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Temperature variation of some combinations of third-order elastic constants of silicon between 300 and 3 °K

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The ultrasonic harmonic generation technique has been used to determine the nonlinearity parameters of silicon between room temperature and 3 °K. By measuring the amplitude of the second harmonic of an initially sinusoidal longitudinal ultrasonic wave propagating along the three principal directions, the temperature dependence of three linear combinations of third-order elastic (TOE) constants of silicon have been studied. Between room temperature and 77 °K, the magnitude of the TOE constants does not vary much as a function of temperature. Between 77 and 3 °K, C_{111} changes by 3.5%, $C_{112} + 4C_{166}$ changes by 11.7%, and $C_{123} + 6C_{144} + 8C_{456}$ changes by -207%. All these combinations are negative at room temperature as well as at low temperatures except $C_{123} + 6C_{144} + 8C_{456}$ which is positive below 8 °K. Room-temperature values of the strain generalized Grüneisen parameters of silicon have been calculated from measured nonlinearity parameters and are compared with existing values. Complete sets of third-order elastic constants at 298, 77, and 4 °K have been calculated by combining our nonlinearity parameters with pressure derivatives of elastic constants measured by Beattie and Schirber [Phys. Rev. B **1**, 1548 (1970)].

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I. INTRODUCTION

Third-order elastic (TOE) constants are of fundamental interest in the study of nonlinear properties of solids which arise from the anharmonicity of the interatomic potential. Measurement of the TOE constants leads to the evaluation of the Grüneisen parameters,^{1,2} thermal expansion, and other anharmonic properties of solids. The TOE constants can be determined from a measurement of the variation of the ultrasonic wave velocity with applied stress,³ or from a measurement of the finite amplitude distortion of an initially sinusoidal ultrasonic wave propagating through the medium.⁴ The later method has been adopted by a number of investigators to determine the room-temperature as well as low-temperature values of some combinations of TOE constants using a capacitive detector technique to measure the amplitudes of the fundamental and the generated second harmonic. The details about the capacitive detector technique and the results of the measurements made on copper,⁵⁻⁷ germanium,^{8,9} and fused silica^{10,11} down to liquid helium temperatures have been reported.

The present study reports the results of measurements made on silicon using previously established techniques to determine the nonlinearity parameters and some combinations of the TOE constants down to very low temperatures. The study was motivated by the fact that silicon shows an anomalous thermal expansion behavior at low temperatures. Below 120 °K, Thermal expansion becomes negative¹² and is

again positive below 20 °K.¹³ The Grüneisen parameter follows a similar behavior at low temperatures.¹⁴ (It is interesting to note that almost all of the solids with diamond lattice structure show a similar behavior.^{12,13,15}) If one uses the quasi-harmonic approximation in the continuum model, calculations of the thermal expansion from second-order elastic (SOE) constants and only room-temperature values of the TOE constants do not predict this anomalous behavior at low temperatures.^{16,17} The present work, which reports some combinations of the TOE constants as a function of temperature, can serve as an additional step toward a solution of the problem.

In Sec. II of this paper the theory on which the experiment is based is given briefly. Section III outlines the experimental procedure and Sec. IV is devoted to the results. Section V constitutes summary and conclusions.

II. THEORY

The theory of the experimental technique used in the present study depends upon the fundamental fact that a sinusoidal ultrasonic wave propagating through a nonlinear medium undergoes a waveform distortion determined by the nonlinearity of the medium.¹⁸ This waveform distortion is characterized by the existence of a second harmonic whose amplitude is proportional to the square of the fundamental amplitude and also proportional to the ratio of the coefficients of the nonlinear terms in the nonlinear wave equation.

TABLE I. Parameters K_2 and K_3 for the three principal directions in a cubic crystal.

