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# Elastic constants and lattice anharmonicity of GaSb and GaP from ultrasonic-velocity measurements between 4.2 and 300 K[*]

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Measurements have been made of the transit times of pulses of 30-MHz longitudinal and transverse ultrasonic waves in sulfur-doped $n$-type single crystals of GaSb and GaP down to 4.2 K. Length-versus-temperature measurements have been made for GaP between 80 and 300 K using a silica dilatometer. Values are presented for the elastic constants $C_{ij}$ at various temperatures. The $C_{ij}$ for GaP below room temperature are the first ever reported. From the low-temperature elastic constants are deduced elastic Debye temperatures of 269.4 K for GaSb and 443.8 K for GaP. Martin's relation between the elastic constants is found to be satisfied no better when the "harmonic" elastic constants rather than room-temperature data are used in it. The temperature dependence of each $C_{ij}$ of GaSb and GaP can be fitted in most of our temperature range by a function having the form suggested by Leibfried and Ludwig to account for lattice anharmonicities. The function contains the average energy of a harmonic lattice oscillator multiplied by a factor $K_{ij}$ whose value is chosen to yield agreement with data at 240 and 4.2 K. For GaSb the value of $K_{12}$ is accounted for mainly by a term containing the thermal expansion, the pressure derivative of $C_{12}$, and the bulk modulus; whereas $K_{11}$ and $K_{44}$ each has a much larger value than can be attributed to the thermal-expansion term. Data on other semiconductors are reviewed and it is found that $K_{12} > K_{11} > K_{44}$ for all III-V semiconductors for which sufficient data are available.

## I. INTRODUCTION

The harmonic components of the forces which bond a solid are mainly responsible for the values observed for the elastic constants. However, the anharmonicity of the material is also reflected in the elastic constants to some extent. By measuring the elastic constants over an appropriate range of temperatures, harmonic and anharmonic effects can be separated. In the absence of applied external stress the contribution of the lattice to the elastic constants is representable by an expression for insulators,[1] i.e.,

$$C^{ad}_{\alpha\beta\sigma\tau} = \frac{\partial^2 F_0}{\partial\mu_{\alpha\beta}\,\partial\mu_{\sigma\tau}} + \gamma^2_{\mathrm{TD}} T\,\frac{C_V \delta_{\alpha\beta}\delta_{\sigma\tau}}{V} - \frac{1}{V}\sum_{qj}\left[\left(\frac{\partial^2\omega_{qj}}{\partial\mu_{\alpha\beta}\,\partial\mu_{\sigma\tau}}\right)\frac{\epsilon_{qj}}{\omega_{qj}} + T c_{qj}\gamma^{qj}_{\alpha\beta}\gamma^{qj}_{\sigma\tau}\right], \quad (1)$$

where $F_0$ is the Helmholtz free energy at absolute zero temperature; the $\mu_{\alpha\beta}$ are strains; $\gamma_{\mathrm{TD}}$ is the thermodynamic Grüneisen parameter and equals $B_T V\beta/C_V$, with $B_T$ the isothermal bulk modulus, $\beta$ the volume thermal-expansion coefficient, and $C_V$ the total heat capacity at constant volume $V$; $T$ is the absolute temperature; $\omega_{qj}$ is the vibrational frequency of the mode characterized by wave vector $q$ and polarization $j$; $\epsilon_{qj}$ is the energy and $c_{qj}$ is the heat capacity of mode $qj$; and $\gamma^{qj}_{\alpha\beta} = -\partial\ln\omega_{qj}/\partial\mu_{\alpha\beta}$.

In analyzing our experimental results we shall use a simplified version of Eq. (1) given earlier by Leibfried and Ludwig.[2] It is

$$C_{ij} = \tilde{C}_{ij}(1 - D_{ij}\bar{\epsilon}) , \quad (2)$$

where $\tilde{C}_{ij}$ are the elastic constants in the harmonic approximation, $\bar{\epsilon}$ is the mean energy per lattice oscillator, and $D_{ij}$ depends on the anharmonicity of the lattice. For our purposes it is adequate to take for the mean oscillator energy $\bar{\epsilon}$, that given by the Debye model. Thus

$$\bar{\epsilon} = \tfrac{3}{8} k\tilde{\Theta} + k\tilde{\Theta} F(T/\tilde{\Theta}) , \quad (3)$$

where $\tilde{\Theta}$ is the Debye temperature in the harmonic approximation and

$$F(T/\tilde{\Theta}) = 3(T/\tilde{\Theta})^4 \int_0^{\tilde{\Theta}/T} \eta^3 (e^\eta - 1)^{-1} d\eta . \quad (4)$$

