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Final Report

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Resonant Ultrasound Spectroscopy Studies of Complex Transition Metal Oxides

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Introduction

The central thrust of this program has been to apply resonant ultrasound spectroscopy (RUS), an elegant and efficient method for determining the elastic stiffness constants of a crystal, to the complex and poorly understood class of materials known as transition metal oxides (TMOs). Perhaps the most interesting and challenging feature of TMOs is their strongly correlated behavior in which spin, lattice, and charge degrees of freedom are strongly coupled. Elastic constants are a measure of the interatomic potentials in a crystal and are thus sensitive probes into the atomic environment. This sensitivity makes RUS an ideal tool to study the coupling of phase transition order parameters to lattice strains.

Personnel History

During the course of this award there have been some significant personnel changes which have had impact on the progress of the proposed work. Dr. Henry E. Bass, the PI for the award provided guidance and expertise that was crucial to the project's overall success. Dr. Veerle Keppens, the Co-PI moved to the University of Tennessee – Knoxville soon after the start date of this project in 2003. At that point, a postdoctoral associate, Gabriella Petelescu, was hired to work with Dr. Keppens to conduct the research. Within two years, Dr. Petelescu's husband was offered a position at Loyola University; thus, she decided to relocate. Shortly thereafter, a postdoctoral associate, Gary Lamberton, was hired to perform the bulk of the proposed work. Dr. Lamberton made progress on the construction of a high temperature RUS apparatus during 2004 – 2005. In the summer of 2005, Dr. Joseph Gladden was hired as a faculty member in the Physics Department and took over the RUS lab at the National Center for Physical Acoustics (NCPA) on the University of Mississippi (UM) campus. Dr. Gladden provided guidance to Dr. Lamberton in regards to the ongoing research. In the summer of 2007, Dr. Gladden devoted 100% of his research efforts toward accomplishing the remaining goals of the project in the short amount of time remaining. Guangyan Li, a graduate student in the Physics Dept. was supported by this grant during 2007 and part of 2008. This final report, prepared by Dr. Gladden, highlights the progress made toward these goals.

The RUS Method

When acoustic vibrations are introduced into a three dimensional solid, certain frequencies will cause a large displacement amplitude response in the solid, or a resonance. Much in the same way oscillating a mass on a spring at just the right frequency will produce large displacements of the mass.

These special frequencies are often called the “natural frequencies” of the system and the types of oscillations they produce are called “normal modes”. Figure 1 shows plots of the deformations of a parallelepiped sample for a number of normal modes. The specific set of natural frequencies of a solid depends on the geometry, mass density, crystallographic orientation, and the elastic constant tensor of the material. While few analytical solutions for 3D normal modes exist, there are good numerical methods for estimating the normal modes for a particular solid. In a RUS measurement, a set of natural frequencies are measured by placing a sample between two transducers; driving one transducer with a swept frequency and monitoring the sample response with the other transducer. Figure 2 shows a frequency sweep for a Zintl thermoelectric (TE) sample measured during the summer of 2007. The resonance peaks measured are then fit with Lorentzian line shapes from which the center frequency and quality factor for each peak are extracted.

Figure 1: First 15 calculated normal modes for a parallelepiped. Red denotes nodal regions and yellow denotes anti-nodes.

The set of measured frequencies are then compared to calculated frequencies for a given set of sample parameters including dimensions, density, crystal orientation (if applicable), and elastic constants. These parameters are then adjusted using a non-linear least squares fitting method until the calculated spectrum best matches the measured spectrum. Other variables that can be adjusted are the three dimension measurements and three Euler angles which are required to rotate the crystal axes to coincide with the parallelepiped axes for anisotropic samples.

Figure 2: The first three resonances of a p-zintl sample at room temperature.

Sample Preparation

RUS analysis assumes the resonators (samples) have a perfect parallelepiped geometry, so samples need to be carefully prepared. Bulk samples are first cut into rough shape with a diamond saw. Each of the 6 surfaces are then polished with diamond paper and polishing jig to produce high quality surfaces with right angle edges and corners. The process is carefully monitored under a microscope. For high temperature measurements, final samples should be at least 1 – 4 mm for each dimension so the weight of the buffer rods does not shift the resonances more than about 0.1%. Just before measurement, samples are typically cleaned with an ultrasonic cleaner in ethanol.

Figure 3: (a) Close-up of the bottom of the lower buffer rod / transducer assembly. (b) Complete high temperature RUS apparatus ready for measurements. The oxygen monitor and electronics are not shown.

