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Compressibility of Polycrystal and Monocrystal Copper: Acoustic-Resonance Spectroscopy[1]

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Using a method used mainly by geophysicists for small specimens—acoustic-resonance spectroscopy (ARS)—we measured the elastic-stiffness constants of centimeter-size copper specimens with rectangular-parallelepiped shapes. The polycrystal consisted of heavily twinned 75-μm crystallites. From the specimens' macroscopic resonance-vibration frequencies (midkilohertz to low-megahertz), we calculated the least-squares elastic-stiffness coefficients, two and three for the two cases. Using the same specimens, we augmented the ARS measurements with conventional pulse-echo-method measurements. Using rod specimens, we measured the Young modulus E and torsional modulus G, and we calculated the bulk modulus B. The less direct and less familiar ARS method gives the same results as a usual pulse-echo method and a rod-resonance method. The small difference between polycrystal and monocrystal values may arise from mobile twin boundaries that contribute a small reversible plastic strain to the intrinsic elastic strain. We list 16 advantages of the ARS method to measure elastic constants.

KEY WORDS: acoustic-resonance spectroscopy; bulk modulus; compressibility; copper; elastic constants; ultrasonics.

1. INTRODUCTION

The compressibility K, or its reciprocal, the bulk modulus B, represents the most fundamental elastic constant because all material states (solid, liquid,

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gas) show a finite compressibility and because K or B relates simply to the internal energy U:

$$B_s = -V\left(\frac{\partial P}{\partial V}\right)_S = V\left(\frac{\partial^2 U}{\partial V^2}\right)_S \tag{1}$$

Here V denotes volume, P pressure, and S entropy. Dynamic measurements (constant entropy) relate simply to static measurements at constant temperature T:

$$B_s^{-1} - B_T^{-1} = -T\beta^2/C_P \tag{2}$$

Here β denotes volume thermal expansivity and C_P specific heat per unit volume at constant pressure. For copper at 298 K, $(B_S - B_T)/B$ equals 1.02%.

The first glimmerings of measuring a solid's compressibility arose in the mid-1800s with the studies by Regnault in 1842 [1], Wertheim in 1848 [2], and Amagat in 1884[3].

Compressibility measurements reached their zenith when Bridgman [4], at Harvard, devoted about 50 years to measuring numerous solids using various high-pressure cells. In 1923, for copper Bridgman [5] reported that $B = 135$ GPa, and in 1949 Bridgman [6] reported that $B = 137.7$ GPa.

Alternative modern approaches to measuring B include high-pressure X-ray diffraction [7] and sound-wave velocities [8]. The latter approach avoids using a pressure cell. Lazarus, in 1949 [9], was the first to use a sound-velocity method for copper, and he found that $B = 139.6$ GPa for a copper monocrystal. A related method, resonance frequencies of bars, was used first by Goens and Weerts in 1936 [10], who found that $B = 138.3$ GPa.

The present study used a relatively old method described by Demarest [11]: acoustic-resonance spectroscopy. Although little used, this method shows enormous potential for both accuracy and simplicity. Like sound-velocity and rod-resonance methods, it avoids a pressure cell. Unlike the latter methods, it requires only a single measurement of a solid's macroscopic vibration frequencies.

2. MATERIALS

The copper polycrystal consisted of a parallelepiped $1.19 \times 1.25 \times 1.46$ cm. The four-nines-purity material came in a half-hard condition from a commercial source. After annealing in vacuum at 600° C for 1.5 h, it had the microstructure shown in Fig. 1. Using Archimedes's method, we found a mass density of $8.934\ \mathrm{g \cdot cm^{-3}}$.

