

time  $\Delta v_i$  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  $\Delta c_{ij}$  were reduced by the misorientation correction for bismuth.

In the case of antimony  $\chi^2$  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.<sup>6</sup> 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,  $\lambda$  = 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)<sup>2</sup> were used by one of us (ERC) to determine the six elastic constants, by the method of least squares.<sup>5</sup> 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  $\text{cm}^{-2}$ . 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  $T_{xy} = (26.00 \pm 0.24) \times 10^{10}$   $\text{cm}^2/\text{sec}^2$  using the adjusted values from Table I, and the diagonal trace for the  $45^\circ$ -cut crystal is  $T_{45^\circ} = (22.22 \pm 0.19) \times 10^{10}$   $\text{cm}^2/\text{sec}^2$ .

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.<sup>1</sup>

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  $10^{-13}$   $\text{cm}^2/\text{dyn}$ , and are in fair agreement with the data of Bridgman<sup>7</sup> 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  $10^{-13}$   $\text{cm}^2/\text{dyn}$ .

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.<sup>2</sup> 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  $10^{10}$   $\text{dyn}/\text{cm}^2$ .

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  $10^{-13}$   $\text{cm}^2/\text{dyn}$ . Bridgman's<sup>8</sup> 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  $10^{-13}$   $\text{cm}^2/\text{dyn}$ .

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

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

$c_{11}$	$c_{13}$	$c_{14}$	$c_{33}$	$c_{44}$	$c_{66}$	$\chi^2$	Remarks
99.4(1)	26.4(4)	21.6(4)	44.5(9)	39.5(5)	34.2(5)	6.4	Near least squares. <sup>a</sup> No correction to experimental data. <sup>b</sup>
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. <sup>b</sup>
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." <sup>c,d</sup>
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 <sup>e</sup>	Same as preceding plus an added misorientation correction. <sup>f</sup>

<sup>a</sup> Described in Ref. 1.

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

<sup>c</sup> Arbitrarily assumed to be  $\pm 1$  cycle of pulse. See Ref. 4.

<sup>d</sup> The basic experimental data for this paper is slightly different from that chosen in Ref. 1.

<sup>e</sup> Data chosen as best in this paper.

<sup>f</sup> Equations (A5)-(A10).

<sup>6</sup> Emmanuel P. Papadakis (private communication).

<sup>7</sup> P. W. Bridgman, Proc. Am. Acad. Arts Sci. **60**, 363 (1925).

<sup>8</sup> Reference 7, p. 305.

TABLE III. Elastic constants  $c_{ij}$  ( $10^{10}$  dyn/cm<sup>2</sup>) of bismuth at room temperature (experimental measurements of ELR used<sup>a</sup>).

$c_{11}$	$c_{12}$	$c_{14}$	$c_{33}$	$c_{44}$	$c_{66}$	$\chi^2$	Remarks
63.50	24.50	7.23	38.10	11.30	19.40	1.7	No least squares. Transducer transit-time correction. <sup>a</sup>
63.22	24.40	7.20	38.11	11.30	19.40	2.6	Near least squares. <sup>b</sup> Transducer transit-time correction. <sup>a</sup>
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 <sup>c</sup>	Same as preceding plus misorientation correction. <sup>d</sup>

<sup>a</sup> See Ref. 2. Ultrasonic video pulse-echo technique used at 12 MHz.

<sup>b</sup> Described in Ref. 1.

<sup>c</sup> Data chosen as best in this paper.

<sup>d</sup> Equations (A5)-(A10).

for Eckstein, Lawson, and Reneker.<sup>2</sup> The 45°-cut crystal trace relation gives  $T_{45^\circ} = (7.911 \pm 0.022) \times 10^{10}$  cm<sup>2</sup>/sec<sup>2</sup> from least squares, while ELR obtain  $T_{45^\circ} = 7.974$  for  $\varphi = 90^\circ$ , and  $T_{135^\circ} = 7.899 \times 10^{10}$  cm<sup>2</sup>/sec<sup>2</sup> 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  $x = \rho v^2$ ,  $\rho$  is the density, and  $v$  the sonic velocity.<sup>9</sup>

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

Here,

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

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

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

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

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

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

and

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

$\theta$  is the angle between a direction of propagation and the positive  $z$  axis,  $\varphi$  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  $\theta$  and  $\varphi$ , 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 <sup>6</sup> cm/sec	Bismuth 10 <sup>6</sup> cm/sec
±Δv <sub>1</sub>	0.00	0.000
±Δv <sub>2</sub>	0.00	0.000
±Δv <sub>3</sub>	0.00	0.000
±Δv <sub>4</sub>	0.00	0.000
±Δv <sub>5</sub>	0.00	0.000
±Δv <sub>6</sub>	0.00	0.000
±Δv <sub>7</sub>	0.00	0.000
±Δv <sub>8</sub>	0.02	0.012
±Δv <sub>9</sub>	0.01	0.006
±Δv <sub>10</sub>	0.00	0.005
±Δv <sub>11</sub>	0.03	0.010
±Δv <sub>12</sub>	0.01	0.008
±Δv <sub>13</sub>	0.01	0.008
±Δv <sub>14</sub>	0.03	0.002