High Temperature RUS Measurements

For high temperature RUS measurements, a vertically oriented tube furnace is used. The sample rests between two 1/8" diameter buffer rods made of thermally stable materials with low acoustic attenuation such as fused quartz or ceramic alumina. The transducers are glued to the other ends of these buffer rods which extend about 6" out the top and bottom of the furnace. This arrangement allows the sample to be heated to very high temperatures while keeping the transducers cool enough to operate. To minimize the chances of oxidation, a very low flow (~ 1 LPM) inert atmosphere fills the sample chamber. The exhaust of the gas flow is monitored for oxygen content and typically kept below about 20 ppm with pure Argon as the inert gas. Based on our initial measurements with the Zintl compounds, we will be switching to a inert gas of 95% Ar and 5% H to further reduce the oxygen content. Photos of the system are shown in Figure 3.

Figure 4: Part of a resonance spectrum for a bulk metallic glass sample showing both sample and buffer rod resonances.

Test Case for the Buffer Rod System

As a test of the buffer rod system, we prepared an aluminum sample. Aluminum was chosen because it has low acoustic attenuation so the resonances peaks are strong and sharp (high Q) and it is a common material with tabulated elastic moduli at elevated temperatures. The Young's and shear moduli as a function of temperature are plotted in Figure 5 along with linear fits. We were able to obtain values of $E = 68.5$ GPa and $G = 25.7$ GPa for the Young's and Shear modulus at room temperature. These values are in agreement literature values of $E = 68 - 70.1$ GPa and $G = 26.0$ GPa. [1] The temperature dependence of these quantities were compared to the work done by Kamm [2] on single crystal aluminum (ours is polycrystalline). The dE/dT we obtained from our measurements is

-0.0375 GPa/°C which compared well with -0.0391 GPa/°C derived from data of Kamm. The shear modulus compared more closely with our results yielding a $dG/dT = -0.0149$ GPa/°C and Kamm's work having a $dG/dT = -0.0143$ GPa/°C. The melting point for aluminum is about 600 C.

Figure 5: Young's and shear moduli for aluminum between room temperature and 400 C. These results were obtained from data acquired using the quartz buffer rod system.

Direct Contact Cell Design and Measurements

One complication with the buffer rod method as described above is that the buffer rods also experience resonances over the frequency ranges of interest. This complicates the data analysis because rod peaks are mixed with sample peaks. Differentiating these peaks is typically done by taking room temperature measurements with direct contact transducers, locating the first 20 - 30 sample peaks, and repeating the measurements with the buffer rods. Overlaying the two spectra allows one to determine which of the peaks are due to sample resonances and which are the buffer rods. However, once the temperature begins to change, all of the peaks shift and if temperature jumps are too large, it again becomes difficult to say with certainty which are the sample peaks. The end result is that even if the temperature range of interest is 700 – 900 C, we still must take data every 50 C from room temperature. This extra time, approximately 1 hour for each temperature point, presents a problem for materials which are very sensitive to oxidation at elevated temperatures such as the Zintl compounds. Figure 4 illustrates the problem.

A significant accomplishment in the past six months is the successful design and construction of a direct contact transducer apparatus using lithium niobate (LN) piezoelectric elements. LN has a high Curie temperature (~1200 C) so that direct contact measurements could in principle be taken over the full temperature range of our furnace. The schematic for the system is shown in Figure 6. We have found however that the limiting factors in the transducer system are electrical contacts and impedance mismatches in the high temperature coaxial cable induces by thermal gradients rather than the piezo elements themselves. We have used our sputtering machine to replace the standard gold lead contacts with platinum and are using silvered epoxy for the coaxial connections. With this system, we have obtained acoustic signals as high as 700 C. Even if the temperature range of interest is higher than 700

C, this system is still helpful because we could begin the process of tracking the peaks with buffer rod measurements above this temperature rather than 23 C, significantly reducing the time the sample must be exposed to the elevated temperatures. Much of the design and construction of the direct contact transducers was performed by Guangyan Li.

Figure 6: (a) High temperature direct contact cell. The top transducer rod assembly slides freely. (b) Detailed view of transducer rod assembly.

