sidered quite fortuitous. That this good agreement is not entirely fortuitous can be seen by using (2.6) to estimate V_0 for N in GaAs:

$$\begin{aligned} V_0(\mathrm{N}:\mathrm{GaAs}) &= V_0(\mathrm{N}:\mathrm{GaP}) - (0.6)(0.5)\ \mathrm{eV} \\ &= -(3.5+0.3)\ \mathrm{eV}, \end{aligned} \qquad (3.6)$$

i.e., V_0 shifts by 0.3 eV on going from the GaP host to GaAs host, whereas to fit the observed binding energies a shift of 0.4 eV is needed. Considering that the only disposable parameter in (3.4) and (3.6) was obtained from analysis of chemical shifts of hydrogenic-donor binding energies, we regard this success as strong evidence for the internal consistency of (2.6), (3.4), and (3.6). If one wishes, one may call this approach the dielectric valence-bond method of treating chemical shifts of impurity states in semiconductors.

The differences in band structure between GaP and Si are rather small for the purposes of treating short-range potentials. Therefore it is of some interest to see what the present model has to say about C substitutional impurities in Si. One has $E_g(\mathrm{SiC}) - E_g(\mathrm{Si}) = 4.5$ eV, compared to $E_g(\mathrm{GaN}) - E_g(\mathrm{GaP}) = 5.8$ eV. Thus the gap shift is smaller. However, as we saw in Sec. 2, $a_{\mathrm{Si}} \sim 0.8$, $a_{\mathrm{GaP}} \sim 0.3$, so that according to (3.3),

$$V_0(\mathrm{C}:\mathrm{Si}) = -(1.6)(4.5)\ \mathrm{eV} = -7.2\ \mathrm{eV}, \qquad (3.7)$$

which is approximately twice the effective depth of N impurities in GaP. In this case the threshold formulas (3.2) and (3.3) no longer apply, but one can say that bound states for C impurities in Si should be deep, with binding energies of order 0.55 eV (half the indirect gap energy).

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Experimental Determination of the Low-Temperature Grüneisen Parameter of Silicon from Pressure Derivatives of Elastic Constants*

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Pressure derivatives of the elastic constants of Si are obtained in fluid and gaseous He at 4 and 77°K on samples in the resistivity range 150–500 Ω cm. The doping level was found to have no effect on these derivatives, and the 4°K values were essentially indistinguishable from those at 77°K. Thus the disparity between the low-temperature limit of the Grüneisen parameter determined from thermal-expansion measurements from 2 to 15°K by Sparks and Swenson and from the 77°K elastic-constant work of McSkimin and Andreatch is not resolved.

I. INTRODUCTION

The low-temperature limit of the Grüneisen parameter γ_0 can be obtained experimentally in two ways. The first method uses directly measured thermodynamic data and the relation $\gamma = \beta B_T V / C_V$, where β is the thermal-expansion coefficient, B_T is the isothermal bulk modulus, and C_V/V is the heat capacity at constant volume per unit volume. The second method, discussed by Daniels,[1] involves a combination of the volume (or pressure) derivatives of the elastic constants. Recent determinations[2,3] of γ_0 by the two techniques have resulted in values differing by more than a factor of 2 in the case of Si in spite of the fact that the estimated uncertainties in each of the methods is of the order of 10%.

This discrepancy might be attributed to the use of 77°K rather than 0°K pressure derivatives in the calculation. However, McSkimin and Andreatch[2] saw essentially no difference between the room-temperature and 77°K values for these derivatives. An examination of the form of the relation between γ_0 and the pressure derivatives of the elastic constants shows that the major contribution stems from dC_{44}/dP. Mason and Bateman[4] have shown that the temperature dependence of C_{44} below 80°K is strongly dependent on doping. While the samples used in the two sets of experiments in question were of relatively high purity, the resistivities of the specimens used by Sparks and Swenson[3] in their thermal-expansion measurements differed from those used by McSkimin and Andreatch[2] in their elastic-constants studies by a factor of 3.

The purpose of this study, then, was to determine whether the pressure dependence of the elastic constants

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[1] W. B. Daniels, Phys. Rev. Letters **8**, 3 (1962).

[2] H. J. McSkimin and P. Andreatch, Jr., J. Appl. Phys. **35**, 2161 (1964).

[3] P. W. Sparks and C. A. Swenson, Phys. Rev. **163**, 779 (1967).

