

time Δv_i is changed, the elastic constants are completely redetermined, and this causes a corresponding change in the adjusted values $v_{i,calc}$. The errors of the six elastic constants Δc_{ij} were reduced by the misorientation correction for bismuth.

In the case of antimony χ^2 became slightly worse by 7% (1.58 to 1.71) and the errors of the elastic stiffness constants for c_{11} , c_{13} , and c_{33} increased slightly, while those for c_{14} , c_{44} , and c_{66} decreased slightly. The trace relations for both semimetals were improved slightly by the application of this correction.

Papadakis has calculated curves for correcting v_7 for diffraction.⁶ His graph is plotted in terms of the phase shift between echoes as a function of $S = z\lambda/a^2$, where z = path length in sample, λ = wavelength, and a = piston (transducer) radius for Waterman's anisotropy parameter b (the coefficient of $\theta^2 v_7$ in Appendix A). The calculation was not possible as our b value for antimony is -9.8 , which exceeds Papadakis's maximum value of -5 . However, assuming the latter anisotropy parameter, the velocity correction for v_7 amounts to -0.1% .

CALCULATIONS AND RESULTS

The fourteen equations of Eckstein, Lawson, and Reneker (ELR)² were used by one of us (ERC) to determine the six elastic constants, by the method of least squares.⁵ A preliminary calculation indicated that the measured velocity v_{11} (see Table I) was inconsistent, a conclusion which was apparent from the trace relations. It was therefore omitted and the remaining thirteen velocities were used to compute a "best" set of elastic constants: $c_{11} = 101.3 \pm 1.6$; $c_{13} = 29.2 \pm 2.2$; $c_{33} = 45.0 \pm 1.5$; $c_{44} = 39.3 \pm 0.7$; $c_{14} = 20.9 \pm 0.4$; $c_{66} = 33.4 \pm 0.6$; and $c_{12} = 34.5 \pm 2.0$ all in units of 10^{10} dyn cm^{-2} . The isothermal correction is negligible. The importance of using a least-squares adjustment of the data in order to determine the elastic constants is that the adjusted velocities which may then be evaluated will satisfy *exactly* all the trace relations in theory.

The trace for the principal-axis-cut crystal of antimony is $T_{xy} = (26.00 \pm 0.24) \times 10^{10}$ cm^2/sec^2 using the adjusted values from Table I, and the diagonal trace for the 45° -cut crystal is $T_{45^\circ} = (22.22 \pm 0.19) \times 10^{10}$ cm^2/sec^2 .

Table I gives the values of the fourteen measured velocities and their least-squares adjusted values. The errors assigned to the adjusted velocities are computed from the full error matrix of the least-squares adjustment and should be used with care since the data are inter-related and cannot be treated as statistically independent. The elastic stiffness constant c_{13} as a result of this computation is found to be 10% higher than the previous finding.¹

The compliances are $s_{11} = 16.31$; $s_{33} = 30.96$; $s_{44} = 38.14$; $s_{12} = -6.15$; $s_{66} = 44.93$; $s_{13} = -6.60$; and $s_{14} = -11.95$ all in units of 10^{-13} cm^2/dyn , and are in fair agreement with the data of Bridgman⁷ who obtains $s_{11} = 17.7$; $s_{33} = 33.8$; $s_{44} = 41$; $s_{12} = -3.8$; $s_{66} = 43$; $s_{13} = -8.5$; and $s_{14} = -8.0$, all in units of 10^{-13} cm^2/dyn .

The fourteen equations were used with the same least-squares procedure as above to determine the six elastic constants of bismuth. The data of Eckstein, Lawson, and Reneker determined by the pulse-echo technique were used.² They state their velocities are accurate to better than 1%, and their principal error arises from the transducer transit-time correction. The "best" set of elastic constants is $c_{11} = 63.7 \pm 0.2$; $c_{13} = 24.7 \pm 0.2$; $c_{33} = 38.2 \pm 0.2$; $c_{44} = 11.23 \pm 0.04$; $c_{14} = 7.17 \pm 0.04$; $c_{66} = 19.41 \pm 0.06$; $c_{12} = 24.9 \pm 0.2$, all in units of 10^{10} dyn/cm^2 .

