Measurement of the elastic constants for Thermoelectric materials: $Ce_{.75}Fe_3CoSb_{12}$ and $CeFe_4Sb_{12}$

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Using resonant ultrasound spectroscopy (RUS), the complete elastic constant matrix will be determined for two single crystal thermoelectric samples of $Ce_{.75}Fe_3CoSb_{12}$ and $CeFe_4Sb_{12}$ with known shape, crystallographic orientation and density. This can be accomplished by measuring a vast amount of resonant frequencies from a sample. The square of these frequencies is dependent upon the product of the elastic constants and linear dimensions of the sample. So, with the known shape, crystallographic orientation, density and linear dimensions, I can obtain the complete elastic moduli from one RUS spectrum from a single sample.

I. INTRODUCTION

The beginning of RUS is credited to geophysics [1]. When the Earth is excited by a major earthquake, geophysicists measured the vibrational modes of the Earth to find the elastic properties of the planet. The first applications of RUS to materials-science was developed by Frazer, LeCraw and Holland. Once RUS hit the mainstream of material-science problems, a series of major improvements in the technology took place. RUS can be used to make important characterizations about materials, and more specifically investigating the elastic constants of thermoelectric materials will help identify what thermoelectric compounds will be the best for thermoelectric power generation.

In the past decade, there has been a huge increase in interest in the field of thermoelectric, which has been driven by the need for more efficient materials for electronic refrigeration and power generation [2]. This experiment is being conducted to investigate the elastic constants of $Ce_{.75}Fe_3CoSb_{12}$ and $CeFe_4Sb_{12}$. Thermoelectric materials can be designed to convert waste heat into electrical energy, and they can also be used in solid-state refrigeration devices [2]. Thermoelectric materials' efficiencies are often characterized by their figure of merit

$$ZT = \frac{S^2\sigma T}{\kappa} \tag{1}$$

where σ is the thermal conductivity, κ is the electrical conductivity, T is the temperature, and S is the Seebeck coefficient, which is defined as

$$S = -\frac{\Delta V}{\Delta T} \tag{2}$$

where ΔV is the thermoelectric voltage seen at the terminals, and ΔT is the temperature difference between the two ends of the material.

The best thermoelectric materials currently used in devices have $ZT \approx 1$ [2]; however, this is not a limit for the figure of merit. In order to increase the figure of merit one must either decrease the thermal conductivity and or increase the electrical conductivity. There is all kinds of research going on to find way to increase the figure of merit. For example, thermoelectric clathrates and filled skutterudites with crystal structures with "Rattlers" [2]. This technique involves the concept of minimum thermal conductivity, which is successfully verified in crystal structures with large empty cages where atoms can be partially or completely filled in such a way that they "rattle," resulting in the scattering of acoustic phonons. At elevated temperatures of 600-800K a $ZT \approx 1.5$ has been achieved in these materials [2].

In this experiment the complete elastic constant matrices of $Ce_{.75}Fe_3CoSb_{12}$ and $CeFe_4Sb_{12}$ will be obtained, analyzed and related to their figures of merit. If either of the samples exhibits low elastic stiffness, this characterization would correlate to a low thermal conductivity, and relatively valuable figure of merit depending on the electrical conductivity of the sample[2]. RUS has become one of the best tools to find the elastic constants in materials, but it is no simple system of measurements and computations.

One of the most notable accomplishments was by Ohno, who created the method to numerically solve the resonant modes of parallelepiped shapes samples with tetragonal, orthorhombic and trigonal symmetries [1]. RUS has the potential to become the most superior technique for extracting information about the elastic constants, the sample shape, the orientation of the crystallographic axis with respect to the sample [3]. Extracting this information is not an easy procedure.

One must compare the measured frequencies with the computed frequencies that are calculated with an initial set of input parameters. The input parameters can be elastic constants, descriptions of the crystallographic orientation or the shape of the sample. The methods for

computing the frequencies of samples with various shapes and symmetries have been for the most part developed by Holland, Demarest, Ohno, Visscher and Migliori (Section II).

