MASTER

C00-623-167

SOLID STATE PHYSICS PROGRAM

THE LOW TEMPERATURE GRUNEISEN PARAMETER OF SOME SEMICONDUCTORS FROM ELASTICITY DATA

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ATOMIC ENERGY COMMISSION

TECHNICAL REPORT NO. 71

CONTRACT NO. AT (11-1)-623

JANUARY, 1971

CASE WESTERN RESERVE UNIVERSITY

UNIVERSITY CIRCLE

CLEVELAND, OHIO 44106

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THE GRÜNEISEN PARAMETER OF SOME
SEMICONDUCTORS FROM ELASTICITY DATA

Abstract

by

DENNIS ALLEN SWYT

The low temperature Grüneisen parameter, γ_L , has been determined from elasticity data for the elemental semiconductors, Si and Ge, and the semiconducting III-V compounds, GaAs, InAs and InSb. Elastic constants were measured from 300 to 4.2°K and pressure derivatives from 300 to 77°K by a conventional pulse echo technique and show good agreement with the results of other workers. The values of γ_L calculated from the present elasticity data are systematically lower than those obtained from low temperature thermal expansion measurements. The difference between γ_L (elastic) and γ_L (thermal) cannot be accounted for by experimental uncertainties and apparently has no basis in present theory.

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ACKNOWLEDGEMENTS

The author wishes to gratefully acknowledge:

Dr. D.E. Schuele, who directed this research, for his generous guidance and encouragement; Dr. C.A. Swenson, for the kind loan of his semiconductor samples; Dr. M.P. Shaw, for the contribution of a specimen boule; and Mrs. Z.M. Clifford, for her conscientious effort in typing this manuscript. The author's wife and parents deserve special consideration for their years of encouragement and sacrifice. The work was supported by the Atomic Energy Commission.

TABLE OF CONTENTS

ABSTRACT	ii
ACKNOWLEDGEMENTS	iii
LIST OF FIGURES	v
LIST OF TABLES	vi
I. INTRODUCTION	1
II. EXPERIMENTAL PROCEDURE	3
III. RESULTS	13
IV. DISCUSSION AND CONCLUSIONS	83
V. REFERENCES	86
VI. APPENDIX	
A. Introduction to continuous wave appendices.	89
A1. General standing wave technique.	91
A2. Sidebands and the continuous approximation.	105
A3. Extension of lossless transmission line analogy to the two transducer case.	107
A4. Polycrystalline aluminum study.	116
A5. An appraisal of the FM technique.	126
B1. The pressure system.	139
B2. Pressure vessel design.	142
B3. Pressure gauge calibration and comparison.	148
C1. The evaluation of uncertainties in low temperature Grüneisen parameters.	157
C2. The Grüneisen parameter of a Debye solid in the quasi-harmonic approximation.	168
C3. The temperature dependence of the Grüneisen parameter, γ_G : real semiconductors.	174

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. The buffer technique.	9
2. Comparison of γ_L from the thermal expansion measurements of Sparks and Swenson and from the present elasticity study.	51
3. The compression of the semiconductors from ultrasonic data according to the Murnaghan logarithmic equation of state.	64
4. The observed temperature dependence of the isothermal bulk moduli.	68
5. A comparison of the bulk moduli of Ge and GaAs.	69
6. The dependence of optical and structural properties on the ionicity of the chemical bond.	80
7. Ratio of the non-central and central force constants in Keating's model for diamond-like crystals as a function of the ionicity of the chemical bond.	81
1A. The resonance of a composite oscillator.	92
2A. Schematic diagram of FM electronics.	97
3A. Schematic diagram of electronics for peak tracing.	98
4A. Sidebands and the modulation index, m.	106
5A. Sample holder for FM measurements.	117
1B. Schematic diagram of pressure system.	140
2B. Pressure vessel and closure rings.	143
3B. Original and redesigned pressure vessels.	144
1C. The temperature dependence of Grüneisen parameter, γ_G , of diamond-like semiconductors and "normal" solids.	175

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1.	Direction cosines of principal axes.	6
2.	Origins and specimen lengths of semiconductors.	7
3.	Bonding materials used at interfaces for different temperatures.	10
4.	Effective elastic constants for longitudinal and shear waves in cubic crystals.	14
5.	Observed transit times and elastic constants for (110) propagation in Si.	15
6.	Observed transit times and elastic constants for (110) propagation in Ge.	16
7.	Observed transit times and elastic constants for (110) propagation in GaAs.	17
8.	Observed transit times and elastic constants for (110) propagation in InAs.	18
9.	Observed transit times and elastic constants for (111) and (001) propagation in InSb.	19
10.	Certain parameters related to the 300°K elastic properties.	20
11.	Sources in the literature of experimentally determined thermal expansion, lattice constant, specific heat, elastic constant, pressure derivative, and Debye temperature data.	21
12.	Effects of orientation corrections on elastic constants.	25
13.	Temperature dependence of the elastic constants of the semiconductors.	26
14.	Thermodynamic data for the semiconductors.	27
15.	Observed pressure derivatives of transit times for Si.	28
16.	Observed pressure derivatives of transit times for Ge.	29

17.	Observed pressure derivatives of transit times for GaAs.	30
18.	Observed pressure derivatives of transit times for InAs.	31
19.	Observed pressure derivatives of transit times for InSb.	32
20.	Adiabatic and isothermal bulk moduli and pressure derivatives.	35
21.	Effect of orientation corrections on pressure derivatives of elastic constants.	36
22.	Observed pressure derivatives of elastic constants at different temperatures.	37
23.	Comparison of results of this study of the elastic constants of Si with those of other workers.	39
24.	Comparison of results of this study of the elastic constants of Ge with those of other workers.	40
25.	Comparison of results of this study of the elastic constants of GaAs with those of other workers.	41
26.	Comparison of results of this study of the elastic constants of InAs with those of other workers.	42
27.	Comparison of results of this study of the elastic constants of InSb with those of other workers.	43
28.	Comparison of the results of this study of the pressure derivatives of the elastic constants of Si with those of other workers.	45
29.	Comparison of the results of this study of the pressure derivatives of the elastic constants of Ge and GaAs with those of other workers.	46
30.	High and low temperature elastic Grüneisen parameters.	48
31.	Comparison of thermal and elastic low temperature Grüneisen parameters.	50

32.	Elastic and calorimetric Debye temperatures.	56
33.	The effects of electrically active impurities on the elastic properties of Si as determined by Hall.	57
34.	Calculation of the temperature derivative of the isothermal bulk moduli.	61
35.	25 kilobar compression data.	63
36.	General compression data.	64
37.	Volume dependent and independent bulk moduli.	67
38.	Relations among the elastic constants for different models of diamond-like crystals.	77
39.	Relations among the elastic constants for different models of diamond-like crystals; evaluated for the 4.2°K data of the present work.	78
1A.	Typical values of parameters employed and observed in FM measurements.	100
2A.	FM system apparatus list.	101
3A.	Typical data and correction coefficients, α and β , for a composite oscillator with two transducers.	111
4A.	Percentage change, ΔF_S and ΔF_B , in observed value of logarithmic pressure derivative of sample resonance frequency due to transducer end effects according to Swyt and Beattie, respectively.	115
5A.	Transducer size and overtone operation effects.	118
6A.	Effects of frequency modulation parameters.	120
7A.	Effects of detector on peak position and spacing.	121
8A.	Pulse echo summary for polycrystalline aluminum.	122
9A.	Transducer end effects in pulse echo measurements on aluminum.	123
10A.	Summary of FM results for transducer size and frequency of operation comparisons:	125

11A.	Summary of FM Data for GaAs	131
12A.	Typical 77°K FM Measurements on Semiconductors	132
13A.	Comparison of Observed and Corrected Pressure Derivatives of Frequency with Pulse Echo Results (F in 10^{-7} /psi).	133
14A.	Trends in FM Measurements.	134
1B.	Pressure system components.	141
2B.	Pressure vessel design data.	146
3B.	Calibration of 10 kbar manganin gauge against the mercury freezing point at 0°C using two different resistance Bridges.	150
4B.	Manganin wire constant based on revised phase transition pressure.	150
5B.	Comparison of 10 kbar and 3 kbar manganin gauges: typical results for total pressure changes of 5 kbar.	152
6B.	Comparison of Heise Bourdon-tube and manganin resistance gauges.	154
7B.	Results of gauge comparisons.	155
1C.	Summary of expressions for changes in elastic constants and their pressure derivatives for changes in transit times and their derivatives.	159
2C.	Expressions for the changes in elastic constants for changes in transit times and their derivatives.	162
3C.	Expressions for changes in pressure derivatives of elastic constants in terms of changes in transit times and their derivatives.	163
4C.	Evaluated changes for Si (effects of 1% change in any variable).	164
5C.	Evaluated changes for InAs (effects of 1% change in any variable).	165
6C.	γ_L and its partial derivatives.	166

INTRODUCTION

Both the Group IV elemental and the III-V compound semiconductors crystallize in structures which exhibit tetrahedral bonding: Si and Ge in the diamond with an FCC space lattice, the III-V compounds in the zinc blende comprised of two interpenetrating FCC lattices. Usually associated with these open structures is a region of negative thermal expansion ($\beta < 0$) at low temperatures. However, small, positive thermal expansions at the lowest temperatures were predicted from elasticity data for Si and Ge¹ and were observed experimentally,² though not with high precision.

With the intent of establishing accurately the magnitude of β for Si and Ge and extending the investigation to III-V compounds, Sparks and Swenson (S&S) made thermal expansion measurements over the range 2 to 30°K.³ For the six semiconductors studied, negative β 's at intermediate temperatures and small, positive β 's at the lowest temperatures were observed. From their own thermal expansion³ and specific heat⁴ data for the same samples, S&S calculated the Grüneisen parameter defined by:

$$\gamma_G = \frac{\beta B_T V}{C_P}$$

Since their data extended into the T^3 region, they were able to calculate the constant low temperature limiting value γ_L . They compared their results for Si and Ge with the γ_L obtained from high pressure elasticity data and observed:

$$\gamma_L(\text{thermal}) > \gamma(\text{elastic}) \quad .$$

Since no basis for the difference exists in the theory and complete elasticity data for the III-V compounds by which further comparisons could be made did not exist, no firm conclusions could be drawn concerning the discrepancy. Whether the difference was systematically fractional or incremental was uncertain.

The present investigation of the high pressure elastic properties of semiconductors was undertaken to shed light on the discrepancy between $\gamma_L(\text{thermal})$ and $\gamma_L(\text{elastic})$ noted by S&S. Where specimen size and geometry would allow, elasticity measurements at as low temperature as possible were to be performed on the identical samples used by S&S. From the low temperature elastic constants and their pressure derivatives, γ_L would be calculated for each semiconductor.

EXPERIMENTAL PROCEDURE

Sample Preparation

Each semiconductor crystal was prepared by the same process of orientation, cutting, polishing and plating. Samples were cut from larger specimens of different shapes and orientation: Ge, InSb, and InAs from approximately circularly cylindrical rods with (111) axes; Si from a (110) cylinder and GaAs from a slab. In each case, the original boule was mounted and x-ray oriented in a goniometer using back reflection Laué photographs. Samples of the order of 1 cm long were cut with a diamond saw with the goniometer fixed to the magnetic table of a wafering machine.

Preparation of parallel faces followed a standard procedure. Samples were x-ray oriented, cemented into steel lapping rings, and lapped on successively finer grades of plate glass-backed emery paper. Kerosene was used as a lubricant with 01, 02, 03, and 04 paper. The lengths of the lapped crystals with (110) orientations which were cut from (111) boules were close to the maximum allowed by the orientation and diameters of the boules. To aid in the adhesion of silver plating and the formation of acoustic bonds, matte finishes were applied using one micron diamond powder with kerosene lubricant on plate glass.

Orientations of the samples in final form were determined from Laué photographs. Ten spots on each photograph were labelled by their Miller indices and positions on the film, and calculations of the direction cosines of the crystals' axes made by a least

squares fit. The angular misorientation of each crystal's parallel faces relative to the basal plane was then determined.

Each crystal was silver plated in order to form the electrical ground for the piezoelectric transducers. Different techniques were tried to determine the most durable plating which could be conveniently obtained. Evaporated films of aluminum and nickel were found to be abraded when a transducer was wrung on. Platinum films deposited by the firing of an organic solution were tough but of an inadequate conductivity; silver films by a similar process, either alone or over the platinum, also were abraded. Finally, silver films formed by chemical deposition in a Rochelle salts process were found to be satisfactory.

Samples were cleansed in preparation for the chemical deposition by a three step process. Each was boiled in an Alconox-distilled water bath and rinsed successively in dilute nitric acid and caustic potash solutions, with rinsings in distilled water after each step. GaAs was found to react with the nitric acid solution; only brief rinsings with very dilute solutions were used thereafter. The samples were plated by immersion in a mixture of solutions which had been prepared previously and stored separately. Slow reaction of the InSb with the plating solution lead to the use of organic silver for its film.

The final form of each sample was that of a somewhat skewed, roughly right circular cylinder, approximately 1 cm in length and diameter. Faces were flat and parallel with deviations in path length of less than .0001 cm over the faces. The direction cosines

and angle of the crystal axis relative to the principle crystallographic axis for each is indicated in Table 1. The source of each specimen and the carrier concentrations of those also used by Sparks and Swenson³ are given in Table 2 along with the room temperature lengths. While it was intended that measurements would be made on all six semiconductors which had been obtained from Sparks and Swenson, the size and shape of some of them precluded this. Only the Ge, InAs, and InSb samples were from boules used by them.

TABLE 1. Direction Cosines of Principal Axes

Element	Axis	l	m	n	$\theta(^{\circ})^*$
Si	(110)	0.7291	0.6843	0.0118	$1^{\circ}56'$
Ge	(110)	0.7108	0.6996	-0.0735	$4^{\circ}12'$
GaAs	(110)	0.7096	0.7046	0.0071	$0^{\circ}18'$
GaAs	(110)	0.7134	0.7006	0.0103	$1^{\circ}3'$
InSb	(001)	0.0433	-0.0233	0.9988	$2^{\circ}48'$
InSb	(111)	0.5789	0.5736	0.5795	$0^{\circ}25'$

*Misorientation of crystal axes with respect to the crystallographic axes.

TABLE 2. Origins and Specimen Lengths of Semiconductors

Element	Length ^A	Resistivity ^A (Ω -cm)	Net Carrier Concentration	Source
Si	1.4341			National Carbon Research
Ge ^B	0.7968	48	$< 10^{17}$	Mono-Silicon
GeAs	0.8786			United Aircraft
InAs ^B	0.8768	0.012	$\sim 2 \cdot 10^{16}$	Texas Instrument
InSb ^B	0.8961	0.024	$< 2 \cdot 10^{16}$	Ohio Semiconductors

A. 300°K

B. Cut from specimen employed in thermal expansion study of Sparks and Swenson
(See Table 11).

THE EXPERIMENT

Transit times for waves of appropriate polarizations propagating in each crystal were determined by a buffer technique.⁵ A block diagram and functional time sequence of the electronics have been given previously.⁶ With a transducer and sample bonded to a cylindrical buffer rod (Figure), the differences in arrival time of pairs of consecutive echoes were measured with a resolution of .1 nanosecond and a reproducibility of ± 0.2 nanosecond. The buffer was of polycrystalline aluminum and the 10MHz transducers of x- and y- cut quartz. Different seal materials were required at different temperatures.

At room temperatures, salol provided seals for both longitudinal and shear waves at buffer-transducer and buffer-sample interfaces. At low temperatures, the seal materials were those which would produce a bond that would not fracture or cause cleavage damage to the fragile samples (Table 3). Seals were generally made in a press at pressures of about 50 psi; No-naq bonds were made by wringing together the surfaces to be bonded. The highly volatile pentane mix was kept from evaporating with rubber cement painted around the edge of the transducer.

At room temperature, measurements were made with the buffer rod and sample in a holder which was immersed in light-weight oil. The temperature was monitored for constancy with a glass thermometer. At 195°K the bath consisted of a closely homogenous mixture of Freon 11 and finely ground dry ice. A copper-constantin thermocouple

Figure 1. The buffer technique

TABLE 3. Bonding Materials Used at Interfaces
for Different Temperatures

T(°K)	Transducer- Buffer	Buffer- Sample	Transducer- Sample
300°	Salol ^A	Salol	No-Naq ^B
195°	No-Naq	Dow #7 ^C	No-Naq
77°	Dow #7	Pentane Mix ^D	Dow #7 ^E
4.2°	Dow #7	Pentane Mix	—

A. Phenyl Salicylate.

B. No-Naq Stopcock Grease (Fisher Scientific Co.).

C. Dow-Corning #7 Silicone Release Agent.

D. 50% Normal and 50% Iso-pentane Mixture.

E. Except for Si, where Dow-Corning Silicone Fluid
(12,500 cp) was used.

referred to an air saturated distilled ice bath was used to monitor temperature. The Freon bath was stable to $\pm 1^\circ$ at a temperature determined from NBS thermocouple tables to be within $.5^\circ\text{C}$ of the sublimation point of CO_2 . The baths of liquid nitrogen and liquid helium in which the sample holder was subsequently immersed were assumed to be at 77° and 4.2° respectively.