Charge Order Transition in LuFe_2O_4

We have recently used the direct contact transducer system to study the charge order transition in the transition metal oxide LuFe_2O_4 in a collaboration with David Mandrus of Oakridge National Lab and Veerle Keppens, an original PI on this grant and now at the University of Tennessee – Knoxville. We present here some preliminary results of this ongoing project. The elastic constants of materials are a measure of the curvature of the interatomic potentials in a crystal and thus are a sensitive probe into phase transitions – often discovering transitions which are missed by other measurement techniques. Also of particular importance to strongly correlated systems in which lattice strain, spin, and charge degrees of freedom are strongly coupled; RUS can provide information about the coupling of the order parameter and strain.

The crystals used in this study were grown using an optical furnace by the Mandrus group at ORNL. The material is very brittle and difficult to handle making polishing a near geometrically perfect parallelepiped extremely difficult. Without a precise geometry, elastic constants can not be obtained, however resonance peaks of a rough cut parallelepiped can be tracked. Since elastic constants are an educated reduction of the natural frequencies, the temperature trends of these

frequencies will match the trends of the elastic constants themselves. Four modes were tracked between room temperature and 200 C. The frequency trends clearly show the broad charge order transition at around 80 C. The shape of the trend suggests a linear coupling between the order parameter and strain. An unexpected feature however is the 'outlier' around 45 C. (see Fig. 7 (left)) Higher resolution data was obtained in the 35 – 60 C range and revealed a strong transition which has a different strain coupling to the order parameter. (see Fig. 7 (right)) The discovery of this new transition and knowledge of the nature of the strain coupling will be important information for theorists working to understand this strongly correlated material.

Figure 7: (Left) Normalized natural frequencies for four modes of a LuFe_2O_4 sample exhibiting a charge order transition near 80 C. (Right) A new transition discovered and more localized near 45 C.

Zintl Phase and Silicon Germanium Thermoelectrics: Current Results and Pending Work

The capability to measure the elastic stiffness tensor at temperatures up to 1000 C has helped spawn a number of additional projects and collaborations. We have recently (Spring 2008) established a project to study Zintl Phase thermoelectric (TE) materials funded through NASA and the Jet Propulsion Laboratory. The initial phase of the project has a budget of \$28,500 lasting through the Fall of 2008. Here we report some preliminary results for a p-type Zintl TE using the buffer rod system and various p and n type silicon germanium (SiGe) materials. By the end of the Summer of 2008 we expect to have enough data for several journal articles. Most of the data shown here was obtained by Guanyan Li.

Room temperature elastic constants were obtained for silicon germanium (as a reference) and p-Zintl TE. Additionally, elevated temperature measurements were performed on the p-Zintl sample using the quartz buffer rod system. At around 500 C, we lost the acoustic signal at which point we cooled the oven and removed the sample. We found significant charring of the sample surface, but no charring of the support structure or buffer rods. As mentioned earlier, the oxygen content of the pure argon gas flow is continuously monitored and never raised above 30 ppm. After analyzing the data, it was found that the quality of the resonance peaks began to degrade above 300 C. We report the elastic constants between room temperature and 300 C in Figure 8 along with temperature coefficients.

Figure 8: Shear and Young's moduli for a p-Zintl thermoelectric compound. Dashed lines are quadratic fits from which the temperature coefficients are obtained.

The newly developed direct contact transducers and improved inert gas system will be used to extend these measurements as high in temperature as high as possible before the sample is destroyed. Material properties of TE compounds are of interest to JPL for the development of next generation electrical power units in deep space probes.

During the Summer of 2008, SiGe samples of five different dopings were studied from room temperature up to 800 – 950 °C. The direct contact transducer system was used up to between 500 and 650 °C, and buffer rods were used at higher temperatures. All of these samples were polycrystalline and well fit assuming elastic isotropy, so the Young's and shear moduli alone completely characterize the material elastically. Figure 9 shows these moduli for the five samples studied. For each sample, 25 – 30 resonances were included in the moduli fit resulting in 0.07 – 0.3 % difference between computed and measured frequencies averaged over all modes. These errors constitute an “good” to “very good” fit for a RUS measurement.

An interesting feature in the n-SiGe sample is the break in the slope just under 200 °C. This behavior is often associated with a phase transition. After the initial heating, the sample was cooled and rescanned in that temperature range and the break in the slope did not repeat which implies the transition is irreversible. The acoustic attenuation also contains useful information near phase transitions as strain energy is coupled into the energy mechanism driving the transition. In a RUS measurement, attenuation is determined by the inverse of the quality factor of the resonances ($1/Q$). Figure 10 shows the temperature trends of $1/Q$ for this sample. The strong peak in attenuation around 150 C (425 K) is well fit with an attenuation model assuming a Arrhenius temperature dependence on the relaxation time. This fit yields an activation energy for the transition of $E_a = 0.27$ eV. Also noteworthy is that the attenuation peak did not repeat upon cooling and reheating the sample. The nature of this transition is as yet unknown, but these measurements have provided some important clues and we are currently working with JPL on better understanding this transition.