If the $\frac{3}{8}k\tilde{\Theta}$ zero-point energy term were not present in $\bar{\epsilon}$, then the harmonic contribution to each elastic constant would be equal to the value at zero temperature or, for all practical purposes, to the value measured at liquid-helium temperatures when electronic effects like those occurring in metals are absent.[3]

In the presence of zero-point vibrations, we have

$$\tilde{C}_{ij} = C_{ij}(0)/(1 - \tfrac{3}{8} k\tilde{\Theta} D_{ij}) . \quad (5)$$

For insulators and high-resistivity semiconductors the $\tilde{C}_{ij}$ can be calculated from Eq. (5) by using values for the $C_{ij}(0)$, $\tilde{\Theta}$, and the $D_{ij}$ which are obtained as follows. The elastic constants measured at liquid-helium temperatures are used for the $C_{ij}(0)$ and to calculate an elastic $\Theta$ to be used in place of $\tilde{\Theta}$. Values for the $D_{ij}$ are obtained by fitting a relation based on Eqs. (2) and (3) to the observed dependences of the elastic constants on temperature.

The characteristic temperature $\Theta$ is an interesting parameter because of its inherent connection with lattice vibrations. The value deduced for it from the low-temperature elastic constants is commonly designated as $\Theta_0^{\text{elas}}$. A temperature-dependent calorimetric $\Theta$ can be deduced from heat-capacity data. When such data extend to low enough temperature, values of the calorimetric $\Theta$ at various temperatures can be extrapolated to zero temperature to yield the quantity $\Theta_0^{\text{cal}}$. Because of the temperature dependence of the calorimetric $\Theta$ even at low temperatures, it is more difficult to deduce $\Theta_0^{\text{cal}}$ from heat-capacity data than to deduce $\Theta_0^{\text{elas}}$ from the elastic constants, since the latter are practically independent of temperature even at the 4.2-K normal boiling point of liquid He.

It has been shown theoretically[4] that $\Theta_0^{\text{cal}}$ should equal $\Theta_0^{\text{elas}}$ even in the presence of anharmonicity and zero-point vibrations, although previous work had claimed, apparently wrongly, that $\Theta_0^{\text{cal}}$ should be less than $\Theta_0^{\text{elas}}$ due to the presence of such effects.[2] The equality of $\Theta_0^{\text{cal}}$ and $\Theta_0^{\text{elas}}$ seems to be true for a wide variety of crystalline solids which includes metals,[5] semiconductors,[6] and some ionic compounds.[7]

In addition to making possible the determination of a characteristic temperature, the low-temperature elastic constants are also useful in determining harmonic elastic constants—as indicated by Eq. (5) and the comments following it—which are appropriate for comparison with theoretical models for harmonic lattice bonding.

For zinc-blende- (ZB) structure compounds, to which group our GaP and GaSb samples belong, there is no theory which is capable of deducing the harmonic force constants from microscopic considerations. However, there is a rather successful model[8] for ZB compounds which utilizes the valence-force-field approach.[9] In this model all interatomic forces are resolved into a bond-stretching force, characterized by a parameter $\alpha$, and a bond-bending force, characterized by a parameter $\beta$. Martin[8] gives expressions for these parameters which allow them to be evaluated from the elastic constants, interatomic spacing, and effective charge. Martin also shows that $\beta/\alpha$ is approximately proportional to $1-f_i$, where $f_i$ is the ionicity,[10] so that given the value of $\beta/\alpha$ for one ZB compound one can estimate the value of $\beta/\alpha$ for any other ZB compound to within 10% if the ionicity of each compound is known. Martin's model does predict that two quantities depending on the elastic constants (and to a lesser extent on the lattice parameter and effective charge) should be equal to each other. Martin found that for all ZB-structure semiconductors this predicted equality is achieved to within 13% when the room-temperature elastic constants are used. Since his model includes only harmonic effects, it would be more appropriate to use the harmonic elastic constants to test his relationship rather than the values measured at room temperature, and we shall do so in analyzing our data on GaSb and GaP.

