

2006-2275: ULTRA-SONIC MEASUREMENT AND COMPUTATION OF ELASTIC CONSTANTS

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Ultra-sonic Measurement and Computation of Elastic Constants

Abstract

We have developed a laboratory exercise using an ultrasonic test system to measure elastic constants in copper single crystals, as well as moduli in polycrystalline samples. This laboratory is coordinated with the Introduction to Physics of Materials class taught to junior-level Materials Science and Engineering majors. Students in the class have usually taken a course in Mechanical Behavior of Solids, and are familiar with macroscopic (and destructive) testing of elastic moduli. This exercise provides an excellent basis for a discussion of the propagation of phonons in solids, the relationship between microscopic and macroscopic properties, destructive vs. non-destructive test methods, and an application of matrix algebra. We have recently added a computational component to the lab: use of density functional theory (using the program Plane Wave Self-Consistent Field, PWSCF) to calculate the elastic constants and compare to the measured values. The free software is part of the Quantum-ESPRESSO package.¹ The use of DFT also allows the demonstration of the nature of the approximations that must be made to solve the many-body Schrödinger equation for electrons in a condensed phase. This follows discussions in the first half of the course about the hydrogen atom and how extending such calculations require approximations due to the many-body problem.

Introduction and Motivation

Materials Scientists and Engineers are increasingly using computational tools to predict material properties, in addition to using analytical tools to measure them. We feel it is essential to incorporate some of these tools, as well as knowledge of the theories on which they are based, into our undergraduate curriculum. One opportunity to do so is in our junior-level Introduction to Physics of Materials course. This is a two-quarter sequence, required by MSE majors, that introduces quantum mechanics and applications to materials and engineering, band structures, cohesive energy, thermal behavior, electrical conduction, etc. The first quarter emphasizes an introduction to quantum mechanics; the second quarter emphasizes applications, and is taught with a weekly two-hour laboratory. One of the lab exercises we have used for several years is the measurement of elastic constants using ultrasonic testing. Most of the students in the class have already taken a course in Mechanical Behavior of Solids, in which they use destructive testing (compression or tension), to measure elastic properties. They have familiarity with moduli, stiffness and compliance from this course, but they have not previously used non-destructive testing (ultrasound). This lab offers an excellent opportunity to expose students to a second method that yields some of the same information they obtained with conventional mechanical testing. We have recently written a follow-up exercise which uses computational free-ware to calculate these same constants. These computations rely heavily on approximations, and students see the limitations of the program when calculating their results that often differ from “book values” by 10-20 percent. This is underscored by the comparison with their measured values, which are much closer to the literature.

I. Ultrasonic measurements of elastic constants in single crystal copper and select polycrystalline samples

Theory

One of the most accurate methods to measure the elastic stiffness constants, c_{ij} , and thus Young's modulus and E and the shear modulus G , is to determine the velocity of long wavelength acoustic wave propagation. Since copper has a face-centered cubic structure, there are three independent elastic constants, C_{11} , C_{12} and C_{44} in Equation (1)

$$\begin{Bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \tau_{yz} \\ \tau_{xz} \\ \tau_{xy} \end{Bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & & & \\ & C_{11} & C_{12} & & & \\ & & C_{11} & & & \\ & sym & & C_{44} & & \\ & & & & C_{44} & \\ & & & & & C_{44} \end{bmatrix} \begin{Bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \gamma_{yz} \\ \gamma_{xz} \\ \gamma_{xy} \end{Bmatrix}, \quad (1)$$

where σ_{xx} , σ_{yy} and σ_{zz} are normal stress, τ_{xy} , τ_{xz} and τ_{yx} are the shear stress, ε_{xx} , ε_{yy} and ε_{zz} are normal strain, γ_{xy} , γ_{yz} and γ_{xz} are the engineering shear strain.²

If the velocity is measured in suitable directions in a single (cubic) crystal, and the density ρ is known, the elastic constants can be found easily using the following equations²:

