Piezo-Raman measurements and anharmonic parameters in silicon and diamond

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Measurements of the frequency shift of optical phonons in Si with uniaxial stress have been performed by Raman spectroscopy using a laser frequency in the region of transparency. A mean deviation of 25% has been found in the phonon deformation potentials as compared with previous results obtained with laser frequencies above the absorption edge. The new values are $p/\omega_0^2=-1.85\pm0.06$, $q/\omega_0^2=-2.31\pm0.06$, and $r/\omega_0^2=-0.71\pm0.02$, and 1.08 ± 0.06 for the Grüneisen parameter γ_G. A valence-force-field model with five anharmonic parameters provides a consistency check between the phonon deformation potentials and the third-order elastic constants of Si. On the basis of this model, existing uniaxial-stress data for the optical phonons of diamond and for the pressure dependence of the second-order elastic constants have been reanalyzed and the corresponding five anharmonic parameters have been determined. In this manner, reliable values for the third-order elastic constants have been obtained for diamond.

I. INTRODUCTION

The harmonic vibrational properties of diamond-type semiconductors are rather well known. The Keating model,[1,2] based on the simple valence-force-field (VFF) approach developed by Musgrave and Pople for diamond,[3] provides an accurate set of values for the second-order elastic constants and for the zone-center optical-phonon frequency. Only two harmonic force constants are necessary for this purpose. In a later study also based on the VFF model, Tubino *et al.*[4] fitted the complete phonon dispersion relations with six spring constants as fitting parameters. Furthermore, bond-charge models[5] and shell models,[6] or a combination of these,[7] produce quite good fits of the phonon dispersion relations. *Ab initio* total-energy calculations in the presence of frozen phonons[8] also predict a good set of harmonic parameters.[9,10]

Despite the agreement between theory and experiment for the harmonic parameters of Si, large discrepancies exist in the internal strain parameter ζ, introduced by Kleinman,[11] which represents the change in bond length under a [111] strain. The experimental values, obtained by x-ray diffraction for silicon,[12–16] range from 0.54 to 0.72, while theories predict values ranging from 0.50 to 0.61.[9,10,17–20] Cousins *et al.*[16] claim that there is an enhancement of the strain near the surface of as much as 35%. Taking into account this surface effect, they obtained an experimental value of $\zeta=0.54\pm0.04$, in agreement with the theoretical ones. We shall return to this point in the Discussion (Sec. VI).

For the anharmonic parameters, on the other hand, the agreement between experimental results and theoretical estimates is not as good as for the harmonic ones. While the third-order elastic constants can be fitted reasonably well with a three-parameter Keating model,[21] we have found that the mode-Grüneisen parameter and the phonon deformation potentials (PDP's) of Si obtained from this model [$\gamma_G=1.05$, $r/\omega_0^2=-0.41$, and $(p-q)/2\omega_0^2=0.59$; see definitions in Sec. IV] are quite different from the experimental values. The parameters $(p-q)/\omega_0^2$ and r/ω_0^2 obtained from *ab initio* calculations also show considerable deviations from some of the experimental values.[9,10]

Vanderbilt *et al.*[22] recently used a generalized Keating model with 12 parameters to fit, by least-squares, a total of 22 data corresponding to harmonic and anharmonic constants. The fitted parameters that describe the dependence of the phonon frequencies on the strain (PDP's), however, are not in agreement with the experimental ones.

The PDP values of several semiconductors have been measured in the past, using laser frequencies either above[23] or below the gap.[24,25] It has been concluded from these studies that there is some relaxation of the stress near the surface (opposite the increase found by Cousins *et al.*[16]), so that the phonon shifts measured in the bulk are between 10% and 30% larger than those observed near the surface. This fact is particularly convincing in the cases of GaAs (Refs. 23 and 24) and InP (Ref. 25), which have been investigated in both ways, i.e., with laser frequencies both above and below the gap. The latter measurements were performed with a cw neodymium-doped yttrium-aluminum-garnet (Nd-YAG) laser ($h\nu=1.165$ eV). For photons of this energy, both GaAs and InP are transparent. AlSb (Ref. 26) and indium-hardened GaAs (Ref. 27) have also been investigated.