Direction	K_2	K_3
[100]	C_{11}	C_{111}
[110]	$\frac{1}{2}(C_{11} + C_{12} + 2C_{44})$	$\frac{1}{4}(C_{111} + 3C_{112} + 12C_{166})$
[111]	$\frac{1}{3}(C_{11} + 2C_{12} + 4C_{44})$	$\frac{1}{6}(C_{111} + 6C_{112} + 12C_{144} + 24C_{166} + 2C_{123} + 16C_{456})$

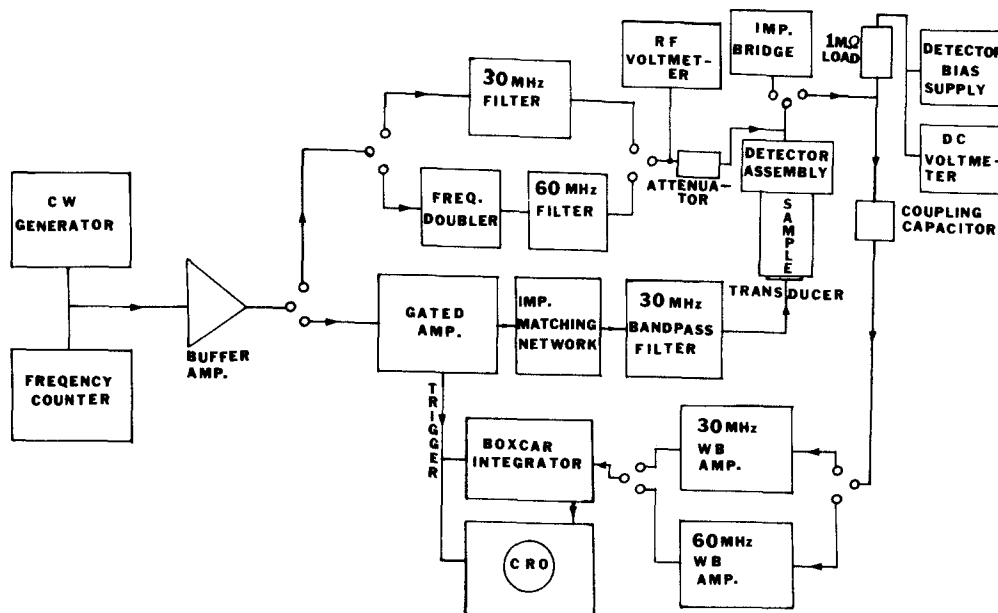


FIG. 1. Block diagram of the room-temperature experimental setup.

Pure mode propagation is possible for longitudinal sound wave propagating along the three principal directions of a cubic crystal. In these special directions the wave equation for longitudinal wave reduces to the form^{4,19}

$$\rho_0 \frac{\partial^2 u}{\partial t^2} = K_2 \frac{\partial^2 u}{\partial a^2} + (3K_2 + K_3) \frac{\partial u}{\partial a} \frac{\partial^2 u}{\partial a^2}, \quad (1)$$

where K_2 and K_3 are, respectively, the linear combinations of SOE and TOE constants given in Table I. Considering an initially sinusoidal disturbance at $a = 0$, the solution to Eq. (1) is of the form⁴

$$u = A_1 \sin(ka - \omega t) + \frac{1}{8} A_1^2 k^2 a \beta \cos 2(ka - \omega t) + \dots, \quad (2)$$

in which a is the propagation distance, $k = 2\pi/\lambda$ is the propagation constant, and A_1 and A_2 are the amplitudes of the

fundamental and the generated second harmonic, respectively. Thus the second-harmonic amplitude is given by

$$A_2 = \frac{1}{8} A_1^2 k^2 a \beta, \quad (3)$$

where the nonlinearity parameter β is defined as

$$\beta = -(3K_2 + K_3)/K_2, \quad (4)$$

which is the negative of the ratio of the nonlinear term to the linear term in the wave equation. β can also be written as

$$\beta = 8(A_2/A_1^2)(1/k^2 a). \quad (5)$$

The parameter K_2 can be determined by measuring the velocities of the ultrasonic waves along the three principal directions. The ratio A_2/A_1^2 is determined by measuring the absolute amplitudes of the fundamental and second harmonic using a capacitive detector.

