1,2")
        sumy+=response[0]
        sumy90+=response[1]
    avgy=sumy/float(num_avg)
avgy90=sumy90/float(num_avg)
data.append([f,avgy,avgy90])
pc_done=(float(i)/float(num_freq)*100)
if pc_done % 10 == 0:
    ctemp,cpress=getTP(navg=tavg)
    ctime=t.time()-t0
    tdata.append((ctime,ctemp,cpress))
    print "%2.0f \t %3.2f \t %3.2f" % (pc_done,ctemp,cpress)
if dump:
    dumpdata=array(data)
    save(dumpfile,dumpdata,fmt='%1.6e',delimiter='\t')
    #plot_update(ctime,ctemp,Tcurv)
if plotit:
    x=array(data)[:,0]
    y=array(data)[:,2]
    plot_update(x,y,Fcurv)

if plotit: Ffigure.display.visible=0
adata=array(data)
f=adata[:,0]
y=adata[:,1]
y90=adata[:,2]
if plotit:
    figframe=figure(scan+1)
    plot(arange(start_freq,end_freq,step),zeros(num_freq))
xlabel("Frequency (Hz)")
ylabel("Signal (mV)")
title("Scan number: %s" % str(scan+1))
show()

##data.insert(0,[start_freq,end_freq,step])
save(ofile,data,fmt='%1.6e',delimiter='\t')
print "===========================
#close('all')

#####
#Release equipment
# WARNING: This should generally be commented out - it resets EVERYTHING!
#####
#ds345.write("*RST")
#sr844.write("*RST")

#Tfigure.display.visible=0

ioff()
end_time=time.time()
duration=(end_time-start_time)/60
T,P=getTP(navg=tavg)

atdata=array(tdata)
temps=atdata[:,1]
times=atdata[:,0]
press=atdata[:,2]
maxtemp=max(temps)
mintemp=min(temps)
maxP=max(press)
minP=min(press)
avgP=average(press)
delP=std(press)
avgtemp=average(temps)
deltemp=std(temps)
#tdata.insert(0,["#Std. Dev. = %3.2f ",deltemp])
#tdata.insert(0,["#Avg. Temp = %3.2f ",avgtemp])
#tdata.insert(0,["#Min. Temp = %3.2f ",mintemp])
#tdata.insert(0,["#Max. Temp = %3.2f ",maxtemp])
save(tempfile,tdata,fmt='%4.2f',delimiter='	')

print "Batch scan complete. 
Time required was %3.2f minutes 
Final Temperature = %.2f" % (duration,tdata[-1][1])
print "=================================================================
Temperature Stats:
Maximum T = %3.2f C
Minimum T = %3.2f C
Average T = %3.2f +/- %2.2f C
Std.Dev. = %3.2f C
=================================================================
Pressure Stats:
Maximum P = %3.2f psi
Minimum P = %3.2f psi
Average P = %3.2f +/- %2.2f psi
Std.Dev. = %3.2f psi
=================================================================
" % (maxtemp,mintemp,avgtemp,(maxtemp-mintemp)/2.,deltemp,maxP,minP,avgP,(maxP-minP)/2.0,delP)
print stats_string
temp_stats_file=open('TP_stats.dat','w')
temp_stats_file.write(stats_string)
temp_stats_file.close()
return 0

########################################################################
#Continuous Scan with Temp monitor

#Continuous Scan with Temp monitor

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def cont_scan_temp(bfile="rusin.txt", tempfile="temps.dat",
    plotit=False, tavg=2, dump=True):
    
    Performs a batch scan and monitors temperature during the scan.
    Usage: batch_scan_temp([bfile="rusin.txt", tempfile="temps.dat",
     plotit=True, tavg=2])
    Output: frequency data files and temperature vs time data file
    Returns: nothing
    
    
    global Tfigure, Ffigure
    try: import visa
    except:
        print '\a'*3
        print "This function requires the PyVISA module. Install this first. \n        Stopping run .."
        return 1
    import time as t
    ion()
    #######
    #Real time plotting flag and make sure all existing plots are closed
    #######
    close('all')
    t.sleep(2)  # let threads release
    start_time=t.time()
    dumpfile="dump.dat"
    #######
    #Read and parse scan parameters and initialize equipment
    #(freqs are in MHz, times in seconds, and amplitude in volts P to P)
    #rusin.dat format:
    # amplitude, time b/t freq. steps, time b/t scans, number of averages
    # start_freq, end_freq, num steps, data file name
    # ........
    #######
    
    def initialize():
        