The effect of lattice anharmonicity on the elastic constants has been represented in Eqs. (1) and (2) and, since we shall use Eq. (2) to analyze our data, it is appropriate to note that an expression for the anharmonicity parameter $D_{ij}$ has been given which is a simplification of that implied by Eq. (1). Since this expression for $D_{ij}$ contains terms whose values are not accessible by other means in the case of ZB-structure compounds, we cannot calculate the complete temperature dependence of the elastic constants. What we can and will do here is to deduce a value for the one term in $D_{ij}$ for which experimentally accessible quantities are available and compare it with the total $D_{ij}$ implied by the experimental temperature dependence of the elastic constants. Specifically, we shall use the expression

$$D_{ij}\bar{\epsilon} = \frac{B}{C_{ij}} \left(\frac{dC_{ij}}{dP}\right)_T \int_0^T \beta\, dT + D_{ij}^{\text{other}}\,\bar{\epsilon} \ , \qquad (6)$$

where, in addition to previously defined quantities, $(dC_{ij}/dP)_T$ is the pressure derivative of elastic constant $C_{ij}$ at constant temperature and $D_{ij}^{\text{other}}$ simply represents the other terms in $D_{ij}$ not included in the first term on the right-hand side of Eq. (6). A value for $D_{ij}^{\text{other}}$ can then be deduced by subtracting the thermal-expansion term in Eq. (6) from the value of $D_{ij}$ deducible from our ultrasonic data.

The purpose of this paper is to report our measurements of the elastic constants of GaSb and GaP which bear on the above questions. We shall deduce values for the characteristic temperature $\Theta$ and the harmonic elastic constants of each compound and use the latter to test Martin's relation. We shall compare the temperature dependence of the elastic constants of our samples with that implied by Eqs. (2), (3), and (6) and with those of other semiconductors.

## II. EXPERIMENTAL DETAILS

### A. Method of obtaining data

A pulse-echo-overlap method[11,12] was used to measure the transit times of ~2-$\mu$sec-wide pulses of longitudinal and transverse ultrasonic waves in our samples to which were bonded appropriate quartz transducers. The electronic components employed were commercial units and included an rf pulse generator (Matec Model 6000), a wide-

TABLE I. Characteristics of the GaSb and GaP samples and identification of the propagation and polarization of the ultrasonic waves employed. Room-temperature values are given for the resistivity, Hall coefficient ($R_H$), and the sample length in the propagation direction.

| Compound | Sample designation | Dopant | Source | Resistivity ($\Omega$ cm) | $-R_H{}^a$ ($cm^3/C$) | Sample length (cm) | Propagation direction | Polarization ($\vec{\mathcal{P}}$) direction |
|---|---|---|---|---|---|---|---|---|
| GaSb | 1*B* | Sulfur | Purdue | 0.117 | 230 | 1.2542 | [100] | $\vec{\mathcal{P}}_\perp$[100] |
| | | | | | | 0.8933 | [110] | [110] |
| | 1*T* | Sulfur | Purdue | 0.067 | 195 | 0.8422 | [110] | [1$\bar{1}$0] |
| | 75*A* | Sulfur | Purdue | 0.066 | 160 | 1.1567 | [110] | [1$\bar{1}$0] |
| | | | | | | 1.1574 | [100] | $\vec{\mathcal{P}}_\perp$[100] |
| GaP | 70 | Sulfur | Monsanto | 0.29 | 43 | 0.9804 | [100] | $\vec{\mathcal{P}}_\perp$[100] |
| | | | | | | 0.9357 | [110] | [110] |
| | | | | | | 0.9357 | [110] | [1$\bar{1}$0] |

[a] Magnetic inductions between 1000 and 5000 G were used for GaSb and an induction of 4000 G was used for GaP.

band amplifier (Arenberg Model WA 600-D), a dual-trace oscilloscope (Hewlett-Packard Type 183A), a decade-divider and dual-delay generator (Matec Model 122), a highly stable cw signal generator (Hewlett-Packard Model 606B), a synchronizer (Hewlett-Packard Model 8708A), and a frequency counter (General Radio Model 1191B). The basic datum was provided by the frequency counter, which measured the frequency from the cw signal generator which was needed to superpose the electrical signals from two ultrasonic echoes selected from the train following each initial ultrasonic pulse, the latter having been produced in the quartz transducer by the applied pulsed rf signal. Care was taken to superpose appropriate cycles within the two echoes by following the procedures outlined by Papadakis.[12] Changes in velocity could be measured to one part in $10^5$. The absolute accuracy of our system was checked by measuring the velocity of [100], [001] shear waves in InSb and comparing the resultant value for $C_{44}$ with the values reported by other workers.[13,14] Our values were within 0.1% of those obtained in Ref. 14 and were even closer to those obtained in Ref. 13 when we used the same values for the density as the previous workers.

