

Elastic Constants of Bismuth

YAKOV ECKSTEIN,* A. W. LAWSON, AND DARRELL H. RENEKER†

Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago, Illinois

(Received May 26, 1960)

The six adiabatic elastic stiffness constants of bismuth have been determined at 301°K by an ultrasonic pulse echo technique. The results are: $c_{11}=63.5$, $c_{33}=38.1$, $c_{44}=11.30$, $c_{66}=19.4$, $c_{14}=+7.23$, and $c_{13}=24.5$, all in units of 10^{10} d/cm². These values were redundantly determined by the measurement of 14 different velocities in four different single crystals of zone-purified bismuth. The velocities are believed accurate to better than 1%, the principal error arising from the uncertainty of the transducer transit time correction. The moduli are in poor agreement with the previously determined static elastic compliance constants reported by Bridgman. Some data on the velocity of sound in bismuth at 98° and at 4.2°K are also presented.

INTRODUCTION

THE acoustic determination of the adiabatic elastic constants of bismuth reported here was instigated in conjunction with measurements of the magneto acoustic-resistance of bismuth.¹ These initial observations were not in agreement with static values reported by Bridgman,² and, indeed, suggested that the latter were in error. However, the initial values were not redundant, nor even unambiguously determined. Because knowledge of the elastic constants is helpful in the theoretical investigation of the electronic band structure, the study was extended to provide more definitive results.

The primitive cell of bismuth is a rhombohedron ($\alpha=57^\circ 41'$) containing two atoms. The body diagonal of the rhombohedron has threefold symmetry and this trigonal axis is commonly designated as the z axis of the crystal. The plane perpendicular to the trigonal axis, containing the center of inversion, contains also three twofold axes and three bisectrices. To specify the other axes, we use the convention described by Cady,³ according to which, a positive y axis is chosen to be along the projection of one edge of the primitive cell on the plane perpendicular to the $[111]$ direction, and the positive x axis is then chosen along the binary axis which completes a right-handed orthogonal system. Such a detailed specification of axes is required in order to determine the sign of c_{14} unambiguously.

The six Voigt elastic constants for this class of crystal ($3m$) may be represented schematically by the matrix,

$$c_{ij} = \begin{vmatrix} c_{11} & c_{12} & c_{13} & c_{14} & 0 & 0 \\ c_{12} & c_{11} & c_{13} & -c_{14} & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ c_{14} & -c_{14} & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & c_{14} \\ 0 & 0 & 0 & 0 & c_{14} & \frac{c_{11}-c_{12}}{2} \end{vmatrix} \quad (1)$$

* Bell Telephone Laboratories Predoctoral Fellow.

† National Science Foundation Predoctoral Fellow. Now at Polychemicals Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware.

¹ D. H. Reneker, *Phys. Rev.* **115**, 303 (1959).² P. W. Bridgman, *Proc. Acad. Arts and Sci.* **60**, 305 (1925).³ W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946), p. 23.

We note in passing that according to the Laval-Raman⁴ formalism, as modified by Joel and Wooster,⁵ a more extended representation is required owing to their use of an unsymmetrical stress tensor. Previous tests⁶⁻⁹ of this theory have been confined to piezoelectric materials in which the issue is confused by complications and experimental difficulties arising from electromechanical interactions. The symmetry in bismuth is such that a direct test of the Laval-Raman theory may be carried out in a simple manner, the test being limited only by the accuracy of the velocity of sound measurements used to determine the elastic constants.

EXPERIMENTAL PROCEDURE

The velocity of sound in the variously oriented crystals was determined by the pulse echo technique at 12 Mc using an apparatus previously described by Lazarus.¹⁰ The delay line of a Dumond 256D oscilloscope was used to measure the difference in arrival time of successive echoes. The delay line was calibrated frequently during the course of the measurements by use of 10- μ sec markers.

The principal source of error in this type of measurement arises from uncertainty about the correction time to be applied for the effective transit time in the transducer. This correction varies in magnitude depending on the relative velocities and lengths of the crystal and transducer. The acoustic mismatch at the crystal-transducer interface, which in turn is also a function of the type and thickness of adhesive used, also produces¹¹ a progressive distortion in the pulse shape of successive echoes. The distortion depends on the phase of the sound wave at the time of its incidence on the interface and thus depends on the frequency and length of the crystal for a given orientation. McSkimin¹² has de-

⁴ J. Laval, *Compt. rend.* **242**, 2502 (1956); C. V. Raman and K. S. Viswanathan, *Proc. Ind. Acad. Sci.* **42**, 1 (1955); **42**, 51 (1955).⁵ N. Joel and W. A. Wooster, *Nature* **182**, 1078 (1958).⁶ Y. LeCorre, *Bull. soc. franç. minéral et crist.* **78**, 1363 (1954).⁷ V. G. Zubov and M. M. Firsova, *Kristallografiya* **1**, 546 (1956).⁸ N. Joel and W. A. Wooster, *Acta Cryst.* **11**, 575 (1958).⁹ H. Jaffe, *Bull. Am. Phys. Soc.* **4**, 427 (1959).¹⁰ D. Lazarus, *Phys. Rev.* **76**, 545 (1949).¹¹ S. Eros and J. R. Reitz, *J. Appl. Phys.* **29**, 683 (1958).¹² H. J. McSkimin, *IRE Trans. on Ultrasonics Eng.* PGUE-5, 25 (1957).