Pressure Measurement

Changes in transit times with pressure to 30,000 psi were measured with the same electronics and a pressure system built expressly for low temperature work (Appendix B). A two-turn Heise bourdon tube gauge was used to monitor the pressure of the helium gas pressure medium. Generally, data consisted of changes in transit time of an individual acoustic echo with corresponding incremental changes in pressure as read on the gauge.

The sample was placed into a holder mounted on the pressure vessel closure plug and sealed into the vessel. The vessel was then pressurized to about 20,000 psi and immersed in the temperature bath. After sufficient time was allowed for thermal equilibrium to be attained, the system was cycled in pressure to eliminate possible transient bond effects. Data was then taken with sufficient time, usually two to four minutes, to reattain equilibrium after each pressure increment.

Generally, three or more runs were made on different echoes for each mode at the temperatures involved (300° , 195° , 77°K). A complete, successful run consisted of a series of points for increas-

ing and decreasing pressure which showed no signs of hysteresis.

RESULTS

Elastic Constants

Except for InSb, the independent elastic constants, C_{11} , C_{12} , and C_{44} , have been determined from measurements of two shear and one longitudinal transit time for waves propagating in the crystal in single directions, i.e., ones close to the (110) axes. For InSb, a longitudinal and a single, degenerate shear transit time were measured for propagation close to (001) and (111) axes in different crystals. The relations between the independent and effective elastic constants appear in Table 4. In any case, the effective elastic constants are calculated according to

$$C_i = \rho v_i^2 = \rho (4L/t_i)^2 \quad (1)$$

where:

v_i = velocity of propagation

L = sample length

t_i = transit time

ρ = density

The observed transit times and the resulting effective elastic constants are given in Tables 5 to 9.

X-ray densities have been calculated from molecular weights and lattice constants (Table 10) and, along with the measured path lengths, corrected for the small effect of thermal expansion. For Si, Ge, and InSb, the explicit dependences of length on temperature given in the references cited in Table 11 were used. For GaAs, the

TABLE 4. Effective Elastic Constants for Longitudinal
and Shear Waves in Cubic Crystal

Direction		Elastic Constant	
Propagation	Polarization	Symbol	Value
(110)	(110)	C	$1/2(C_{11} + C_{12} + 2C_{44})$
(110)	(110)	C'	$1/2(C_{11} - C_{12})$
(110)	(001)	C_{44}	C_{44}
(001)	(001)	C_{11}	C_{11}
(001)	any shear	C_{44}	C_{44}
(111)	(111)	C_{1L}	$1/3(C_{11} + 2C_{12} + 4C_{44})$
(111)	any shear	C_{1S}	$1/3(C_{11} + C_{44} - C_{12})$

TABLE 5. Observed Transit Times and Elastic Constants for
(110) Propagation in Si

T (°K)	Length (cm)	Density (g/cm ³)	Mode	Transit Time (μsec)	Elastic Constant (10 ¹² dynes/cm ²)
300°	1.4341	2.3294	(110)	3.1386	1.9453
			(1 $\bar{1}$ 0)	6.1320	.50963
			(001)	4.9074	.79571
195°	1.4338	2.3308	(110)	3.1288	1.9579
			(1 $\bar{1}$ 0)	6.1085	.51364
			(001)	4.8951	.79987
77°	1.4337	2.3311	(110)	3.1248	1.9629
			(1 $\bar{1}$ 0)	6.1033	.51452
			(001)	4.8857	.80295
4.2°	1.4338	2.3310	(110)	3.1223	1.9662
			(1 $\bar{1}$ 0)	6.1049	.51431
			(001)	4.8851	.80315

TABLE 6. Observed Transit Times and Elastic Constants
for (110) Propagation in Ge

T (°K)	Length (cm)	Density (g/cm ³)	Mode	Transit Time (μsec)	Elastic Constant (10 ¹² dynes/cm ²)
300°	.7968	5.3247	(110)	2.9378	1.5668
			(1 $\bar{1}$ 0)	5.7831	.40433
			(001)	4.5104	.66469
195°	.7964	5.3334	(110)	2.9229	1.5838
			(1 $\bar{1}$ 0)	5.7477	.40961
			(001)	4.4799	.67422
77°	.7960	5.3400	(110)	2.9136	1.5943
			(1 $\bar{1}$ 0)	5.7209	.41352
			(001)	4.4588	.68076
4.2°	.7960	5.3402	(110)	2.9071	1.6015
			(1 $\bar{1}$ 0)	5.7080	.41541
			(001)	4.4560	.68164

TABLE 7. Observed Transit Times and Elastic Constants
for (110) Propagation in GaAs

T (°K)	Length (cm)	Density (g/cm ³)	Mode	Transit Time (μsec)	Elastic Constant (10 ¹² dynes/cm ²)
300°	.87859	5.3170	(110)	3.3550	1.4585
			(1 $\bar{1}$ 0)	7.0929	.32631
			(001)	5.2560	.59428
195°	.87799	5.3281	(110)	3.3368	1.4755
			(1 $\bar{1}$ 0)	7.0674	.32892
			(001)	5.2279	.60111
77°	.87759	5.3352	(110)	3.33190	1.4920
			(1 $\bar{1}$ 0)	7.0276	.33280
			(001)	5.2040	.60690
4.2°	.87754	5.3344	(110)	3.3148	1.4954
			(1 $\bar{1}$ 0)	7.0169	.33373
			(001)	5.1990	.60791

TABLE 8. Observed Transit Times and Elastic Constants
for (110) Propagation in InAs

T (°K)	Length (cm)	Density (g/cm ³)	Mode	Transit Time (μsec)	Elastic Constant (10 ¹² dynes/cm ²)
300°	.8768	5.6668	(110)	4.0340	1.0708
			(1 $\bar{1}$ 0)	9.5562	.1908
			(001)	6.6404	.39519
195°	.8764	5.6736	(110)	4.0076	1.0853
			(1 $\bar{1}$ 0)	9.4958	.19331
			(001)	6.6054	.39951
77°	.8762	5.6787	(110)	3.9829	1.1062
			(1 $\bar{1}$ 0)	9.4230	.19640
			(001)	6.5719	.40376
4.2°	.8760	5.6821	(110)	3.9667	1.1085
			(1 $\bar{1}$ 0)	9.4138	.19681
			(001)	6.5589	.40543

TABLE 9. Observed Transit Times and Elastic Constants
for (111) and (001) Propagation in InSb

T (°K)	Length (cm)	Density (g/cm ³)	Mode*	Transit Time (μsec)	Elastic Constant (10 ¹² dynes/cm ²)
300°	.8961	5.7776	(001) _L	5.1142	.66557
			(001) _S	7.5832	.30272
	.8679		(111) _L	4.6179	.87022
			(111) _S	9.6065	.20109
195°	.8957	5.7853	(001) _L	5.0880	.67271
			(001) _S	7.5326	.30693
	.8675		(111) _L	4.5783	.88573
			(111) _S	9.5039	.20555
77°	.8955	5.7892	(001) _L	5.0378	.68633
			(001) _S	7.4860	.31083
	.8673		(111) _L	4.5478	.89786
			(111) _S	9.4238	.20911
4.2°	.8953	5.7931	(001) _L	5.0042	.69573
			(001) _S	7.4774	.31161
	.8671		(111) _L	4.5389	.90159
			(111) _S	--	--

* L (longitudinal) and S (shear) polarization.

TABLE 10. Certain Parameters* Related to the 300°K Elastic Properties

Element	Si	Ge	GaAs	InAs	InSb
MW (molecular weight) (grams.mole)	28.09	72.60	72.32	94.87	118.29
a (lattice constant) (Å ^o)	5.43080	5.65769	5.65315	6.05838	6.47877
ρ (density) (grams/cm ³)	2.3294	5.3247	5.3170	5.6668	5.7776
V (specific volume) (cm ³)	12.059	13.635	13.601	16.741	20.474
β (volume expansion) (10 ⁻⁶ /°K)	6.99	17.3	7.15	13.5	15.1
C _p (heat capacity) (cal/mole °K)	4.796	5.590	5.525	5.710	5.910
B _T (bulk modulus) (10 ¹² dynes.cm ²)	0.9873	0.7886	0.7361	0.6121	0.4652
P _t (phase transition pressure in kbar)	195-200	120-125	240-250	1100-1103	23

* For source of data, see Tables 11.

TABLE 11. Sources in the literature of experimentally determined thermal expansion, lattice constant, specific heat, elastic constant, pressure derivative (P), and Debye temperature data.

<u>Elastic Constants</u>		
<u>Element</u>	<u>T(°K)</u>	<u>Source</u>
Si	77-300° (P)	H.J. McSkimmin and P. Andreatch, Jr., J. Appl. Phys. <u>35</u> , 2161 (1964).
	4.2-300°	John J. Hall, Phys. Rev. <u>161</u> , 756 (1967).
	300° (P)	J. Chapman, M.S. Thesis, Case Inst. Tech., (1961).
Ge	77-300° (P)	H.J. McSkimmin and P. Andreatch, Jr. J. Appl. Phys. <u>34</u> , 651 (1963).
	77-300°	A.E. Kadyshevitch, Sov. Phys. Solid State <u>9</u> , 1467 (1968).
	4.2-200°	L.J. Brunner and R.W. Keyes, Phys. Rev. Letters <u>7</u> , 55 (1961).
GaAs	300° (P)	H.J. McSkimmin, et al., J. Appl. Phys. <u>38</u> , 2362 (1967).
	300°	T.B. Bateman, et al., J. Appl. Phys. <u>30</u> , 544 (1959).
	300°	J.R. Drabble and A.J. Brammer, Sol. St. Comm. <u>4</u> , 467 (1966).
	300°	C.W. Garland and K.C. Park, J. Appl. Phys. <u>33</u> , 759 (1962).
InAs	4.2-300°	D. Gerlich, J. Appl. Phys. <u>34</u> , 2915 (1963); <u>35</u> , 3062 (1964).
	4.2-300°	R. Reifengerger, M.J. Keck, and J. Trivisonno, J. Appl. Phys. <u>40</u> , 5403 (1969).
InSb	300°	H.J. McSkimmin, et al., Bull. Am. Phys. Soc. 11, 111 (1956).
	77-300°	R.J. Slutsky and C.W. Garland, Phys. Rev. <u>113</u> , 167 (1959).

Thermal Expansion

<u>Element</u>	<u>T(°K)</u>	<u>Source</u>
Si, Ge, InSb	40-300°	D.F. Gibbons, Phys. Rev. <u>112</u> , 136 (1958).
GaAs	40-300°	S.I. Novikova, Sov. Phys. Solid State <u>7</u> 2170 (1966).
All	4.2-40°	P.W. Sparks and C.A. Swenson, Phys. Rev. <u>163</u> , 779 (1967).
InAs	40-300°	Estimated from general shape of III-V family of curves, low temperature data of Sparks and Swenson, and an average value at 184°.

Specific Heat

Si, Ge	4.2-300°	P. Flubacher, et al., Phil Mag. <u>4</u> , 273 (1959).
All III-V	30-300°	T.C. Cetas, et al., Phys. Rev. <u>174</u> , 835 (1968).
All III-V	30-300°	U. Piesbergen, Z. Naturforsch <u>184</u> , 141 (1963).

Lattice Constants

Si, Ge	300°	D.N. Batchelder and R.O. Simmons, J. Appl. Phys. <u>36</u> , 2864 (1961).
InAs, GaAs	300°	G.V. Ozolin'sh, et al. Sov. Phys. Cryst. <u>7</u> , 691 (1963).
InSb	300°	G. Giesecke and H. Pfister, Acta Cryst., <u>369</u> (1958).

Debye Temperature

Si, Ge	P. Flubacher, et al., loc. cit.
All III-V	T.C. Cetas, et al., loc. cit.

Phase Transition Pressures

<u>Element</u>	<u>T(°K)</u>	<u>Source</u>
All		S. Minomura and H.G. Drickamer, J. Phys. Chem. Solids <u>23</u> , 451 (1962).

dependence was calculated by a numerical integration of the thermal expansion data indicated. For InAs, an estimate was made of the length changes from the character of the family of thermal expansion curves of the III-V compounds and experimental high and low temperature values. For the other semiconductors, the total length change between 300° and 4.2°K is less than about .1%; since the total neglect of that change would contribute only that much error to the elastic constants and would be within the general experimental uncertainty, the approximation approach is effective.

Finally, in the case of the (110) crystals, the small effects of misorientation on the elastic constants were compensated by a computer perturbation calculation using the direction cosines of Table 1. The InSb results are uncorrected for this effect. A comparison of the orientation corrected and uncorrected 300° elastic constants appears in Table 12 and the final adiabatic elastic constants and bulk moduli for all temperatures in Table 13.

Pressure Derivatives of Elastic Constants

Basic data used in the calculation of the pressure derivatives of the elastic constants appear in Tables 10 and 14. The pressure derivatives are calculated from the observed transit time changes (Tables 15 to 19), according to

$$\frac{dC_i}{dp} = \frac{d}{dp} \left[\frac{4\rho L^2}{t_i^2} \right] = C_i \left[\frac{1}{3B_T} - \frac{2}{t_i} \left(\frac{dt_i}{dp} \right) \right] \quad (2)$$

TABLE 12. Effects of Orientation Corrections on Elastic Constants
(Oriented/Unoriented)

Element	C_{11}	C_{12}	C_{44}	C	C'	B_s
Si	1.6590	.6416	.7958	1.9461	.5087	.9807
	1.6592	.6400	.7957	1.9453	.5096	.9797
Ge	1.2970	.4914	.6697	1.5639	.4028	.7599
	1.3064	.4978	.6647	1.5668	.4043	.7673
GaAs	1.1904	.5379	.5943	1.4585	.3263	.7554
	1.1905	.5379	.5943	1.4585	.3263	.7554
InAs	0.8663	.4848	.3953	1.0708	.1908	.6120
	0.8664	.4848	.3952	1.0708	.1908	.6118
InSb	0.6656	.3669	.3011	0.8174	.1494	.4665
	_____	_____	_____	_____	_____	_____

Elastic Constants in 10^{12} dynes/cm²

TABLE 13. Temperature Dependence of the Elastic Constants of the Semiconductors

Element	T(°K)	C_{11}	C_{12}	C_{44}	C	C'	B_s
Si	300	1.6590	0.6416	0.7958	1.9461	0.5087	0.9807
	195	1.6714	0.6461	0.8000	1.9587	0.5127	0.9878
	77	1.6740	0.6472	0.8031	1.9637	0.5133	0.9895
	4.2	1.6773	0.6502	0.8033	1.9670	0.5135	0.9926
Ge	300	1.2970	0.4914	0.6694	1.5639	0.4028	0.7599
	195	1.3096	0.4934	0.6790	1.5805	0.4081	0.7655
	77	1.3174	0.4954	0.6856	1.5910	0.4120	0.7681
	4.2	1.3257	0.4979	0.6865	1.5982	0.4139	0.7738
GaAs	300	1.1904	0.5379	0.5943	1.4585	0.3263	0.7554
	195	1.2032	0.5454	0.6012	1.4755	0.3289	0.7647
	77	1.2178	0.5523	0.6070	1.4920	0.3328	0.7741
	4.2	1.2211	0.5537	0.6080	1.4954	0.3337	0.7762
InAs	300	0.8663	0.4848	0.3953	1.0708	0.1908	0.6120
	195	0.8790	0.4925	0.3996	1.0853	0.1932	0.6213
	77	0.8918	0.4992	0.4038	1.0993	0.1963	0.6303
	4.2	0.8997	0.5063	0.4055	1.1085	0.1967	0.6374
InSb	300	0.6656	0.3669	0.3011	0.8174	0.1494	0.4664
	195	0.6727	0.3707	0.3069	0.8286	0.1510	0.4714
	77	0.6863	0.3759	0.3108	0.8419	0.1552	0.4794
	4.2	0.6957	0.3799	0.3116	0.8494	0.1579	0.4851

