

Elastic Moduli of Indium Antimonide*

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By using the composite resonator technique, the elastic moduli of InSb have been measured as a function of temperature between 77°K and 700°K. The results give good agreement with Born-Smith dynamic lattice theory if nearest neighbor interactions alone are considered. The value of θ_D is found to be 208°K by using Sutton's method. High-temperature behavior of the constants is discussed.

INTRODUCTION

THE elastic constants of crystalline materials and their behavior as a function of temperature provide fundamental information of the mechanical and thermodynamical properties. There exists a great deal of interest in the intermetallic semiconductors formed from the elements of the III_B and V_B columns of the periodic chart. Of these, indium antimonide is one that has received extensive attention to its optical, electrical, and thermal properties.¹ The elastic constants are the first results of a program at the National Bureau of Standards to study the mechanical properties of these materials.

EXPERIMENTAL

The experimental technique is largely the same that was reported by Hunter and Siegel.² Standing waves of integral half-wavelengths are set up in the samples when they are excited in the appropriate resonant modes. One part of a composite 2-part resonator consists of a fused quartz rod whose frequency was matched very closely to that of a quartz piezoelectric crystal. This composite was constructed by cementing the quartz crystal onto the rod with a resin-type cement giving a permanent room temperature bond. The sample is cemented with a mixture suggested by Sutton,³ consisting, by weight, of two parts Na₂SiF₆, one part BaSO₄, ground fine. The cementing process consists of clamping the 2-part resonator in a jig; a spring-loaded plunger butts the sample up against the fused silica rod. Between the sample and rod is placed a small amount of the cement mixed with sodium silicate which is allowed to set for 24 hours or more. This cement was used at all temperatures between 77°K and 673°K. Figure 1 shows the 3-part composite in its clamp with

radiation shield in place. The clamp is at a displacement node on the quartz.

The block diagram, Fig. 2, shows the essentials of the measuring circuit. The oscillator was tuned to the series resonance point of the resonator and the frequency and mechanical Q of the composite resonator determined.

The quartz crystal and silica rod were matched such that the respective resonant frequencies differed less than 1% over the entire temperature range. The 3-part composite had about the same frequency variation with respect to the 2-part resonator. The following relation between the resonant frequency of the sample and the

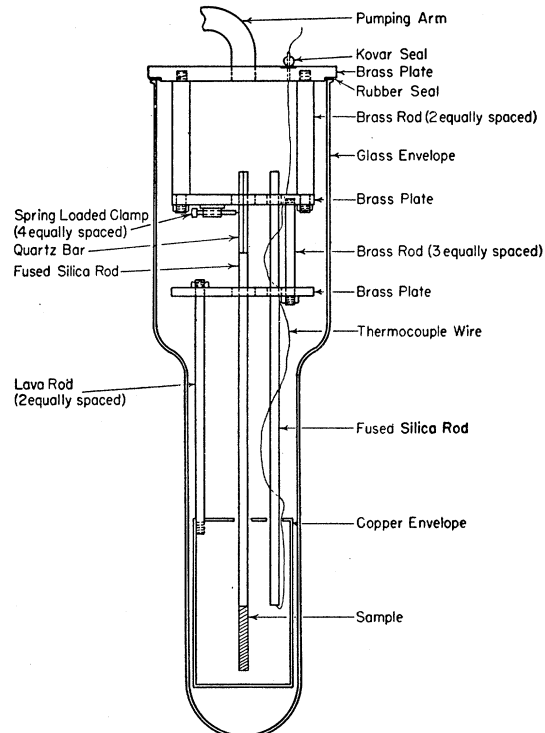


FIG. 1. The experimental apparatus was designed to keep the quartz transducer at temperatures below 100°C. Above this temperature a large loss peak interferes with decrement measurements. A suitable refrigerant is placed in a Dewar about the lower part of the envelope for temperatures below room temperature. An oven in the same position gives a range of temperatures up to 500°C.

* This research was supported by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command.

¹ A partial list of references includes: H. Weiss, Z. Naturforsch. 8A, 463 (1953); Harmon, Willardson, and Beer, Phys. Rev. 95, 699 (1954); Breckenridge, Blunt, Hosler, Frederikse, Becker, and Oshinsky, Phys. Rev. 96, 571 (1954); H. P. R. Frederikse and E. V. Mielczarek, Phys. Rev. 99, 1889 (1955); H. P. R. Frederikse and R. F. Blunt, Proc. Inst. Radio Engrs. 43, 1828 (1955); Hrostowski, Morin, Geballe, and Wheatley, Phys. Rev. 100, 1672 (1955).