Wave in the [100] direction

$$\text{Longitudinal velocity, } v_L = \sqrt{\rho \cdot C_{11}} \quad (2)$$

$$\text{Transverse velocity, } v_T = \sqrt{\rho \cdot C_{44}} \quad (3)$$

Wave in the [110] direction

$$\text{Longitudinal velocity, } v_L = \sqrt{\frac{1}{2} \rho \cdot (C_{11} + C_{12} + 2C_{44})} \quad (4)$$

$$\text{Transverse velocity, } v_{T1} = \sqrt{\rho \cdot C_{44}} \quad (5)$$

$$v_{T2} = \sqrt{\frac{1}{2} \rho \cdot (C_{11} - C_{12})} \quad (6)$$

Wave in the [111] direction

$$\text{Longitudinal velocity, } v_L = \sqrt{\frac{1}{3} \rho \cdot (C_{11} + 2C_{12} + 4C_{44})} \quad (7)$$

$$\text{Transverse velocity, } v_{T2} = \sqrt{\frac{1}{3}\rho \cdot (C_{11} - C_{12} + C_{44})} \quad (8)$$

Although there are two modes of transverse (shear) propagation, these are degenerate in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, but not in the $\langle 110 \rangle$ direction. Hence there are seven equations to solve for the three unknown stiffness constants, and the problem is over determined.

Once the stiffness constants are determined, the compliance constants may be determined using equations (9) – (11), which follow from inversion of the stiffness matrix in equation (1)².

$$C_{44} = 1/S_{44} \quad (9)$$

$$C_{11} - C_{12} = (S_{11} - S_{12})^{-1} \quad (10)$$

$$C_{11} + 2C_{12} = (S_{11} + 2S_{12})^{-1} \quad (11)$$

The compliance constants may then be used to determine the anisotropic values for Young's modulus³:

$$\frac{1}{E_{[100]}} = s_{11} \quad (12)$$

$$\frac{1}{E_{[110]}} = s_{11} - \frac{1}{2}[(s_{11} - S_{12}) - \frac{1}{2}s_{44}] \quad (13)$$

$$\frac{1}{E_{[110]}} = s_{11} - \frac{2}{3}[(s_{11} - S_{12}) - \frac{1}{2}s_{44}] \quad (14)$$

In addition to the measurements on single crystal copper samples, the longitudinal and transverse velocities in polycrystalline materials may be measured. In this case the samples are assumed to be isotropic, and the corresponding values of Young's modulus E , the shear modulus G , and Poisson's ratio ν , may be determined from:

$$G = \frac{E}{2(1+\nu)} \quad (15)$$

$$v_L = \sqrt{\frac{E(1-\nu)}{\rho(1+\nu)(1-2\nu)}} \quad (16)$$

$$v_T = \sqrt{\frac{G}{\rho}} \quad (17)$$

Equipment, Materials and Supplies

For example: Matec Ultrasonic Inspection system comprised of a Pentium III PC, SR 9000 pulser/ receiver card, SR9010 100 MHz data acquisition card, and MUIS-32 Digital Oscilloscope Emulation Software. (Matec Instrument Companies, Inc. 56 Hudson St., Northborough, MA 01532; phone: 508-393-0155).

Three copper single crystals ~ 5 mm x 5 mm x 5 mm; cut with faces parallel to $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$, respectively. (Faces are polished.)

Longitudinal transducer: M5025-L (Matec 50MHz, 0.25 inch diameter faceplate)

Shear transducer: MQ520-F (Matec 20 MHz, 0.25 inch diameter faceplate)

Coupling media: glycerin or molasses for longitudinal and shear waves, respectively.

Polycrystalline samples: alumina, aluminum, copper, nickel. Dimensions: ~ 3 mm thick, with areas larger than the 0.25 inch diameter transducer faceplates.