Elastic Constants in 10^{12} dynes/cm²

TABLE 14. Thermodynamic Data for the Semiconductors^a

Element	T(°K)	v^b	C_p^c	β^d	$(\frac{\partial \beta}{\partial T})_p^e$	A_o^f
Si	300	12.059	4.796	6.99	6.00	8.64
	195	12.052	3.656	5.17	5.90	4.06
	77	12.050	1.188	-2.15	5.40	0.86
	4.2	12.051	0.129*	0.65*	46.0	0
Ge	300	13.635	5.590	17.3	24.0	39.6
	195	13.612	4.984	14.3	60.0	20.0
	77	13.595	2.529	3.81	137.0	1.11
	4.2	13.595	0.692*	5.78*	--	0
GaAs	300	13.602	5.525	7.15	8.5	6.82
	195	13.573	5.066	5.73	22.0	3.15
	77	13.555	2.648	1.08	67.4	0.09
	4.2	13.557	0.874*	6.43*	459	0
InAs	300	16.741	5.710	13.5	12.0	24
	195	16.721	5.305	10.5	24.0	9
	77	16.706	3.259	1.5	183	.2
	4.2	16.696	2.489*	7.5*	--	0
InSb	300	20.474	5.910	15.1	12.0	26.4
	195	20.447	5.589	13.1	24.0	13.8
	77	20.433	3.889	1.8	183	0.16
	4.2	20.419	5.110*	--	--	0

^a) See Table 11 for sources of data. b) (cm³). c) (cal/mole°K). d) (10⁻⁶/°K).

e) (10⁻⁸/°K). f) $A_o = \frac{\beta^2 B_{TV}}{C_p} \cdot 10^{-4}$

TABLE 15. Observed Pressure Derivatives of Transit Times
for Si (10^{-7} μ sec/psi)

300°K					
(110)		(1 $\bar{1}$ 0)		(001)	
Echo	$\frac{1}{N}(dt/dp)$	Echo	$\frac{1}{N}(dt/dp)$	Echo	$\frac{1}{N}(dt/dp)$
3	-2.528	10	+0.500	11	-1.019
8	-2.539			12	-1.081
				13	-0.969
				14	-0.973
	-2.534 ± 0.006		+0.500 ± 0.050		-1.011 ± 0.045
195°K					
7	-2.430	10	+0.480	10	-0.988
8	-2.485			11	-1.041
8	-2.464			12	-0.957
				12	-1.018
				13	-1.036
				14	-1.008
	-2.460 ± 0.023		+0.480 ± 0.020		-1.008 ± 0.029
77°K					
6	-2.444	10	+0.500	7	-0.932
7	-2.356			8	-0.983
10	-2.500			11	-1.001
11	-2.496			13	-1.026
				14	-1.014
	-2.449 ± 0.058		± 0.490 ± 0.010		-0.991 ± 0.033

TABLE 16. Observed Pressure Derivatives of Transit

Times for Ge (10^{-7} μ sec/psi)

300°K					
(110)		(110)		(001)	
Echo	$\frac{1}{N}(\frac{dt}{dp})$	Echo	$\frac{1}{N}(\frac{dt}{dp})$	Echo	$\frac{1}{N}(\frac{dt}{dp})$
5	-3.921	10	0.845	9	-2.453
6	-3.874	11	0.968	9	-2.426
7	-3.901	12	0.987	10	-2.416
		14	0.845	10	-2.333
		15	0.823		
	-3.899 ±0.019		+0.890 ±0.080		-2.432 ±0.016
195°K					
6	-3.671	10	0.810	8	-2.415
7	-3.606	15	0.811	8	-2.426
8	-3.686	15	0.847	9	-2.276
		15	0.905		
	-3.654 ±0.035		+0.840 ±0.040		-2.421 ±0.005
77°K					
6	-3.665	5	0.912	3	-2.420
7	-3.677	5	0.910	7	-2.468
		8	0.837	8	-2.411
		8	0.881	9	-2.479
		14	0.910		
		15	0.977		
	-3.671 ±0.006		+0.904 ±0.042		-2.415 ±0.050

TABLE 17. Observed Pressure Derivatives of Transit
Times for GaAs (10^{-7} μ sec/psi)

300°K					
(110)		(1 $\bar{1}$ 0)		(001)	
Echo	$\frac{1}{N}(\frac{dt}{dp})$	Echo	$\frac{1}{N}(\frac{dt}{dp})$	Echo	$\frac{1}{N}(\frac{dt}{dp})$
8	-4.136			8	-2.549
9	-4.101			9	-2.523
10	-4.139			9	-2.519
10	-4.102				
11	-4.161				
11	-4.034				
	-4.112 ± 0.040				-2.530 ± 0.019
195°K					
8	-4.122			8	-2.377
9	-4.074			8	-2.396
10	-4.141			9	-2.349
11	-4.026			9	-2.378
11	-4.066				
12	-4.059				
	-4.081 ± 0.039				-2.375 $\pm .017$
77°K					
10	-4.020		+0.320	9	-2.257
11	-4.057			10	-2.240
12	-4.058				
	-4.045 ± 0.028		+0.320 ± 0.016		-2.248 $\pm .008$

TABLE 18. Observed Pressure Derivatives of Transit

Times for InAs (10^{-7} μ sec/psi)

300°K					
(110)		(1 $\bar{1}$ 0)		(001)	
Echo	$\frac{1}{N}(\frac{dt}{dp})$	Echo	$\frac{1}{N}(\frac{dt}{dp})$	Echo	$\frac{1}{N}(\frac{dt}{dp})$
5	-5.947	8	+5.216	4	-1.189
6	-5.905	9	+5.348	5	-1.190
7	-6.007				
	-5.953 ± 0.042		+5.282 ± 0.066		-1.190 ± 0.001
195°K					
				4	-1.281
8	-5.670	8	+5.152	4	-1.259
9	-5.653	9	5.168	10	-1.794
7	-5.526	10	5.238	10	-1.257
	-5.616 ± 0.064		+5.186 ± 0.037		-1.273 ± 0.015
77°K					
3	-5.397	9	5.016	5	-1.131
6	-5.708	10	5.030	6	-1.120
7	-5.760				
8	-5.749				
	-5.667 ± 0.155		+5.023 ± 0.007		-1.125 $\pm .005$

TABLE 19. Observed Pressure Derivatives of Transit Times for
InSb (10^{-7} $\mu\text{sec/psi}$) *

300° K							
(001) _L		(001) _S		(111) _L		(111) _S	
Echo	$\frac{1}{N}(\frac{dt}{dp})$	Echo	$\frac{1}{N}(\frac{dt}{dp})$	Echo	$\frac{1}{N}(\frac{dt}{dp})$	Echo	$\frac{1}{N}(\frac{dt}{dp})$
5	1.064	8	-2.177	8	-8.795	8	+0.909
5	1.091	9	-2.184	9	-8.764	8	+0.898
6	1.064	10	-2.041			9	+0.946
6	1.106					9	+0.982
7	1.071					9	+0.987
7	1.083					10	+0.972
8	1.084						
	1.079 ±0.019		-2.134 ±0.066		-8.789 ±0.015		+0.940 ±0.043
195° K							
5	1.095	10	-2.028	9	-8.534	8	+1.298
5	1.077	11	-2.031	10	-8.614	9	1.275
6	1.075	12	-2.081	10	-8.642	9	1.275
7	1.061			11	-8.647	10	1.164
7	1.076						1.140
8	1.067						1.278
	1.075 ±0.013		-2.047 ±0.025		-8.609 ±0.045		1.231 ±0.065

(continued)

TABLE 19. (continued)

77° K							
(001) _L		(001) _S		(111) _L		(111) _S	
Echo	$\frac{1}{N}(\frac{dt}{dp})$	Echo	$\frac{1}{N}(\frac{dt}{dp})$	Echo	$\frac{1}{N}(\frac{dt}{dp})$	Echo	$\frac{1}{N}(\frac{dt}{dp})$
5	1.018	7	-2.523	7	-8.578	8	+1.241
6	1.035	10	-2.432	9	-8.560	9	1.316
6	1.0112	11	-2.464	10	-8.545	10	1.214
7	1.116						
	1.070		-2.473		-8.561		+1.257
	±0.045		±0.038		±0.013		±0.043

* L (longitudinal) and S (shear) polarization.

where B_T , the isothermal bulk modulus (Table 20), is

$$B_T = B_S \left[1 + \frac{8^2 VT}{C_P} B_S \right]^{-1} \quad (3)$$

An exact calculation⁷ of the small effects of misorientation for the (110) crystals has been made and a comparison of the oriented and unoriented derivatives appears in Table 21. No corrections were made for InSb. The final pressure derivatives of the effective and independent elastic constants for temperatures of 300°, 195°, and 77° appear in Table 22.

Uncertainties

The probable uncertainties in the elastic constants of the five semiconductors are dependent upon the uncertainties in the transit times (.1%), the path lengths (.02%) and the relative magnitudes of the longitudinal and shear constants. The .25% uncertainty in each observed elastic constant gives rise to those in the independent elastic constants given by:

$\frac{C_{11}}{\pm .5\%}$	$\frac{C_{12}}{\pm .85-1.25\%}$	$\frac{C_{44}}{\pm .25\%}$	$\frac{B_S}{\pm .75\%}$
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where the uncertainty in C_{12} decreases in the series Si, Ge, GaAs, InAs, and InSb.

For the (110) crystals, orientation corrections were generally less than .01, .25, and .01% respectively for C_{11} , C_{12} , and C_{44} . For Ge, a 4° misorientation necessitated changes of .7, 1.3, and .4%. Since measurements along the (001) axis are less

TABLE 20. Adiabatic and Isothermal Bulk Moduli and Pressure Derivatives

Element	T(°K)	B_s	$(\partial B_s / \partial p)_T$	B_T	$(\partial B_T / \partial p)_T$
Si	300	.9807	4.456	.9788	4.464
	195	.9878	4.369	.9874	4.374
	77	.9895	4.366	.9895	4.363
Ge	300	.7599	5.369	.7569	5.356
	195	.7655	5.059	.7650	5.050
	77	.7681	5.140	.7680	5.139
GaAs	300	.7554	4.774	.7549	4.775
	195	.7647	4.791	.7644	4.798
	77	.7741	4.859	.7741	4.856
InAs	300	.6120	4.813	.6105	4.842
	195	.6213	4.738	.6207	4.754
	77	.6300	4.542	.6300	4.546
InSb	300	.4664	4.757	.4652	4.834
	195	.4714	4.814	.4707	4.852
	77	.4794	4.915	.4794	4.917

Bulk moduli in 10^{12} dynes/cm²

TABLE 21. Effect of Orientation Corrections on Pressure Derivatives of Elastic Constants (Oriented/Unoriented)

Element	$(\frac{dC_{11}}{dp})$	$(\frac{dC_{12}}{dp})$	$(\frac{dC_{44}}{dp})$	$(\frac{dC}{dp})$	$(\frac{dC'}{dp})$	$(\frac{dB_s}{dp})$
Si	4.527	4.424	0.747	5.223	.0501	4.444
	4.528	4.420	0.746	5.220	.0540	4.456
Ge	5.317	5.339	1.366	6.694	-.0110	5.332
	5.365	5.371	1.342	6.710	-.0032	5.369
GaAs	4.907	4.708	1.092	5.830	0.099	4.774
	4.907	4.708	1.092	5.830	0.099	4.774
InAs	4.546	4.951	0.421	5.167	-0.203	4.816
	4.544	4.948	0.421	5.167	-0.202	4.813
InSb	4.550	4.860	0.461	5.166	-0.155	4.757
	-----	-----	-----	-----	-----	-----

TABLE 22. Observed Pressure Derivatives of Elastic Constants at Different Temperatures

Element	T(°K)	$(\frac{dC_{11}}{dp})$	$(\frac{dC_{12}}{dp})$	$(\frac{dC_{44}}{dp})$	$(\frac{dC}{dp})$	$(\frac{dC'}{dp})$	$(\frac{dB_s}{dp})$
Si	300	4.53	4.42	0.75	5.22	.054	4.46
	195	4.44	4.33	0.75	5.13	.055	4.37
	77	4.43	4.33	0.74	5.13	.054	4.37
Ge	300	5.32	5.34	1.37	6.71	-.003	5.37
	195	5.02	5.02	1.39	6.42	+.004	5.06
	77	5.09	5.11	1.40	6.51	-.001	5.14
GaAs	300	4.91	4.71	1.09	5.83	.100	4.77
	195	4.92	4.73	1.05	5.88	.100	4.79
	77	4.99	4.79	1.02	5.92	.100	4.86
InAs	300	4.55	4.95	0.42	5.17	-.202	4.81
	195	4.35	4.76	0.44	4.99	-.202	4.74
	77	4.52	4.92	0.41	5.13	-.202	4.54
InSb	300	4.55	4.86	0.46	5.17	-.160	4.76
	195	4.60	4.92	0.46	5.22	-.160	4.81
	77	4.71	5.02	0.45	5.32	-.160	4.92

sensitive to misorientation, although the (001) crystal was about $2\text{-}1/2^\circ$ of axis no corrections were made. The increased uncertainty in the observed elastic constants for InSb due to this omission is probably about .25%, which raises the uncertainty in the directly measured C_{11} and C_{44} to $\pm .5\%$.

Finally, when some consideration is made for the small effects of diffraction, bond and guided wave phenomena, realistic maximum uncertainties for all five semiconductors are likely to be:

C_{11}	C_{12}	C_{44}	B_S
$\pm .5\%$	$\pm 1.5\%$	$\pm .5\%$	$\pm 1.0\%$

Agreement between the observed elastic constants and those appearing in the literature is generally good and within probable uncertainties (Tables 23 through 27). The constants C_{11} and C_{44} agree within .25% and C_{12} within 1%. For Ge, apparently a large C value leads to a C_{11} and a C_{12} which are 1 and 2% higher respectively than those of other workers (Table 24). Apparently the InAs data of Gerlich shows some irregularities (Table 26).

The pressure derivatives of the elastic constants are considered to be accurate to $\pm 5\%$. That these measurements reflect the time resolution and absolute accuracy of the electronics is indicated by two facts. One, the arithmetic average of the RMS deviations in the derivatives, dt/dp , multiplied by the total pressure change, happens to correspond with the least count of the time base:

TABLE 23. Comparison of Results of the Study of the Elastic Constants of Si with Those of Other Workers*

Reference	T(°K)	C_{11}	C_{12}	C_{44}	B_s
McSkimmin	300	1.65767	.63925	.79619	.9787
	77	1.67719	.64975	.80355	.9922
Hall	300	1.6564	.6394	.7951	.9784
	4.2	1.6754	.6492	.8024	.9913
Chapman	300	1.6604	.6424	.7958	.9817
Author	300	1.6590	.6416	.7958	.9807
	195	1.6714	.6461	.8000	.9878
	77	1.6740	.6472	.8031	.9895
	4.2	1.6773	.6502	.8033	.9926

Elastic Constants in 10^{12} dynes/cm²

*For sources of data, see Table 11.

TABLE 24. Comparison of Results of this Study of the Elastic Constants of Ge with Those of Other Workers*

Reference	T(°K)	C_{11}	C_{12}	C_{44}	B_s
McSkimmin	300	1.28529	.48260	.66799	.75016
	77	1.31141	.49227	.68163	.76532
Kadyshevitch	300	1.282	.475	.668	.744
	77	1.302	.486	.678	.758
Brunner	195	--	--	.671	--
	77	--	--	.679	--
	4.2	1.299	.487	.680	.758
Author	300	1.2970	.4914	.6697	.7599
	195	1.3096	.4934	.6790	.7655
	77	1.3174	.4954	.6856	.7681
	4.2	1.3257	.4979	.6865	.7738

Elastic Constants in 10^{12} dynes/cm²

*For sources of data, see Table 11.

TABLE 25. Comparison of Results of this Study of the Elastic Constants of GaAs with Those of Other Workers*

Reference	T(°K)	C_{11}	C_{12}	C_{44}	B_s
McSkimmin	300	1.1877	.5372	.5944	.7540
Bateman	300	1.188	.538	.594	.755
Drabble	300	1.1904	.5384	.5952	.756
Garland and Park	300	1.181	.532	.594	.748
	77	1.221	.566	.599	.788
	0	1.226	.571	.600	.789
Author	300	1.1904	.5379	.5943	.7554
	195	1.2032	.5454	.6012	.7647
	77	1.2178	.5523	.6070	.7741
	4.2	1.2211	.5537	.6080	.7762

Elastic Constants in 10^{12} dynes/cm²

*For sources of data, see Table 11.

TABLE 26. Comparison of Results of this Study of the Elastic Constants of InAs with Those of Other Workers*

Reference	T(°K)	C_{11}	C_{12}	C_{44}	B_s
Gerlich	293	.8329	.4526	.3959	.5794
	77	.8465	.5001	.3968	.6156
	4.2	.8980	.5025	.3924	.6343
Trivisonno	300	.8674	.4854	.3956	.6127
	195	.8734	.4930	.3995	.6198
	77	.8955	.5025	.4031	.6335
	4.2	.8997	.5065	.4040	.6376
Author	300	.8663	.4848	.3953	.6120
	195	.8790	.4925	.3996	.6213
	77	.8918	.4992	.4038	.6303
	4.2	.8997	.5063	.4055	.6374

Elastic Constants in 10^{12} dynes/cm²

* For sources of data, see Table 11.