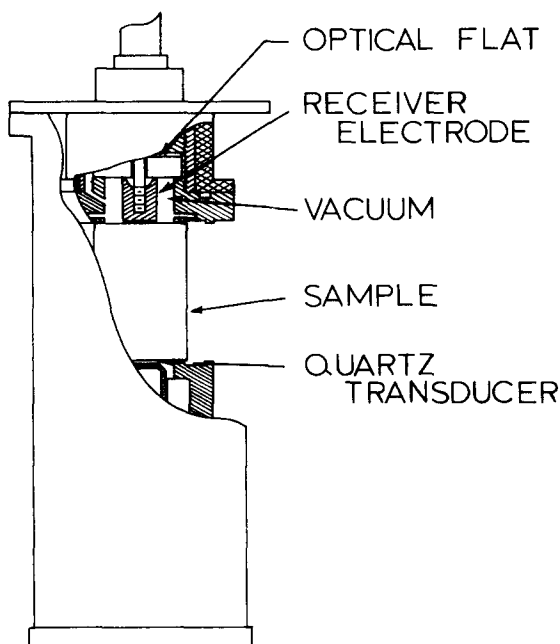


FIG. 2. Cutaway view of the low-temperature assembly.

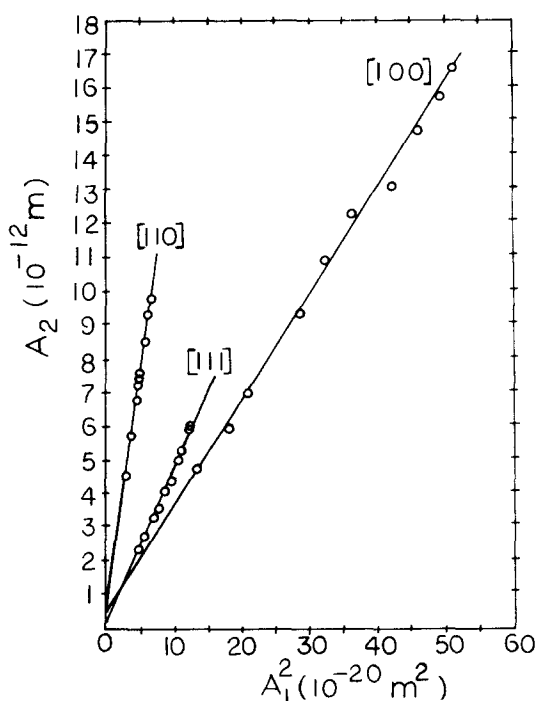


FIG. 3. Variation of second-harmonic amplitude with square of the fundamental amplitude at room temperature.

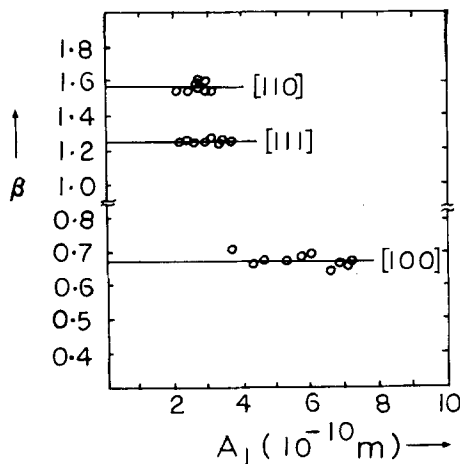


FIG. 4. Variation of the dimensionless parameter β with the fundamental amplitude at room temperature.

III. EXPERIMENTAL TECHNIQUE

A. Room-temperature measurements

The experimental technique used is essentially the same as the one used for germanium.⁹ The block diagram of the apparatus used for making room-temperature measurements is shown in Fig. 1. A pulsed rf wave of frequency of approximately 30 MHz is applied to an x-cut quartz transducer bonded to one end of the sample. The air gap capacitive receiver used is described in detail elsewhere.⁵ The receiver electrode is 1.016 cm in diameter and the distance between the sample and the electrode, both being optically flat, is on the order of 5 to 10 μm . A dc bias on the order of 150 V is applied across the gap through a large resistance of value $\approx 1\text{M}\Omega$. Provision is made to place a substitutional signal on the capacitive receiver so that accurate amplitude measurements can be made. Details of the measurement procedure are described elsewhere.⁹