Procedure

The ultrasonic measurement system used in this experiment works in the pulse-echo mode. A single transducer is coupled to one of the faces of a copper sample, using the appropriate coupling media. Students use the digital oscilloscope to measure the time between the generated pulse and the echo from the opposite face of the crystal. The velocity of wave propagation is twice the thickness of the sample divided by this measured time of flight. These measurements are repeated with both transducers and each of the three copper single crystal samples. The two modes of shear propagation in the $\langle 110 \rangle$ are observed when that sample is rotated on the face of the transducer. Longitudinal and transverse velocities may likewise be measured for the polycrystalline samples, which are assumed to be isotropic.

Typical Results

Table 1. Acoustic velocity (longitudinal and transverse waves) in single crystal copper

Cu	Thickness (m)	Time (μ sec) longitudinal	v_L (m/sec)	Time (μ sec) transverse	v_T (m/sec)
$\langle 100 \rangle$.00391	1.78, 1.768	4408	2.808	2789
$\langle 110 \rangle$.0048	1.98, 1.948	4959	6.020	1621
$\langle 110 \rangle$				3.384 (rotate 90°)	2884
$\langle 111 \rangle$.00622	2.456, 2.436	5109	5.992	2077

Table 2. Values of elastic stiffness constants

Constant	Measured velocities & equation:	Experimental value (GPa)	Literature value ^{3,4} (GPa)
C_{11}	Eq (2); Eq (4,5,6,8)	174, 175	168
C_{44}	Eq (3); Eq (4,5,6,8)	69.5; 68.7	75
C_{12}	Eq (7); Eq (4,5,6,8)	124; 127	121

The difference between experimental measurements and literature values is between 4-8%.

II. PWSCF computation of elastic constants in copper

Theory

The first quarter of the Introduction to Physics of Materials course acquaints students with quantum mechanics, and introduces the so-called “many-body problem” encountered when solving for electronic structure: the concept that even for the simple He molecule, the Schrödinger equation cannot be solved exactly because there are more than two particles present. The electron-electron interactions (even with only two electrons in the system) complicate the physics, and require one to approximate the form of the Hamiltonian, and solve iteratively. Ignoring these interactions is not a good approach; in that case the calculated energy of the ground state of He (-54.4 eV) is very different from the measured value (-24.6 eV).

Density Functional theory (DFT) represents an approach to solving this many-body problem that has emerged as the theoretical framework that yields the most optimal balance of accuracy and computational efficiency. DFT is a parameter-free computational method that yields true predictions for the cohesive, electronic and thermodynamic properties of materials. The theory is able to treat systems with covalent, ionic and metallic bonding with comparable accuracy and represents an invaluable tool to aid in the design, development and understanding of materials and their properties.

This lab is intended to familiarize students with DFT calculations, using software that is representative of many such programs that have become available to the materials science community over the past decade. The specific program used here is called Plane Wave Self-Consistent Field (PWSCF), and it is freely available on <http://www.pwscf.org>¹. This portion of the lab involves the calculation of elastic constants using DFT methods, which will be compared to the measured values that were determined using ultrasonic methods. DFT uses as input only the atomic numbers of the atoms in the system (in this case, Cu with $Z=29$) as well as the geometry of the crystal structure (strained and unstrained). All the numbers that are calculated represent true computational predictions that result from solving the many-body Schrödinger equation with the approximations underlying the DFT theory. Due to the approximations which must be made to make these calculations tractable, the difference between the calculated and measured values is often on the order of 10-20 percent.

The PWSCF DFT code is used to compute the energy for some selected deformed Cu structures (Figure 1). Three deformation modes are considered sequentially: (A) hydrostatic compression; (B) volume conserving orthorhombic strain; (C) volume conserving monoclinic strain.

The energy vs. the deformation is fit to determine the three independent elastic constants described in Equation 1.