        Initialize equipment settings:
        amplitude, phase"

        ifile=open(bfile, 'r')
        lines=ifile.readlines()
        amp=float(lines[0].split(',')[0])
        df_time=float(lines[0].split(',')[1])
        ds_time=float(lines[0].split(',')[2])
        num_avg=int(lines[0].split(',')[3])
ifile.close()
time.sleep(0.5)
cmd="AMPL %.2fVP" % amp
time.sleep(0.5)
ds345.write(cmd)
print ''''
==========================
Beginning Batch scan:
Amplitude = %1.2f
Number of scans = %i
Number of averages = %i
Temperature = %.2f
==========================
'''' % (amp,len(lines)-1,num_avg,tdata[-1][1])

return df_time,ds_time, num_avg,lines[1:]

def tc_poly(x):
    ## For 0 - 1300C range (+/- 0.06C)(N-type)
    a0=0.000000000
    a1=3.8783277E-2
    a2=-1.1612344E-6
    a3=6.9525655E-11
    a4=-3.0090077E-15
    a5=8.8311584E-20
    a6=-1.6213839E-24
    a7=1.669362E-29
    a8=-7.3117540E-35
    return a0+a1*x+a2*x**2+a3*x**3+a4*x**4+a5*x**5+a6*x**6+a7*x**7+a8*x**8

def get_temp():
    vsum=0
    for i in range(tavg):
        v=dmm.ask_for_values(":meas:volt:dc?")
        #t.sleep(0.5)
        vsum+=float(v[0])
    v=(vsum/tavg)*1E6
    temp=tc_poly(v)
    ctime=t.time()-t0
    tdata.append([ctime,temp])
    # print "Temp = %.2f C" % temp
    return temp

#######
#Connect to equipment
#######
ds345=visa.instrument("GPIB::%i"%DS345_GPIB)
sr844=visa.instrument("GPIB::%i"%SR844_GPIB)
dmm=visa.instrument("GPIB::%i"%DMM_GPIB)

tdata=[]
t0=t.time()
get_temp()

df_time,ds_time,num_avg,scans=initialize()

#if plotit: Tcurv,Tfigure=plot_init(ttext="Monitoring Temperature")
global Tfigure

#####
#Begin scans, update plots, and dump data
#####

for scan in range(0,len(scans)):
    params=scans[scan].split(',','
    start_freq=float(params[0])*1e6
    if start_freq < 0:
        print '===============
NOTICE: Skipping a scan.
=============='
        continue
    end_freq=float(params[1])*1e6
    num_freq=int(params[2])
    ofile=params[3].strip()
    ofilerooot=ofile[:-4]
    if len(params)==5:
        num_avg=int(params[4])
        print "Changing number of averages for this scan to: ",num_avg
        step=(end_freq-start_freq)/float(num_freq)
        fmid=(end_freq-start_freq)/2.+start_freq
        data=[]
        if plotit:
            Fcurv,Ffigure=plot_init(ttext="Resonance Data",xtext="Freq (Hz)",
ytext="Signal (mV)")
            global Ffigure
        print "Beginning scan %i of %i: %6.0f to %6.0f with step size %4.0f
        ...
        % (scan+1,len(scans),start_freq,end_freq,step)
        start_temp=get_temp()
        ds345.write("FREQ %f" % start_freq)
t.sleep(0.5)
sr844.write("APHS")
        for i in range(0,num_freq+1):
            f=start_freq+i*step
            ds345.write("FREQ %f" % f)
if i == 0: t.sleep(ds_time)
sumy=sumy90=0.
for j in range(0,num_avg):
    t.sleep(df_time)
    response=sr844.ask_for_values("SNAP?1,2")
    sumy+=response[0]
    sumy90+=response[1]

avgy=sumy/float(num_avg)
avgy90=sumy90/float(num_avg)
data.append([f,avgy,avgy90])

pc_done=(float(i)/float(num_freq)*100)
if pc_done % 10 == 0:
    ctemp=get_temp()
    ctime=t.time()-t0
    print "At %.1f" % pc_done + " percent done, temperature is: %.2f C" % ctemp
    if dump:
        dumpdata=array(data)
        save(dumpfile,dumpdata,fmt=’%1.6e’,delimiter=’\t’)
#plot_update(ctime,ctemp,Tcurv)
if plotit:
    x=array(data)[:,0]
    y=array(data)[:,2]
    plot_update(x,y,Fcurv)

if plotit: Ffigure.display.visible=0
adata=array(data)
f=adata[:,0]
y=adata[:,1]
y90=adata[:,2]
if plotit:
    figframe=figure(scan+1)
    plot(arange(start_freq,end_freq,step),zeros(num_freq))
xlabel("Frequency (Hz)")
ylabel("Signal (mV)")
title("Scan number: %s" % str(scan+1))
show()