After the fundamental and second-harmonic signals are measured by the boxcar integrator, the continuous-wave substitutional signal is introduced at the capacitive receiver. The 60-MHz second-harmonic substitutional signal is derived by doubling the 30-MHz signal with a ring bridge mixer. These two signals are adjusted to give the same output from the boxcar integrator as the acoustic signals and are then measured with the rf voltmeter. Measurements are made for different fundamental amplitudes. The SOE constants are determined from the room-temperature velocity

measurements and they agree well with the values reported by McSkimin²⁰ and McSkimin *et al.*²¹

The samples used in the measurements are single crystals of silicon having lengths of 2.5171, 2.5222, and 2.5248 cm along the [100], [110], and [111] orientations, respectively. The sample ends are lapped and polished until they are optically flat and parallel to within 15 in. of arc. The ends are then made conductive by coating with approximately 1000 Å of copper.

B. Cryogenic measurements

The electronic apparatus for making measurements at low temperatures is essentially the same as that for room-temperature measurements. The cryogenic system is described in detail in a previous paper.⁹ With the apparatus it is possible to make measurements from room temperature down to liquid helium temperature ($\approx 3^\circ\text{K}$). Liquid nitrogen is used to lower the temperature down to 78 °K, and then liquid helium is used to make measurements down to 3 °K. When low-temperature measurements are made, a cellulose tape adhesive is used to bond the transducer to the sample. Only relative measurements need be taken with the cryogenic apparatus. Both the frequency and amplitude of the fundamental remain constant throughout the measurements. A variable gap capacitive detector²² is used to compensate for the effects of differential thermal expansion. The sample arrangement is shown in Fig. 2. Adjustments are made in the capacitive detector bias voltage at various temperatures to compensate for the variation in the second-harmonic amplitude. Germanium and platinum sensors are used for accurate temperature measurements. A low-power heater is used to increase the temperature in steps of $\approx 8^\circ\text{K}$. The sensors and the heater outputs are powered and controlled by an Artronix temperature controller. Keeping everything constant except the second-harmonic bias voltage, measurement of β as a function of temperature is reduced to a measurement of the bias voltage necessary to maintain a constant second-harmonic amplitude as the temperature is varied. The second-harmonic amplitude A_2 of the ultrasonic wave at two different temperatures T_1 and T_2 are then related by

$$A_2(T_2)/A_2(T_1) = V_b(T_1)/V_b(T_2). \quad (6)$$

All the measurements are made relative to the room-temperature amplitude and bias voltage values. Measurements are done from 3 °K to room temperature at intervals of $\approx 8^\circ\text{K}$.

TABLE II. Room-temperature values of the nonlinearity parameter β and the parameters K_3 of silicon.

Orientation of sample	Length of sample (cm)	β	$K_2^a \times 10^{11}$ (dyn/cm ²)	Present experiment	$K_3 \times 10^{12}$ dyn/cm ²	
					Experimental values of McSkimin <i>et al.</i> ^a	Theoretical values of Keating ^b
[100]	2.5171	2.0336	16.5779	-8.34 ± 0.11	-8.25	-8.21
[110]	2.5222	4.6887	19.4470	-14.95 ± 0.22	-14.75	-15.68
[111]	2.5248	3.7500	20.4031	-13.77 ± 0.12	-13.31	-13.58

^aReference 21.

^bReference 23.

TABLE III. Comparison of isentropic strain generalized Grüneisen parameters to the Brugger-Grüneisen parameters for silicon.

Grüneisen γ from β measured in the present experiment			Grüneisen γ from Brugger's theory		
$\gamma_{11}^s(1,[100])$	$\gamma_{11}^s(1,[110])$	$\gamma_{11}^s(1,[111])$	$\gamma_{11}^s(1,[100])$	$\gamma_{11}^s(1,[110])$	$\gamma_{11}^s(1,[111])$
1.01	1.17	0.63	0.99	1.40	1.08

IV. RESULTS

A. Room-temperature nonlinearity parameters of Si

The variation of the absolute amplitude of the second harmonic with the square of the fundamental amplitude for all the three orientations is plotted in Fig. 3. The straight lines show a well-defined linear variation of A_2 with A_1^2 . The lines do not pass through the origin because of residual noise. The slope of the line in each case is the best fit to the value of the nonlinearity parameter. In Fig. 4 we have plotted the dimensionless parameter β calculated for various values of the fundamental amplitude. In view of the fact that the measurements depend upon absolute measurements of displacement amplitudes of the order of 10^{-3} Å, the scatter of the data in Fig. 4 is not excessive.