In this work we present Raman data for the zone-center phonon frequency ω_0 of Si under uniaxial stress, taken with a cw Nd-YAG laser. In this case it was necessary to work at liquid-N_2 temperature in order to make Si transparent to this radiation. We have obtained from this experiment a set of phonon deformation potentials p, q, and r which are somewhat higher and more accurate

than those obtained previously.[28,29] We have performed a fit to all available anharmonic constants related to vibrations at the center of the Brillouin zone using a Keating model which includes two additional VFF anharmonic force constants that were omitted in Keating's original work.[21] First, the two harmonic force constants and the internal-strain parameter ζ were obtained from a fit to the second-order elastic constants and the zone-center optical-phonon frequency; the value of ζ established in this way (=0.533) agrees well with those extracted from *ab initio* calculations. Using this set of harmonic force constants, plus the five anharmonic VFF parameters, we obtained a satisfactory fit to existing anharmonic data, a fact which emphasizes the need for incorporating the additional two anharmonic force constants introduced here.

In view of the experience gained in the analysis of the anharmonic parameters of Si, we decided to test the validity of this model further by reanalyzing data available for diamond. In this case, however, the only values known from experiments are those of p, q, and r, and the pressure derivatives of the second-order elastic constants. We have found a value of $\zeta=0.13$ from the fit of the two harmonic parameters to the zone-center optical-phonon frequency and to the second-order elastic constants. This value differs from the one (=0.21) found in the pioneering work of Martin,[2] but agrees quite well with the most recent determination by synchrotron radiation ($\zeta=0.125$).[30] Furthermore, including the two additional VFF anharmonic parameters in diamond leads, after fitting, to a complete set of third-order elastic constants unavailable otherwise.

In Secs. II and III the experimental techniques and the results from the piezo-Raman data are discussed. In Sec. IV we present the Keating model with the five anharmonic parameters and explicit expressions for the third-order elastic constants, the Grüneisen parameter, and the phonon deformation potentials. Section V includes numerical results and the fitting procedure. Discussion and conclusions are presented in Sec. VI.

II. RAMAN MEASUREMENTS

The Raman-scattering measurements were taken at 110 K. At this temperature the indirect gap of Si practically coincides with the photon energy of the Nd-YAG laser radiation. A germanium detector and conventional synchronous detection was used. The samples were parallelepipeds of $15\times1.5\times1.5$ mm^3 and $15\times1.0\times1.0$ mm^3 size and were cut in the directions [100],[010],[001] (*a* samples) and [111],[11$\bar{2}$],[$\bar{1}$10] (*c* samples). In the *c* samples the stress was applied along the [111] direction. A third sample (*d*) oriented along [110], [001], and [1$\bar{1}$0] was also used for checking the consistency of the data. The material used was commercial high-purity Si obtained from Wacker Chemitronics (Burghausen, FRG).

The measurements were taken in the right-angle configuration. A Dove prism was used to align the image of the beam through the sample with the entrance slit of the monochromator. A Hg line ($h\nu=1.098$ eV) was used to ensure the reproducibility of the measurements. Other experimental details can be found in Ref. 24.

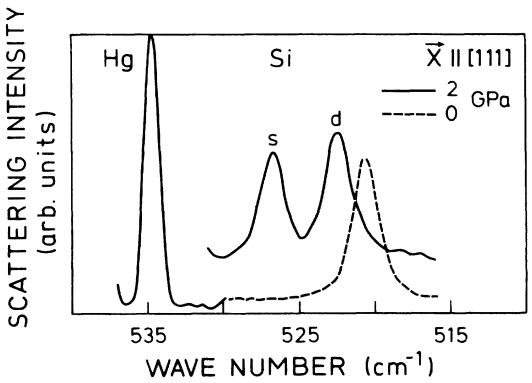

FIG. 1. Effect of a uniaxial stress along the [111] direction on the Raman phonon of Si at 110 K. At 2 GPa the doublet and singlet components are clearly defined. The Hg line was used for calibration. The spectra have been displaced for clarity.