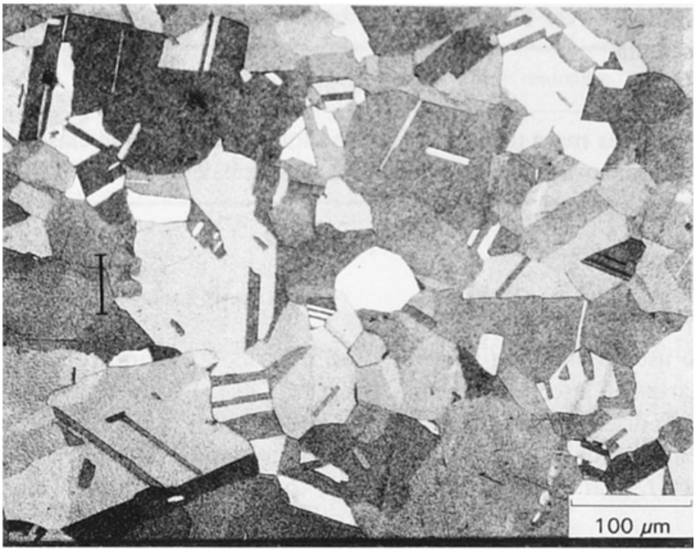

Fig. 1. Microstructure of studied polycrystal. Grains are equiaxed, twinned heavily, and show an average size of about 75 μm.

Our crystal, with five-nines purity, was a roughly 1-cm rectangular parallelepiped with (110), ($\bar{1}$10), and (001) faces. After being cut from a larger crystal, it was annealed in vacuum at 600° C for 1 h. Using Archimedes's method, we found a mass density of 8.937 g · cm^{-3}. A crystal with the above orientation enables direct measurement of four principal C_{ij}: C_{11}, C_{44}, $C' = (C_{11} - C_{12})/2$, and $C_L = (1/2)(C_{11} + C_{12} + 2C_{44})$.

3. MEASUREMENT METHODS

In this study, we used three measurement methods.

3.1. Pulse-Echo Superposition

We used a traveling-wave pulse-echo-superposition method described previously [12]. Briefly we used 5-MHz x-cut and ac-cut quartz transducers bonded with phenyl salicylate. Ultrasonic waves were reflected from flat and parallel surfaces of a rectangular-parallelepiped specimen. We determined sound velocities v by the relationship

$$v = 2l/t \tag{2}$$

Here l denotes the specimen thickness and t the round-trip transit time for an ultrasonic wave. These velocities convert to elastic stiffnesses C by the usual formula

$$C = \rho v^2 \quad (4)$$

Here ρ denotes mass density. From the longitudinal-mode elastic modulus C_l and the shear-mode elastic modulus C_t, we calculated the bulk modulus by

$$B = C_l - (4/3)\, C_t \quad (5)$$

3.2. Marx Oscillator

We used a standing-wave method described previously [13]. Briefly, two quartz-rod oscillators (one driver, one gage) were cemented to rod-shape cylindrical specimens measuring about 5 mm in diameter and several centimenters long. From the extensional-mode specimen resonance frequency f, near 50 kHz, we calculated the Young modulus from

$$E = 4\rho f^2 l^2 \quad (6)$$

Here l denotes specimen length. A similar relationship holds for the torsion-mode modulus G. From E and G, we calculated the bulk modulus by