² L. Hunter and S. Siegel, Phys. Rev. 61, 84 (1942).

³ P. M. Sutton, Phys. Rev. 91, 816 (1953).

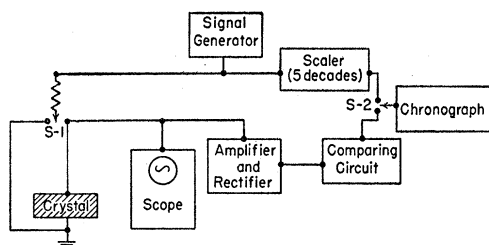


FIG. 2. A schematic block diagram of the apparatus. With $S-1$ and $S-2$ in the appropriate positions the signal generator is tuned to the series resonant frequency of the crystal. The output pulse of the fifth decade of the scaler is used to turn the chronograph on and off. The lower circuit is for measuring the logarithmic decrement of the crystal.

resonant frequency of the 2-part composite was used:

$$f_s = f_3 + e(f_3 - f_2) - \frac{\pi^2 e(e^2 - 1)(f_3 - f_2)^3}{3 f_2^2},$$

where f_2 = resonant frequency of 2-part composite, f_3 = resonant frequency of 3-part composite, f_s = resonant frequency of sample, $e = m_2/m_s$, m_2 = mass of 2-part composite, and m_s = mass of sample. This relationship results from ignoring higher-order terms in an expansion³ of an expression due to Rose.⁴

Two composite resonators were used; the first, which gave a longitudinal vibration mode, was a $-18.5^\circ X$ -cut crystal⁵ cut into a square prism $0.5 \times 0.5 \times 5$ cm, cemented onto fused silica rod.⁶ This 2-part composite was known as *ER2*. The second was a quartz cylinder⁷ cut with length along X -axis, cemented onto a fused silica cylindrical rod. This 2-part composite was known as *DR2* and gave a torsional vibration mode. *ER2* resonated at 49.874 kilocycles/second at room tempera-

TABLE I. Data at 27°C pertinent to determining the elastic constant of InSb.

Sample	l_0 cm	f_s (long.) cycles/sec	f_t (torsion.) cycles/sec	ρ_0 ^a	a_0 ^b Å
C39 (100)	2.7238	50 066.2	42 146.9	5.7751 ± 0.0003	6.4782
No. 2 (111)	3.5852	50 085.3			
	Temperature range $^\circ\text{C}$			α^c —Average coeff. of linear thermal expansion per $^\circ\text{C}$	
	-190 to -60			3.9×10^{-6}	
	-60 to -20			4.4	
	-20 to +20			4.7	
	+20 to 60			4.9	
	60 to 100			5.0	
	100 to 150			5.2	
	150 to 200			5.4	
	200 to 250			5.5	

^a Measured by C. T. Collett, Capacity, Density, and Fluid Meters Section, National Bureau of Standards, Washington, D. C.

^b Swanson, Fuyat, and Ugrinic, National Bureau of Standards Circular 539, Vol. IV, 1955 (unpublished), p. 73.

^c P. Hidnert and R. K. Kirby, Length Section, National Bureau of Standards, Washington, D. C.

⁴ F. Rose, Phys. Rev. **49**, 50 (1936).

⁵ Supplied by F. Phelps, Quartz Section, Boulder Laboratories, National Bureau of Standards.

⁶ From Tube Department, General Electric Company, Nela Park, Ohio.

⁷ August E. Miller Laboratories, North Bergen, New Jersey.

ture while *DR2* resonated at 40.090 kilocycles/second at the same temperature.

InSb cylinders of 5-mm diameter were prepared by cementing oriented square prisms onto brass dowels which could be placed in a small lathe. The crystals were turned down to cylinders of the proper diameter using the sand blast from an air-abrasive unit as the cutting tool.

Temperature was measured by placing iron-constantan thermocouples at the end of a dummy 2-part composite resonator which was clamped near the real resonator. The thermocouples were commercial duplex type, taken from a roll out of which a segment was calibrated by the Thermometry Section of the National Bureau of Standards. The over-all accuracy of the temperature measurements is estimated to be better than 1°C .