The compliances are $s_{11} = 25.7$; $s_{33} = 40.83$; $s_{44} = 116.4$; $s_{12} = -8.13$; $s_{66} = 67.6$; $s_{14} = -21.6$; $s_{13} = -11.33$, all in units of 10^{-13} cm^2/dyn . Bridgman's⁸ results are $s_{11} = 26.9$; $s_{33} = 28.7$; $s_{44} = 104.8$; $s_{12} = -14.0$; $s_{66} = 81.2$; $s_{14} = 16.0$; $s_{13} = -6.2$, all in units of 10^{-13} cm^2/dyn .

The principal-axis trace relation, or T_{xy} gives $(9.623 \pm 0.041) \times 10^{10}$ cm^2/sec^2 from our least-squares results, versus $T_x = 9.580$ and $T_y = 9.654 \times 10^{10}$ cm^2/sec^2 .

TABLE II. Elastic-stiffness constants c_{ij} (10^{10} dyn/cm^2) of antimony at room temperature.

c_{11}	c_{13}	c_{14}	c_{33}	c_{44}	c_{66}	χ^2	Remarks
99.4(1)	26.4(4)	21.6(4)	44.5(9)	39.5(5)	34.2(5)	6.4	Near least squares. ^a No correction to experimental data. ^b
99.5 \pm 2.2	25.3 \pm 2.6	21.5 \pm 0.6	45.0 \pm 0.9	40.3 \pm 0.7	33.9 \pm 0.7	4.9	Least squares (ERC). No correction to experimental data. ^b
101.4 \pm 1.5	29.4 \pm 2.1	20.9 \pm 0.5	45.0 \pm 1.4	39.2 \pm 0.8	33.4 \pm 0.8	1.58	Least squares (ERC). Data corrected for "transit time." ^{c,d}
101.3 \pm 1.6	29.2 \pm 2.2	20.9 \pm 0.4	45.0 \pm 1.5	39.3 \pm 0.7	33.4 \pm 0.6	1.71 ^e	Same as preceding plus an added misorientation correction. ^f

^a Described in Ref. 1.

^b Made by the rf pulse-echo technique (longitudinal principally at 10 MHz; shear principally at 5 MHz) of Ref. 1.

^c Arbitrarily assumed to be ± 1 cycle of pulse. See Ref. 4.

^d The basic experimental data for this paper is slightly different from that chosen in Ref. 1.

^e Data chosen as best in this paper.

^f Equations (A5)-(A10).

⁶ Emmanuel P. Papadakis (private communication).

⁷ P. W. Bridgman, Proc. Am. Acad. Arts Sci. 60, 363 (1925).

⁸ Reference 7, p. 305.

TABLE III. Elastic constants c_{ij} (10^{10} dyn/cm²) of bismuth at room temperature (experimental measurements of ELR used^a).

c_{11}	c_{12}	c_{14}	c_{33}	c_{44}	c_{66}	χ^2	Remarks
63.50	24.50	7.23	38.10	11.30	19.40	1.7	No least squares. Transducer transit-time correction. ^a
63.22	24.40	7.20	38.11	11.30	19.40	2.6	Near least squares. ^b Transducer transit-time correction. ^a
63.7 ± 0.3	24.6 ± 0.2	7.20 ± 0.04	38.1 ± 0.2	11.26 ± 0.04	19.38 ± 0.07	1.4	Near least squares (ERC), plus preceding correction.
63.7 ± 0.2	24.7 ± 0.2	7.17 ± 0.04	38.2 ± 0.2	11.23 ± 0.04	19.41 ± 0.06	0.93 ^c	Same as preceding plus misorientation correction. ^d

^a See Ref. 2. Ultrasonic video pulse-echo technique used at 12 MHz.

^b Described in Ref. 1.

^c Data chosen as best in this paper.

^d Equations (A5)-(A10).

for Eckstein, Lawson, and Reneker.² The 45°-cut crystal trace relation gives $T_{45^\circ} = (7.911 \pm 0.022) \times 10^{10}$ cm²/sec² from least squares, while ELR obtain $T_{45^\circ} = 7.974$ for $\varphi = 90^\circ$, and $T_{135^\circ} = 7.899 \times 10^{10}$ cm²/sec² for $\varphi = -90^\circ$.

Tables II and III summarize the effects of different data processing on the elastic-stiffness constants of antimony and bismuth, respectively, and represent additional measurements on the original specimens taken by one of us (deB).