##data.insert(0,[start_freq,end_freq,step])
ofilename=ofileroot+"_%3.1f.dat" % start_temp
save(ofilename,data,fmt=’%1.6e’,delimiter=’\t’)
print "="
#close(’all’)

#####
#Release equipment
# WARNING: This should generally be commented out - it resets EVERYTHING!

```python
#ds345.write("*RST")
#sr844.write("*RST")

#Tfigure.display.visible=0

ioff()
end_time=time.time()
duration=(end_time-start_time)/60
get_temp()

atdata=array(tdata)
temps=atdata[:,1]
times=atdata[:,0]
maxtemp=max(temps)
mintemp=min(temps)
avgttemp=average(temps)
deltemp=std(temps)
#tdata.insert(0, ['#Std. Dev. = %3.2f '%deltemp])
#tdata.insert(0, ['#Avg. Temp = %3.2f '%avgttemp])
#tdata.insert(0, ['#Min. Temp = %3.2f '%mintemp])
#tdata.insert(0, ['#Max. Temp = %3.2f '%maxtemp])
save(tempfile,tdata,fmt='%4.2f',delimiter='\t')

print "Batch scan complete. \n Time required was %3.2f minutes \n Final Temperature = %.2f" % (duration,tdata[-1][1])
print "=============\nTemperature Stats: Maximum temp = %3.2f C Minimum Temp = %3.2f C Average Temp = %3.2f +/- %2.2f C Std.Dev. = %3.2f C =============
" % (maxtemp,mintemp,avgttemp,(maxtemp-mintemp)/2.,deltemp)
print temp_stats_string
temp_stats_file=open('temp_stats.dat','w')
temp_stats_file.write(temp_stats_string)
temp_stats_file.close()

return 0
```

```python
#Batch_scan()
```

```python
def batch_scan(bfile="rusin.txt",dump=True,plotit=False):
```
Performs a batch scan with parameters read from bfile.
Usage: batch_scan([bfile="rusin.txt"])
Output: frequency data files
Returns: nothing

try: import visa
except:
    print '\a'*3
    print "This function requires the PyVISA module. Install this first. \n    Stopping run .."
    return 1
import time as t
#####
#Real time plotting flag and make sure all existing plots are closed
#####
if plotit: close('all')
t.sleep(2)    # let threads release
start_time=t.time()
#####
#Read and parse scan parameters and initialize equipment
#(freqs are in MHz, times in seconds, and amplitude in volts P to P)
#rusin.dat format:
#    amplitude, time b/t freq. steps, time b/t scans, number of averages
#    start_freq, end_freq, num steps, data file name
#    .........
#####
def initialize():
    ''' Initialize equipment settings:
        amplitude, phase'''
    ifile=open(bfile,'r')
    lines=ifile.readlines()
    amp=float(lines[0].split(',')[0])
    df_time=float(lines[0].split(',')[1])
    ds_time=float(lines[0].split(',')[2])
    num_avg=int(lines[0].split(',')[3])
    ifile.close()
    t.sleep(0.5)
    cmd="AMPL %.2fVP" % amp
    t.sleep(0.5)
    ds345.write(cmd)
    print '''
    ============== 
Beginning Batch scan:
    Amplitude = %1.2f
Number of scans = %i
Number of averages = %i

==========================
'' % (amp,len(lines)-1,num_avg)

return df_time,ds_time, num_avg,lines[1:]

####
#Connect to equipment
####
ds345=visa.instrument("GPIB::%i"%DS345_GPIB)
sr844=visa.instrument("GPIB::%i"%SR844_GPIB)

df_time,ds_time,num_avg,scans=initialize()

