

veloped an ingenious resonant scheme for avoiding this inherent difficulty of the pulse echo technique. In our case, the errors were reduced to a minimum by the empirical procedure of determining the time interval between echoes with and without a dummy transducer attached to the reflecting end of the sample. The change in time interval produced by addition of the dummy was used to estimate the effective transit time correction for the identical driving transducer. The transit time correction so determined varied between 0.02 and 0.06  $\mu$ sec. Most of the samples employed in these measurements were somewhat over 1 cm in length. Hence, the correction at most is of the order of 1% in velocity.

The bismuth single crystals were cut from a zone refined bar whose impurity concentration is estimated to be about 1 ppm. The crystal blocks approximately  $1 \times \frac{3}{4}$  in. in cross section were ground so their ends were flat and parallel to within 0.0001 in.

Most of the measurements of sound velocity were made at room temperature, actually 301°K. No effort was made to control the temperature accurately because of the small temperature coefficients of the elastic constants. Measurements made at helium and liquid nitrogen temperatures were made using the cryostat previously described by Reneker.<sup>1</sup>

The orientation of the crystals was determined to within  $\pm 1^\circ$  by the standard Laue back reflection x-ray technique. The problem of ascertaining the directions of the positive  $x$  and positive  $y$  axes in the crystal was resolved as follows. One notes that on a stereographic projection, such as that given by Vickers<sup>13</sup> for the larger rhombohedral unit cell containing eight atoms per unit cell, the three positive  $x$  axes point in the  $[01\bar{1}]$ ,  $[\bar{1}01]$ , and  $[1\bar{1}0]$  directions and the three positive  $y$  axes point in the  $[\bar{2}11]$ ,  $[1\bar{2}1]$ , and  $[11\bar{2}]$  directions. For crystals not oriented along principal axes, we specify the orientation by polar angles  $\theta$  and  $\varphi$ , where  $\theta$  is the angle between the direction of propagation and the  $z$  axis and  $\varphi$  is the angle between the  $xz$  plane and the plane containing the  $z$  axes and the propagation direction. In our case, we are concerned only with  $\theta = 45^\circ$ , and  $\varphi = \pm 90^\circ$ . The differentiation between  $\varphi = +90^\circ$  and  $\varphi = -90^\circ$  is based on the fact that for  $\varphi = -90^\circ$  a very strong reflection corresponding to the (100) planes in Vicker's diagram occurs  $11.5^\circ$  from the center of the Laue picture. No such strong reflection occurs for  $\varphi = +90^\circ$ . In addition, the identification may be checked by the occurrence of a relatively strong spot on the  $\varphi = +90^\circ$  picture corresponding to the (111) planes at an angular distance of about  $26.5^\circ$  from the center.

## RESULTS

Fourteen independent velocities were measured at room temperature on an X-cut, a Y-cut, a  $\theta = 45^\circ$ ,  $\varphi = +90^\circ$ , and a  $\theta = 45^\circ$ ,  $\varphi = -90^\circ$  crystal. The velocities are given in Table I. Using the method described

TABLE I. Observed velocities of sound on bismuth at 301°K.

Symbol	Direction of propagation	Velocity in $10^5$ cm/sec	Mode
$v_1$	$x$ axis	$2.540 \pm 0.022$	Longitudinal
$v_2$	$x$ axis	$1.550 \pm 0.009$	Fast shear
$v_3$	$x$ axis	$0.850 \pm 0.004$	Slow shear
$v_4$	$y$ axis	$2.571 \pm 0.018$	Longitudinal
$v_5$	$y$ axis	$1.407 \pm 0.009$	Shear polarized along $x$
$v_6$	$y$ axis	$1.022 \pm 0.006$	Shear polarized along $y$
$v_7$	$z$ axis	$1.972 \pm 0.015$	Longitudinal
$v_8$	$z$ axis	$1.074 \pm 0.011$	Degenerate shear <sup>a</sup>
$v_9$	$\theta = 45^\circ, \varphi = +90^\circ$	$2.082 \pm 0.019$	Longitudinal
$v_{10}$	$\theta = 45^\circ, \varphi = +90^\circ$	$1.522 \pm 0.017$	Shear polarized along $x$
$v_{11}$	$\theta = 45^\circ, \varphi = +90^\circ$	$1.150 \pm 0.006$	Shear polarized along $\theta = 95^\circ$
$v_{12}$	$\theta = 45^\circ, \varphi = -90^\circ$	$2.441 \pm 0.041$	Longitudinal
$v_{13}$	$\theta = 45^\circ, \varphi = -90^\circ$	$0.910 \pm 0.003$	Shear polarized along $x$
$v_{14}$	$\theta = 45^\circ, \varphi = -90^\circ$	$1.055 \pm 0.006$	Shear polarized along $135^\circ$