The sample was mounted in a spring-loaded copper holder suspended in a liquid-helium Dewar flask shielded with liquid nitrogen. Temperatures were measured with a commercial (Cryocal) Ge resistance thermometer, a platinum resistance thermometer (Artronix), or copper constantan thermocouple. All of the measurements on GaP and some of the measurements on GaSb were made in a variable-temperature metal (Cryogenic Associates) Dewar with a commercial temperature controller (Princeton Applied Research Model 152) with a GaAs diode sensor (Lake Shore Cryotronics TG-100P). Some of the GaSb measurements were made in a double-glass Dewar, in which case the temperature was allowed to drift up slowly (1 K every few minutes). Repetition of some of these measurements using the controlled system yielded identical results.

*X*-cut and *AC*-cut optically polished quartz disks coaxially plated with chrome-gold (from Valpey Corp.) with fundamental frequencies of 10 or 30 MHz were used as transducers. They were bonded to the samples with Dow Corning 200 fluid of 1000 or 12500-centistoke viscosity or Nonaq stopcock grease.

### B. Samples

Various characteristics of the samples are listed in Table I. The reason for using sulfur-doped samples was to minimize electronic contributions to the elastic constants, since for these samples the concentration of electrons in the conduction band became very small at low temperatures. We avoided using the most common *n*-type GaSb (doped with Te), for example, because in such material electrons remain in the conduction band down to low temperatures and consequently, because there are (111) conduction-band valleys lying only ~ 0.08 eV above the (000) conduction-band minimum, certain of the elastic constants might be affected because of interband or intervalley electron transfer caused by the ultrasonic stress.

The crystalline direction perpendicular to the flat parallel faces of a sample was chosen so that ultrasonic waves could be propagated whose velocities would *not* be affected by the piezoelectricity of the sample, as are the velocities of [111] longitudinal waves and [110], [001] shear waves.[15]

The crystals were oriented to within 0.1° using x rays and a Bragg diffractometer, and samples were cut from them using a wire saw. Hall and

TABLE II. Elastic constants and density of GaSb.

| Temperature (K) | $C_{11}$ ($10^{11}$ dyn/cm$^2$) | $C_{12}$ ($10^{11}$ dyn/cm$^2$) | $C_{44}$ ($10^{11}$ dyn/cm$^2$) | Density (g/cm$^3$) |
|---|---|---|---|---|
| 296 | 8.834 ± 0.2%<br>(8.847 ± 0.3%)[a]<br>(8.849 ± 0.3%)[b] | 4.023 ± 0.2%<br>(4.032 ± 0.7%)[a]<br>(4.037 ± 0.5%)[b] | 4.322 ± 0.2%<br>(4.318 ± 0.2%)[a]<br>(4.325 ± 0.3%)[b] | 5.619 |
| 77 | 9.052 ± 0.2%<br>(9.078 ± 0.3%)[a] | 4.113 ± 0.2%<br>(4.139 ± 0.7%)[a] | 4.435 ± 0.2%<br>(4.432 ± 0.2%)[a] | 5.638 |
| 4.2 | 9.082 ± 0.2%<br>(9.091 ± 0.3%)[a] | 4.131 ± 0.2%<br>(4.146 ± 0.7%)[a] | 4.447 ± 0.2%<br>(4.440 ± 0.2%)[a] | 5.638 |

[a] Reference 23.

[b] Reference 17.

resistivity samples were cut close to the ultrasonic samples whenever possible. One or two sets of flat parallel surfaces were prepared on each ultrasonic sample by lapping on glass plates using a 9-$\mu$m alumina-glycerin-water slurry and then polishing on nylon cloths with successively smaller alumina powders mixed with distilled water. These sample surfaces were measured to be flat to better than 0.5 $\mu$m (using a He light source and an optical flat) and to be parallel to better than 5 sec of arc using an electronic thickness measuring instrument (Brown and Sharpe Model 579-992). Sample thickness was measured to within 0.5 $\mu$m using the above Brown and Sharpe instrument in conjunction with standard gauge blocks.