II. BACKGROUND

Before going into the complicated computations of the eigenfrequencies in RUS, a review of crystalline elasticity should be noted. A material becomes deformed when forces are applied to that material. We can denote $u_i(x_k), i, k = 1, 2, 3$ as the displacement of a point along the ith axis whose coordinates were x_k before deforming. A strain tensor can be constructed to describe the deformation.

$$e_{kl} = \frac{1}{2}\Big(\frac{\partial u_k}{\partial x_l} + \frac{\partial u_l}{\partial x_k}\Big) \tag{3}$$

Assuming that the strains are small makes all the second-order terms negligible. e_{kk}, the diagonal elements of the strain tensor, are measurements of the extension per unit length of the kth axis. e_{kl}, the off-diagonal elements of the strain tensor, are measurements of the change in the angle between the k and l axes. We can now define a stress tensor σ_{ij} that describes the forces related to the deformation. i denotes the ith component of a force acting on a unit area with its normal along the jth axis. In linear elasticity a generalized Hooke's Law shows that

$$\sigma_{ij} = C_{ijkl} e_{kl} \tag{4}$$

where C_{ijkl} are the elastic constants. From work done on physical properties of crystals by John Frederick Nye and the work accomplished on the theory of elastic waves in crystals by S. Cusac and A. Miller, it has been shown that the elastic constants are the second derivatives of the free energy with respect to strain [5, 6]. It seems there are 81 independent elastic constants; however, assuming there are no net body torques acting on the material we can simplify the amount of elastic constants. For cubic crystals, it can be shown that $\sigma_{ij} = \sigma_{ji}$; therefore, i and j are commutable [3]. It is clear from equation (3), one can see that k and l are also interchangeable. The result is a decrease from 81 independent elastic constants to 36. There is another simplification that can be made: the strain energy must be a function only of the state of the material. Knowing this we can conclude $C_{ijkl} = C_{klij}$, and this fact reduces the amount of independent elastic constants to only 21. Any further decrease in elastic constants depends on the symmetry of the crystal that is being examined. The equations of motion can be derived by noting the forces acting on an infinitesimal cube of the material with volume dx dy dz. Now if we neglect body forces, the net force exists from the different stresses acting on the different faces of the cube, or in other words, it is due to the spatial variation of the stress [1]. Applying Newton's second law

$$\frac{\partial \sigma_{ij}}{\partial x_j} = \frac{\rho \partial^2 u_i}{\partial^2 t} \tag{5}$$

where ρ is the mass density. Now combining equations (3), (4) and (5), and using what we found earlier, $C_{ijkl} = C_{klij}$, the equation of motion can be written as [3]

$$\frac{C_{ijkl}\partial^2 u_k}{\partial x_j \partial x_l} = \frac{\rho \partial^2 u_i}{\partial^2 t} \tag{6}$$

Solving equation (6) turns out to be a very difficult task, so we have to rely on approximations to find solutions.

III. THEORETICAL COMPUTATIONS

RUS measurements are used on samples that are free vibrators, and because there is no analytical solution for a free vibrating solid, one must use approximations to solve the problem. The work done by William M. Visscher, Albert Migliori, Thomas M. Bell and Robert A. Reinert [4], shows that the displacements are expanded in some suitable set of basic functions. Taking the derivatives of the Lagrangian with respect to expansion coefficients and equating them to zero can determine the extremum. The result is a generalized eigenvalue problem in which kinetic and potential energies are defined by large matrices . The eigenvalues give the square of the resonant frequencies, and the eigenvectors give the displacements. The computational part of RUS consists of calculating a large matrix, finding the eigenvalues, and then utilizing the eigenvectors to determine the corrections to the set of input parameters to work out a match between the computed and measured frequencies.