A thick copper radiation shield is placed about the lower end of the silica rod and the sample. This shield

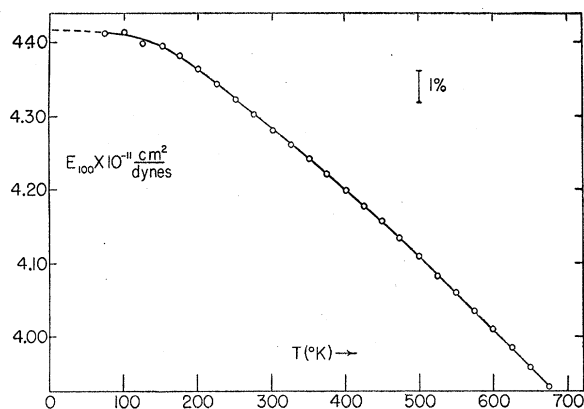


FIG. 3. Young's modulus for InSb for the (100) axis. The modulus is assumed to be free as measured. The misorientation of 4° in the sample has been corrected for in the figure.

is supported by lava rods. The entire assembly is placed in a Pyrex vacuum envelope.

Elevated temperatures are maintained by placing an oven around the Pyrex envelope. The ambient temperature of the experimental environs varied by no more than 2°C . The reproducibility of resonant frequencies for heating and cooling cycles was very good ($\pm 2 \times 10^{-6}$). Temperatures below room temperature were attained by placing a flask of liquid N_2 around the envelope. A pressure of one mm He gas around the sample served to lower the sample temperature to 77°K . The exchange gas was removed and the system allowed to warm up for temperatures intermediate between 77°K and 300°K .

This arrangement was not as satisfactory for low temperatures as for high temperatures, principally because silica has a large loss peak due to relaxation processes near 77° . An apparatus suitable for measurements down to liquid helium temperature has been constructed.

Crystal orientations were determined by the Laue back reflection method.

Both samples were cut from boules drawn from the melt by the Kyropoulos method.

RESULTS

Two InSb crystals were used during this investigation. One had its length in the $\langle 111 \rangle$ direction within one degree. The other had its length along the $\langle 100 \rangle$ direction within four degrees. These samples were designated InSb No. 2 and C39, respectively. Table I has pertinent data on these crystals for room temperature.

The Young's modulus of a sample was determined from its resonant frequency f_s when used with ER2. Similarly, the rigidity modulus was determined with DR2.

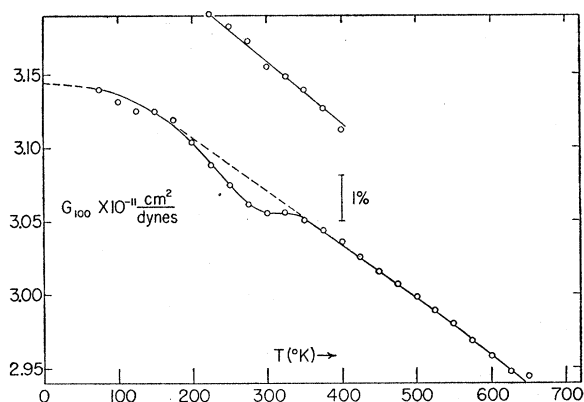


FIG. 4. "Free" rigidity modulus for InSb for the $\langle 100 \rangle$ axis. The measured modulus was assumed to be the "pure" modulus in the slightly misoriented sample. Both the conversion to the "free" modulus and the orientation correction have been made in the figure. Whether the dip in the modulus below room temperature is real or due to the use of household cement as a bonding agent has not been determined. On subsequent runs the sample suffered a small chip fracture on the side which destroyed the cylindrical symmetry to a certain degree. The upper curve shows the modulus to be almost linear in this region. The dip was assumed to be transitory and values along the dotted line were used for C_{44} .

These moduli are related to the frequency f_s by

$$M(T) = 4l^2 f_s^2 \rho = 4l_0^2 \rho_0 f_s^2(T) / \left(1 + \int_{300}^T \alpha dT \right),$$

where l is sample length, ρ is the density, T is the temperature, α the coefficient of linear expansion, and M is the proper modulus. Table I lists the values of α , l_0 , and ρ_0 used.