In Table II we tabulate the values of β obtained by a least-squares fit to the data from all the plotted points for all the three principal directions. The parameter K_3 for all the three directions are evaluated from β and are presented in the table. The K_3 values used for evaluation are also given. The room-temperature TOE constants of Si have been reported by McSkimin *et al.*²¹ who measured the variation of ultrasonic wave velocities with hydrostatic pressure and uniaxial stress. The K_3 values calculated from their TOE constants are also tabulated for comparison. It may be noted that the nonlinearity parameters obtained from these two entirely different techniques agree well within experimental uncertainties.

Keating²³ has theoretically evaluated all the six TOE constants of silicon in terms of three anharmonic first- and

second-neighbor force constants and two harmonic force constants. We have calculated the K_3 values from these TOE constants, and these values are also tabulated in Table II for comparison. Keating's theoretical values agree very well with the experimental values showing that Keating's model is a very good approximation for silicon.

A simple method has been proposed²⁴ to evaluate the isentropic strain generalized Grüneisen parameters from the nonlinearity parameters measured directly in harmonic generation experiments. Following this approach we have evaluated the Grüneisen parameter along the three principal directions. These values are reproduced in Table III along with the values calculated from Brugger's theory.¹ The two values agree well for the [100] direction, agree reasonably well for the [110] direction, but do not agree for the [111] direction. Further investigations are underway to trace out the origin of the disagreement.

B. Temperature variation of the nonlinearity parameters of silicon

In Fig. 5 we have plotted the data obtained for the parameter K_3 for the three orientations of silicon as a function of temperature from 3 to 300 °K. The SOE constants as a function of temperature have been plotted by McSkimin²⁰ from room temperature to 77 °K. We measured the velocities, and hence the SOE constants at different temperatures below 77 °K down to 3 °K, and found that these values agree with the curves of McSkimin extrapolated to 0 °K. For cal-

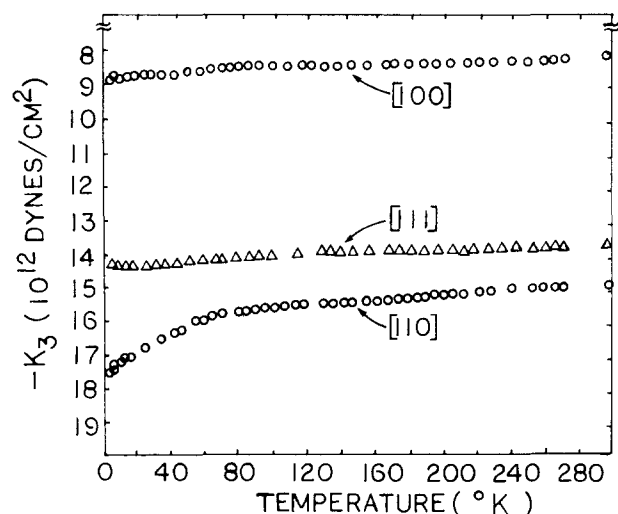
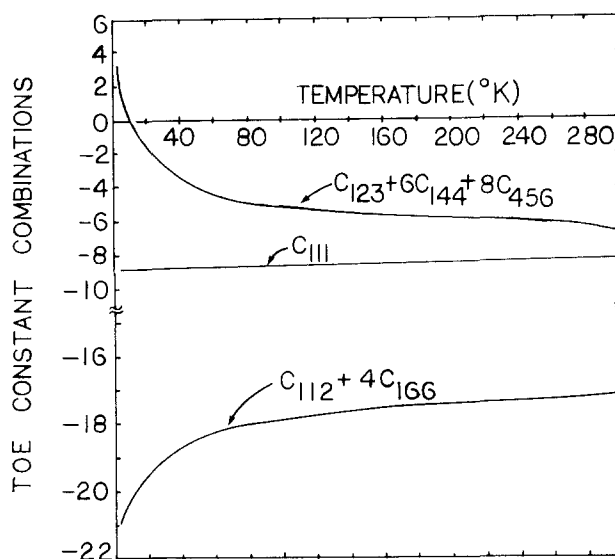
FIG. 5. Temperature variation of the nonlinearity parameters K_3 along the three principal directions.