TABLE 27. Comparison of the Results of this Study of the Elastic Constants of InSb with Those of Other Workers*

Reference	T(°K)	C_{11}	C_{12}	C_{44}	B_s
McSkimmin	300	.6717	.3665	.3018	.4667
Slutsky and Garland	300	.6669	.3645	.3020	.4653
	200	.6744	.3670	.3076	.4695
	77	.6872	.3753	.3111	.4793
	0	.6918	.3788	.3132	.4831
Author	300	.6656	.3669	.3011	.4664
	195	.6727	.3707	.3069	.4714
	77	.6863	.3759	.3108	.4794

Elastic Constants in 10^{12} dynes/cm²

*For sources of data, see Table 11.

$$\langle \Delta(dt/dp) \rangle_{av}(P_f - P_o) = (.03 \pm .02 \times 10^{-7} \text{ } \mu\text{sec/psi}) \times$$

$$(30,000 \text{ psi}) = .09 \pm .06 \text{ nsec} \approx .1 \text{ nsec.} \quad (4)$$

Second, the bourdon gauge agrees within .01% in linearity and .5% in absolute pressure with a calibrated manganin gauge (Appendix 33). Within the 5% limits, agreement of the observed elastic constant pressure derivatives with those of other workers is reasonably good (Tables 28 and 29).

Grüneisen Parameter

The low temperature Grüneisen parameter, γ_L , is given in the quasi-harmonic approximation, Appendix C1, for an anisotropic solid by:

$$\gamma_L = \frac{\sum_{i=1}^3 \int_{\Omega} C_i^{-3/2} \gamma_i(\theta, \phi) d\Omega}{\sum_{i=1}^3 \int_{\Omega} C_i^{-3/2} d\Omega} \quad (5)$$

The mode gammas, under the assumption of non-dispersive propagation, become

$$\gamma_i = -\frac{1}{6} + \frac{B_T}{2} \frac{1}{C_i} \left(\frac{dC_i}{dp} \right)_T, \quad (6)$$

where $(dC_i/dp)_T$ is the pressure derivative of the effective elastic constant $C_i = \rho v_i^2$.

A computer program for the calculation of γ_L by numerical

TABLE 28. Comparison of the Results of this Study of the Pressure Derivatives of the Elastic Constants of Si with Those of Other Workers*

Reference	T(°K)	$\frac{dC_{11}}{dp}$	$\frac{dC_{12}}{dp}$	$\frac{dC_{44}}{dp}$	$\frac{dB_s}{dp}$
Hall	300	4.26±.21	4.15±.21	0.72±.05	4.19
Chapman	300	5.16±.23	5.06±.23	0.79±.02	5.09
McSkimmin	300	4.33±.21	4.19±.36	0.80±.10	4.24
	77	4.29	4.20	0.75	4.23
Beattie and Schirber	77	4.25±.13	4.11±.13	0.80±.02	4.16±.21
	4.2	4.19	4.02	0.80	4.08
Author	300	4.52±.23	4.42±.23	0.75±.05	4.46
	195	4.43	4.33	0.75	4.36
	77	4.43	4.33	0.74	4.36

*For sources of data, see Table 11.

TABLE 29. Comparison of the Results of this Study of the Pressure Derivatives of the Elastic Constants of Ge and GaAs with Those of Other Workers*

Reference	T(°K)	$\left(\frac{dC_{11}}{dp}\right)$	$\left(\frac{dC_{12}}{dp}\right)$	$\left(\frac{dC_{44}}{dp}\right)$	$\left(\frac{dB_s}{dp}\right)$
GaAs					
McSkimmin	300	4.63	4.42	1.10	4.49
Author	300	4.91	4.71	1.09	4.77
Ge					
McSkimmin	300	5.03±.25	4.31±.22	1.40±.07	4.55
	77	5.06	4.36	1.29	4.59
Author	300	5.32±.27	5.34±.27	1.37±.07	5.33
	195	5.06	5.02	1.39	5.03
	77	5.09	5.10	1.40	5.09

*For sources of data, see Table 11.

integration of the weighted mode gammas over the solid angle has been described by Schuele and Smith.⁸ Along with γ_L , the high temperature parameter, γ_H , where:

$$\gamma_H = \frac{\sum_{i=1}^3 \int \gamma_i(\theta, \phi) d\Omega}{\sum_{i=1}^3 \int d\Omega}, \quad (7)$$

and an integral to which the Debye temperature, θ_D , is proportional, are calculated. The input includes the independent elastic constants, C_{11} , C_{12} , and C_{44} , their pressure derivatives, and the isothermal bulk modulus. The results for the three temperatures at which pressure measurements were made are given in Table 30. γ_L ranges from .38(Ge, GaAs) to -.01(InAs).

The probable uncertainty in γ_L may be computed from the experimental uncertainties in the transit times and their pressure derivatives and the partial derivatives of γ_L with respect to these parameters by:

$$P_Y = \sqrt{\sum_{i=1}^3 \left(\frac{\partial \gamma}{\partial t_i} \right)^2 \Delta t_i^2 + \sum_{i=1}^3 \left(\frac{\partial \gamma}{\partial t'_i} \right)^2 \Delta t'_i{}^2} \quad (8)$$

where the summation is over the three modes and t'_i denotes the pressure derivative of t_i (Appendix C2).

γ_L was therefore calculated for each of six different sets of input data corresponding to a change in each experimental observable with the five others held constant. The partial deriva-

TABLE 30. High and Low Temperature Elastic Grüneisen Parameters*

	T(°K)	Si	Ge	GaAs	InAs	InSb
γ_H	300	.464	.701	.677	.415	.443
	195	.473	.681	.667	.404	.446
	77	.475	.685	.664	.377	.455
γ_L	300	.218	.380	.375	-.008	.0414
	195	.214	.379	.363	-.006	.0389
	77	.215	.380	.356	-.010	.0418

* Present work.

tives of γ_L are evaluated numerically as :

$$\left(\frac{\partial \gamma}{\partial t}\right) = \frac{\gamma(t+\Delta t) - \gamma(t)}{\Delta t} \quad (9)$$

This procedure has been carried out for the 77° data of Si and InAs (Appendix C2). The results indicate uncertainties* in γ_L for these two semiconductors which are relatively independent of the magnitude of γ_L :

$$\begin{aligned} \gamma_L(\text{Si}) &= .218 \pm .016 \\ \gamma_L(\text{InAs}) &= -.010 \pm .007 \end{aligned} \quad (10)$$

This independence is related to the fact that the pressure derivatives of the transit times reflect the resolution of the time base. The uncertainty in any (dt/dp) is about the same, independent of the value of (dt/dp).

In Table 31 are shown the low temperature Grüneisen parameters which are the product of this study and those of the thermal expansion experiment of Sparks and Swenson (S.S.).³ That the former are systematically lower than the latter is apparent (Figure 2). A linear least squares fit yields:

$$\gamma_L(\text{thermal}) = 0.97 \gamma_L(\text{elastic}) + -.25 \quad (11)$$

Such a discrepancy has been noted by SS and has given impetus to the present work. The source of the offset is still not evident,

*The normal distribution factor of .67 which should appear in Eq. 8 has been purposely omitted.

TABLE 31. Comparison of Thermal and Elastic Low Temperature Grüneisen Parameters*

	Si	Ge	GaAs	InAs	InSb
Present Work	.22	.38	.36	-.01	.04
Beattie	.22	---	---	---	---
Sparks and Swenson	.43	.65	.60	.32	.22

*For sources of data, see Table 11.

Figure 2. Comparison of γ_L from the thermal expansion measurements of Sparks and Swenson and from the present elasticity study.

although its existence for all the semiconductors under consideration is confirmed.

Both the basic elasticity and thermal expansion data show good internal and external consistency. There is agreement, where measurements overlap, with the results of other studies. For example, the thermal expansion of Ge over the range 15 to 35°K by SS agrees within experimental uncertainty with that measured by Carr, et al.,² although the correspondence for Si is not quite as good. Measurements in the actual T³ region have been done, however, only by SS. The elastic constants and their temperature and pressure dependence as observed by different workers have been shown above to exhibit similar consistency. With the apparent validity of both thermal and elastic data in mind, some consideration may still be given to the experimental conditions which might give rise to the discrepancy.

First to be considered is the systematic deviation introduced by an error in the calibration of the thermal expansion apparatus. An inductance bridge was used by SS to measure the change in length of the sample with temperature. The change in output voltage, dV/dT , due to a length change, dL/dT , is given by:

$$\frac{dL}{dT} = k \frac{dV}{dT} \quad (12)$$

The calibration constant, k , was determined from a plot of output voltage as a function of path length (as measured with a micrometer). A linear dependence to a maximum change of about 1mm was

observed at room temperatures. A change of calibration of less than 1% was observed at 4.2°K for where length changes in the angstrom region occur. Since β (hence, γ_L) is proportional to k :

$$\beta = 3\alpha = 3 \left(\frac{1}{L} \frac{dL}{dT} \right)$$

$$\gamma_L \sim \beta = \frac{1}{L_o} \left(\frac{dL}{dT} \right) = \frac{1}{L_o} \left(k \frac{dV}{dT} \right) \quad (13)$$

an error in calibration, Δk , would lead to an observed thermal expansion given by

$$\beta_{\text{obs}} = \beta_{\text{true}} + \frac{\Delta k}{L_o} \left(\frac{dV}{dT} \right) \quad (14)$$

Evidence for the absence of such an error is of two kinds: (1) the agreement with the results of workers mentioned above and (2) internal consistency; the same β was observed for a sample of Ge before and after it had been cut in half.

Another possible source of an offset error in β would be a T^3 dependence within the apparatus itself, such as in a spacer, which was not accounted for. That this is simply another form of "calibration" error is shown by the following:

$$\left(\frac{dL}{dT} \right)_{\text{obs}} = \left(\frac{dL}{dT} \right)_{\text{sample}} + \left(\frac{dL}{dT} \right)_u$$

$$= (a_s L_s T^3 + a_u L_u T^3) \quad (15)$$

$$\gamma_L \sim \beta = a_s T^3 \left(1 + \frac{a_u L_u}{L_s} \right) \quad (16)$$

The evidence for the absence of this type of error rests directly on the agreement between the two Ge measurements and indirectly on the fact that the sample lengths (~ 10 cm) were apparently greater than other parts (e.g. a 2cm quartz spacer) which could exhibit T^3 dependence.

It has been observed that since the elastic data was taken at 77°K, perhaps helium temperature measurements of elastic constants are necessary.³ The analysis in Appendix C2 indicates that in order for γ_L to increase to the values determined by the thermal expansion experiment, large changes in derivatives would be necessary. Since only small changes occur in the elastic constants between 300° and 4.2° and in their pressure derivatives between 300° and 77°, a simple extrapolation is insufficient. That measurements are necessary in the T^3 region may be true. However, pressure measurements on Si by Beattie and Schirber⁹ indicate no precipitous change between 77° and 4.2°K, in fact almost no change at all.

Finally, the discrepancy may be indicative of a failure of the Debye model to adequately describe these semiconductors, since no basis in theory for the difference exists (Appendix C1 and 3). Since the electronic¹⁰ and anharmonic¹¹ contributions to the internal energy would not be expected to cause unusual behavior, independent of detailed lattice structure the semiconductors should

behave at low enough temperatures as a quasi-harmonic, anisotropic continuum. That this is somewhat true is indicated by the excellent agreement between Debye temperatures, θ_D , as calculated from thermal and elastic data (Table 32). Although the semiconductors diverge at intermediate temperatures (the negative expansion region) from Debye-like behavior, both the specific heat and the thermal expansion exhibit at extremely low temperatures a pronounced T^3 dependence. According to theory, the acoustic measurements represent the effects of a portion of the lattice frequency spectrum which gives rise to this T^3 region; the model itself has been shown for many solids to adequately deal with this aspect. Thus, real disagreement for the semiconductors studied between elastic and thermal parameters would be theoretically significant.

Since single crystal semiconductors with controlled doping levels have, in general, only recently been prepared, the effects of substitutional and electronic impurities are not completely known. Although there has been no systematic study of the effects of impurities on elastic and thermal properties, some scattered data, specifically for Si and Ge, exist. The results of the experiment by Hall¹² given in Table 33 are representative of impurity effects in elastic properties. The data indicates that a change in impurity level from 10^{-4} ppm to 10^2 ppm changes elastic constants by as much as 3%. There is quantitative agreement with similar results for Si and Ge by Beilin, et al.¹³ θ_D (elastic) and γ_L (elastic), calculated by the present investigator from Hall's data, also appear in the Table. The doping leads to a reduction

TABLE 32. Elastic and Calorimetric Debye Temperatures*

θ_D (°K)	T (°K)	Si	Ge	GaAs	InAs	InSb
Elastic (Author)	300	646.0	370.6	344.0	248.0	201.7
	195	647.9	372.9	345.6	249.5	203.2
	77	648.9	375.0	347.4	251.1	205.1
	4.2	649.0	375.2	347.8	251.5	206.0
Elastic (Others)	300	--	--	--	249	--
	77	647.8	374.0			
	4.2	648.7	--	345±3	234	205.8±1
Calorimetric		645	374	346.7±1.5	250.9±.7	206.6±.6

* For sources of data, see Table 11.

TABLE 33. The Effect of Electrically Active Impurities on the Elastic Properties of Si as Determined by Hall*

Property	Pure Si	Doped Si ($\sim 2 \cdot 10^{19}$ P/cm ³)
C_{11}	1.6754	1.6382
C_{12}	.6492	.6684
C_{44}	.8024	.7797
C	1.9647	1.9330
C'	.5131	.4849
B_T	.9913	.9917
dC_{11}/dp	4.258	4.179
dC_{12}/dp	4.150	4.166
dC_{44}/dp	0.722	0.742
dC/dp	4.926	4.915
dC'/dp	0.054	0.0065
dB_T/dp	4.186	4.170
γ_H	.4537	.4599
γ_L	.2043	.1978
$\theta_D (^{\circ}K)$	648.7°	636.2°

Elastic Constants in Units of $10^{12}/\text{cm}^2$

* Ref. 12.

in θ_D (elastic) of 12.5° (or 2%) and in γ_L of .0065(or 3%). A similar reduction in θ_D (thermal) has been observed in low temperature specific heat measurements on pure and doped Ge.¹⁴ It would be expected that the change in the lattice properties which reduces θ_D would increase the thermal expansion. An increase of about 5% in β , associated with the weakening of the covalent bonds, has been seen in high temperature thermal expansion of Ge; however, the difference in β between pure and doped samples decreased with temperature until it becomes zero around 90°K .¹⁵ The low temperature behavior is unknown. Thus, although γ_L (elastic) has been shown to decrease with doping, the behavior of γ_L (thermal) has not been determined. Finally, the experimental evidence indicates that an impurity effect capable of significantly changing γ_L (thermal) would probably manifest itself in the Debye temperature and the elastic constants.

Compressional Equation of State

Compression data at high pressure may be obtained by a number of techniques. The dependence of volume on pressure may be measured directly or obtained indirectly, e.g., from shock wave studies. One convenient means, however, is to extract information from low pressure ultrasonic data. The results of sound velocity measurements at pressures normally less than a few kilobars can be reliably extrapolated to pressure of hundreds of kilobars in continuous, analytic functions. The means and rationale have been

developed by several authors.

The compressional equation of state for cubic solids

$$P = P(V/V_0) = \left[\frac{B_0}{B'_0} \left(\frac{V_0}{V} \right)^{B'_0} - 1 \right] \quad (17)$$

where:

$$B_0 = B_T(T, V_0) \quad (\text{isothermal bulk modulus})$$

$$B'_0 = \left(\frac{\partial B_T}{\partial P} \right)_{T, V=V_0}$$

$$V_0 = V(T, P=0) \quad (\text{molar volume at zero pressure}) ,$$

has been derived by Murnaghan.¹⁶ He assumed that both the adiabatic, B_S , and isothermal, B_T , bulk moduli vary linearly with pressure:

$$B_T(P) = B_T(P=0) + B'_T P$$

$$B_S(P) = B_S(P=0) + B'_S P \quad (19)$$

Since acoustic measurements at different temperatures yield the adiabatic bulk modulus, $B_S(V, T)$, and its pressure derivative, $(\partial B_S(V, T)/\partial P)_T$, a means of reducing the acoustic data to a constant temperature and volume basis is necessary. The isothermal bulk modulus, $B_T(V)$, may be calculated from the adiabatic, $B_S(V)$, according to the familiar thermodynamic relation:

$$B_T(V) = B_S(V) \left[1 + \alpha B_S(V) \right]^{-1} \quad (20)$$

where

$$A = \frac{\beta^2 VT}{C_p}$$

β = thermal expansion

C_p = molar heat capacity at constant pressure.