####
#Begin scans, update plots, and dump data
####
for scan in range(0,len(scans)):
    params=scans[scan].split(',
    start_freq=float(params[0])*1e6
    if start_freq < 0:
        print '===============
NOTICE: Skipping a scan.
===============
        continue
    end_freq=float(params[1])*1e6
    num_freq=int(params[2])
    ofile=params[3].strip()
    if len(params)==5:
        num_avg=int(params[4])
        print "Changing number of averages for this scan to: ",num_avg
        step=(end_freq-start_freq)/float(num_freq)
        fmid=(end_freq-start_freq)/2.+start_freq
        data=[]
        if plotit: fcurv,ffigure=plot_init(ttext="Resonance Data",
                                               xtext="Freq (Hz)",ytext="Signal (mV)")
        print "Beginning scan %i of %i: %6.0f to %6.0f with step size %4.0f
... \n" % (scan+1,len(scans),start_freq,end_freq,step)
        ds345.write("FREQ %f" % start_freq)
        t.sleep(0.5)
        sr844.write("APHS")
        for i in range(0,num_freq+1):
            f=start_freq+i*step
            ds345.write("FREQ %f" % f)
            if i == 0: t.sleep(ds_time)
            sumy=sumy90=0.
for j in range(0,num_avg):
    t.sleep(df_time)
    response=sr844.ask_for_values("SNAP?1,2")
    sumy+=response[0]
    sumy90+=response[1]

avgy=sumy/float(num_avg)
avgy90=sumy90/float(num_avg)
data.append([f,avgy,avgy90])

pc_done=(float(i)/float(num_freq)*100)
if pc_done % 10 == 0:
    print "%.1f ", pc_done +"% done"
    if dump:
        dumpfile="dump.dat"
        dumpdata=array(data)
        save(dumpfile,dumpdata,fmt='%.6e',delimiter='\t')

if plotit: plot_update((f-start_freq),avgy,fcurv)
adata=array(data)
f=adata[:,0]
y=adata[:,1]
y90=adata[:,2]

if plotit:
    figure.display.visible=0
    figure(scan+1)
    plot(f,y)
    xlabel("Frequency (Hz)"")
    ylabel("Signal (mV)"")
    title("Scan number: %s" % str(scan+1))
    show()

    # 8/14/2008
    data.insert(0,[start_freq,end_freq,step])
    save(ofile,data,fmt='%.6e',delimiter='\t')
    print "==========================
    #close('all')

    #######
    #Release equipment
    #######
    #ds345.write("*RST")
    #sr844.write("*RST")

    end_time=t.time()
duration=(end_time-start_time)/60

    print "Batch scan complete. Time required was %3.2f minutes" % duration
C.2 Batch Script for Temperature and Pressure Elastic Constants Fits

import os, sys, time, math, thread

isotherm=sys.argv[0]

#Therm exp. shift per degC
dlt=11.2E-6

#Executable params
rusexec='auto_cubicmrq.exe'
rusinput='xyzmrq.dat'
spectrafile='allfreqs.dat'

user='jgladden'
output={} # dict containing all mrq output for each temp
MRQFILE='mrqhdr.dat'

NOTELINE='PdH: Temp = '

def num_proc():
    """
    Determines the number of processors a host is running and updates the 
    ’hostinfo’ dict.
    Returns the number of processors (as integer).
    """
    result=os.popen('cat /proc/cpuinfo')
    cpudata=result.readlines()
numproc=0
for line in cpudata:
    if line.split(':') [0] == 'processor': numproc += 1
return numproc

def num_proc_mac():
    """
    Same as above, but on MacOSX.
    """
    result=os.popen('system_profiler | grep Cores')
    #print type(result)
    cpuinfo=result.readlines()
    numproc=int(cpuinfo[0].split(':') [1])
    return numproc

def adj_dims(mrqlines,temp):
    temp=temp-23.5 #adjust so no change at room temp, change is local
dx=dldt*temp
dy=dx
dz=dx
    cij=mrqlines[1].split(', ')[0:3]
e1= float(mrqlines[1].split(', ')[3])
e2= float(mrqlines[1].split(', ')[4])
e3= float(mrqlines[1].split(', ')[5])
density= float(mrqlines[3].split(', ')[0])
order= int(mrqlines[3].split(', ')[1])
numfr= int(mrqlines[3].split(', ')[2])
new_e1=e1*(1.0+dx)
new_e2=e2*(1.0+dx)
new_e3=e3*(1.0+dz)
new_density=density*e1*e2*e3/(new_e1*new_e2*new_e3)
global new_rho
new_rho=new_density
print "Current density = ", new_density
mrqlines[1]="%1.4f, %1.4f, %1.4f, %1.4f, %1.4f
\n (float(cij[0]), float(cij[1]), float(cij[2]), new_e1, new_e2, new_e3)
mrqlines[3]="%1.3f, %i, %i \n" % (new_density, order, numfr)
return mrqlines

def parse_in(temp):
    """
    Reads in the list of freqs. for a given temperature and the mrq. header file.
    Returns a list of lines for the new 'trigmrqin.dat' file
    (but does not write them to a file).
    """
    OFILE='xyzmrq.dat'
mrqf=open(MRQFILE,'r')
mrqlines=mrqf.readlines()