### C. Determination of elastic constants from data

The velocity of each type of ultrasonic wave was deduced from the measured transit time and the sample length. The elastic constants were in turn deduced from the velocities and the sample density. The relations used to obtain the elastic constants from the velocities[16] are

$$\rho_M v^2_{[110],[110]} = \tfrac{1}{2}(C_{11}+C_{12}+2C_{44}) \,, \tag{7}$$

$$\rho_M v^2_{[110],[\bar{1}10]} = \tfrac{1}{2}(C_{11}-C_{12}) \,, \tag{8}$$

$$\rho_M v^2_{[100],\vec{\varphi}_\perp [100]} = C_{44} \,, \tag{9}$$

where $\rho_M$ is the density and the sets of subscripts on each velocity $v$ give the propagation and polarization $\vec{\varphi}$ direction of the ultrasonic wave.

In computing the velocities and elastic constants for both GaSb and GaP we used our measured sample lengths and room-temperature densities from the literature.[17,18] For lower temperatures we used sample lengths and densities corrected for thermal contraction. For GaSb we used thermal-expansion data from the literature.[19] However, since thermal-expansion data have not be been reported previously for GaP below 300 K, we measured the contraction of our [100]-length GaP sample using a commercial silica dilatometer system (Theta Industries), and found the contraction to be close to that of Ge and GaAs down to 120 K. Therefore GaAs thermal-expansion data from the literature[20] were used to correct for the thermal contraction of GaP down to 77 K. To within the accuracy needed, it was adequate to assume that no significant change of length took place below 77 K. This is reasonable in view of the thermal-expansion coefficient of various type-IV and -III-V semiconductors at low temperatures.

## III. RESULTS AND DISCUSSION

### A. Elastic constants

Elastic-constant values for GaSb at selected temperatures are listed in Table II. It may be noted that our tabulated values at 4.2 and 77 K are slightly larger than those plotted in or implied by Fig. 1. This is because our tabulated values are based on data obtained using all three samples listed in Table I, while the plotted points are based on data for only one or two samples. The differences between the tabulated and plotted values are not significant, since they are of about the same size as our estimated experimental errors. The agreement between our results and representative values of previous workers indicates the high absolute accuracy of our results.

Table III contains elastic constants of GaP at a few temperatures. It can be seen from Table III that our 300-K values for $C_{11}$ and $C_{44}$ are within experimental error of the only previously reported values,[21] while our value of $C_{12}$ at 300 K is about 2.5% greater than that reported previously. This discrepancy exceeds that expected from the combined stated experimental errors, and we have no explanation for it. It seems unlikely that the discrepancy is due to different samples having been used in the two investigations because of the agreement between the values of the other elastic constants. Also, when we checked for consistency using a [111] longitudinal wave in another GaP sample

TABLE III. Elastic constants and density of GaP.

| Temperature (K) | $C_{11}$ ($10^{11}$ dyn/cm$^2$) | $C_{12}$ ($10^{11}$ dyn/cm$^2$) | $C_{44}$ ($10^{11}$ dyn/cm$^2$) | Density (g/cm$^3$) |
|---|---|---|---|---|
| 300 | 14.14 ± 0.2%<br>(14.12 ± 0.21%)[a] | 6.398 ± 0.2%<br>(6.253 ± 0.65%)[a] | 7.028 ± 0.1%<br>(7.047 ± 0.24%)[a] | 4.1297 |
| 180 | 14.282 ± 0.2% | 6.461 ± 0.2% | 7.101 ± 0.1% | 4.1377 |
| 70 | 14.375 ± 0.2% | 6.513 ± 0.2% | 7.139 ± 0.1% | 4.1417 |
| 5 | 14.387 ± 0.2% | 6.520 ± 0.2% | 7.143 ± 0.1% | 4.1417 |

[a] Reference 21.

of unknown dopant, we obtained a value of $C_{12}$ within our stated experimental error.

In order to obtain a value for $\Theta_0^{\text{elas}}$ we used the relation from deLaunay[22]:

$$\Theta_0^{\text{elas}} = \frac{h}{k}\left(\frac{9N}{4\pi V}\right)^{1/3}\left(\frac{C_{44}}{\rho_M}\right)^{1/2}\left(\frac{9f(s,t)}{18+\sqrt{3}}\right)^{1/3}, \quad (10)$$

where $f(s,t)$ is an anisotropy function depending on $s$ and $t$ with $s=(C_{11}-C_{44})/(C_{12}+C_{44})$ and $t=(C_{12}-C_{44})/C_{44}$. Values for $f(s,t)$ were obtained from Table I of Ref. 22. We found upon inserting the elastic constants measured at liquid-helium temperatures into the above relation that