<sup>a</sup> Owing to the degeneracy of the shear modes of propagation along the trigonal axis, internal conical refraction occurs and the transmitting crystal must be laterally displaced with respect to the receiving crystal in order to detect the pulses.

by Mason,<sup>14</sup> we may relate these velocities to the elastic constants by the equations<sup>15-17</sup>:

$$\rho v_1^2 = c_{11} \quad (2)$$

$$\rho v_5^2 = c_{66} = \frac{1}{2}(c_{11} - c_{12}) \quad (3)$$

$$\rho v_3^2 = c_{44} \quad (4)$$

$$\rho v_7^2 = c_{33} \quad (5)$$

$$\rho v_{13}^2 = \frac{1}{2}(c_{66} + c_{44}) - c_{14} \quad (6)$$

$$\rho v_{10}^2 = \frac{1}{2}(c_{66} + c_{44}) + c_{14} \quad (7)$$

$$\rho v_2^2 = \frac{1}{2}[(c_{66} + c_{44}) + \{(c_{44} - c_{66})^2 + 4c_{14}^2\}^{\frac{1}{2}}] \quad (8)$$

$$\rho v_3^2 = \frac{1}{2}[(c_{66} + c_{44}) - \{(c_{44} - c_{66})^2 + 4c_{14}^2\}^{\frac{1}{2}}] \quad (9)$$

$$\rho v_4^2 = \frac{1}{2}[(c_{11} + c_{44}) + \{(c_{44} - c_{11})^2 + 4c_{14}^2\}^{\frac{1}{2}}] \quad (10)$$

$$\rho v_6^2 = \frac{1}{2}[(c_{11} + c_{44}) - \{(c_{44} - c_{11})^2 + 4c_{14}^2\}^{\frac{1}{2}}] \quad (11)$$

These are the equations which we have used to determine all the constants, except  $c_{13}$ . In addition, we have four additional relations

$$2\rho v_{12}^2 = \frac{1}{2}(c_{11} + c_{33}) + c_{44} + c_{14} + \left\{ \left( \frac{1}{2}c_{11} - \frac{1}{2}c_{33} + c_{14} \right)^2 + (c_{13} + c_{44} + c_{14})^2 \right\}^{\frac{1}{2}} \quad (12)$$

$$2\rho v_{14}^2 = \frac{1}{2}(c_{11} + c_{33}) + c_{44} + c_{14} - \left\{ \left( \frac{1}{2}c_{11} - \frac{1}{2}c_{33} + c_{14} \right)^2 + (c_{13} + c_{44} + c_{14})^2 \right\}^{\frac{1}{2}} \quad (13)$$

<sup>14</sup> W. P. Mason, *Physical Acoustics and the Properties of Solids* (D. van Nostrand Company, Inc., Princeton, New Jersey, 1958), p. 368.

<sup>15</sup> These formulas have also been given by Bhimasenacker but are repeated here because there are some typographical errors in his paper. Some formulas derived in the manner described by Mayer and Hiedemann are slightly different, apparently because they neglect certain nonzero off diagonal matrix elements of Eq. (1) in deriving their Eq. (7).

<sup>16</sup> J. Bhimasenacker, *Proc. Ind. Acad. Sci.* **A29**, 200 (1949).

<sup>17</sup> W. G. Mayer and E. A. Hiedemann, *Acta Cryst.* **12**, 1 (1959).

<sup>13</sup> W. Vickers, *J. Metals* **9**, 827 (1957).