Reprinted from THE PHYSICAL REVIEW, Vol. 148, No. 2, 575–579, 12 August 1966
Printed in U. S. A.

Least-Squares Determination of the Elastic Constants of Antimony and Bismuth

ALEXANDER DE BRETTEVILLE, JR.
Institute for Exploratory Research, U. S. Army Electronics Command, Fort Monmouth, New Jersey

AND

E. RICHARD COHEN
North American Aviation Science Center, Thousand Oaks, California

AND

ARTHUR D. BALLATO AND IRVING N. GREENBERG
Electronic Components Laboratory and Institute for Exploratory Research, U. S. Army Electronics Command, Fort Monmouth, New Jersey

AND

SEYMOUR EPSTEIN
Electronic Components Laboratory, U. S. Army Electronics Command, Fort Monmouth, New Jersey
(Received 28 September 1965; revised manuscript received 8 April 1966)

A least-squares determination of the elastic stiffness constants of antimony (using the data of Epstein and de Bretteville) and bismuth (using the data of Eckstein, Lawson, and Reneker) at room temperature was made by one of us (ERC). In the previous determination of the elastic constants of antimony and bismuth certain errors were not considered. They are considered in this paper. The antimony constants are: $c_{11}=101.3\pm1.6$; $c_{13}=29.2\pm2.2$; $c_{33}=45.0\pm1.5$; $c_{44}=39.3\pm0.7$; $c_{14}=20.9\pm0.4$; $c_{66}=33.4\pm0.6$; and $c_{12}=34.5\pm2.0$ all in units of 10^{10} dyn cm^{-2}. The bismuth constants in the same units are: $c_{11}=63.7\pm0.2$; $c_{13}=24.7\pm0.2$; $c_{33}=38.2\pm0.2$; $c_{44}=11.23\pm0.04$; $c_{66}=19.41\pm0.06$; $c_{12}=24.9\pm0.2$; $c_{14}=7.17\pm0.04$.

INTRODUCTION

THE earlier paper of Epstein and de Bretteville on ultrasonic velocity measurements in antimony and bismuth at room temperature did not include a least-squares determination, in depth, of the elastic constants of these crystals.[1] Since the number of wave velocities measured for different propagation and polarization directions was larger than the number of elastic moduli for these crystals, such a determination would increase the accuracy of the computed values of the elastic constants. The least-squares determination is presented in this paper along with an analysis of the sources of experimental error and the final best values of the elastic constants of antimony and bismuth. The data for bismuth were taken from Eckstein, Lawson, and Reneker.[2]

VELOCITY ERRORS AND CORRECTIONS

The errors in measuring the echo time using the rf pulse-echo technique, in regard to the antimony measurement, are: (1) the uncertainty of measuring from the crest of one wave in one echo train (11 periods for shear and 20 periods for longitudinal waves) to the crest of the corresponding cycle in an adjacent train;

[1] S. Epstein and A. de Bretteville, Jr., Phys. Rev. **138**, A771 (1965).

[2] Y. Eckstein, A. W. Lawson, and D. H. Reneker, J. Appl. Phys. **31**, 1535 (1960).

(2) the transit time or round-trip time in the quartz transducer which is also intertwined with the phase shift caused by the reflection of the ultrasonic waves at the transducer including the bonding agent[3]; (3) the instrument error of the oscilloscope; (4) the error due to room-temperature changes on the transducer sample system; (5) misorientation of the crystal; (6) diffraction.

Item (1) above is the largest error of all and is assumed to be one cycle per round-trip time. The latter assumption is acknowledged to be both arbitrary and generous. The uncertainty of the velocity because of this is $|\Delta v_i^{\text{set}}| = |v_{i,m}^2/2l_i f_r|$, where $v_{i,m}$ is the measured velocity without any correction, l_i the length of the sample, f_r is the resonant frequency or reciprocal of the period of the quartz transducer, and i refers to one of fourteen velocity measurements. If the error were assumed to be n integer cycles, the above formula would be multiplied by a factor n. The total error is the root-square sum of the measured error $\Delta v_{i,m}$ (due to the scattering of the measurements) and the $\Delta|v_i^{\text{set}}|$ described or $\Delta v_i = \{\Delta v_{i,m}^2 + (v_{i,m}^2/2f_r l_i)^2\}^{1/2}$. This formula is used to compute the total error in the measured velocity for antimony listed in Table I under measured velocity, plus a small misorientation correction given later in Table IV.

Eros and Reitz[4] have shown by a graphical analysis of the reflection and transmission of the rf pulse at the sample transducer interface, how to eliminate the error Δv_i^{set}, which they call the "transit time." Since the correction was not made in the antimony experiment[1] the correction formula Δv_i was necessary.

TABLE I. Observed velocities of sound in antimony at room temperature.