A relation between the pressure derivatives of the adiabatic and isothermal moduli, which proceeds from differentiation of the above expression, has been given by Overton:¹⁷

$$\begin{aligned} \left(\frac{\partial B_T(V)}{\partial P} \right)_T &= \left(\frac{\partial B_S(V)}{\partial P} \right)_T + A \left(1 - \frac{2}{\beta B_T} \left(\frac{\partial B_T}{\partial P} \right)_T - 2 \left(\frac{\partial B_S}{\partial P} \right)_T \right) \\ &+ A^2 \left(\left(\frac{\partial B_S}{\partial P} \right)_T - 1 - \frac{1}{\beta^2} \left(\frac{\partial \beta}{\partial T} \right)_P \right) \end{aligned} \quad (21)$$

The basic data necessary for the evaluation of this expression appear in Table 14. Since the elastic constants but not their temperature derivatives were measured at different temperatures, the small temperature derivative of B_T has been approximated. A least squares fit of B_T as a function of T (Table 34),

$$B_T = b_0 + b_1 T + b_2 T^2, \quad (22)$$

was performed. Thus,

$$\left(\frac{\partial B_T}{\partial T} \right)_P = b_1 + 2b_2 T. \quad (23)$$

The condition $(\partial B_T / \partial T)_P = 0$ at $T = 0$ has not been imposed.

TABLE 34. Calculation of $(\partial B_T / \partial T)_p$

Element	T(°K)	$B_T(\text{exp})$	$B_T(\text{Calc})^a$	$(\frac{dB_T}{dT})_p^b$	$\frac{1}{B_T}(\frac{dB_T}{dT})_p$
Si ¹	300	.9788	.9799	-6.94	-7.08x10 ⁻⁵
	195	.9874	.9864	-4.83	-4.90
	77	.9895	.9907	-2.47	-2.49
	4.2	.9926	.9920	--	--
Ge ²	300	.7569	.7573	-6.26	-8.26
	195	.7650	.7636	-5.53	-7.29
	77	.7680	.7696	-4.79	-6.22
	4.2	.7738	.7730	--	--
GaAs ³	300	.7549	.7547	-11.3	-14.9
	195	.7644	.7650	-8.53	-11.1
	77	.7741	.7733	-5.44	-7.04
	4.2	.7762	.7766	--	--
InAs ⁴	300	.6105	.6106	-8.77	-14.4
	195	.6207	.6202	-8.75	-14.1
	77	.6300	.6307	-8.74	-13.9
	4.2	.6374	.6371	--	--
InSb ⁵	300	.4652	.4651	-12.9	-27.9
	195	.4707	.4709	-11.5	-24.5
	77	.4794	.4791	-9.9	-20.7
	4.2	.4851	.4852	--	--

a). (10¹² dynes/cm²)

b). (10⁵ dynes/cm² °K)

* Fit to $B=B_0+B'T+B''T^2$ implies that the condition

$(\frac{dB}{dT})_{T=0} = 0$ was not imposed.

$$1. B(\text{Si}) = .9920 - (.923 \cdot 10^{-5})T - (1.003 \cdot 10^{-7})T^2$$

$$2. B(\text{Ge}) = .7732 - (4.28 \cdot 10^{-5})T - (0.330 \cdot 10^{-7})T^2$$

$$3. B(\text{GaAs}) = .7767 - (3.43 \cdot 10^{-5})T - (1.307 \cdot 10^{-7})T^2$$

$$4. B(\text{InAs}) = .6375 - (8.73 \cdot 10^{-5})T - (.007 \cdot 10^{-7})T^2$$

$$5. B(\text{InSb}) = .4856 - (8.86 \cdot 10^{-5})T - (0.683 \cdot 10^{-7})T^2$$

TABLE 35. 25 Kilobar Compression Data (300°): V/V_0

P(kbar)	Si	Ge	GaAs	InAs	InSb
0	1.0000	1.0000	1.0000	1.0000	1.0000
2.5	0.9975	0.9968	0.9968	0.9960	0.9948
5.0	0.9950	0.9936	0.9936	0.9921	0.9897
7.5	0.9925	0.9905	0.9905	0.9883	0.9848
10.0	0.9901	0.9875	0.9874	0.9846	0.9800
12.5	0.9877	0.9845	0.9844	0.9809	0.9754
15.0	0.9853	0.9816	0.9815	0.9773	0.9708
17.5	0.9830	0.9788	0.9786	0.9738	0.9664
20.0	0.9807	0.9759	0.9757	0.9704	0.9621
22.5	0.9784	0.9732	0.9729	0.9671	0.9580
25.0	0.9762	0.9705	0.9702	0.9638	0.9539*

* Above Phase Transition Pressure.

Figure 3. The compression of the semiconductors from ultrasonic data according to the Murnaghan logarithmic equation of state.

TABLE 36. General Compression Data (300°): V/V_0

P(kbar)	Si	Ge	GaAs	InAs	InSb
0	1.0000	1.0000	1.0000	1.0000	1.0000
25	0.9762	0.9705	0.9702	0.9638	0.9539*
50	0.9551	0.9457	0.9448	0.9341	--
75	0.9364	0.9245	0.9229	0.9090	--
100	0.9195	0.9060	0.9036	0.8874*	--
125	0.9041	0.8896*	0.8864	--	--
150	0.8900	--	0.8710	--	--
175	0.8771	--	0.8570	--	--
200	0.8651*	--	0.8442	--	--
225	--	--	0.8324	--	--
250	--	--	0.8215*	--	--

*Above Phase Transition Pressure (Minomura, S. and H. G. Drickamer, J. Phys. Chem. Solids, 23, 451 (1927))

$$\beta B_T \neq \text{constant.} \quad (26)$$

The temperature independence of the compression data is attributed then to the inherently small changes in B_T and $(\partial B_T / \partial P)_T$ with temperature and the relative insensitivity at low pressures ($P \lesssim B_T$) of the Murnaghan equation to changes in these quantities.

The differences in behavior exhibited by the semiconductors can be made more apparent by a reduction of the bulk moduli to a constant volume basis. Under the assumption that $(\partial^2 B / \partial^2 V)$ is small, it follows that

$$B(V', T) = B(V, T) + \left(\frac{\partial B}{\partial V} \right) (V' - V) = B(V, T) \left[1 - \left(\frac{\partial B}{\partial P} \right) \left(\frac{V' - V}{V} \right) \right] \quad (27)$$

For $V' = V(T=0) = V^0$,

$$B(V^0, T) = B(V, T) \left[1 - \left(\frac{\partial B}{\partial P} \right) \left(\frac{V^0 - V}{V} \right) \right] \quad (28)$$

$B_T(V)$ and $B_T(V^0)$ are given in Table 37 and shown as functions of temperature for the semiconductors in Figure 4. The curves for Ge and GaAs lie within the same error bars. Two effects are indicated by the Figure. First, the greater curvature in $B_T(V)$ associated with the more ionic compounds; second, the retention of curvature for the ionic compounds when moduli are reduced to a constant volume basis. This second effect is clearly demonstrated by the comparison of Ge and GaAs in Figure 5. In this case, the two semiconductors are isoelectronic and have approximately the same reduced mass, yet the temperature derivatives of $B_T(V_0)$ are quite different:

$$\left(\frac{\partial \ln B_T(V_0)}{\partial T} \right)_P (\text{Ge}) \sim 10^{-6} \quad (29a)$$

TABLE 37. Volume Dependent and Independent Bulk Moduli

Element	T(°K)	($\Delta V/V_o$)	$B_S(V)$	$B_T(V)$	$B_S(V_o)$	$B_T(V_o)$
Si	300	6.6	.9807	.9788	.9836	.9817
	195	0.8	.9878	.9874	.9881	.9877
	77	-0.8	.9895	.9895	.9892	.9892
	4.2	0.0	.9926	.9926	.9926	.9926
Ge	300	29.4	.7599	.7569	.7719	.7688
	195	12.5	.7655	.7650	.7703	.7698
	77	0.0	.7681	.7680	.7681	.7680
	4.2	0.0	.7738	.7738	.7738	.7738
GaAs	300	33.2	.7554	.7549	.7674	.7669
	195	11.8	.7647	.7644	.7690	.7687
	77	-1.5	.7741	.7741	.7735	.7735
	4.2	0.0	.7762	.7762	.7762	.7762
InAs	300	27.0	.6120	.6105	.6200	.6185
	195	15.0	.6213	.6207	.6215	.6251
	77	6.0	.6300	.6300	.6320	.6320
	4.2	0.0	.6374	.6374	.6374	.6374
InSb	300	26.9	.4664	.4652	.4724	.4712
	195	13.7	.4714	.4707	.4745	.4738
	77	6.9	.4794	.4794	.4810	.4810
	4.2	0.0	.4851	.4851	.4851	.4851

Bulk Moduli in 10^{12} dynes/cm².

Figure 4. The observed temperature dependence of the isothermal bulk moduli.

Figure 5. A comparison of the bulk moduli of Ge and GaAs.

$$\left(\frac{\partial \ln B_T(V_0)}{\partial T} \right)_p (\text{GaAs}) \sim 10^{-4} \quad (29b)$$

Since the contribution of the zero point energy to the total energy dominates at low temperatures, $B_T(V_0)$ approaches a constant value. With an increase in temperature, however, the anharmonic contributions within the vibrational spectrum lead to the softening of the solid manifested by a decrease in $B_T(V_0)$. The greater degree of such an effect for the ionic solids would also be indicated by a strong temperature dependence in the Grüneisen parameter, represented in the difference between the limiting high and low temperature values.

Elastic Constants and Microscopic Models

In general, the elasticity, cohesive energies, and detailed lattice dynamical properties of crystalline solids may be derived from the analytic potential energy function associated with a given model. Beginning, however, with the early work of Born,²⁰ successful descriptions of the lattice properties of ionic solids have been attained using parametric potential energy functions. In these cases, the interatomic forces which bind atoms in crystals are treated in terms of parameters which are often arbitrary and unrelated to the fundamental electronic properties of the crystal. Because of the success of this approach to ionic (and metallic) solids, the trend has been to accommodate the models to covalent structures by the introduction of more parameters, until their number has often approached or exceeded the number of available experimental quanti-

ties required to evaluate them.²¹ Further, the interest of theorists in diamond-like crystals has been primarily in the collective electron behavior of semiconduction; thus, no quantum mechanical treatment has been done which might relate the force constants or otherwise alleviate the situation. The elastic constants of mixed ionic-covalent crystals have been used mostly, therefore, as fitting parameters in conjunction with optical, infrared and slow neutron dispersion data. In this context, although no detailed calculations based on the results of this work will be made, some consideration will be given to the significance of the few theoretical treatments of elastic properties which yield explicit relations between the elastic and interatomic force constants. The α and β used are not necessarily the same in each model.

Born and von Kármán^{22,23} in a rigid ion (RI) calculation for diamond used two nearest neighbor (1NN) force constants, α (central) and β (non-central), with the result:

$$\begin{aligned} C_{11} &= \frac{\alpha + \beta}{4a} \\ C_{12} &= \frac{\alpha - 2\beta}{4a} \\ C_{44} &= \frac{2/3\beta(\alpha + 5\beta)}{4a(\alpha + \beta)} \end{aligned} \quad (30)$$

where a is the NN distance. These elastic constants are related by the "Born relation",

$$\frac{4C_{11}(C_{11} - C_{44})}{(C_{11} + C_{12})^2} = 1 \quad (31)$$

An independent development of the Born RI model has been reported by Keating²⁴ with the elastic constants given by:

$$\begin{aligned} C_{11} &= \frac{\alpha + \beta}{4a} \\ C_{12} &= \frac{\alpha - \beta}{4a} \\ C_{44} &= \frac{3\beta(\alpha + \beta/4)}{4a(\alpha + \beta)} \end{aligned} \quad (32)$$

with the relation

$$\frac{4C_{11} C_{44}}{(3C_{11} + C_{12})(C_{11} - C_{12})} = 1 \quad (33)$$

In any case, where the RI model has been applied to the lattice dynamics of diamond-like crystals, the results have not been inspiring. Agarwal²⁵ used five force constants in treating diamond, while Herman²⁶ and Pope²⁷ used twenty-one for Ge. These works indicate that the inclusion of interactions out to at least the sixth neighbors necessary to produce a good fit to dispersion data yields non-unique values of force constants.

As an improvement on the RI model, the shell model (SM) which treats deformable ions, has been proposed by Dick and Overhauser,²⁸ developed by Cochran,²⁹ Cowley and others,³⁰ and quantum mechanically justified by Tolpygo³¹ and Sinha.³² Slow neutron spectra (C (Ref. 33), Si (Ref. 34), Ge (Ref. 35), GaAs (Ref. 36)) have been analyzed in terms of the SM: for C by Tolpygo,³⁷ C and Si by Kucher³⁸ and Sirota,³⁹ for Ge by Demindenko,⁴⁰

for all four by Dolling and Cowley,⁴¹ and for many ZnS compounds by Kaplan and Sullivan.⁴² These studies have consistently indicated that in its lowest order approximation, the SM cannot account for the experimental observations. The inclusion of higher order interactions leads to parameters which compensate for the deficiency of the model by assuming non-unique or unrealistic values. An illustrative example is the work of Kaplan and Sullivan.⁴² Unable to obtain a fit with 1NN force constants, they included small, realistic 2NN values and obtained multiple fits with ionic charges varying between +.5 and -2.0. With no theoretical criteria by which a proper fit may be chosen, the resulting inability to distinguish between strongly ionic or covalent bonding is a serious shortcoming.

Since the formulations of the RI and SM generally have been done in terms of the cartesian coordinates of the basic crystal structure, translational and rotational invariance have been imposed as auxiliary conditions. Further, redundancies among coordinates of necessity were removed explicitly. A more natural approach to the tetrahedrally bonded diamond structure (which is still basically cubic) involves force constants which describe changes in bond lengths, interbond angles and other valence coordinates. This valence force field model (VFFM) involves force constants which need not be related to insure invariance or eliminate redundancies. Further, because of the degree of saturation of covalent bonds, the bond stretching force constants should be somewhat independent of environment, i.e., a C=C bond should have the same constant in a molecule or a crystal.²⁴

The VFFM for diamond has been proposed by Musgrave and Pople⁴³ and calculations of phonon dispersion curves based on it made with good results by McMurry, et al.⁴⁴ for diamond and Nusimovici, et al.⁴⁵ for CdS.

Using valence coordinates and an assumed form of the potential energy function, Vukcevic⁴⁶ has derived explicit forms for the elastic constants and their pressure dependences. Since he excludes long range interactions by employing only 1NN force constants, the results are applicable only to diamond:

$$\begin{aligned} C_{11} &= \alpha + 2\beta \\ C_{12} &= \alpha - \beta \\ C_{44} &= \alpha + \beta/2 \end{aligned} \quad (34)$$

where α (central), β (non-central). The elastic constants are related by

$$\frac{5(C_{11}-C_{12})}{9(C_{11}-C_{44})} = 1 \quad (35)$$

Keating²⁴ following the lead of Musgrave and Pople⁴³ used the VFFM. After concluding that all purely 1NN interactions are central only, he used one 1NN central force constant and a 2NN non-central constant to obtain

$$\begin{aligned} C_{11} &= \frac{\alpha + 3\beta}{4a} \\ C_{12} &= \frac{\alpha + \beta}{4a} \\ C_{44} &= \frac{\alpha + \beta}{a(\alpha + \beta)} \end{aligned} \quad (36)$$

which are related by

$$\frac{2C_{44}(C_{11} + C_{12})}{(C_{11} - C_{12})(C_{11} + 3C_{12})} = 1 \quad (37)$$

Both Vukceвич⁴⁶ and Keating²⁴ avoided the non-physical results inherent to Born's original approach.²³ In Keating's calculation the bulk modulus is still a function of the non-central constant, although this is allowable since the 2NN non-central interaction of the VFF contributes to the strain energy when the bond length is changed but the bond angles are not.²⁴

An extension of Keating's work to heteropolar crystals must take into account the long range coulomb forces associated with an effective charge. By adding a screened rigid-ion effective charge at the lattice site (the magnitude of which is determined from optical data), Martin^{47,48} has been able to calculate the elastic constants of all the diamond and zinc blende crystals:

$$\begin{aligned} C_{11} + 2C_{12} &= \frac{\sqrt{3}}{4a} (3\alpha + \beta) - .355 SC_0 \\ C_{11} - C_{12} &= \frac{\sqrt{3}}{4a} \beta + 0.053 SC_0 \\ C_{44} &= \frac{\sqrt{3}}{4a} (\alpha + \beta) - .136 SC_0 - C_5^2 \end{aligned} \quad (38)$$

where

$$C = \frac{\sqrt{3}}{4a} (\alpha + \beta) - .266 SC_o$$

$$C_o = \frac{e^2}{a^2}$$

$$\zeta = C^{-1} \frac{\sqrt{3}}{4a} (\alpha - \beta) - .294 SC_o$$

and S is an effective charge parameter related to the optical mode splitting. In this case

$$\frac{2C_{44}(C_{11} + C_{12} - C'')}{(C_{11} - C_{12})(C_{11} + 3C_{12} - 2C'') + .831 C''(C_{11} + C_{12} - C'')} = 1 \quad (39)$$

reduces to Keating's form for neutral bonding ($C''=0$).