mrqlines[0]=NOTELINE+str(press)+'
'
new_mrqlines=adj_dims(mrqlines,temp)
nummodes=int(mrqlines[3].split(','))[2])

mrqf.close()

speclines=specdata[str(press)]

temp=float(temp)

for i in range(len(speclines)):
    new_mrqlines.append(speclines[i])

outf=open(OFILE,'w')
outf.writelines(mrqlines)
outf.close()

return new_mrqlines, nummodes

def parse_all_in():
    specs=open(spectrafile,'r').readlines()
    specdata={}
    temp=specs[0]
    presslist=specs[1].split()
    for press in presslist:
        specdata[press]=[]
    for mode in range(2,len(specs)-1):
        freqs=specs[mode].split()
        if freqs[0][0]=='-':
            for i in range(1,len(freqs)):
                freqs[i]='-'+freqs[i]
        for i in range(len(presslist)): #freq,press in freqs,presslist:
            specdata[presslist[i]].append(freqs[i]+'
')
    return presslist,specdata,temp

def parse_out(mrqout,nummodes):
    """
    Read output from 'mrqout.txt' file and extract the last set of Cij values and RMS error.
    These results are appended to the 'results' dict.
    """
    #fitf=open('mrqout.txt','r').readlines()
    E=mrqout[-3].split()[-1]
    #sigma=mrqout[-1].split()[-1]
    c11=float(mrqout[-(nummodes+6)].split()[0])
    c12=float(mrqout[-(nummodes+6)].split()[1])
    c44=float(mrqout[-(nummodes+6)].split()[2])
    #print c11,c12,c44
\[ B = \frac{1.0}{3.0} \times (c_{11} + 2.0 \times c_{12}) \]
\[ C' = \frac{1.0}{2.0} \times (c_{11} - c_{12}) \]
\[ G = c_{44} \]
\[ \text{error} = \text{mrqout[-5].split()[-1]} \]
\[ \text{results} = [\text{str}(c_{11}), \text{str}(c_{12}), \text{str}(c_{44}), \text{error}] \]
\[ \text{return results} \]

```python
def start_run(temp, press):
    
    Begins a 'trigmrqrot.exe' run on a remote host.
    Writes input file through an 'echo' command, runs the fit, and writes results to a local mrqout_temp.dat file.
    Updates 'hostjobs' dict when fit for that temp is done.
    Returns: list of strings with the contents of the

    ""
    print "=================================
    print "Started: Pressure = %.1f" % press

    cmddir=cmddir1
    proc1=os.popen('ps ax |grep '+rusexec).readlines()
    if numcpu==2 and len(proc1) > 1:
        cmddir=cmddir2
    (mrqlines,nummodes)=parse_in(temp)
    mrqfile=open(rusinput,'w')
    mrqfile.writelines(mrqlines)
    mrqfile.close()
    cmd= cmddir+rusexec
    mrqout=os.popen(cmd).readlines()
    results=parse_out(mrqout,nummodes)
    if totalPass==2: results=nextPass(mrqlines,results,nummodes)
    output.update({press:results})
    mrqout.insert(0,NOTELINE+str(press)+'
    fname='%smrq_%.1f.dat' % (cmddir1,press)
    f=open(fname,'w')
    f.writelines(mrqout)
    f.close()
    print results
    print "\n=================================
    return

def nextPass(mrqlines,results,nummodes):
    print results
    c11,c12,c44,e1,e2,e3=mrqlines[1].split(',')
    c11=results[0]
    c44=results[2]
```

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mrqlines[1]=c11+','+c12+','+c44+','+e1+','+e2+','+e3
mrqlines[2]='0,1,0,0,0,0\n'

mrqfile=open(rusinput,'w')
mrqfile.writelines(mrqlines)
mrqfile.close()
cmd=cmddir1+rusexec
mrqout=os.popen(cmd).readlines()
results=parse_out(mrqout,nummodes)
return results

#Make connections to the required number of hosts and divy up jobs
numcpu=num_proc()
print '='*30
print "Found %i processors" % numcpu
print '='*30

#Force to use 1 processor
numcpu=1
totalPass=2

#move files
import subprocess as sub
cmd='cp allfreqs_'+isotherm+'.dat allfreqs.dat'
sub.Popen(cmd,shell=True)
time.sleep(1)

presslist,specdata,temp=parse_all_in()
presslist.sort()

outdata=[]
data=[]
for press in presslist:
    tmp=[]
    tmp.append(press)
    outdata.append([str(press)]+output[press])
    tmp=tmp+map(float,output[press])
    data.append(tmp)