$$\Theta_0^{\text{elas}} = 269.4 \pm 0.2 \text{ K for GaSb},$$

$$\Theta_0^{\text{elas}} = 443.8 \pm 0.2 \text{ K for GaP}.$$

Furthermore, we found that $[f(s,t)]^{1/3} = 0.679$ for GaSb and 0.677 for GaP. In fact, if one makes a plot of $\Theta_0^{\text{elas}}$ versus $(C_{44}/\rho_M)^{1/2}$ data for III-V semiconductors and Ge and Si, all the data fall very close to a straight line, indicating the approximate constancy of $f(s,t)$. The value for GaSb was computed using the lowest-temperature data points shown in Fig. 1 and is equal to within one part in 1000 to that computed using the tabulated low-temperature constants.

Our value of $\Theta_0^{\text{elas}}$ for GaSb is very close to the value of 268 K obtained from previous low-temperature elastic-constant data[23] and even closer to the value of 270 ± 2 K obtained for $\Theta_0^{\text{cal}}$ from heat-capacity data.[24] Similar close agreement between $\Theta_0^{\text{elas}}$ and $\Theta_0^{\text{cal}}$ seems to be the usual rule for III-V compound semiconductors, provided that the heat capacity is measured to temperatures low enough so that extrapolation to $T=0$ is feasible.[24] This indicates that only long-wavelength elastic waves contribute to the thermal as well as to the elastic properties of the lattice of GaSb and other III-V's at low enough temperatures.

Departures from the frequency-squared law for the density of phonon states which have been observed by inelastic neutron scattering[25] and which are important for the heat capacity at higher temperatures[26] are thus not important in the zero-temperature limit.

For GaP no previous value for $\Theta$ is available with which to compare ours. However, a value of 445 K has been determined for GaP from room-temperature elastic-constant data by Weil and Groves[21] using a somewhat different, less accurate method[27] than the one we employed. In order to compare their results with ours we used the method of deLaunay[22] to obtain a room-temperature value of $\Theta^{\text{elas}}$ from their data and then extrapolated this value down to 5 K by using the temperature dependence

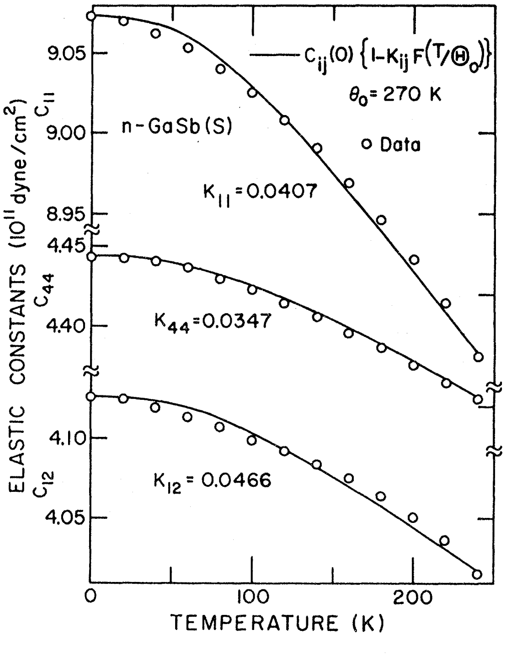

FIG. 1. Elastic-constant data for $n$-GaSb(S) (open circles) plotted vs temperature and curves (solid lines) calculated from Eqs. (2) and (3). $K_{ij}$'s were determined by requiring a fit at the highest and lowest temperature.

we found for $\Theta^{\mathrm{elas}}$ using our own data on GaP. This procedure gave a value of 445 K, in good agreement with our 443.8-K value.

Heat-capacity data for GaP have been reported to no lower than[28] 55 K, so that no value for $\Theta_0^{\mathrm{cal}}$ is available for this material. In order to make a comparison with our value of $\Theta_0^{\mathrm{elas}}$ for GaP we note that using room-temperature heat-capacity data[28] and the Debye model one obtains a calorimetric $\Theta$ of 493 K. This value is about 11% higher than our $\Theta_0^{\mathrm{elas}}$. The size of the disagreement is probably to be expected in view of the fact that the zero- and room-temperature values of $\Theta^{\mathrm{cal}}$ differ by about 6% in the case of GaAs and by about 11% in the case of GaSb, even though $\Theta^{\mathrm{cal}}$ for each of these substances exhibits a much larger (but nonmonotonic) total variation with temperature.[26]