A. The Lagrangian

The derivation of these computations starts with the Lagrangian for a 3D elastic body [3],

$$L = \frac{1}{2}\int_V (\rho\omega^2 u_i^2(r) - C_{iji'j'} u_{i,j}(r) u_{i',j'}(r))dV \tag{7}$$

in this case, we assume there is an $exp(i\omega t)$ time dependence. The subscripts are to be summed over, i, j , i', j' =1, 2, 3. The subscripts separated by commas imply a differentiation with respect to the subscripts appearing on the right-hand side of the comma. Expanding the displacements in equation (7) we can utilize a new equation

$$u_i(r) = a_{i\alpha}\Phi_\alpha(r) \tag{8}$$

where $a_{i\alpha}$ are the expansion coefficients and $\Phi_\alpha(r)$ are the basis functions. The basis functions are chosen depending on the shape of the sample. The important thing here is to be able to integrate the basis functions and their derivatives over the volume of the sample.

Thanks to the research on dynamic methods of measuring the elastic properties of solids that Moises Levy, Henry E. Bass, and Richard R. Stern [7] and to the research on free vibration of a rectangular parallelepiped crystal and its application to determination of elastic constants of orthorhombic crystals done by Susumu Ohno [8], we know that the best choice for $\Phi_\alpha(r)$ is the Legendre polynomials. there are three components of the displacement that are expanded in equation (8), and each component has its own set of expansion coefficients. Now, substituting equation (8) into the Lagrangian results in

$$L = \frac{1}{2}\Big(a_{i\alpha}a_{i'\alpha'}\rho\omega^2\int_V \Delta_{ii'}\Phi'_\alpha(r)dV - a_{i\alpha}a_{i'\alpha'}\int_V C_{iji'j'}\Phi_{\alpha',j}(r)\Phi_{\alpha',j'}(r)dV\Big) \quad (9)$$

This can be written in a shorter manner as

$$L = \frac{1}{2}((\rho\omega^2)a^T Ea - a^T\Gamma a) \quad (10)$$

B. The Generalized Eigenvalue Problem

Now the integrals from equation (9) are the elements of the matrices E and Γ. For L to be an extremum, the derivatives of L with respect to each of the expansion coefficients must be set to equal zero, and now a derivation for a generalized eigenvalue equation can be made as

$$\Gamma a = (\rho\omega^2)Ea. \quad (11)$$

The eigenvalues can be calculated by $\lambda = \rho\omega^2$. the eigenvectors, a, are the expansion coefficients. To calculate the resonant frequencies for a 3D elastic body, basically one calculates Γ and E if need be and finding the eigenvalue of equation (11). The eigenvectors will be useful for fitting the calculated resonant frequencies with the measured values. The elements of E and Γ are calculated using two terms from the expansion of $u(r)$ from equation (8). For a rectangular parallelepiped the normalized Legendre polynomials ($\bar{P}_n(x) = \sqrt{\frac{(2n+1)}{2}}P_n(x)$ with P_n being the usual Legendre polynomials) are the basis functions, and the expansion of the displacement becomes

$$u(r) = \frac{a_{i\lambda\mu v}}{\sqrt{L_1L_2L_3}}\bar{P}_\lambda(X)\bar{P}_\mu(Y)\bar{P}_v(Z)\hat{e}_i \qquad X = \frac{x}{L_1} \quad Y = \frac{y}{L_2} \quad Z = \frac{z}{L_3} \quad (12)$$

In this case, i=1, 2, 3 corresponds to the x, y and z components of $u(r)$, the e_i are the unit vectors, the sample dimensions in the x, y and z directions are $2L_1$, $2L_2$ and $2L_3$ respectively, and the reduced coordinates are, X, Y, Z. Setting p with a set $i\lambda\mu v$ equal to q with a set $i'\lambda'\mu'v'$ allows for the calculation of the matrices. The elements of E and Γ are given by

$$E_{pq} = \delta_{ii'}\int_{-1}^{1}\int_{-1}^{1}\int_{-1}^{1}\bar{P}_\lambda(X)\bar{P}_{\lambda'}(X)\bar{P}_\mu(Y)\bar{P}_{\mu'}(Y)\bar{P}_v(Z)\bar{P}_{v'}(Z)dXdYdZ \quad (13)$$

and

$$\Gamma_{pq} = \sum_{j=1}^{3}\sum_{j'=1}^{3}\frac{C_{iji'j'}}{L_jL'_j}\int_{-1}^{1}\int_{-1}^{1}\int_{-1}^{1}\frac{\partial(\bar{P}_\lambda(X)\bar{P}_\mu(Y)\bar{P}_v(Z))}{\partial X_j}\times\frac{\partial(\bar{P}_{\lambda'}(X)\bar{P}_{\mu'}(Y)\bar{P}_{v'}(Z))}{\partial X_{j'}}dXdYdZ \quad (14)$$