In Table 38 the relations between the elastic constants for the models discussed are summarized and evaluated for the 4.2°K data of the present study. The table gives an indication of the basis for some tentative conclusions about the models. Born's RI must be considered inadequate for the highly covalent diamond for which it was developed. The agreement for Si and Ge is accidental since they have less saturated bonds; this is even more true of the III-V compounds since they do not conform to Born's prediction that

$$C_{12} - C_{44} < 0 \quad (40)$$

Besides the failure of Born's model to adequately treat the elastic constants, it is parametric, α and β are not derived and cannot be used to predict other mechanical or thermal properties.

TABLE 38. Relations Between Elastic Constants for Different Models of Diamond-like Crystals

Born: (Ref. 22)

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

Born (Keating): (Ref. 23)

$$\frac{4C_{11} C_{44}}{3C_{11} + C_{12})(C_{11} - C_{12})} = 1$$

Vukceovich: (Ref. 45)

$$\frac{5(C_{11} - C_{12})}{9(C_{11} - C_{44})} = 1$$

Keating: (Ref. 23)

$$\frac{2C_{44}(C_{11} + C_{12})}{(C_{11} - C_{12})(C_{11} + 3C_{12})} = 1$$

Martin: (Ref. 46)

$$\frac{2C_{44}(C_{11} + C_{12} - C'')}{(C_{11} - C_{12})(C_{11} + 3C_{12} - 3C_{12} - 2C'') + .832C''(C_{11} + C_{12} - C'')} = 1$$

TABLE 39. Relations Between Elastic Constants for Different Models of Diamond-like Crystals: Evaluated for the 4.2° K Data of the Present Work

	B.	B.(K.)	V. .	K.	M.
C(diamond)*	1.49	1.29	1.05	1.00	1.00
Si	1.08	1.09	.65	.99	.99
Ge	1.02	1.02	.72	.94	.94
GaAs	(.95)	(.95)	(.60)	(.89)	.93
InSb	(.92)	(.90)	(.46)	(.86)	.92
InAs	(.90)	(.86)	(.44)	(.83)	.92

*McSkimmin and Bond, Phys. Rev., 105, 116 (1957).

The virtue of Vukceвич's approach⁴⁶ (which gives good agreement for diamond for which it is most appropriate) is that it also produces expressions for the strain dependence of the elastic constants of diamond.

The VFF approach of Keating²⁴ to the covalent diamond structure and Martin to the heteropolar zinc blende are the most interesting. Although basically parametric, Martin's expressions have been used by him⁴⁸ to correlate the elastic constants of a great many diamond and zinc blende crystals on an ionicity scale* developed by Phillips.⁴⁹

In Figure 7 is shown the ratio of the non-central to central force constants β/α for many zinc blende compounds as a function of ionicity as determined by Martin.⁴⁷ As is apparent, the non-central contribution to the elastic constants is largest for the most covalent crystals and decreases to zero for purely ionic solids in the manner

$$\frac{\beta}{\alpha} \sim 1 - f_i \quad 0 < f_i < 1$$

Since the relation between the elastic constants and the effective charge was shown by Martin⁴⁷ to be satisfied to within about 10% for many crystals, the elastic constants for any zinc blende crystal can be empirically predicted with the same expected accuracy. Only

*The scale, based on optical spectroscopic data, has been used successfully to correlate a host of properties associated with the chemical bond;⁴⁹ included are the type of electron transitions under optical excitation⁵⁰ and basic crystal structure (Fig. 6). It has been shown that those and only those crystals with an ionicity, f_i , less than a critical value are stable in a tetrahedrally coordinated structure.

Figure 6. The dependence of properties on the ionicity of the bond.

Figure 7. Ratio of the non-central and central force constants in Keating's model for diamond-like crystals as a function of the ionicity of the chemical bond.

the measured bond length and calculated ionicity need be used.

DISCUSSION AND CONCLUSIONS

Although the nature of the covalent bond is not fully understood, much of the behavior of the tetrahedrally coordinated solids which exhibit this kind of bonding can at least qualitatively be explained. Specifically, the origin of the macroscopic thermodynamic properties can be seen to be primarily structural, i.e., the result of the motion and interactions at the lattice sites. Although the bonding is obviously an electronic property, it is not the result of the kind of collective electron behavior which in metals strongly affects or dominates thermal properties. Thus, the behavior of diamond-like solids can be explained in part in terms of the effect of atomic motion on an unspecified anharmonic potential. Although specific lattice dynamical and elastic properties could be derived if the analytic form of such a potential were known, the trend has not been such as would lead to the development of such a function. Understandably, theoretical interest in the diamond-like semiconductors has been primarily concerned with the electronic properties related to semiconduction. Thus, theoretical treatments have primarily involved band and pseudopotential calculations. The alternate approach has been the treatment of optical and neutron spectra by shell model calculations. However, enough evidence exists to indicate that the covalent bond is an entity in itself and not amenable to treatment as if it were metallic (the pseudo-potential approach) or ionic (the shell model approach) in nature. Thus, the treatment of covalency as a perturbation is an

attempt to alter basic character and, by necessity, involves large numbers of OPW's or shell model parameters to obtain minimal success.

The more fruitful approach seems to be one tailored specifically for the covalent tetrahedral structures and includes the development of an analytic potential energy function (which is easy to say). For this reason, the development of the VFFM is significant; by the use of valence coordinates, the problems of formalism are eliminated and the physics of the interactions may be treated directly. Thus, a proposed potential energy function can be formulated and tested through a detailed calculation of elastic properties (including their strain dependence) and other lattice properties. This is what Vukcevic⁴⁶ has begun for the homopolar diamond. The next logical step would be the calculation within the context of Martin's model⁴⁷ of the strain dependence elastic properties of the heteropolar zinc blende crystals. Thus, the details of the lattice spectrum and the temperature dependence of γ_G could be calculated for any diamond-like solid. However, there is at present no model to account quantitatively for γ_G at any temperature; in any case, γ_L should be independent of the detailed lattice structure and be represented by both thermal and elastic data. Thus, the problem of the observed difference between γ_L (thermal) and γ_L (elastic) is primarily an experimental one.

The absence of unquestionably reliable data (in terms of confirmed thermal expansion and high pressure elastic data at the low temperature temperatures) leaves the discrepancy an open

question which suggests further study which includes:

- (1) pressure measurements in the T^3 region (which implies a refinement of methods such as the FM technique)
- (2) remeasurement of the thermal expansion (with direct calibration in the range where measurements are actually made).

One course of action suggested for this investigator is the systematic investigation of the low temperature Grüneisen parameter of metals, oxides, ionic and covalent solids based on the most current and reliable low temperature elastic and thermal data. Since the small differences between γ_L (elastic) and γ_L (thermal) observed in other studies have generally been attributed to experimental uncertainty, it would be of interest to determine γ_L for many solids by exactly the same procedure to eliminate that as one variable. The discrepancy observed in this study could then be judged in the context of a broader picture.

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Appendix A appears as a separate technical report:

"The Measurement of the Pressure Derivatives of Elastic
Constants by a Frequency Modulation Technique: An
Evaluation"

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Atomic Energy Commission

C00-623-168

January, 1971

APPENDIX B1

Pressure System

The system for the generation, control and measurement of the high pressures needed is a simple, straightforward one using commercial components (Figure 1B). A two-stage air-driven compressor is used. The pump is actuated by filtered, compressed air delivered from a reservoir. Dry, oil-less helium gas from a standard cylinder (1000-2500 psi) is compressed to a maximum 30,000 psi and delivered to the pressure vessel by a simple system of regulating valves and high pressure tubing. Pressure is monitored by a two-turn bourdon tube gauge. The components are listed in Table 1B.

-96-

Figure 1B. Schematic diagram of pressure system.

TABLE 1B. Pressure system components.

COMPRESSOR (American Instrument; No. 46-14021, horizontal, two stage, diaphragm type; (30,000 psi)).

REGULATING VALVES (Scientific Systems; 60,000 psi, hard seat valves; torque handles).

GAUGE (Heise Bourdon Tube; 16", 2 turn, thermally compensated, 30,000 psi).

TUBING and FITTINGS (High Pressure Equipment).

AIR COMPRESSOR (1 1/2 HP; 150 psi; 50 CFM, 30 gal.).

APPENDIX B2

Pressure Vessel Design

Pressure vessels based on two different designs have been used in the low-temperature pressure derivative experiment. Each with essentially the same dimensions was constructed from Beryloc-25 by similar processes of machining and heat-treating. Fracture under pressure of a vessel based upon the early design led to slight but significant design and fabrication changes. General features and closure seals were identical.

Received in half-hard heat treatable temper, rough machined, its residual stresses resulting from cold work relieved by heat treatment, each rod was finish machined into the final form of the pressure vessel (Figure 2B). Closure for the vessel was achieved by a V-ring and groove assembly (Figure 3B) which extruded indium against the wall of the vessel and the screw-in plug. Small leaks at low temperatures and high pressure were eliminated with the addition of an indium O-ring and Berylco armor ring. Electrical leads were brought out through the plug using conical stainless-steel feed-throughs, each coated with a machined 5 mil epoxy layer. After each receptacle was tinned with indium and a second, uncured layer of epoxy applied to each cone, the cones were seated under oil pressure of approximately 45,000 psi. These modified pipestone feed throughs, if carefully made, had a reasonable lifetime under pressure and temperature cycling. Room temperature seals of the same type have a manifold increase in lifetime.

The relevant design factors of the early vessel which failed

Figure 2B. Pressure vessel and closure rings.

ARMOR RING

INDIUM

UPPER
SLIP RING

V-RINGS

LOWER
SLIP RING

Figure 3B. Original and redesigned pressure vessels.

and the one presently used are indicated in Table 2B. Maximum stress values have been calculated from rule-of-thumb formulae¹

$$\tau \text{ (shearing stress)} = p_i \left(\frac{k^2}{k^2 - 1} \right)$$

$$\sigma_t \text{ (tensile stress)} = p_i \left(\frac{k^2 + 1}{k^2 - 1} \right)$$

$$\sigma_R \text{ (radial stress)} = p_i$$

where p_i is the hydrostatic pressure and k is the ratio of inner to outer diameters. Indicated also in Table 2B are the different stresses generated by 30,000 and 50,000 psi internal pressures and the internal pressures at which a given stress equals the maximum stress for the material employed. As indicated, Beryloco 25 exhibits high elastic strength (the highest of any Cu base alloy) and, further, has high endurance and resistance to distortion due to greater strain relief.² Both designs have calculated stresses at the working pressure which are reasonable fractions of the limiting values of the strength of the material. However, the vessel based on the earlier design failed.

With a relatively short load-cycle history, an initial pressurization to 45,000 psi at room temperature, and about 50 pressurizations to 30,000 psi at temperatures down 77°K, the vessel fractured under oil pressure of 50,000 psi. Apparently a crack at the intersection of the interior base and sidewall propagated plastically

TABLE 2B: Pressure Vessel Design Data

(10 ³ psi)	p	Γ	σ_t	σ_R
Vessel 1	30.0	37.0	44.1	30.0
(k=2.29)	50.0	61.8	73.5	50.0
ID = 1.49"	76.9	95.0	-	-
OD = .65"	133.0	-	159.0	-
	195.0	-	-	195.0
Vessel 2	30.0	35.7	41.1	30.0
(k=2.50)	50.0	59.5	69.0	50.0
ID = 1.875"	79.8	95.0	-	-
OD = .75"	141.0	-	195.0	-
	195.0	-	-	195.0

where p: pressure
 Γ : shearing stress
 σ_t : tensile stress
 σ_R : radial stress

along a path approximately bisecting the right angle at the intersection and cleanly breaking the vessel into two pieces.³ Evidence (location of fracture, texture of mating surfaces) indicates a failure due to inherent stress concentrations rather than fatigue or a casting imperfection.

The second vessel incorporates changes in design and fabrication based on the experience with the first. A hemispheric bottom for the chamber and a corner with the maximum allowable radius for the closure-ring receptacle have been included. These radii have been lapped, inspected and relapped to remove cracks or machining marks. The resulting vessel, with essentially the same ratio of external to internal diameters, as the early vessel, has survived an even greater load-cycle use.

1. Pressure Vessel Design, John Harvey, 1963.
2. Brush-Beryllium Data Sheet.
3. The desirability of failure under plastic flow with the resulting lack of shrapnel is apparent.

APPENDIX B3

Pressure Gauge Calibration and Comparisons

Direct calibration of a manganin coil pressure gauge against the freezing point of mercury at 0°C has been made. Comparison of this gauge with a second, one regularly used for pressure derivative measurements, and of the second and a bourdon-tube gauge has also been done. Deviations from linearity for each pair of gauges is less than .05%, with the calibration of each gauge differing by no more than .5% from any other.¹ A maximum of .5% is considered to be the uncertainty in the original calibration against the freezing point. There is a .1% of full scale uncertainty stated by the manufactures for the bourdon-tube gauge.

Resistance gauges used in this lab consist of nominally 300Ω coils of #40 manganin wire with double silk insulation, the wire loosely wound in a multiple layer on a coil form. Efforts are made to insure a strain-free coil. The calibration is a linear one with the resistance determined at pressures of one atmosphere and that of the freezing point of mercury at 0°C . The change in volume of the mercury with no pressure change is used as evidence of the phase transition according to the following procedure.

The pressure gauge in its own plug and a pressure intensifier within the pressure vessel form a unit with the pump which actuates

1. For a discussion of manganin gauges, see: Boren, M., et al., Rev. Sci. Instr., 36, 1456 (1965).

the intensifier. While the pressure gauge coil is maintained nominally at 25°C, the mercury in a cup within a separate pressure vessel is immersed in a distilled water ice bath of 0°C. The second vessel is joined to the intensifier vessel by about two feet of stainless tubing. Connected to the atmospheric side of the low pressure end of the intensifier piston is a burette partially filled with oil. Changes in the position of the intensifier, hence, changes in the volume of the high pressure system, may be inferred from the changes in the level of the burette.

New continuously-triple distilled mercury was placed in the cup in the pressure vessel which was then immersed in the ice bath and left to come to equilibrium overnight.

Resistance, hence pressure, was measured as a function of the level of oil in the burette, corresponding to volume. In the single phase region, equilibrium was achieved in about 5 minutes after pressure changes; during the phase change, about 15 minutes was necessary. The gauge resistance at the plateau of the graph of resistance against volume corresponds to the value at the freezing point of the mercury. An average was taken of all values of gauge resistance in the two-phase region.

Results of typical runs involving two different resistance bridges appear in Table 3B. The value of pressure above atmospheric employed is 7.568×10^9 dynes/cm², based on the most recent determination of the pressure at the phase transition.² Other recently deter-

2. R.S. Dadson, and R.G. Greig, Brit. J. Appl. Phys., 16, 1711 (1965).

TABLE 3B. Calibration of 10 kbar manganin gauge against the mercury freezing point at 0°C using two different resistance bridges.

	Bridge L & N	Wolff
$R_o (\Omega)$	301.924	301.588
$R_l (\Omega)$	0.358	0.370
$\Delta R = R_p - R_o$	5.304	5.302
$R = \frac{\Delta p}{\Delta R} (10^9 \text{ dynes/cm}^2)$	1.4268	1.4274
$K = k(R_o - R_l) (\text{kbar})$	430.3	430.0

TABLE 4B. Manganin wire constant based on revised phase transition pressure.

	K(kbar)	
	Bridgeman ^A	Revised ^B
Daniels	423.2	427.5
Chapman	426.5	430.8
Author		430.2 ^C

A. $\Delta p = 7.492 \cdot 10^9 \text{ dynes/cm}^2$ (See footnote 2) .

B. $\Delta p = 7.568 \cdot 10^9 \text{ dynes/cm}^2$ (See footnote 3) .

C. Values from 408 to 435 kbar have been obtained from investigations of the piezoresistivity of manganin (See E. Baris, E. Williams, and C. Skoog, J. Appl. Phys. 41, 5155 (1970)).

mined values of 7.567 (Johnson and Newhall, 1953)³ and 7.565 (Newhall, et al.)⁴ are in essential agreement with this value and differ by about 1% from the widely used Bridgman value⁵ now considered to be in error. Also indicated in Table 4B are values of the wire constant, k, determined on different occasions in this laboratory. Since these earlier calibrations were based on Bridgman's value of the freezing point pressure, calculations for both the Bridgman and new values are given. The two most recent calibrations of Chapman and the present work agree within 0.15% while differing from the earlier calibration of Daniels' by about .6%.