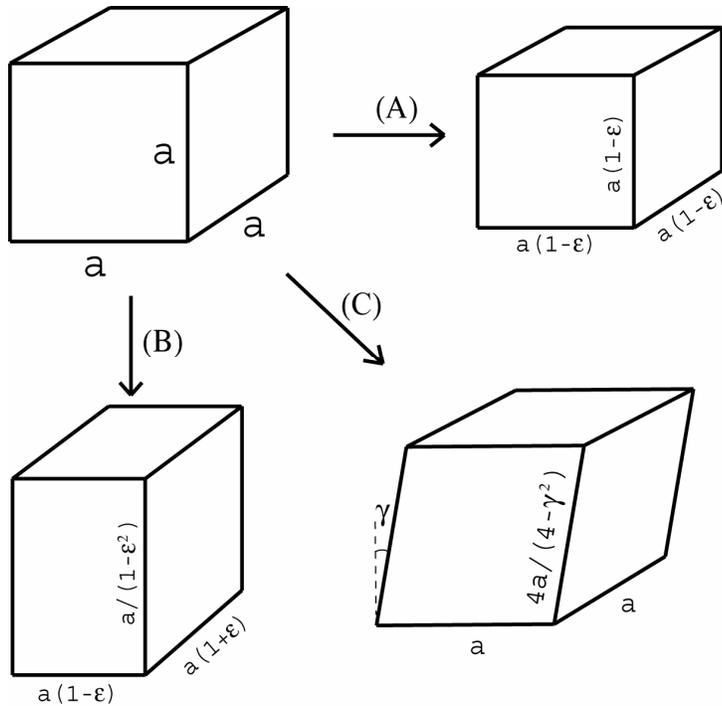


Figure 1. Three deformation modes used to compute the three independent elastic constants for FCC Cu. (A) hydrostatic compression; (B) volume conserving orthorhombic strain; (C) volume conserving monoclinic strain

Part I – Bulk Modulus/ Hydrostatic deformation

The first deformation mode to consider is that of hydrostatic deformation, illustrated in Figure 1A. This will allow us to determine the bulk modulus, $B = (C_{11} + 2C_{12})/3$. In this case, the energy can be expressed using the so-called Birch-Murnaghan equation of state:

$$E(V) = E_0 + \frac{B_0 V}{B_0'} \left[\frac{(V_0/V)^{B_0'}}{B_0' - 1} + 1 \right] - \frac{B_0 V_0}{B_0' - 1} \quad (18)$$

where $E(V)$ is the energy per atom calculated from PWSCF code, and V is the atomic volume. There are four fitting parameters in Eq.18: V_0 is the equilibrium volume corresponding to the lowest energy E_0 , $B_0 = (C_{11} + 2C_{12})/3$ is the bulk modulus and $B_0' = \partial B_0 / \partial P$ is the partial derivative of bulk modulus with respect to the pressure. Fitting Eq. (18) to energies calculated as a function of volume is the first step in this lab section. From the resulting fit we can obtain not only the bulk modulus, but also the equilibrium lattice constant a , which is the basis for the next two steps in calculation.

Part II – Elastic Constant, C_{12} from orthorhombic deformation

The next mode of deformation considered (Figure 1B) makes the initially cubic cell orthorhombic in shape. The strains are defined so that the total volume of the strained

orthorhombic cell and the initial (undeformed) cubic cell are the same. For this volume conserving orthorhombic strain deformation, the elastic energy is a quadratic function with respect to the strain ε :

$$E(\varepsilon) = E_0 + V_0(C_{11} - C_{12})\varepsilon^2 \quad (19)$$

where E_0 and V_0 are the fitting quantities we obtained in the first step by fitting Eq. (18). Fitting the energy vs. the strain in Eq. (19) allows us to compute the elastic constant $C' = C_{11} - C_{12}$. Combining this result with the equilibrium bulk modulus B_0 computed from Eq. (18) we have:

$$C_{11} = B + \frac{2}{3}C' \quad C_{12} = B - \frac{1}{3}C' \quad (20)$$

There is one remaining single-crystal elastic constant for a cubic material, namely C_{44} . This can be obtained by calculating the energy as a function of imposed shear strain and fitting to a form analogous to Eq. (20). For technical reasons these calculations turn out to be much more computationally demanding than the calculations of C' and B , and they are also less accurate. Given the two-hour lab time (this run took nearly one hour), this calculation is not included.