[4] W. P. Mason and T. B. Bateman, Phys. Rev. Letters **10**, 151 (1963).

of Si displayed any unexpected temperature dependence between 77 and 4°K or an equally unexpected dependence upon doping in the range of resistivity (100–500 Ω cm) of the samples used in the above-mentioned experiments. Measurements are reported of the pressure derivatives of C_{11}, C_{12}, and C_{44} for Si at 77 and 4°K on samples spanning the doping levels of the samples investigated by McSkimin and Andreatch[2] and by Sparks and Swenson.[3]

The experimental techniques employed are treated in some detail in Sec. II. Our results and discussion are found in Sec. III.

II. EXPERIMENTAL TECHNIQUE

The choice of experimental technique for measuring changes in the elastic constants will depend upon the method used to apply hydrostatic pressure at helium temperatures. Hydrostatic pressures to ~10 kbar are feasible for this type of experiment using solid He, but this technique requires somewhat involved seals and closures and requires temperature cycling of the specimen for each pressure change.[5] Thus liquid instead of solid He was chosen as the pressure transmitting medium. The low freezing pressure of He (~2100 psi at 4.0°K) puts stringent requirements on the sensitivity of the acoustic velocity measurement. The maximum velocity shift in Si for this pressure is on the order of one part in 10^4, thus sensitivities on the order of one part in 10^7 are desirable. The technique chosen was to measure the change in the resonant frequency of a composite resonator consisting of the sample and two bonded transducers. The necessary sensitivity is available if the frequency modulation method of Melcher, Bolef, and Merry[6] is used.

Experimentally, one transducer is driven by a cw rf signal and the acoustic signal produced is detected by the other transducer. A mechanical resonance is indicated by a maximum in the detected acoustic signal. The rf signal was supplied by a Hewlett-Packard (HP) 608F generator stabilized with a HP 8708A synchronizer. The fine tuning provision in the synchronizer allows the setting of a frequency to within ±5 Hz at 50 MHz. This frequency was monitored with a counter. The acoustically generated signal was amplified and measured with a HP 8405A vector voltmeter.

Several methods of determining the resonant frequencies of the composite resonator were used. The simplest is to adjust the frequency for a maximum reading on the vector voltmeter. This allows a frequency determination with an accuracy of about ±100 Hz at 50 MHz. A second method is to slowly sweep the frequency and plot the signal amplitude against frequency on an X-Y recorder. A set of such peaks at different pressures is shown in Fig. 1. Resolution of the center of these peaks on this graph is better than ±50 Hz but, depending upon the frequency and shape of the particular peak and the frequency lock point on the synchronizer, the resolution could be as bad as ±200 Hz. The third and most accurate method is the frequency-modulation technique.[6] A small frequency modulation is impressed on the rf signal. The center of the resonance peak is indicated when the received signal is modulated at twice the modulation frequency. For this experiment the modulation frequency was 10 Hz and the output of the vector voltmeter examined on an oscilloscope. The frequency swing was set so that the amplitude of the 20-Hz signal was less than 5% of the amplitude of the detected signal, thus ensuring that only the peak was seen and that nonsymmetrical line shapes of the resonance did not affect the measurement. The accuracy of this method was such that the center frequency of the resonant peak could be determined to ±10 Hz in 50 MHz.

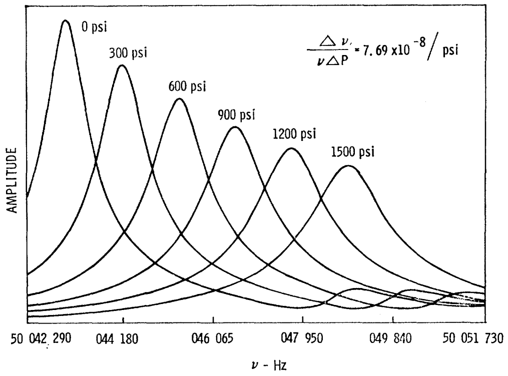

FIG. 1. Signal amplitude as a function of frequency at different pressures. Note the broadening of the resonance peak with increasing pressure. There was no fine structure on this peak although some can be seen on the high-frequency side of it.

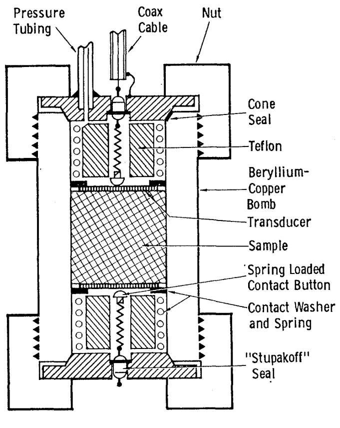

FIG. 2. Schematic diagram of the pressure bomb.