After this direct calibration of the 10 kilobar gauge, the 3 kilobar gauge used for most pressure derivative work was connected to that system and the two gauges compared. The resistance of each gauge was measured on the same bridge. A DPDT switch was used and it was carefully cleaned, both to minimize stray resistance effects. The data of this comparison is indicated in Table 5B.

Finally, the 3 kilobar gauge was connected to the bourdon-tube gauge system and these two gauges compared. While the pressure medium of the bourdon gauge was helium gas, that of the

-
3. D.P. Johnson and N.H. Newhall, Trans. Amer. Soc. Mech. Engrs., 75, 301 (1953).
 4. D.H. Newhall, et al., in High Pressure Measurements, A.A. Giardini and E.C. Lloyds, Washington, Butterworths, p.339 (1963).
 5. P.W. Bridgman, Proc. Amer. Acad. Arts Sci., XLVII, P.347 (1912).

TABLE 5B. Comparison of 10 kbar ($R_0 = 302.156$) and 3 kbar ($R_0 = 297.478\Omega$) manganin gauges: typical results for total pressure changes of 70,000 psi (5 kbar).

$\Delta R_{10}^A (\Omega)$	$\Delta R_3^B (\Omega)$	$\Delta R_{10}(\text{calc})$	$\Delta R_{10} - \Delta R(\text{calc})$
0	0	0	0
0.512	0.499	0.513	+0.001
0.973	0.954	0.973	0
1.356	1.332	1.356	0
1.668	1.636	1.664	-0.004
2.179	2.144	2.179	0
2.629	2.588	2.629	0
3.334	3.283	3.333	-0.001
2.162	2.128	2.163	+0.001
1.896	1.865	1.896	0
1.568	1.540	1.507	-0.001
1.396	1.370	1.395	-0.001
0.778	0.762	0.779	+0.001
0.286	0.273	0.284	-0.002
0.056	0.050	0.058	+0.002
0	0	0	0

manganin gauge was always oil, its housing acting as a reservoir. The data for one run of this comparison appears in Table 6B.

Calculations based on the calibration against the mercury freezing point and the comparison of each pair of gauges is shown in Table 7B. The deviations from linearity in the case of each gauge - gauge measurement were less than .05%.

As means of comparing the bourdon tube gauge with the two manganin gauges, the gauge constant, k , was calculated for the 3 kbar gauge by three separate means. Systematic differences in pressure as measured by the three gauges would appear as a discrepancy between the constants calculated. First, the gauge constant is calculated from the wire constant determined by the Hg calibration:

$$k = \frac{K}{(R_0 - R_2)} ;$$

second, by a point-by-point comparison with the 10 kbar gauge:

$$k = k_{10k} \left(\frac{\Delta R_{10k}}{\Delta R_{3k}} \right) ;$$

third, by a point-by-point comparison with the bourdon-tube gauge:

$$k = \frac{\Delta P_H \times (\text{units conversion})}{\Delta R_{3k}} .$$

The three constants lie within experimental uncertainty of each other; the average of these values have a standard deviation of less than .25%. This result indicates the absence of any system-

TABLE 6B. Comparison of Heise bourdon-tube and manganin resistance gauges.

$\Delta p_H (10^3 \text{ psi})$	$\Delta R_3 (\Omega)$	$\Delta R_3 (\text{calc})$	$\Delta R_3 - \Delta R_3 (\text{calc})$
0	0	0	0
2.985	0.147	0.147	0
6.200	0.290	0.290	0
9.020	0.435	0.433	-0.002
12.105	0.569	0.569	0
15.060	0.719	0.720	+0.001
17.705	0.835	0.835	0
20.990	1.001	1.001	0
24.390	1.152	1.152	0
27.010	1.286	1.287	+0.001
28.375	1.342	1.341	-0.001
28.000	1.372	1.372	0

TABLE 7B. Results of gauge comparisons.

Gauge constant of 3 kbar manganin gauge calculated from:

1. Direct point-by-point measurement against Heise gauge.
2. Direct point-by-point measurement against 10 kbar gauge.
3. The wire constant determined by direct calibration of the 10 kbar gauge against Hg freezing point.

Method	k (kbar/ Ω)
<p>Heise</p> $\left(\frac{\Delta R_{3k}}{\Delta p_{\text{Heise}}} \right) \times \left(\frac{\text{psi}}{\text{kbar}} \text{ conversion} \right)$	1.453
<p>10k</p> $\left(\frac{\Delta R_3}{\Delta R_{10}} \right) \times k_{10k}$	1.446
<p><u>Wire constant</u></p> $K \times (R_o - R_l)$	1.450
<u>Average</u>	$1.450 \pm .0035$

atic difference in pressure as determined by the three different gauges (Table 7B).

APPENDIX CI

Evaluation of Uncertainties in Low Temperature Grüneisen Parameters

The probable uncertainty in the low temperature Grüneisen parameter, γ_L , may be evaluated from the uncertainties in the observed transit times and their pressure derivatives according to

$$\Delta\gamma = \sqrt{\sum_{\alpha} \left(\frac{\partial\gamma}{\partial t_{\alpha}} \right)^2 (\Delta t_{\alpha})^2 + \sum_{\alpha} \left(\frac{\partial\gamma}{\partial t'_{\alpha}} \right)^2 (\Delta t'_{\alpha})^2}, \quad (1)$$

where α denotes the mode of propagation in the [110] direction,

Δt_{α} is the experimental uncertainty in the transit time,

t'_{α} , of the α mode,

and $\Delta t'_{\alpha}$ is the uncertainty in the pressure derivative, t'_{α} , of the transit time.

Since the input to the computer program which calculates γ_L includes the independent elastic constants, C_{11} , C_{12} , C_{44} , their pressure derivatives, and the isothermal bulk modulus, B_T , explicit expressions for the changes in these quantities with changes in t_{α} and t'_{α} must be developed. γ_L may then be computed for six different sets of input data corresponding to changes in each experimental observable with the five others held constant. (The effect of the small uncertainty in the density, ρ , and the length, L , is neglected.) The partial derivatives of γ_L may then be evaluated numerically as

$$\left(\frac{\partial \gamma}{\partial t} \right) = \frac{\gamma(t+\Delta t) - \gamma(t)}{\Delta t} \quad (2)$$

In order to calculate the dependence of the elastic constants on the changes in transit times, C_{11} , C_{12} , and C_{44} may be written in the general form

$$C_{ij} = \sum_{\alpha} b_{\alpha}^{ij} C_{\alpha} \quad (3)$$

where α denotes longitudinal ($\alpha=L$) or one of the two shear modes ($\alpha=1S$; $\alpha=2S$) for $[110]$ propagation. For convenience, the superscripts ij on b_{α}^{ij} may be suppressed. The coefficients b_{α} for the different modes are indicated in Table IC along with a summary of the expressions for changes in the elastic constants and pressure derivatives for changes in t_{α} and t'_{α} .

The partial derivative of C_{ij} with respect to the transit time, t_{α} , may be calculated directly when C_{ij} is given in terms of a summation over the modes with a dummy subscript, x :

$$\begin{aligned} \frac{\partial}{\partial t_{\alpha}} C_{ij} &= \frac{\partial}{\partial t_{\alpha}} \sum_x b_x C_x \\ &= \frac{\partial}{\partial t_{\alpha}} \sum_x b_x \left(\frac{4\rho L^2}{t_x^2} \right) \\ &= - \frac{2b_{\alpha} C_{\alpha}}{t_{\alpha}} \quad (4) \end{aligned}$$

since

$$\begin{aligned} \frac{\partial t_x}{\partial t_{\alpha}} &= 0 \text{ for } x \neq \alpha \\ &= 1 \text{ for } x = \alpha \end{aligned}$$

TABLE 1C. Summary of expressions for changes in elastic constant and their pressure derivatives for changes in transit times and their derivatives.

$$\Delta(t_{\alpha})C_{ij} = - \frac{2b_{\alpha} C_{\alpha} \Delta t_{\alpha}}{t_{\alpha}}$$

$$\Delta(t'_{\alpha})C_{ij} \equiv 0$$

$$\Delta(t_{\alpha}) \left(\frac{dC_{ij}}{dp} \right) = \frac{2C_{\alpha} \Delta t_{\alpha}}{t_{\alpha}} \left[b_{\alpha} \left(\frac{3t'_{\alpha}}{t_{\alpha}} - A \right) + 3A^2 a_{\alpha} C_{ij} \right]$$

$$\Delta(t'_{\alpha}) \left(\frac{dC_{ij}}{dp} \right) = - \frac{2b_{\alpha} C_{\alpha} t'_{\alpha}}{t_{\alpha}}$$

where

$$t' = (dt/dp)$$

$$A = 1/3B_T$$

and the coefficients a_x and b_x are:

	b_x			a_x
	(11)	(12)	(44)	
L(C)	1	1	0	1
1S(C')	1	-1	0	-1/3
2S(C ₄₄)	-1	-1	1	-1

By denoting the change in C_{ij} with changes in t_α by $\Delta(t_\alpha)C_{ij}$, the change in C_{ij} becomes

$$\begin{aligned}\Delta(t_\alpha)C_{ij} &= \left(\frac{\partial C_{ij}}{\partial t_\alpha} \right) \Delta t_\alpha \\ &= - \frac{2b_\alpha C_\alpha \Delta t_\alpha}{t_\alpha}\end{aligned}\quad (5)$$

Since the elastic constants are not functions of the pressure derivatives of the transit times, t'_α , the change in C_{ij} with changes in t'_α is zero, hence,

$$\Delta(t'_\alpha)C_{ij} \equiv 0$$

To evaluate $(\partial B_T / \partial t_\alpha)$, the approximation

$$B_T \approx B_S$$

is made and B_T written as a sum over the modes

$$B_T = \sum_{\alpha} a_{\alpha} C_{\alpha},$$

where $a_L = 1$, $a_{1S} = -1/3$, and $a_{2S} = -1$. Thus,

$$\begin{aligned}\frac{\partial}{\partial t_\alpha} B_T &= \frac{\partial}{\partial t_\alpha} \sum_{\alpha} a_{\alpha} C_{\alpha} \\ &= a_{\alpha} \frac{\partial C_{\alpha}}{\partial t_\alpha} \\ &= - \frac{2a_{\alpha} C_{\alpha}}{t_\alpha}\end{aligned}\quad (6)$$

The partial derivatives of (dC_{ij}/dp) may similarly be calcu-

lated from

$$\begin{aligned} \frac{dC_{ij}}{dp} &= \sum_x b_x \left(\frac{dC_x}{dp} \right) \\ &= \sum_x b_x C_x \left[\frac{1}{3B_T} - \frac{2}{t_x} \left(\frac{dt_x}{dp} \right) \right] \\ &= \sum_x b_x C_x \left[\frac{1}{3B_T} - \frac{2t'_x}{t_x} \right] \end{aligned} \quad (7)$$

Differentiation and straightforward algebra lead to the expressions

$$\Delta(t_\alpha) \left(\frac{dC_{ij}}{dp} \right) = \frac{2C_\alpha \Delta t_\alpha}{t_\alpha} \left[b_\alpha \left(\frac{3t'_\alpha}{t_\alpha} - A \right) + 3A^2 a_\alpha C_{ij} \right] \quad (8)$$

where

$$A = \frac{1}{3B_T}$$

and

$$\Delta(t'_\alpha) \left(\frac{dC_{ij}}{dp} \right) = - \frac{2b_\alpha C_\alpha \Delta t'_\alpha}{t_\alpha} \quad (9)$$

Explicit formal expressions for changes in the elastic constants and their pressure derivatives based on Table 1C are given in Tables 2C and 3C. Numerical expressions for Si and InAs are given in Tables 4C and 5C respectively. Table 6C shows the results of computer calculations of γ_L , including the partial derivatives. With the values of the partial derivatives indicated, the series expansions of γ_L to first order,

TABLE 2C. Expressions for the changes in elastic constants for changes in transit times and their derivatives.

Variable	ΔC_{11}	ΔC_{12}	ΔC_{44}	ΔB_T
t_L	$-2C \left(\frac{\Delta t_L}{t_L} \right)$	$-2C \frac{\Delta t_L}{t_L}$	0	$-2C \left(\frac{\Delta t_L}{t_L} \right)$
t_{1S}	$-2C' \left(\frac{\Delta t_{1S}}{t_{1S}} \right)$	$2C' \left(\frac{\Delta t_{1S}}{t_{1S}} \right)$	0	$2C' \left(\frac{\Delta t_{1S}}{t_{1S}} \right)$
t_{2S}	$2C_{44} \left(\frac{\Delta t_{2S}}{t_{2S}} \right)$	$2C_{44} \left(\frac{\Delta t_{2S}}{t_{2S}} \right)$	$-2C_{44} \left(\frac{\Delta t_{2S}}{t_{2S}} \right)$	$\frac{2}{3}C_{44} \left(\frac{\Delta t_{2S}}{t_{2S}} \right)$
t'_L	0	0	0	0
t'_{1S}	0	0	0	0
t'_{2S}	0	0	0	0

TABLE 3C.

Expressions for changes in pressure derivatives of elastic constants in terms of changes in transit times and their derivatives.

	$\Delta \left(\frac{dC_{11}}{dp} \right)$	$\Delta \left(\frac{dC_{12}}{dp} \right)$	$\Delta \left(\frac{dC_{44}}{dp} \right)$
t_L	$2C\Delta_L(3T_L - A + 3A^2C_{11})$	$2C\Delta_L(3T_L - A + 3A^2C_{12})$	$2C\Delta_L(3A^2C_{44})$
t_{1S}	$2C'\Delta_{1S}(3T_{1S} - A - A^2C_{11})$	$-2C'\Delta_{1S}(3T_{1S} - A + A^2C_{12})$	$-2C'\Delta_{1S}(A^2C_{44})$
t_{2S}	$-2C_{44}\Delta_{2S}(3T_{2S} - A + 3A^2C_{11})$	$-2C_{44}\Delta_{2S}(3T_{2S} - A + 3A^2C_{12})$	$2C_{44}\Delta_{2S}(3T_{2S} - A - 3A^2C_{44})$
t'_L	$-2C \left(\frac{\Delta t'_L}{t_L} \right)$	$-2C \left(\frac{\Delta t'_L}{t_L} \right)$	0
t'_{1S}	$-2C' \left(\frac{\Delta t'_{1S}}{t_{1S}} \right)$	$-2C' \left(\frac{\Delta t'_{1S}}{t_{1S}} \right)$	0
t'_{2S}	$2C_{44} \left(\frac{\Delta t'_{2S}}{t_{2S}} \right)$	$2C_{44} \left(\frac{\Delta t'_{2S}}{t_{2S}} \right)$	$-2C_{44} \left(\frac{\Delta t'_{2S}}{t_{2S}} \right)$

where $A = \frac{1}{3B_T}$ and $\Delta_\alpha = \frac{\Delta t_\alpha}{t_\alpha}$

TABLE 4C. Evaluated changes for Si (effects of 1% change in any variable).

Variable	C_{11}	C_{12}	C_{44}	dC_{11}	dC_{12}	dC_{44}	B_T
0	1.659	0.6416	0.7958	4.5300	4.4200	0.7500	0.9799
t_L	1.620	0.6027	0.7958	4.400	4.2788	0.7607	0.9409
t_{1S}	1.649	0.6518	0.7958	4.528	4.4191	0.7491	0.9901
t_{2S}	1.675	0.6575	0.7799	4.541	4.4362	0.7259	0.9852
t'_L	1.659	0.6416	0.7958	4.5072	4.3972	0.7500	0.9799
t'_{1S}	1.659	0.6416	0.7958	4.5292	4.4208	0.7500	0.9799
t'_{2S}	1.659	0.6416	0.7958	4.5324	4.4224	0.7476	0.9799

DATA INVOLVED

C_{11}	C_{12}	C_{44}	C	C'	B_T	dC_{11}	dC_{12}	dC_{44}	t_L	t_{1S}	t_{2S}
1.659	0.6416	0.7958	1.946	.5087	.9799	4.530	4.420	0.750	-1.17	+1.17	-.299

Elastic Constants (10^{12} dynes/cm²)

dC 'S dimensionless

T (10^{-12} cm²/dyne)

TABLE 5C. Evaluated changes for InAs (effects of 1% change in any variable).