To ensure the E and Γ remain finite, the series for expansion of $u(r)$ must be truncated at some point. Visscher, Migliori, Bell and Reinert accomplished this [9] by requiring

$$\lambda + \mu + v \leq R \quad (15)$$

where R is some integer. This condition leads to another important result

$$N = \frac{(R+1)(R+2)(R+3)}{6} \tag{16}$$

The rank of the matrices will be 3N because each component of the displacement will have N terms in the expansion. R=10 is generally a good compromise between accuracy and computational overhead [8]. In summary, to calculate the vibrational eigenfrequencies of a sample, one must solve equation (11) with a convenient choice of basis functions and a fitting truncation of the expansion for equation (12). The matrix elements are found in equations (13) and (14) for the specific case of a rectangular parallelepiped and normalized Legendre polynomials as the basis functions.

IV. GOALS

The main objective of this research is to obtain the complete elastic matrix for $Ce_{.75}Fe_3CoSb_{12}$ and $CeFe_4Sb_{12}$. Once I achieve my main goal, I will analyze and examine the differences in the elastic properties of both thermoelectric materials. Lastly, I will relate the elastic properties of these two thermoelectric samples and make a prediction on which sample would be the better material for a thermoelectric generator.

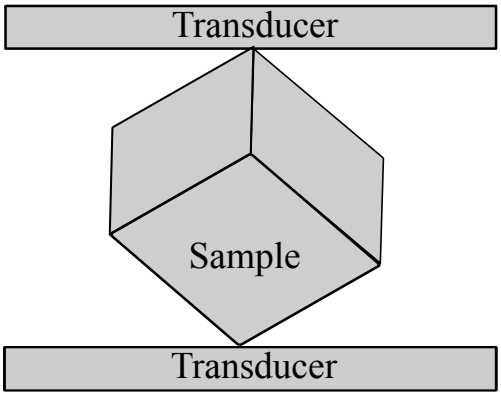

FIG. 1. A schematic of a typical RUS setup. The top piezoelectric transducer drives frequencies through the sample, and the bottom piezoelectric transducer records the resonant response and outputs a resonant ultrasound spectroscopy spectrum.

V. METHOD

RUS is based on the measurement of the vibrational eigenmodes of samples that are usually in the shape of parallelepipeds [2]. A schematic of the experimental apparatus can be seen in figure 1. The experimental setup for RUS is shown in Figure 1. A parallelepiped shaped sample will be held between two piezoelectric transducers. One transducer drives a range of frequencies from as little as 100 kHz to as much as 2 MHz. The other transducer records the resonant responses of the sample, and captures a RUS spectrum. When a large response is obtained, the frequency of the driving transducer corresponds to one of the sample's eigenfrequencies. The complete elastic constant matrix can be obtained from a single RUS spectrum if the sample shape, crystallographic orientation, and density are known.

VI. RESOURCES

The experiment will have to be performed in the lab with a resonant ultrasound spectroscopy system. We will examine two thermoelectric samples, $Ce_{.75}Fe_3CoSb_{12}$ and $CeFe_4Sb_{12}$, that are already available in the physics department. Some standard literature sources will be required, but most research and information is available online. All resources for this project are readily available in the physics department.

VII. BUDGET

No funds will be necessary for the completion of this project.

VIII. TIMELINE

- August 2015: Learning and training of the RUS system with known samples.
- September 2015: Data collection for thermoelectric samples of $Ce_{.75}Fe_3CoSb_{12}$ and $CeFe_4Sb_{12}$.
- October 2015: Data analysis of the collected RUS spectrums and complete elastic constant matrices from the $Ce_{.75}Fe_3CoSb_{12}$ and $CeFe_4Sb_{12}$ samples.
- November 2015: Begin writing paper and preparing presentations on all research and work accomplished.

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