Requirements for Computation

The PWSCF software is run from a Linux operating system. A graphical user interface (GUI) called PWGUI is used to perform the calculations.

The following parameters must be defined in the input file:

- 1) Pseudo-potential: This represents the effective electrostatic potential that a valence electron feels as it interacts with a given “ion” (i.e., an atomic nucleus and associated core electrons) in a crystal. In this calculation, the pseudo-potential describes the interactions of the 3d and 4s electrons with the Cu ion. We use an ultra-soft pseudo-potential, GGA (PBE96).
- 2) Cut-off energy for plane wave and charge density: In PWSCF, a truncated Fourier transform is used to expand the periodic wave functions and charge density for the valence electrons. The cutoff energy is a measurement of the truncation. Higher cut off energies provide more accurate results, but require more computation time.
- 3) k point mesh in first-Brillouin zone: PWSCF uses discrete points to perform integrations over the energy bands (i.e., energy as a function of wavenumber). These discrete points used in the numerical integrations are referred to as k points. A denser k point mesh provides more accurate results, but requires more computer time.

In general one needs to pay special attention to these settings in performing DFT calculations. The settings for cutoff energy and k point mesh we will use are given to guarantee the convergence of energy within 0.001 eV per atom.

Procedure

The PWGUI window is used to input the system parameters. A self-consistent field is chosen. The lattice is specified: FCC Bravais lattice, with cell dimensions in atomic units (i.e. 6.94 Bohr radii). The kinetic energy cutoffs for the wavefunction and charge density are set to 30 and 360

Rydberg, respectively. Optional variables are also chosen: smearing (on) and 0.01 for Gaussian spreading. The atomic label (Cu) and mass (64) and the pseudo-potential file (Cu.pbe-d-rrkjus.UPF) are selected. The k-point mesh values nk1, nk2 and nk3, are set to 15. The energy and pressure are calculated for the lattice constant that was chosen initially. These are recorded. The lattice constant is changed in the cellsm(1) field and the computation is repeated. This is done 5-9 times, in the range of lattice constant between 6.2 and 7.1. Energy vs. volume is plotted and fit to determine the equilibrium energy and volume and the bulk lattice constant.

The equilibrium lattice constant is determined from the equilibrium volume ($= a^3/4$) determined above. This serves as input for the first calculation in part II (determining $c^2 = c11 - c12$). This time the Bravais lattice index is set to orthorhombic face-centered. The cell dimensions are specified are a in celldm(1), b/a in celldm(2) and c/a in celldm(3). Other parameters are the same as above. The computation is run for zero strain (the equilibrium lattice constant, then re-run as a function of strain. Students fill in the following table:

Strain ε	$a = a_0*(1-\varepsilon)$	$b = a_0*(1+\varepsilon)$	$c = a_0/(1-\varepsilon^2)$	b/a	c/a	Energy E(ε)
0						
0.01						
0.02						
0.03						

Results

The first series of calculations, in which energy is determined as a function of cell volume in the range of 6.2 to 7.2 Bohr radii³, yield the following plot:

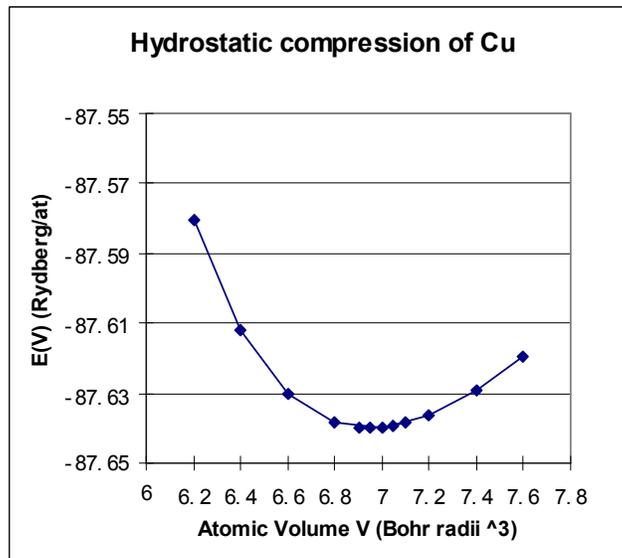


Figure 2. Energy vs. atomic volume data from calculations using hydrostatic deformation.