The pressure bomb is illustrated in Fig. 2. The end seals are simple cone seals. The rf lead-ins are "Stupakoff" seals soldered to the beryllium copper bomb with

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[5] A. G. Beattie, J. R. Neighbours, and J. E. Schirber, Phys. Rev. **175**, 599 (1968).

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TABLE I. Measured values of dv/vdP in units of 10^{-8}/psi.

	160 Ω cm		580 Ω cm	
	77°K	4.0°K	77°K	4.0°K
v_l	7.70±0.21	7.59±0.13	7.70±0.13	7.58±0.11
v_{s1}	1.58±0.08	1.58±0.07	1.61±0.12	1.54±0.09
v_{s2}	−1.17±0.20	−1.06±0.17	−1.17±0.11	−1.18±0.12

low-melting (∼70°C) solder. In general these seals were reliable, although a few did crack and develop small leaks after repeated temperature-pressure cycling. The pressure was applied through stainless-steel pressure tubing from He cylinder and measured with a Heise gauge. The uncertainty in the pressure readings was about ±5 psi. All pressures are relative to an atmospheric pressure of ∼625 Torr.

The samples were cylindrical single crystals of silicon, 1.25 cm in diameter and 1.9 cm long. They were oriented with flat and parallel ends lying within $\frac{1}{2}°$ of (110) planes. The samples were ordered[7] with resistivities of 150 and 410 Ω cm to duplicate the samples of Sparks and Swenson[3] and of McSkimin and Andreatch,[2] respectively. Four terminal measurements indicated resistivities of 160 and 580 Ω cm (±10%). The transducers were coaxially plated X- and Y-cut quartz with a 10-MHz fundamental frequency. They were bonded to the samples with a Dow-Corning 200 fluid of 200 000 centistokes viscosity. All bonds were carefully wrung on and then compressed overnight under 50 psi. Attempts to use Nonaq and a lower viscosity DC 200 fluid were not successful, since the bonds broke soon after freezing. For the shear wave measurements, the axes of the samples and transducers were aligned to within ±1° using Laue back reflection patterns from both the samples and transducers.

The experimental procedure was as follows. First, a frequency sweep about 8 MHz wide was made around the harmonic of the transducer to determine the approximate frequencies of the resonances and their relative strengths. The frequencies of the 10 to 15 strongest resonances were then determined at "zero" pressure. The pressure was raised to about 1600 psi and the frequencies again determined. Experimental data were taken around both 50 and 70 MHz for all pressure derivatives.

The sensitivity of the experimental method is such that accuracies of better than ±1% in the pressure derivatives should be easily achievable. Previous work with velocity shifts produced by magnetic fields showed that $\Delta\nu/\nu$ was a function only of the field and was the same for all the mechanical resonances examined. However, in this experiment it was found that while the $\Delta\nu/\nu$ for any given resonance was reproducible until the temperature or bond was changed, different answers were obtained from different resonances. A closer examination showed that for some resonances $\Delta\nu/\nu$ was nonlinear in pressure while for others, even while linear, the slopes $\Delta\nu/\nu\Delta P$ could vary as much as 10%. The most erratic behavior of this type was traced to poor bonds. However, even extreme care in making the bonds did not eliminate this problem.

The application of hydrostatic pressure to a composite resonator produces several effects in addition to a change in the acoustic velocity in the sample. The lengths of the sample, the bonds, and the transducers all change as do the velocities in the transducers and bonds. Changes in the lengths of the transducers and sample and the change in the acoustic velocity in the transducers enter as corrections in the calculation of the pressure derivatives of the elastic constants. Changes in the bonds can be ignored, in a first approximation, because of their very small length. However, there are more subtle effects involving the bonds and transducers which are thought to account for the nonlinear behavior and variation in slope of the different resonant peaks.

The resonant frequencies of the composite resonator depend not only on the lengths and velocities of the various components but also on the phase shifts when the acoustic waves are reflected from the ends of the resonator, i.e., from the transducers. Williams and Lamb[8] have investigated phase shifts from bonded transducers and find that these phase shifts can differ considerably from 180°, the difference depending on both the bond characteristics and the deviation from the transducer resonant frequency. These phase shifts are the reason that the apparent amplitudes of the resonances in a composite resonator are very sensitive to exact matching of the resonant frequencies of the two transducers,[9] even though a loaded transducer is a low-Q device. A velocity-shift measurement using a composite resonator will not be affected by these variations in phase as long as the variable producing the velocity change (for instance, a magnetic field) does not affect the bonds or transducers. However, changing pressure (or temperature to a lesser degree) changes both the bond length and the transducer frequency and thus the phase shifts. Since the phase-shift variations are not linear with frequency change or bond length change, one should not expect the apparent changes in velocity to be linear in pressure.