### B. Test of Martin's relationship

As mentioned in the Introduction, Martin,[8] employing a modified valence-force-field approach, has derived a relationship involving the elastic constants (and other quantitites) which seems to be satisfied rather well, even when room-temperature elastic-constant data are used in it. The relationship is

$$M=\frac{2C_{44}(C_{11}+C_{12}-C')}{(C_{11}-C_{12})(C_{11}+3C_{12}-2C')+0.831C'(C_{11}+C_{12}-C')}=1\,, \tag{11}$$

where $C'=0.314\,SC_0$, $C_0=e^2/r^4$, with $e$ being the electronic charge and $r$ the nearest-neighbor distance, and $S=(e_B^*/e)^2/\kappa_\infty$, with $e_B^*$ being the Born effective charge and $\kappa_\infty$ the high-frequency dielectric constant.

We find that for GaSb $M=1.072$ if use is made of the low-temperature values of $C'$ and $C_0$ and harmonic elastic constants [deduced by applying Eq. (5) to our data] and that $M=1.071$ using room-temperature quantities in Eq. (11). For GaP we find that $M=1.052$, using low-temperature values of $C_0$ and $C'$ and harmonic elastic constants, and that the same value is calculated for $M$ using room-temperature data. Thus the validity of Martin's relationship is not improved by using harmonic elastic constants in it.

### C. Temperature dependence of the elastic constants

Figures 1 and 2 show, respectively, our elastic-constant results for GaSb and GaP plotted as a function of temperature. It can be seen that the data can be fitted quite well by a function which is a consequence of Eqs. (2) and (3) if $\tilde{\Theta}$ is replaced by $\Theta_0^{\mathrm{elas}}$ and $K_{ij}=D_{ij}k\Theta_0/(1-\frac{3}{8}k\Theta_0 D_{ij})$, where for brevity we have written $\Theta_0$ for $\Theta_0^{\mathrm{elas}}$ both in the expression for $K_{ij}$ and in the figures.

For both GaSb and GaP we found that $K_{12}>K_{11}>K_{44}$ (see Figs. 1 and 2). Wondering whether this was generally true for III-V compounds, and perhaps for Ge and Si also, we have reviewed data which are available in the literature[6] and have found that the above inequalities do hold for the three other III-V's whose elastic constants have been reported below room temperature (i.e., GaAs, InAs, and InSb). However, for Ge $K_{11}>K_{44}>K_{12}$ and for Si $K_{12}>K_{44}>K_{11}$. Table IV shows values of $K_{ij}$ upon which these statements are based.

The value of each $K_{ij}$ needed to fit our GaSb data is larger than that implied by the first term in Eq. (6). A specific comparison is made in Table V, which shows that the thermal-expansion term accounts for most of the temperature dependence of $C_{12}$ but for only about one-third of that of $C_{11}$ and for only about one-fifth of that of $C_{44}$. The difference between the observed change of each $C_{ij}$ with temperature and that calculated from the thermal expansion we attribute to the term containing $D_{ij}^{\mathrm{other}}$ in Eq. (6). Thus the difference provides an approximate measure of the anharmonicities involved

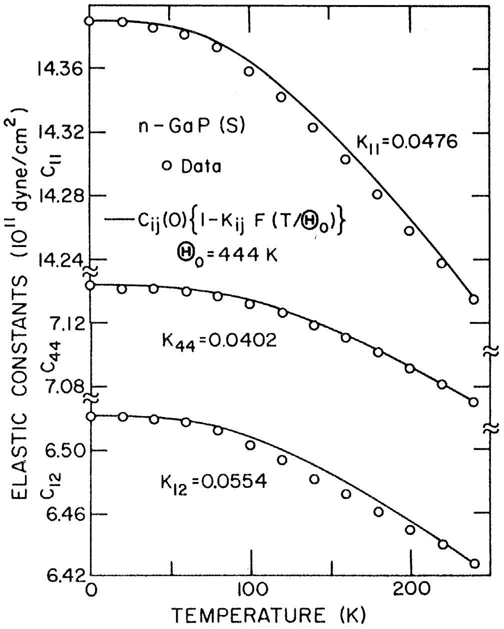

FIG. 2. Elastic-constant data for $n$-GaP(S) (open circles) plotted vs temperature and curves (solid lines) calculated from Eqs. (2) and (3). $K_{ij}$'s were determined by requiring a fit at the highest and lowest temperature.