FIG. 6. Variation of some combinations of TOE constants with temperature.

TABLE IV. TOE constants of silicon at various temperatures.

TOE Constant $\times 10^{12} \text{ dyn cm}^{-2}$	4 K	77 K	298 K
C_{111}	-8.80 ± 0.16	-8.49 ± 0.14	-8.34 ± 0.11
C_{112}	-5.15 ± 0.26	-5.24 ± 0.31	-5.31 ± 0.32
C_{144}	$+0.74 \pm 0.08$	-0.49 ± 0.10	-0.95 ± 0.24
C_{123}	$+0.27 \pm 0.24$	-0.08 ± 0.20	-0.02 ± 0.18
C_{166}	-3.85 ± 0.07	-3.23 ± 0.08	-2.96 ± 0.12
C_{456}	-0.40 ± 0.11	-0.21 ± 0.34	-0.074 ± 0.22

culations of K_3 as a function of temperature, the plotted values²⁰ of K_2 as a function of temperature have been used. The K_3 values for the [100], [110], and [111] directions vary by 5.3%, 15.2%, and 4.1%, respectively, between room temperature and 3 °K. The data for the [100] and [111] directions are quite smooth and are nearly parallel to the temperature axis. The variation is maximum for the [110] direction between 77 and 3 °K, the variation being as high as 11%. The TOE constant C_{111} appears in the nonlinearity parameters along the three directions and could definitely be subtracted out from K_3 [110] and K_3 [111]. So we can get two more combinations of TOE constants, viz., $C_{112} + 4C_{166}$ and $C_{123} + 6C_{144} + 8C_{456}$. The temperature variation of these two combinations along with that of C_{111} are plotted in Fig. 6.

As can be seen from Fig. 6, the variation of these combinations of TOE constants with temperature is not very great down to 77 °K. But between 77 and 3 °K, there is a considerable variation in some of them. In particular, the combination $C_{123} + 6C_{144} + 8C_{456}$ crosses zero at 8 °K and becomes positive below that temperature. Since these are the TOE constants which would play a significant role in the transverse modes, the lack of agreement between the theoretically calculated value of thermal expansion from elastic data and measured thermal expansion values might be attributed to the theoretical assumption that the TOE constants are independent of temperature.

Results on ultrasonic harmonic generation can be combined with the hydrostatic pressure derivatives of the elastic constants of cubic materials to determine the complete set of TOE constants. The complete theory and equations are given by Wallace.²⁵ We have combined our results with the pressure derivatives of the elastic constants of silicon measured by Beattie and Schirber²⁶ at 4.0 and 77 °K and by McSkimin and Andreatch²⁷ at 298 °K and evaluated the complete set of TOE constants of silicon at these temperatures. The results are given in Table IV. The agreement with theoretical values²³ is good.

V. SUMMARY AND CONCLUSIONS

The present measurements have been carried out to verify whether silicon shows a similar nonlinear behavior to germanium as the temperature is lowered down to liquid helium temperatures. The measurements indicate that there is a definite temperature dependence for some of the TOE

constants of silicon. The variation is similar to that of germanium.⁹ Using pressure derivative data²⁶ we have evaluated all six TOE constants at 298, 77, and 4 °K; however, the detailed variation with temperature has not been evaluated. From our data, the combinations $C_{123} + 6C_{144} + 8C_{456}$ and $C_{112} + 4C_{166}$ are most sensitive to temperature variations. It has been observed that these combinations for copper do not show much variation with temperature.²⁸ Similar studies on crystals with other kinds of bonding between atoms may shed more light on the physical properties of solids.

ACKNOWLEDGMENT

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