$$B = (1/3)\, EG/(3G - E) \quad (7)$$

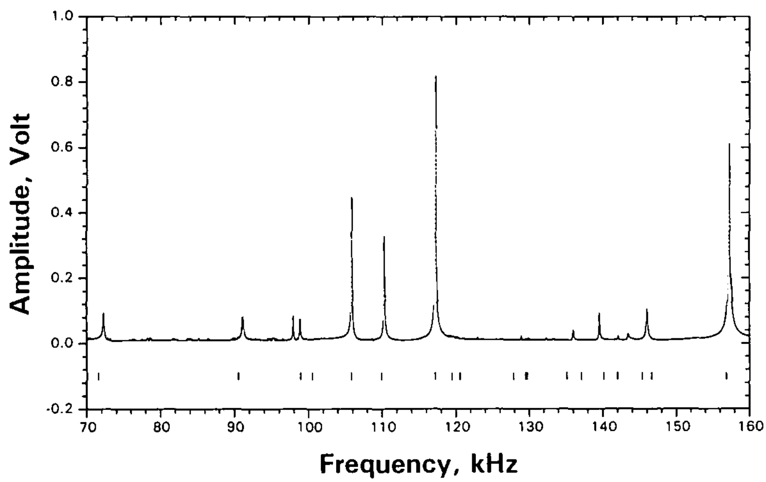

Fig. 2. Voltage–frequency spectrum for polycrystalline specimen. Resonance frequencies give the elastic stiffnesses. Resonance–peak widths give the internal frictions, which are not reported here. Bars near the bottom represent the predicted frequencies: corresponding low-intensity resonance peaks are not visible in this scale.

Table I. Bulk Modulus (GPa) of Polycrystal and Monocrystal Copper

Structure	ARS	Pulse echo	Rod resonance	Literature
Polycrystal	136.0 ± 1.0	137.3 ± 0.1	137.6 ± 0.5	142 ± 4
Monocrystal	138.4 ± 0.8	138.3 ± 0.4	In progress	138.1 ± 2.0

3.3. Acoustic-Resonance Spectroscopy

We described this method previously [14]. Briefly, using two PZT piezoelectric transducers we excite and detect the specimen's natural macroscopic vibration frequencies. An inverse calculation leads to the least-squares elastic stiffnesses C_{ij}. From these, the bulk modulus arises simply:

$$B = (1/3)(C_{11} + 2C_{12}) \tag{8}$$

Figure 2 shows the resonance spectrum.

4. RESULTS

Table I summarizes our measurement results together with values from the literature, as summarized by Ledbetter and Naimon [15].

5. DISCUSSION

Considering first the polycrystal, we see that our three measurement methods give essentially the same result: $B = 137.0 \pm 0.9$ GPa, or $\pm 0.6\%$. Comparison with the main literature value leads to little that is useful because its uncertainty is large. However, we all know that some measurements are preferred over others. Thus, we cite Bridgman's value [6], $B = 137.7$ GPa, which agrees with ours.

For the monocrystal, our two measurement methods give $B = 138.4 \pm 0.1$. This agrees with the average literature value: 138.1 ± 2.0.

The difference between our monocrystal and polycrystal values suggests that B(poly) may be actually less than B(mono). Examination of the microstructure (Fig. 1) shows a high annealing-twin density. If the twin boundaries are mobile under a small alternating stress, then they would contribute a small reversible plastic strain that would decrease the effective elastic stiffness, for both longitudinal and shear modes.

Finally, we want to emphasize that ARS values agree with pulse-echo and resonant-rod values. This study represents, we think, the first application of ARS to metals. (Previous studies focused on oxides [16] and oxide superconductors [17].) The ARS method offers numerous advantages.

1. Simple specimen geometry: sphere, cylinder, cube, parallelepiped, others.
2. One specimen (instead of four[5] or more).
3. Small specimen: 1 mm or less.
4. One measurement (instead of nine[5] or more).
5. Simultaneous elastic-constant and internal-friction measurements.
6. No tranducer, bonding, electrode corrections; weak specimen–transducer coupling.
7. Shorter measurement time.
8. One run (instead of nine) for temperature measurements.
9. Possible simultaneous frequency-dependence study using overtones.
10. No specimen-geometry requirement for relative values of principal elastic constants (versus temperature or pressure).
11. Complete automation possible for small specimen-to-specimen differences.
12. No need to cut and prepare various orientations (especially valuable for monocrystals).
13. No diffraction and sidewall effects.
14. Very accurate measurements (based on frequency) possible.
15. Wide range of transducer choices.
16. No precise specimen dimensioning required.

6. CONCLUSIONS

During this study, we reached three principal conclusions.

1. An accurate bulk modulus B for copper results from acoustic-resonance spectroscopy (ARS).
2. Annealing twins in the polycrystal possibly cause the B(mono) to exceed slightly the B(poly).
3. ARS, pulse-echo, and rod-resonance values agree within 0.6%.

[5] This number assumes orthotropic symmetry, or nine independent elastic constants.

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