TABLE IV. Elastic Debye temperature at $T = 0$ K and values of factors needed to fit the temperature dependence of the elastic constants in terms of the thermal energy of an average harmonic-lattice oscillator.

| | $\Theta_0^{\text{elas}}$ (K) | $K_{11}$ | $K_{12}$ | $K_{44}$ | Source of $\Theta_0^{\text{elas}}$ and data to calculate $K_{ij}$ |
|---|---|---|---|---|---|
| Si | 649 | 0.048 | 0.086 | 0.056 | Ref. 6 |
| GaP | 444 | 0.048 | 0.055 | 0.040 | Present work |
| Ge | 375 | 0.051 | 0.038 | 0.046 | Ref. 6 |
| GaAs | 348 | 0.054 | 0.055 | 0.041 | Ref. 6 |
| GaSb | 270 | 0.041 | 0.046 | 0.035 | Present work |
| InAs | 252 | 0.052 | 0.062 | 0.033 | Ref. 6 |
| InSb | 206 | 0.037 | 0.045 | 0.026 | Ref. 6 |

TABLE V. Fractional changes in the elastic constants of GaSb between 80 and 240 K. The thermal-expansion contribution $-(B/C)(dC_{ij}/dP)\int\beta\, dT$ was calculated using the room-temperature value of $dC_{ij}/dP$ from Ref. 31 of the text and the thermal expansion obtainable from Ref. 19 of the text.

| | $ij$ | $-\dfrac{B}{C_{ij}}\dfrac{dC_{ij}}{dP}\displaystyle\int_{80\text{ K}}^{230\text{ K}}\beta\, dT$ | $\dfrac{C_{ij}\text{ (240 K)} - C_{ij}\text{ (80 K)}}{C_{ij}\text{ (80 K)}}$ |
|---|---|---|---|
| | 11 | $-7.4\times10^{-3}$ | $-20\times10^{-3}$ |
| GaSb | 12 | $-15\times10^{-3}$ | $-22\times10^{-3}$ |
| | 44 | $-3.1\times10^{-3}$ | $-17\times10^{-3}$ |

in the last two terms in Eq. (1).

Inspection of data on other semiconductors reveals similar differences between the values of a particular $K_{ij}$ deduced from the temperature dependence of the elastic constants and that implied by the thermal-expansion term in Eq. (6). Furthermore, for a particular pair of $ij$ the thermal-expansion term calculated for each different semiconductor listed in Table IV (except for GaP, for which pressure data are lacking) has a rather similar value. This can be understood empirically as the consequence of the fact that all these semiconductors except[29] Si are characterized by very similar amounts of thermal expansion,[30] and by rather similar values of the factor[6,31] $(B/C_{ij})(dC_{ij}/dP)$ for each particular pair of $ij$. More specifically, $(B/C_{11})(dC_{11}/dP)$ is close to 3.2 for all the III-V's and Ge and is about 2.7 for Si; $(B/C_{12})(dC_{12}/dP)$ ranges from a low of 6.2 for InSb to a high of 8.3 for Ge; and $(B/C_{44})(dC_{44}/dP)$ ranges from a low of 0.65 for InAs to a high of 1.5 for Ge.

Since for GaP the pressure derivatives of the elastic constants have not been measured, we cannot calculate the contribution of the thermal expansion to the temperature dependence of the elastic constants. However, in view of the fact that each $B/C_{ij}$ factor has a value for GaAs which agrees to within 10% or better with that found for GaSb (and the already noted similarity of the thermal expansions of III-V's), it seems likely that the thermal-expansion contribution to the temperature dependence of the elastic constants of GaP will also be less than that needed to account for the $K_{ij}$ values, as was true in the case of our GaSb sample.

## IV. CONCLUSION

Information about both harmonic and anharmonic lattice forces in GaSb and GaP can be obtained from measurements of the elastic constants as a function of temperature. Division of the temperature dependence into a calculable and an inaccessible part shows that the third-order term, which has the same temperature dependence as the thermal expansion, is too small to account for all of the temperature dependence of the elastic constants and that higher-order terms must be considered. The equality of $\Theta_0^{\text{elas}}$ and $\Theta_0^{\text{cal}}$ is confirmed for GaSb, indicating that only long-wavelength elastic modes are involved in the heat capacity of GaSb at lowest temperatures. Unfortunately, calorimetric data for GaP do not exist to low enough temperatures to allow us to compare our $\Theta_0^{\text{elas}}$ with $\Theta_0^{\text{cal}}$.

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