Using Voigt's notation⁸ we have the following relations between the compliance moduli (S_{ij}) and the Young's (E) and rigidity (G) moduli:

$$S_{11} = 1/E_{100}, \quad S_{44} = 1/G_{100}, \quad S_{11} + S_{44} + 2S_{12} = 3/E_{111}.$$

Figures 3, 4, and 5 show the experimental values of the moduli as functions of temperature. The S_{11} and

⁸ R. F. S. Hearman, *Revs. Modern Phys.* 18, 409 (1946).

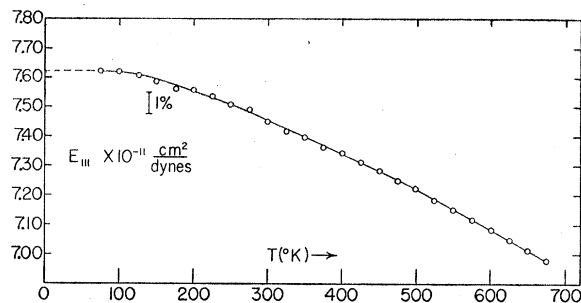


FIG. 5. The Young's modulus along the $\langle 111 \rangle$ axis. It was assumed to be the free modulus and no correction for orientation was made.

S_{44} values were corrected for the four degrees the sample axis was off the true crystallographic $\langle 100 \rangle$ axis.⁹ This misorientation also necessitated converting the measured rigidity modulus from the "pure" to the "free" modulus.⁸

Tables II and III list the elastic moduli and moduli of compliance, respectively, at 100° intervals. These values are several percent lower than those reported by McSkimin *et al.*¹⁰ at room temperature.

DISCUSSION

A. Lattice Theory

A dynamic theory of the diamond lattice for nearest neighbor interaction has been worked out by Born¹¹ and developed further by Smith.¹² The diamond lattice

TABLE II. Moduli of elasticity, in units of 10^{11} dynes/cm².

T (°K)	C_{11}	C_{12}	C_{44}
0	6.66	3.35	3.14
100	6.649	3.351	3.137
200	6.607	3.345	3.107
300	6.472	3.265	3.071
400	6.312	3.166	3.034
500	6.131	3.039	2.998
600	5.906	2.888	2.958

TABLE III. Moduli of compliance, in units of 10^{-12} cm²/dyne.^a

T (°K)	S_{11}	$-S_{12}$	S_{44}
0	2.26	0.76	3.18
100	2.268	0.760	3.188
200	2.291	0.770	3.218
300	2.335	0.783	3.256
400	2.380	0.795	3.296
500	2.432	0.806	3.336
600	2.494	0.819	3.381

^a The values at 300°K are estimated to be within 1%. The error at other temperatures is probably somewhat larger, i.e., between 1 and 2%. The fourth significant figure is given in all cases, except the zero degree extrapolated value, to indicate the temperature variation of the constants.

⁹ W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946).

¹⁰ McSkimin, Bond, Pearson, and Hrostowski, *Bull. Am. Phys. Soc. Ser. II*, 1, 111 (1956).

¹¹ M. Born, *Ann. Physik* 44, 605 (1914).

¹² H. M. J. Smith, *Proc. Roy. Soc. (London)* 241, 105 (1948).

TABLE IV. A comparison of results of first neighbor forces lattice theory.

	$\left[\frac{4C_{11}(C_{11}-C_{44})}{(C_{11}+C_{12})^2}\right]$	$\nu \times 10^{-12} \text{ sec}^{-1}$ calc.	$\lambda_l(\mu)$	$\lambda_0(\mu)$ measured
Si	0.99 ^a	19.8	15	16.5 ^d
Ge	1.02 ^b	11.6	27	29 ^d
InSb	0.94	6.66	46	52 ^{e,f}
ZnS	0.89 ^c	11.76	23	26 ^f

^a H. J. McSkimin, J. Appl. Phys. 24, 988 (1953).

^b M. E. Fine, J. Appl. Phys. 26, 863 (1955).

^c S. Bhagavantam, Proc. Indian Acad. Sci. 41, 72 (1955).

^d R. J. Collins and H. Y. Fan, Phys. Rev. 93, 676 (1954).

^e W. G. Spitzer and H. Y. Fan, Phys. Rev. 99, 1893 (1955).

^f H. Yoshinaga, Phys. Rev. 100, 753 (1955).

is made up of two interpenetrating, identical, face-centered cubic lattices. The zinc blende structure is similar except the two face-centered cubic lattices have different atoms at the points of the respective sublattices. The Born-Smith theory should not be strictly applicable to zinc blende structures, and indeed does break down for the case for Smith's extension to include central-force, next-nearest neighbor interactions. However, if we consider nearest neighbors only, even the highly ionic ZnS crystal gives good agreement.