#write all results to a tab delim file
ofile=open('alldata.dat','w')
ofile.write('# Temp = '+isotherm)
ofile.write('#Press(psig) c11(GPa) c12(GPa) c44(GPa) error(%) rho(g/cc)
')
for i in range(len(data)):
    ofile.write('%.1f ' % data[i][0])
    for j in range(1,len(data[i])): if j==1 or j==2 or j==3: data[i][j]=100.0*data[i][j] #Convert to GPa
        ofile.write('%.4f ' % data[i][j])
    ofile.write('%.5f ' % rhos[i])
ofile.write('
')
ofile.close()

#cp results files
cmd='cp alldata.dat alldata_'+isotherm+'.dat'
su.Popen(cmd,shell=True)

C.3 Batch Script for High Temperature Elastic Constants Fits

#Works with the 'auto_isomrq' rus file input/output.
# Reads all spectra at once from 'spectrafile' in form:
# 23.5 50.0 100.4
#  fr1  fr1  fr1
#  fr2  fr2  fr2
#

import os, sys, time, math, thread

dldt=11.2E-6
# Executable params
rusexec='auto_cubicmrq.exe'
rusinput='xyzmrq.dat'
spectrafile='allfreqs.dat'

user='jgladden'
output={}  # dict containing all mrq output for each temp
MRQFILE='mrqhdr.dat'
cmddir1='./working1/
cmddir2='./working2/
NOTELINE='PdH: Temp = '

def num_proc():
    """
    Determines the number of processors a host is running and updates the
    'hostinfo' dict.
    Returns the number of processors (as integer).
    """
    result=os.popen('cat /proc/cpuinfo')
    cpudata=result.readlines()
    numproc=0
    for line in cpudata:
        if line.split(':') [0] == 'processor\t': numproc +=1
    return numproc

def adj_dims(mrqlines, temp):
    temp=temp-23.5  # adjust so no change at room temp, change is local
    dx=dldt*temp
    dy=dx
    dz=dx
    cij=mrqlines[1].split(',' )[0:3]
    e1=float(mrqlines[1].split(', ') [3])
    e2=float(mrqlines[1].split(', ') [4])
    e3=float(mrqlines[1].split(', ') [5])
    density=float(mrqlines[3].split(', ') [0])
    order=int(mrqlines[3].split(', ') [1])
    numfr=int(mrqlines[3].split(', ') [2])
    new_e1=e1*(1.0+dx)
    new_e2=e2*(1.0+dx)
    new_e3=e3*(1.0+dz)
    new_density=density*e1*e2*e3/(new_e1*new_e2*new_e3)
    print "Current density = ", new_density
    mrqlines[1]='%1.4f, %1.4f, %1.4f, %1.4f, %1.4f, %1.4f
    (float(cij[0]), float(cij[1]), float(cij[2]), new_e1, new_e2, new_e3)
    mrqlines[3]="%1.3f, %i, %i
      (new_density, order, numfr)
def parse_in(temp):
    """
    Reads in the list of freqs. for a given temperature and the mrq. header file.
    Returns a list of lines for the new 'trigmrqin.dat' file
    (but does not write them to a file).
    """
    OFILE='xyzmrq.dat'
    mrqf=open(MRQFILE,'r')
    mrqlines=mrqf.readlines()
    mrqlines[0]=NOTELINE+str(temp)+'\n'
    new_mrqlines=adj_dims(mrqlines,temp)
    nummodes=int(mrqlines[3].split(\',\') [2])
    mrqf.close()

    speclines=specdata[str(temp)]

    temp=float(temp)

    for i in range(len(speclines)):
        new_mrqlines.append(speclines[i])

    outf=open(OFILE,'w')
    outf.writelines(mrqlines)
    outf.close()
    return new_mrqlines, nummodes

def parse_all_in():
    specs=open(spectrafile,'r').readlines()
    specdata={}
    temps=specs[0].split()
    for temp in temps:
        specdata[temp]=[]
    for mode in range(1,len(specs)-1):
        freqs=specs[mode].split()
        if freqs[0][0]=='-':
            for i in range(1,len(freqs)):
                freqs[i]='-' + freqs[i]
        for i in range(len(temps)):
            freq,freq, temp in freqs,
            temps:
                specdata[temps[i]].append(freq[i]+'\n')
    return temps,specdata