Figure 9: Young's and shear moduli for variously doped SiGe materials. Closed symbols are results obtained with the direct contact transducers and open symbols resulted from buffer rod measurements.

Figure 10: Acoustic attenuation of n-SiGe averaged over 30 modes before and after a thermal cycle. The smooth solid line represents a fit using an Arrhenius relaxation model with $E_a = 0.27$ eV.

Software Development

Once the resonance spectra of a given sample is experimentally obtained, the list of frequencies is used to determine the elastic constants of the material through a nonlinear fitting routine. Given the sample geometry, mass density, crystal orientation (if applicable), and an initial guess for the elastic

tensor, a resonance spectrum is computed using the Raleigh-Ritz principle. The computed and measured spectra are compared and elastic constants are adjusted until a minimum in the sum of the squares of the differences is found. The code to perform the calculations was developed over a decade ago.

For materials of high symmetry, such as isotropic or cubic, an optimization scheme can be utilized which allows the fits to complete in typically less than a few minutes. However for lower symmetry crystals such as trigonal, this optimization can not be employed and the fits typically run 45 – 60 minutes. For temperature resolved measurements involving spectra at 20 – 50 different temperatures, the computation time becomes significant. Since the analysis of each spectra is completely independent, it is an “embarrassingly parallel” problem. We have developed a set of Python scripts which read a ASCII text file containing the frequency lists for each temperature, build an input file for the fitting program and stores the results for each temperature. The script can be given a pool of machines connected via the internet, connect to each machine through SSH and determine the number of processing cores. The fits are then divided up accordingly, processed, and all results reassembled by the client machine and stored locally. The parallelization and automation of this process greatly shortens the time to final results for low symmetry materials. This script is also useful for isotropic or cubic samples for which we have data at many temperature points. To maintain consistency, the fit parameters for each temperature must be the same and the design of this software provides a convenient method of batch processing all the temperature data with a few user supplied commands.

An additional Python program was developed to speed the analysis of samples with poor quality resonances. Analyzing 20 peaks at 50 different temperatures quickly reveals the scale of the task at hand. The script plots the magnitude of the resonances peaks for 8-10 temperatures on one plot. The user can then zoom in on one peak, use a mouse to click on the top of the peak for each temperature and save the center frequencies for each temperature to a file. The user can then pan to the next peak and repeat the process, thereby quickly building up the frequency lists for input into the fitting routines described above. For higher quality peaks, we typically perform a non-linear fit on each peak using a Lorentzian line shape and extract the center frequency from the fit parameters. This method provides the most reliable values for the center frequencies, but can become problematic for low quality and strongly overlapping peaks. These scripts can be made available to anyone who would find them useful by contacting J.R. Gladden (jgladden@phy.olemiss.edu).

Scholarly Output and Final Remarks

To date, one manuscript entitled *Acoustic Modes of Finite Length Homogeneous and Layered Cylindrical Shells: Single and Multiwall Carbon Nanotubes* has been published in the Journal of Applied Physics [JAP **104**, 033524 (2008)]. Additionally, contributed presentations were given at the APS March Meeting in 2008, an invited presentation was given at the Acoustic Society of America Meeting in November 2007, and posters were presented at the DOE – EPSCoR meetings in West Virginia (2005) and Golden, CO (2007).

Over the final year of the project (2007), significant advancements in equipment design and data analysis have been achieved and collaborations between ORNL and JPL have been established. We expect the RUS investigations into the charge order transition to result in a significant publication in the coming months. The Zintl phase and SiGe thermoelectric material project with JPL currently underway will also result in several publications within 12 months. This DOE EPSCoR award will be cited in these coming publications. Through this grant, the DOE has enabled the construction of a high temperature RUS apparatus with the capability of measuring the elastic stiffness tensor of a crystal between room temperature and 1000 C. While low temperature Physics is mature, high temperature material properties and phase transitions remains a rather under developed field, one for which this DOE project has provided an important resource. We expect many future collaborations with materials physicists and engineers will result.

References

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- [2] G. N. Kamm and G. A. Alers, *J Appl Phys* **35**, 327 (1964)