In this theory, one relates the elastic constants (C_{ij}) to the lattice force constants α and β :

$$C_{11} = \alpha/a, \quad C_{12} = (2\beta - \alpha)/a, \quad C_{44} = (\alpha^2 - \beta^2)/a\alpha,$$

where a is the lattice constant and the elastic constants are related by the expression

$$4C_{11}(C_{11} - C_{44}) / (C_{11} + C_{12})^2 = 1.$$

When one calculates the highest optical mode of vibration, i.e., where the lattice wave vector \mathbf{q} is zero, one gets

$$\nu = (1/2\pi)(8C_{11}a/m)^{1/2},$$

where m is taken as the mean atomic mass and ν is the frequency of vibration.

Table IV shows for comparison purposes the results for Si, Ge, InSb, and ZnS using this theory.

B. Debye Temperature

The mean Debye characteristic temperature θ_D of the InSb crystal can be easily calculated using a method due to Sutton.¹³ Using the 0°K values of elastic constants, one finds for the velocity of sound the mean value

$$v_m = 2.26 \times 10^5 \text{ cm/sec},$$

and $\theta_D = 208^\circ\text{K}$. Keesom and Pearlman¹⁴ report $\theta_D = 200 \pm 5^\circ\text{K}$ from the specific heat measurements on InSb.

C. High-Temperature Behavior

The behavior of the elastic constants at the higher temperatures is of interest. In Fig. 6 we have plotted the two shear moduli, C_{44} and $(C_{11} - C_{12})/2$. These

¹³ P. M. Sutton, Phys. Rev. 99, 1826 (1955).

¹⁴ P. H. Keesom and N. Pearlman (private correspondence).

along with the bulk modulus $(C_{11} + 2C_{12})/3$, which is shown divided by 2, must each be positive if the lattice is to be stable. The ratios $2C_{44}/(C_{11} - C_{12})$ and $2(C_{11} + 2C_{12})/3(C_{11} - C_{12})$ are also shown. It can be seen that the bulk modulus is decreasing most rapidly over the observed temperature range, where the upper temperature is approximately 100° below the melting point. The behavior of these moduli between 700°K and 800°K should be most interesting. If $(C_{11} - C_{12})/2$ goes to zero before C_{44} , the compound then goes into what Born¹⁵ calls the gel state where a hydrostatic stress exists as in a liquid, but an elastic resistance against shearing remains. The fact that the bulk modulus is decreasing the most rapidly indicates an instability condition where cohesion of the lattice is decreasing.

SUMMARY

The elastic constants for the semiconductor indium antimonide have been measured as a function of tem-

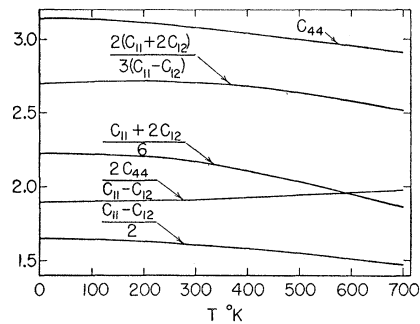


FIG. 6. The fundamental moduli, C_{44} , $(C_{11} - C_{12})/2$, and $\frac{1}{2}[(C_{11} + 2C_{12})/3]$, and their ratios are shown. The moduli are in units of 10^{11} dynes/cm². The bulk modulus is decreasing the most rapidly over the observed temperature range.

perature using the composite resonator technique. Those constants have been compared with other semiconductors of the diamond and zinc blende structure. The Born-Smith nearest neighbor theory has been found to give varying degrees of agreement with all the types in Table IV. That agreement varies from excellent in the case of highly homopolar bonds (Si and Ge) to fair in the case of ZnS which has some ionic character. Finally a value for θ_D was determined to compare with specific heat data.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the excellent technical skills W. J. McKean and J. M. Smith gave to this project. I wish to thank N. Koenig who took the Laue photos and assisted in their interpretation. P. Hidnert and his colleague R. K. Kirby were most cooperative in providing the values of the coefficients of linear expansion. D. E. Roberts who grew the large well-defined single crystals made the experiment possible.

¹⁵ M. Born, J. Chem. Phys. 1, 591 (1939).