def parse_out(mrqout,nummodes):
    """
    Read output from 'mrqout.txt' file and extract the last set of
    Cij values and RMS error.
    """
These results are appended to the 'results' dict.

```python
#fitf=open('mrqout.txt','r').readlines()
E=mrqout[-3].split()[-1]
#sigma=mrqout[-1].split()[-1]
c11=float(mrqout[-(nummodes+6)].split()[0])
c12=float(mrqout[-(nummodes+6)].split()[1])
c44=float(mrqout[-(nummodes+6)].split()[2])
B=(1.0/3.0)*(c11+2.0*c12)
Cprime=(1.0/2.0)*(c11-c12)
G=c44
error=mrqout[-5].split()[-1]
results=[str(c11), str(c12), str(c44),error]
return results
```

def start_run(temp):
    """
    Begins a 'trigmrqrot.exe' run on a remote host.
    Writes input file through an 'echo' command, runs the fit, and writes results to a local mrqout_temp.dat file.
    Updates 'hostjobs' dict when fit for that temp is done.
    Returns: list of strings with the contents of the
    """
    print "================================"n
    print "Started: Temp = %.1f" % temp

    cmddir=cmddir1
    proc1=os.popen('ps ax |grep '+rusexec).readlines()
    if numcpu==2 and len(proc1) > 1:
        cmddir=cmddir2
    (mrqlines,nummodes)=parse_in(temp)
    #cmd='mv %strigmrqin.dat %strigmrqin_old.dat' % (cmddir,cmddir)
    #os.system(cmd)
    mrqfile=open(rusinput,'w')
    mrqfile.writelines(mrqlines)
    mrqfile.close()
    cmd= cmddir+rusexec
    mrqout=os.popen(cmd).readlines()
    results=parse_out(mrqout,nummodes)
    output.update({temp:results})
    mrqout.insert(0,NOTELINE+str(temp)+'
')
    fname='%smrq_%.1f.dat' % (cmddir1,temp)
    f=open(fname,'w')
    f.writelines(mrqout)
    f.close()
```
print results
print "\n="*'30
return

#Make connections to the required number of hosts and divy up jobs
numcpu=num_proc()
print '='*'30
print "Found %i processors" % numcpu
print '='*'30

#Force to use 1 processor
numcpu=1

temps,specdata=parse_all_in()
print temps
#print specdata
ttemps=list(temps)
jobs_per_cpu=int(math.ceil(float(len(temps))/float(numcpu)))

jobs=0
for temp in temps:
    mrqout=start_run(float(temp))
    #mrqout=threading.start_new_thread(start_run,(float(temp))

temps=output.keys()
temps.sort()
outdata=[]
data=[]
for temp in temps:
    tmp=[]
    tmp.append(temp)
    outdata.append([str(temp)]+output[temp])
    tmp=tmp+map(float,output[temp])
data.append(tmp)

#write all results to a tab delim file
ofile=open('alldata.dat','w')
ofile.write('#Temp(C)\t c11(GPa) \t c12(GPa) \t c44(GPa) \t error(%)\n')
for i in range(len(data)):
    ofile.write('%.1f \t' % data[i][0])
    for j in range(1,len(data[i])):
        ofile.write('%.5f \t' % data[i][j])
    ofile.write('
')
C.4 Exponential Fit for Equilibrium Dynamics Data Plots

This script is used to fit tracked peak to an exponential function for the equilibrium dynamics monitoring data. 
NOTE: The 'dir' must be changed to the current directory before use.

# Method of picking starting point for peak fit:
# 1: start at lower 1/3 of scan
# 2: start at middle of scan
# 3: start at upper 2/3 of scan
# 4: automatically pick from max of magnitude of data
centerFmethod=4
temp=os.getcwd()[-3:]

close('all')
def getFiles(dir):
    startdir=os.getcwd()
    os.chdir(dir)
    files=glob.glob('peaktrack*.dat')
    times=[]
    for file in files:
        time=float(file.split('_')[1][1:5])
        print time
        times.append(time)
    os.chdir(startdir)
def residuals(p, y, x, xi):
    err = y - funct(p, x, xi)
    return err

def funct(params, x, xi):
    pbg = params[0:2]
    p1 = params[2:6]
    if Npeaks > 1: p2 = params[6:10]
    if Npeaks > 2: p3 = params[10:14]
    if Npeaks == 1: return bkgrnd(pbg, x, xi) + lor(p1, x)
    if Npeaks == 2: return bkgrnd(pbg, x, xi) + lor(p1, x) + lor(p2, x)
    if Npeaks == 3: return bkgrnd(pbg, x, xi) + lor(p1, x) + lor(p2, x) + lor(p3, x)