One other point that can lead to erroneous measurements is the dispersion in the phase velocities caused by the finite dimensions of the sample. This dispersion, which is predicted by the high-frequency solutions of the Pochhammer-Chree equations,[10] will have little effect at most frequencies. However, for resonances very close to the "jump" frequencies, the rapid dispersion of the phase velocity can give shifts in the resonant fre-

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[10] H. J. McSkimin, J. Acoust. Soc. Am. **28**, 484 (1956); M. Redwood and J. Lamb, Proc. Phys. Soc. (London) **B70**, 136 (1957).

quency quite independent of any change in the actual velocity.

III. RESULTS AND DISCUSSION

The measured frequency shifts for the three velocities along the [110] axis are given in Table I, where $v_l=[(C_{11}+C_{12}+2C_{44})/2\rho]^{1/2}v_{s1}=(C_{44}/\rho)^{1/2}$ and $v_{s2}=[(C_{11}-C_{12})/2\rho]^{1/2}$. Each frequency shift is an average of the measured shifts of at least 10 resonances near 50 MHz and 10 near 70 MHz. Weak resonances or those with fine structure were not used. The uncertainty quoted is the standard deviation. The pressure derivatives of the elastic constants can be calculated from the fractional change in resonant frequency by means of

$$\frac{dC}{CdP}=2(1+\alpha)\frac{dv}{vdP}+\tfrac{1}{3}K-2\alpha\frac{dW}{W_0dP},$$

where $\alpha=2av/lc$, K is the compressibility calculated from the elastic constants, l the sample length, a the transducer length, v the velocity of sound in the sample, c the velocity of sound in the transducer, and $W_0^{-1}\,dW/dP$ the pressure derivative of the "natural velocity" of the transducers as discussed by McSkimin, Andreatch, and Thurston.[11] The elastic constants of silicon were not measured in this experiment, except for rough measurements of the velocities to check on the mode being propagated. Instead, McSkimin and Andreatch's[2] values for 77°K and Hall's[12] values for 4.2°K were used. The values of $W_0^{-1}\,dW/dP$ for the transducers were taken from McSkimin *et al.*[11] for 77°K and were assumed to be good at 4.0°K.

Pressure derivatives of the elastic constants are given in Table II. The uncertainties given reflect only the uncertainties in the frequency shifts and an estimated uncertainty in the "zero pressure" frequency of ±50 Hz due to irreversible pressure induced changes in the bond length. The uncertainty in the elastic constants and compressibility are estimated to be less than 0.5% which is well below the quoted errors. While $W_0^{-1}\,dW/dP$ for the shear transducer changed by 17% from between 298 and 77°K, even a change of 20% between 77 and 4°K would change dC_{44}/dP at 4°K by less than 0.5%. The uncertainties quoted in Table II are felt to be realistic barring any unknown systematic error. The agreement with the 77°K values of McSkimin and Andreatch[2] is quite good. The uncertainties given for their values are calculated from their estimates of maximum probable errors and appear to be conservative.

Table II. Pressure derivatives of the elastic constants.

	160 Ω cm		580 Ω cm		McSkimin
	77–K	4.0°K	77°K	4.0°K	77°K
dC_{11}/dP	4.25±0.13	4.19±0.09	4.25±0.10	4.18±0.08	4.29±0.21
dC_{12}/dP	4.11±0.13	4.02±0.09	4.10±0.10	4.05±0.08	4.20±0.36
dC_{44}/dP	0.80±0.02	0.80±0.02	0.81±0.03	0.79±0.03	0.75±0.10

It is apparent in Table II that any change in the pressure derivatives of the elastic constants between 77 and 4.0°K is within the experimental uncertainty. A calculation of the low-temperature Grüneisen constant from the data gives a value of $\gamma_0=0.24\pm0.02$ which is in good agreement with the value of 0.21 calculated from McSkimin and Andreatch's[2] data. No dependence on doping level of the value of the pressure derivatives of the elastic constants of Si was observed. The disagreement between the value of γ_0 calculated from the elastic constants and the value $\gamma_0=0.44$, calculated by Sparks and Swenson[3] from their thermal-expansion data, therefore still exists. Recent thermal-expansion data on Si by Ibach[13] agree with earlier data of Carr *et al.*,[14] and differ systematically with the results of Sparks and Swenson above 20°K. However, only the data of Sparks and Swenson go to low enough temperatures (<15°K) to be useful in calculating the *limiting* value of the Grüneisen parameter.

ACKNOWLEDGMENT

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