Variable	C_{11}	C_{12}	C_{44}	dC_{11}	dC_{12}	dC_{44}	B_T
0	0.8919	0.4942	0.4038	4.5200	4.923	0.4140	0.6303
t_L	0.8699	0.4772	0.4038	4.388	4.773	0.4214	0.6083
t_{1S}	0.8880	0.5031	0.4038	4.526	4.915	0.4144	0.6342
t_{2S}	0.9000	0.5073	0.3957	4.518	4.926	0.4076	0.6330
t'_L	0.8919	0.4992	0.4038	4.497	4.898	0.4140	0.6303
t'_{1S}	0.8919	0.4992	0.4038	4.518	4.925	0.4140	0.6303
t'_{2S}	0.8919	0.4992	0.4038	4.521	4.924	0.4120	0.6303

DATA INVOLVED

C_{11}	C_{12}	C_{44}	C	C'	B_T	dC_{11}	dC_{12}	dC_{44}	t_L	t_{1S}	t_{2S}
0.8919	0.4992	0.4038	1.0993	0.1964	0.6303	4.520	4.553	0.414	-2.07	+ .773	-.248

Elastic Constants (10^{12} dynes/cm²)

dC (dimensionless)

t (10^{-12} cm²/dyne)

TABLE 6C. γ_L and its partial derivatives.

Element	Parameter varied by 1%	γ_L	$\Delta\gamma_L$	$\left(\frac{\partial\gamma_L}{\partial t_\alpha}\right)^*$
Si	-	0.21774	0	-
	t_L	0.21210	-0.00584	-0.1870
	t_{1S}	0.22357	+0.00564	+0.0924
	t_{2S}	0.21625	-0.00169	-0.0346
	t'_L	0.21967	+0.00173	+0.047
	t'_{1S}	0.21997	+0.00204	+0.047
	t'_{2S}	0.21957	+0.00163	+0.111
InAs	-	-0.01020	0	-
	t_L	-0.00455	+0.00565	+0.1419
	t_{1S}	-0.00695	+0.00326	+0.0345
	t_{2S}	-0.01309	-0.00289	-0.0440
	t'_L	-0.00984	+0.00036	+0.0044
	t'_{1S}	-0.01124	-0.00104	-0.0143
	t'_{2S}	-0.01065	+0.00045	+0.0276

* Partial derivatives with respect to transit times, t , in units of $(\mu\text{sec})^{-1}$; those for pressure derivatives of transit times in $(10^{12} \text{ dynes/cm}^2)$.

$$\gamma_L = \gamma_{Lo} + \sum_{\alpha} \left(\frac{\partial \gamma}{\partial t_{\alpha}} \right) \Delta t_{\alpha} + \sum_{\alpha} \left(\frac{\partial \gamma}{\partial t'_{\alpha}} \right) \Delta t'_{\alpha} ,$$

may be written for Si and InAs:

$$\begin{aligned} \gamma_L(\text{Si}) = & .218 - .187\Delta t_L + .0924\Delta t_{1S} - .0346\Delta t_{2S} + .148\Delta t'_L \\ & + 1.744\Delta t'_{1S} + 0.545\Delta t'_{2S} \end{aligned}$$

and

$$\begin{aligned} \gamma_L(\text{InAs}) = & -.010 + .142\Delta t_L + .0345\Delta t_{1S} - .044\Delta t_{2S} \\ & + .0173\Delta t'_L + .135\Delta t'_{1S} + .182\Delta t'_{2S} \end{aligned}$$

for t in μsec and t' in $\mu\text{sec}/(10^{12} \text{ dynes/cm}^2)$. The contribution of each term in the above expressions for generous uncertainties of 1% in transit times and $\pm 0.044 \mu\text{sec}/(10^{12} \text{ dynes/cm}^2)$ in pressure derivatives (an average of RMS deviations of measurements for all modes) are given by

$$\begin{aligned} \gamma_L(\text{Si}) = & .218 \pm .0058 \pm .0056 \pm .0017 \pm .0021 \pm .0125 \pm .0049 \\ = & .218 \pm .016 \end{aligned}$$

and

$$\begin{aligned} \gamma_L(\text{InAs}) = & -.010 \pm .0057 \pm .0033 \pm .0029 \pm .0002 \pm .0006 \pm .0012 \\ = & -.010 \pm .007 \end{aligned}$$

APPENDIX C2

Grüneisen Parameter of a Debye Solid in the Quasi Harmonic Approximation.

A realistic first approximation which takes into account anharmonicity treats a crystal as a collection of $3N$ harmonic oscillators with volume dependent eigenfrequencies.^{1,2} The volume dependence in this "quasi-harmonic approximation may be expressed in terms of a mode gamma, γ_i , as

$$\gamma_i = \frac{-d \ln \omega_i}{d \ln V},$$

where i denotes the i th normal mode. This microscopic parameter is related to macroscopic crystal parameters in the following way.

The internal energy of the crystal lattice may be written as

$$U = U_0(V) + U'_0(V) + U''(V, T)$$

where

U_0 : energy of the static lattice

$U'_0(V)$: zero point energy of the harmonic oscillators

$U''(V, T)$: vibrational energy

The free energy of the crystal,

$$F = U - TS = U - T \int_0^T \frac{C_V}{T} dT,$$

where $C_V = (\partial U / \partial T)_V$, is related to the thermal expansion by

$$B_T \beta = - \frac{\partial^2 F}{\partial V \partial T},$$

where B_T is the isothermal bulk modulus. Substitution of U and F into the above yields

$$B_T \beta = \frac{C_V}{V} \gamma$$

where $\gamma = \frac{\sum_i C_i \gamma_i}{\sum_i C_i}$ and $C_i = (\partial \bar{E}_i / \partial T)_V$ is the Einstein specific heat of the i th normal mode.

In the low temperature region ($T < \theta_D/50$), the crystal may be treated as an anisotropic continuum and standard Debye theory applied, with the Debye density of states

$$g(\bar{\omega}) d\omega \sim \sum_{i=1}^3 \frac{\omega^2 d\Omega d\omega}{v_i^3(\theta, \phi)}$$

where $d\Omega$ is an element of solid angle and the sum is over mode type. The density of states can be used to evaluate γ_L according to

$$\gamma_L = \frac{\sum_{i=1}^3 \int_{\Omega} v_i^{-3} \gamma_i(\theta, \phi) d\Omega}{\sum_{i=1}^3 \int_{\Omega} v_i^{-3} d\Omega}$$

The mode gamma, γ_i , may be calculated from the pressure derivative of the elastic constant of that mode. From the definition of the elastic constant:

$$C_i = \rho v_i^2$$

where ρ is the density, the assumption of non-dispersive propagation:

$$\omega_i = v_i(\theta, \phi)k$$

where k is the wave number, and the definition of the mode gamma,

γ_i , it follows that:

$$\gamma_i = -\frac{1}{6} + \frac{B_T}{2} \frac{1}{C_i} \left(\frac{dC_i}{dT} \right)_T$$

At low temperatures, Debye theory predicts the same temperature dependence for both the specific heat and the thermal expansion :

$$C_V = C_0 (T/\theta_D)^3$$

$$\beta = \beta_0 (T/\theta_D)^3$$

where θ_D , the Debye characteristic temperature, is given by:

$$\theta_D = \text{constant} \times \int_{\Omega} v_i^{-3}(\phi, \theta) d\Omega$$

In this T^3 region, it follows from the temperature dependences of C_V , and β , that

$$\left(\frac{\partial \gamma}{\partial T} \right) = 0$$

and

$$\gamma_L = \left(\frac{\beta V B_T}{C_V} \right) \text{ for } T \rightarrow 0$$

Thus, γ approaches a constant limiting value, γ_L , which is finite and, though not necessarily, non-zero, at low temperatures.

At high temperatures, each individual oscillator becomes fully excited. The specific heat approaches the classical limit and the Grüneisen parameter, due to equal weighting of the individual modes, becomes

$$\gamma_H = \frac{1}{4\pi} \int_{\Omega} \sum_i \gamma_i(\theta, \phi) d\Omega$$

Since β and C_V approach limiting values,

$$\left(\frac{\partial \gamma_G}{\partial T} \right) \rightarrow 0$$

and γ is again given by the Grüneisen relation:

$$\gamma_H = \left(\frac{\beta B_T V}{C_V} \right) \quad T \gg \theta_D$$

Again the model yields a Grüneisen parameter which is equivalent in terms of thermal and elastic parameters.

At intermediate temperatures, as more modes become excited and to greater degrees, both C_V and β (hence, γ) increase smoothly from their low temperature values to the high. Thus normal behavior for a Debye-like solid involves a positive thermal expansion which increases with temperature and a specific heat characterized by a temperature independent θ_D . The behavior of the thermal expansion can be understood in terms of the frequency spectrum of the quasi-harmonic oscillators; this spectrum determines the specific heat and the thermal expansion.

The thermal expansion may alternatively be written:⁴

$$\beta = \frac{C_V}{V} \frac{1}{\bar{\omega}} \frac{d\bar{\omega}}{dp}$$

where $\bar{\omega}$ is the average oscillator frequency. For the model presently under consideration, all frequencies depend on the volume in the same way, although the dependence may differ between acoustic branches. The frequency distribution for the Debye-like solid is given by:

$$g(\omega) = c\omega^2$$

where the total number of states is constant and determined by a cut-off frequency, $\omega_{\max}$. When the atoms in a solid are brought together by increasing pressure, the amplitude of their vibrations decreases and the frequency increases. The cut-off frequency shifts toward a higher value so that some additional higher frequencies are excited. Since the total number of excited states remains constant, there is a reduction in the number of low frequency vibrations and $d\omega/dp > 0$.⁵ This behavior is characteristic then of a "normal" solid with positive thermal expansion.

APPENDIX C2

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APPENDIX C3

The Temperature Dependence of the Grüneisen Parameter, γ_G , Real Semiconductors

Although the "Grüneisen" parameters associated with different physical quantities are generally not equivalent, under certain conditions those associated with thermal and elastic properties are. For Debye-like solids, both the Debye temperature, θ_D , and the low temperature Grüneisen parameter, γ_L , may be calculated from elasticity or thermal expansion and specific heat data. Thus, since the internal consistency of the quasi-harmonic approximation for a Debye model and its appropriateness for specific solids have been demonstrated, the question of whether a real semiconductor may be treated in this manner is pivotal. It will be shown that while significant deviation from Debye-like behavior is exhibited by semiconductors at intermediate temperatures, they behave "normally" at high and extremely low temperatures. In Figure 1C is shown γ_G (defined by the Grüneisen relation) as a function of temperature for both a Debye-like solid and a diamond-like semiconductor. The difference is apparently characteristic of all the tetrahedrally bonded semiconductors.

The "normal" behavior of the ideal solid is a simple increase in γ_G from the low to the high temperature limiting values with $(\partial\gamma_G/\partial T)$ becoming zero at both extremes.¹ This behavior contrasts sharply with that exhibited by the real solids considered here. Generally, γ_G for the semiconductors, beginning at $T=0$, increases with temperature, decreases through zero until a minimum is reached,

Figure 1C. The temperature dependence of Grüneisen parameter, γ_G , of diamond-like semiconductors and "normal" solids.

TABLE 7C. Features of the General $\gamma(T)$ Curve for Specific Semiconductors

	Si	Ge	GaAs	InAs	InSb
γ_L (thermal)	.44	.66	.58	.28	.21
(elastic)	.22	.38	.38	-.01	.04
γ_{min} (thermal)	-.40	-.10	-.24	-.44	-.95
γ_H (thermal)	.48	.73	.75	--	.50
(elastic)	.45	.68	.67	.43	.45
$T_1(T_1/\theta_D)$	19°(.03)	15°(.04)	13°(.04)	5°(.02)	5°(.02)
$T_{min}(T_{min}/\theta_D)$	29°(.045)	23°(.06)	22°(.06)	18°(.07)	15°(.07)
$T_2(T_2/\theta_D)$	120°(.185)	38°(.10)	40°(.11)	--	55°(.25)
θ_D (thermal)	645°	374°	347°	251°	207°
θ_D (elastic)	649°	375°	348°	251°	206°

then increases until a high temperature limiting value is approached. The most striking aspect of this curve is the region of negative thermal expansion corresponding to the negative gamma. Those features which the two curves have in common and those by which they differ may be considered in the light of several experimental and theoretical observations.

At extremely low temperatures, the semiconductors clearly possess a Debye-like T^3 region. Both the specific heat and the thermal expansion have this temperature dependence (although the region for C_p and β have slightly different upper limits):^{2,3}

$$C_p \sim (T/\theta_D)^3 \quad (T/\theta_D) \lesssim .006$$

$$\beta \sim (T/\theta_D)^3 \quad (T/\theta_D) \lesssim .02$$

The argument, that regardless of a crystal's detailed lattice structure, the lowest excited states are quantized long elastic waves, is consistent with this observation.⁴ Further, the electronic contribution to the specific heat at low temperatures is in this case, negligible compared to that of the lattice.⁵

Thus, the thermal (vibrational) free energy of the real crystal depends on velocities precisely as in harmonic crystals and the equivalence of properties calculated from thermal and elastic data for this region follows.

The question of anharmonic effects, other than those accounted for by the volume dependence of the eigenfrequencies, arises. That such effects can be expected to be minor is evidenced by the small

thermal expansion and the only slight temperature dependence of the elastic constants.⁵ There is some indication⁶ that any anharmonic contribution to the free energy to lowest order would be proportional to T^4 and, thus.

$$\theta_D(\text{anharmonic}) = \theta_D(\text{harmonic}) + \text{constant}.$$

Such a contribution to the free energy would still imply, however, that

$$\theta_D(\text{elastic}) \equiv \theta_D(\text{thermal})$$

and the equivalence of thermal and elastic parameters would be maintained.

At high temperatures ($T > \theta_D$) the thermal expansion and specific heat, with minor variations, exhibit normal behavior.* Both θ_D and γ_G approach maximum values, although θ_D decreases after having passed through a flat maximum (classical region).⁷ At intermediate temperatures, where

$$.02 < T/\theta_D < .5,$$

the semiconductors have prominent minima in the curves of θ_D and γ_G .

Neither these minima nor the fall of θ_D at high temperature ($T \gg \theta_D$) can be accounted for by harmonic lattice theory. The departure from Debye-like behavior at low temperatures in both the speci-

* Specific heat data are conventionally represented by a temperature-dependent characteristic temperature, θ_D , much as thermal expansion data are expressed by a temperature dependent γ_G , defined by the Grüneisen relation.

fic heat and the thermal expansion reflects the distinctive character of the frequency spectra, especially that of the transverse modes, of the semiconductors. That the transverse acoustic modes lead to a reduction in γ_G , even to the point of driving it negative, has been predicted⁸ and discussed^{1,9,10} in terms of particular models. The existence of negative mode gammas has been indicated by experimental neutron-diffraction¹¹ and elastic¹² studies. Thus, the origin of a negative thermal expansion lies in the nature of the frequency spectra which give rise to negative gammas for transverse modes.

Support has been given for the, at times, dominant effect of transverse vibrations by Phillips.¹³ With a frequency distribution, moments of frequency, and appropriate singularities based on slow neutron data, he was able to calculate a specific heat curve which accurately fit experimental data. The results indicate that the shape of the specific heat curve is sensitive only to that of the transverse acoustic mode distribution. Thus, the distribution which gives rise to negative mode gammas can at certain temperatures emphasize them, producing an average γ and thermal expansion which are negative.

Such a frequency distribution would have certain atypical properties. For a frequency, ω' , below which effectively all modes are excited and above which none are, it would show

$$\frac{d\omega}{dp} < 0 \quad \text{for } \omega < \omega' ;$$

that is, an increase in pressure leads in some frequency interval

to an increase in the number of low frequency vibrations. For these conditions, β and γ would be negative. Although the theoretical model, either atomistic or phenomenological, which adequately describes this behavior has yet to be developed, the qualitative behavior is somewhat understood.

For example, the negative thermal expansion can be understood in terms of structural effects, i.e., those resulting from the interactions of atoms at the lattice sites. The modes γ which determine the thermal expansion are dependent upon the relative motions of planes of atoms during excitation. The negative mode γ are related to the motion of atoms in planes perpendicular to nearest neighbor bonds which are not in the planes. Since shear waves give motion normal to the bond directions, the interatomic distances are increased beyond those which minimize the potential energy. Further, since the potential function is a symmetric, the "effective spring constants" decrease, the eigenfrequencies decrease, and the mode γ (which describes the volume dependence of the eigenfrequency) is negative. Since compressional and optic modes have positive γ , competition between the positive and negative contributions determine the sign of γ_G and, hence, β . Since the magnitude of each mode γ is determined by the number of atoms in each plane which contribute positively or negatively, the lattice structure determines each mode γ . As opposed to NaCl, the ZnS structure has more atoms which give negative contributions. Although this analysis is simplistic and neglects many body effects, the qualitative conclusions

are supported by calculations based on models of NaCl and ZnS structures. For NaCl, γ_G may be negative for somewhat unusual potentials; for ZnS, however, γ_G may be negative for any reasonable potential.¹⁴

APPENDIX C3

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