Symbol	Direction propagation	Mode	Measured velocity 10^5 cm/sec	Adjusted velocity 10^5 cm/sec
v_1[a]	x axis	Longitudinal	3.92 ± 0.08	3.891 ± 0.03
v_2[b,a]	x axis	Fast shear polarized along z	2.92 ± 0.14	2.930 ± 0.020
v_3[b,a]	x axis	Shear polarized along y	1.53 ± 0.04	1.508 ± 0.013
v_4	y axis	Longitudinal	3.99 ± 0.09	4.011 ± 0.026
v_5	y axis	Shear polarized along x	2.24 ± 0.05	2.23 ± 0.026
v_6	y axis	Shear polarized along z	2.24 ± 0.06	2.217 ± 0.018
v_7	z axis	Longitudinal	2.61 ± 0.09	2.591 ± 0.042
v_8	z axis	Degenerate shear	2.45 ± 0.08	2.423 ± 0.022
v_9	$\theta = 45° \varphi = 90°$	Longitudinal	3.19 ± 0.18	3.230 ± 0.032
v_{10}[b]	$\theta = 45° \varphi = 90°$	Shear polarized along x	2.92 ± 0.06	2.924 ± 0.020
v_{11}	$\theta = 45° \varphi = 90°$	Shear polarized along $\theta = 45°$	1.28 ± 0.05	1.801 ± 0.040
v_{12}	$\theta = 135° \varphi = -90°$	Longitudinal	4.14 ± 0.10	4.192 ± 0.025
v_{13}[b]	$\theta = 135° \varphi = -90°$	Shear polarized along x	1.49 ± 0.04	1.518 ± 0.013
v_{14}	$\theta = 135° \varphi = -90°$	Shear polarized along $\theta = 135°$	1.51 ± 0.09	1.531 ± 0.041

[a] Dr. H. J. McSkimin kindly measured the three velocities, on this crystal by now accidentally severely damaged, by the buffered-pulse-superposition method. He obtained: $v_1 = 3.84(3)$; $v_2 = 2.93(0)$; and $v_3 = 1.47(4)$ all multiplied by 10^5 cm/sec. Only v_3 is outside the range of our experimental error.

[b] Although the inequality relations, $v_2 > v_{10}$ and $v_{13} > v_3$ are not satisfied for the measured velocity they are satisfied for the adjusted velocity, which are the more accurate values, obtained from the computer program. When the errors of the measured velocity are taken into account they are not incompatible with the inequality relations.

The transducer transit-time correction, item (2) above, was not made because of the uncertainty in the round-trip echo time mentioned in item (1). One can easily show that the transit-time error (neglecting bonding agent) is $-(f_r)^{-1}$, or one period, the minus sign meaning it should be subtracted from the round-trip echo time. The additional phase shift due to the transducer and bonding agent is probably small since the wave frequency is very close to the resonance frequency of the transducer, and the waves are assumed to be in a steady-state condition in the transducer. In order to check the latter assumption, the rf pulse width was increased from 2-μsec width at 5 MHz (10 periods) to about 3-μsec (15 periods), and finally to 4-μsec width (20 periods). In each case, the change if any in the first echo train was observed, as well as the echo time to the adjacent train. The results show that the shape of the first echo (other than a corresponding increase in the length of the echo train) appeared unaffected, in the first two cases, as well as the echo time, while this was not true for the last case.

The instrument error of the Tektronix 585A oscilloscope is given as: "Accuracy is typically within 1%, and in all cases within 3% of panel reading." The timing circuit of the oscilloscope was checked with a Tektronix Time Mark Generator 180-S1 and found to be well within 1%.

The effect of thermal expansion on the velocity in an antimony crystal, for a 20°C rise above room temperature, is negligible for the trigonal axis (maximum coefficient of expansion direction) and amounts to less than 0.1%.

The velocity error correction due to misorientation, which does not change the elastic constants over 1%, is given in Appendix A. The correct procedure would have been to determine the exact misorientation by x-ray back-reflection photographs and apply the correction to the velocity v_i instead of treating the correction as a random error as described in Appendix A. The χ^2 value, or $\sum(v_{i,\text{calc}} - v_{i,\text{obs}}/\Delta v_i)^2$, where $v_{i,\text{obs}}$ is the measured velocity with correction for misorientation, $v_{i,\text{calc}}$ is the calculated velocity obtained from Eq. (A1), and Δv_i is the error in velocity as described in detail above, decreased 34% (1.41 to 0.93) for bismuth after making the misorientation correction. One might expect only a small decrease in χ^2 because of the increase of Δv_i, but not such a large percentage change. In reality this is a gross simplification. Our basic assumption is that the χ^2 sum above should be a minimum, in order to obtain the best values of the six elastic constants. The consequence of this assumption, without going into detail, is that the coefficients of the six normal equations[5] used for determining the best value of the elastic constants contain the fourteen Δv_i as weights. Each

[3] H. J. McSkimin, J. Acoust. Soc. Am. **33**, 1 (1961).

[4] S. Eros and J. R. Reitz, J. Appl. Phys. **29**, 683 (1958).

[5] E. R. Cohen, K. M. Crowe, and J. W. M. DuMond, *Fundamental Constants of Physics* (Interscience Publishers, Inc., New York, 1957), pp. 235–244.