# Define model function with all adjustable parameters in a
tuple called 'params'
def lor(params, x):
    xo = params[0]
    Q = params[1]
    A = params[2]
    phi = params[3]
    return A * (x / xo * cos(phi) + (1.0 - (x / xo)**2) * Q * sin(phi)) / ((x / xo)**2 + (1.0 - (x / xo)**2)**2 * Q**2)

def bkgrnd(params, x, xi):
    a0 = params[0]
    a1 = params[1]
    return a0 + a1 * (x - xi)

def runFit(file):
    # close('all')

data = np.loadtxt(file)

data = data[1:]
xdata = data[3:, 0]
ydata = data[3:, 2]

if centerFmethod == 1: centerF = min(xdata) + 1 * (max(xdata) - min(xdata)) / 3.
if centerFmethod == 2: centerF = min(xdata) + 1 * (max(xdata) - min(xdata)) / 2.
if centerFmethod == 3: centerF = min(xdata) + 2 * (max(xdata) - min(xdata)) / 3.
if centerFmethod == 4:
ydata2 = data[3:, 1] - data[6, 1]
ydatamag = sqrt(ydata2**2 + ydata**2)
centerF=xdata[argmax(ydatamag)]

xi=xdata[0]
Npeaks=1

pname = (['A0', 'A1', 'Fo', 'Q', 'A', 'phi'])

params0=[0.00, 0.00, centerF, 3000, 0.001, 3]
plsq = leastsq(residuals, params0, args=(ydata, xdata, xi), maxfev=2000)
fitfreq=plsq[0][2]
fitQ=plsq[0][3]
plot(xdata, ydata, 'r-', ms=4)
plot(xdata, funct(plsq[0], xdata, xi), 'b-')
xlabel('Frequency (kHz)')
ylabel('Amplitude (mV)')

print '=============================
print "Final parameters for " + file
for i in range(len(pname)):
    print "%s = %.4f " % (pname[i], plsq[0][i])

return fitfreq, fitQ

files, times=getFiles(dir)

data=[]
Npeaks=1

startdir=os.getcwd()
os.chdir(dir)

figure(1)

for file in files:
    freq, Q=runFit(file)
data.append((times[files.index(file)], freq, Q))

def expresiduals(p, y, x):
    err = y-expfit(p, x)
    return err

def expfit(params, x):
    A0=params[0]
import numpy as np
import os
import matplotlib.pyplot as plt

x = np.array([1, 2, 3, 4, 5])
y = np.array([10, 20, 30, 40, 50])

tc = params[1]
offset = params[2]
return A0*(1-exp(-x/tc))+offset

#times=array(times)
#freqs=array(freqs)/1000
data.sort()
data = array(data)
#data.sort(axis=0)
times = data[:, 0]
freqs = data[:, 1]
Q = data[:, 2]

params0 = [1000, 10, freqs[0]]
plsq = leastsq(expresiduals, params0, args=(freqs, times), maxfev=2000)
print
print "Time Constant = %3.2f, Freq Change = %3.3f" % (plsq[0][1], plsq[0][0]/1000)
figure(2)
xfit = linspace(min(times), max(times), 100)
plot(times, freqs, 'o')
plot(xfit, expfit(plsq[0], xfit), 'r-')
xlabel("Time (min)")
ylabel("Freq (kHz)")
title("PdH: P="+dir[-14:-11]+" psia, T="+temp+: tau=%2.2f"%plsq[0][1]+" min")
figure(3)
plot(times, 1/Q, '-o')
ylabel('Attenuation (1/Q)')
xlabel('Time (min)')
show()

np.savetxt('equilib.dat', data)

os.chdir(startdir)

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VITA

Rasheed Adewale, Adebisi received his Bachelor of Science degree in Engineering Physics from Obafemi Awolowo University, Ile-Ife, Nigeria in July 2000. After a year of national service and a couple of years of employment in the research and marketing services. He started his Master of Science studies in Engineering Physics at the Obafemi Awolowo University. Mid-way into the graduate studies, January 2006, he got offer for a job as a research officer at the Engineering Materials Development Institute in Akure, Nigeria.

Seven months after in August 2006, he had to quit the job and seek a postgraduate degree in Physics upon receiving a generous graduate assistantship from the University of Mississippi (UM), United States of America. He worked as a teaching assistant in the department of Physics and Astronomy for five semesters. In the summer of 2007, he joined the Resonant ultrasound spectroscopy (RUS) group as a research assistant. This was the beginning of his four years dissertation journey with Dr. Joseph Gladden as his advisor.