ACKNOWLEDGMENTS

The authors would like to thank Professor Jesse W. M. DuMond of California Institute of Technology for his interest and helpful suggestions with regard to the problem; Dr. H. J. McSkimin of Bell Telephone Laboratories, Murray Hill, New Jersey, for his advice concerning echo-time corrections; Leon Leskowitz and Joyce Nickelson of our laboratory for checking the elastic-stiffness calculations of North American Aviation Science Center; Dr. Emmanuel P. Papadakis of the Bell Telephone Laboratories, Allentown, Pennsylvania for helpful suggestions; Professor H. B. Huntington of Rensselaer Polytechnic Institute; Dr. M. J. P. Musgrave of the National Physical Laboratory, England; and H. A. Osborne for mechanical design and fabrication. Special thanks are due Professor D. I. Bolef of Washington University.

APPENDIX A: MISORIENTATION CORRECTION

The velocity error due to misorientation can be calculated from the following determinant for point group $\bar{3}m$, where $x = \rho v^2$, ρ is the density, and v the sonic velocity.⁹

$$\begin{vmatrix} A-x & H & G \\ H & B-x & F \\ G & F & C-x \end{vmatrix} = 0. \quad (\text{A1})$$

Here,

$$A = c_{11} \sin^2 \theta \cos^2 \varphi + \frac{1}{2} (c_{11} - c_{12}) \sin^2 \theta \sin^2 \varphi + c_{44} \cos^2 \theta + 2c_{14} \sin \theta \cos \theta \sin \varphi,$$

$$B = \frac{1}{2} (c_{11} - c_{12}) \sin^2 \theta \cos^2 \varphi + c_{11} \sin^2 \theta \sin^2 \varphi + c_{44} \cos^2 \theta - 2c_{14} \sin \theta \cos \theta \sin \varphi,$$

$$C = c_{44} \sin^2 \theta + c_{33} \cos^2 \theta,$$

$$F = c_{14} \sin^2 \theta (1 - 2 \sin^2 \varphi) + (c_{13} + c_{44}) \sin \theta \cos \theta \sin \varphi,$$

$$G = 2c_{14} \sin^2 \theta \sin \varphi \cos \varphi + (c_{13} + c_{44}) \sin \theta \cos \theta \cos \varphi,$$

and

$$H = \frac{1}{2} (c_{11} + c_{12}) \sin^2 \theta \sin \varphi \cos \varphi + 2c_{14} \sin \theta \cos \theta \cos \varphi.$$

θ is the angle between a direction of propagation and the positive z axis, φ is the angle in the basal plane measured from the positive x axis counterclockwise to the projection of the direction of propagation on the basal plane.

The equations for the three velocities are, neglecting G and H which are small and would be zero for a perfectly oriented principal axis and 45°-cut crystal,

$$\rho v^2 = A, \quad (\text{A2})$$

$$\rho v^2 = (B+C) + \{(B-C)^2 + 4F^2\}^{1/2}, \quad (\text{A3})$$

$$\rho v^2 = (B+C) - \{(B-C)^2 + 4F^2\}^{1/2}. \quad (\text{A4})$$

Equations (A2)-(A4) were differentiated with respect to velocity in terms of θ and φ , and solved for the error $\pm \Delta v_i$ by inserting the appropriate elastic-stiffness constants c_{ij} , velocities v_i , and the value $\Delta \theta = \pm 1^\circ$ for

TABLE IV. Velocity errors due to misorientation for antimony and bismuth.

Symbol	Antimony 10 ⁵ cm/sec	Bismuth 10 ⁵ cm/sec
$\pm \Delta v_1$	0.00	0.000
$\pm \Delta v_2$	0.00	0.000
$\pm \Delta v_3$	0.00	0.000
$\pm \Delta v_4$	0.00	0.000
$\pm \Delta v_5$	0.00	0.000
$\pm \Delta v_6$	0.00	0.000
$\pm \Delta v_7$	0.00	0.000
$\pm \Delta v_8$	0.02	0.012
$\pm \Delta v_9$	0.01	0.006
$\pm \Delta v_{10}$	0.00	0.005
$\pm \Delta v_{11}$	0.03	0.010
$\pm \Delta v_{12}$	0.01	0.008
$\pm \Delta v_{13}$	0.01	0.008
$\pm \Delta v_{14}$	0.03	0.002

⁹ J. B. Wachtman, Jr., W. E. Tefft, D. G. Lam, Jr., and R. P. Stinchfield, J. Res. Natl. Bur. Std. 64A, 219 (1960).