Values determined from the curve-fit in Figure 2 are: $E_0 = -87.64997$ Rydberg, $V_0 = 83.6556$, $B=0.00865$ Rydberg/Bohr radius = 127.30648 GPa (compare with literature value of 142.0267 GPa⁵, $B' = 5.00649$, $a = 6.9425391$ Bohr radii = 3.6726032 Å (compare with a literature value

of 3.6Å at 0K⁵.) The goodness of fit is affected by the number of points chosen, as well as cutoff energies and mesh size.

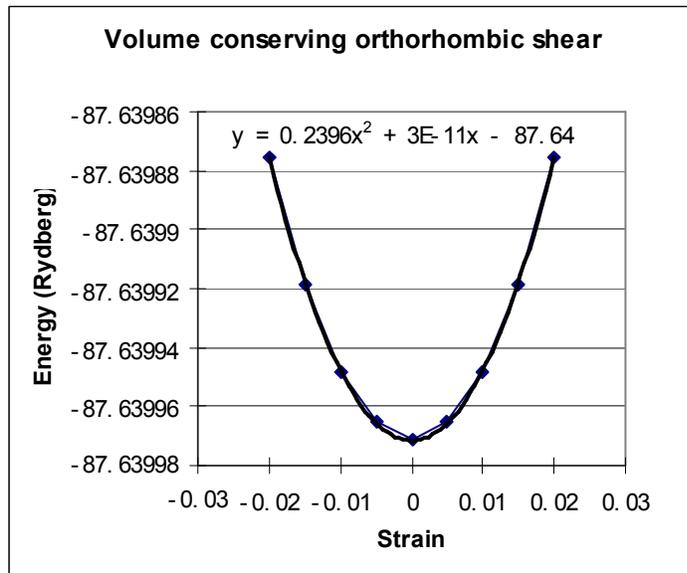


Figure 3. Energy vs. strain from calculations using orthorhombic deformation.

The curve-fit in figure 3 is used to determine $C' = C_{11} - C_{12} = .002856096 = 42.03462$ GPa

Combining equations for B and C' (equation 20):

$$C_{11} = 155.3 \text{ GPa (compare to } 176.2 \text{ GPa, } 0\text{K}^5; 12\% \text{ error)}$$

$$C_{12} = 113.3 \text{ GPa (compare to } 124.94 \text{ GPa at } 0\text{K}^5; 9\% \text{ error)}$$

Deliverable

The students are expected to complete a laboratory report on the two-part exercise. The report should include a summary of the experimental data, represented in Tables I and II and the corresponding values for the elastic constants determined computationally, i.e. from figures 2 and 3. The students are expected to compare these with literatures values and discuss the results. One benefit of the exercise is that students see how such values may be computed, but that the computed values may not be accurate. In this case the experimental determination is closer to “book values” than the computation.

Conclusions

We have developed a two-part laboratory in which elastic constants for copper are determined both experimentally and computationally. The experimental measurements are straightforward, easy and relatively quick to do; all aspects of the laboratory that students appreciate. The ultrasonic technique used for these measurements exposes students to a non-destructive determination of values they have previously measured with more conventional mechanical testing (tensile or compression tests). A wide range of polycrystalline samples may be tested. Use of single crystal copper samples underscores the anisotropic elastic properties of cubic

materials, and the underlying physics. We feel the computational portion is an effective illustration of the use of density functional theory, introduced at the undergraduate level. By comparing the computational results with the measured results, as well as literature values, students are exposed to both the power and limitations of the DFT technique.

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