III. RESULTS

Figure 1 shows two spectra, at 0 and 2 GPa, taken from sample *c* with the polarizer at 45° and no analyzer. The singlet and doublet components are clearly resolved. (This was not the case with the previous measurements, which were performed above the gap and at room temperature.[28,29]) Most of the present data were taken with stresses up to ~1.2 GPa to avoid possible complications from nonlinearities.

Figures 2 and 3 show the shift of the phonon frequencies with uniaxial stress applied in either the [001] or [111] direction, respectively. The solid lines are least-squares fits to the experimental points, while the dashed ones represent the calculated shifts due to the hydrostatic content of the applied stress. The fits yield the following slopes: For hydrostatic shift,

$$\Delta\omega_H=1.88\pm0.05\ \text{cm}^{-1}/\text{GPa}\ ;$$

for singlet-doublet splitting,

$$\Delta\omega_{[111]}=2.31\pm0.08\ \text{cm}^{-1}/\text{GPa}\ ;$$

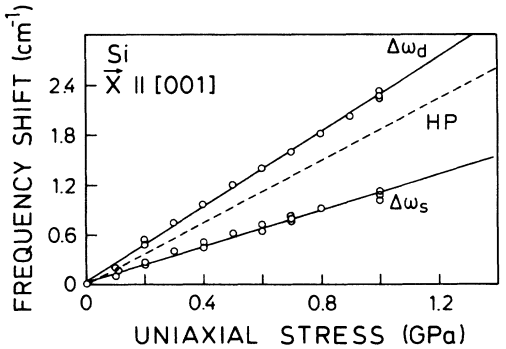

FIG. 2. Frequency shifts of the singlet and doublet components measured with stress along [001]. Solid lines are linear least-squares fits to the experimental points. The dashed line shows the calculated shift corresponding to the hydrostatic component.

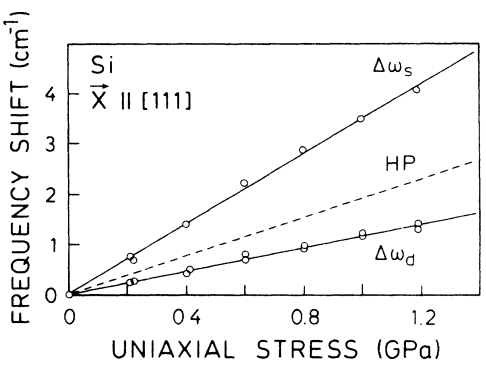

FIG. 3. Same as Fig. 2 for stress along [111].

for single-doublet splitting,

$$\Delta\omega_{[001]} = -1.16 \pm 0.12 \text{ cm}^{-1}/\text{GPa} .$$

In Table I we compile the Grüneisen parameter γ_G of the Raman-active phonon of Si and the three PDP values deduced from the above shifts, together with the corresponding values from other experimental and theoretical determinations. Let us recall that $\gamma_G = -(p+2q)/6\omega_0^2$ and that $p-q$ and r represent the single-doublet splitting under [100] and [111] compression, respectively. For $X \| [110]$ the analysis shows that the triple degeneracy of the zone-center phonon is completely removed and the three new singlet components at frequencies ω_1, ω_2, and ω_3 have their eigenvectors along [110], [001], and [1$\bar{1}$0], respectively.[23–25] The right-angle–scattering geometry with incidence along [001] and detection along [1$\bar{1}$0] allows the observation of all three components with incident (scattered) polarizations along [110] ([001]), [110] ([110]), and [1$\bar{1}$0] ([001]), respectively. Measurements of the components ω_1, ω_2, and ω_3 produced the slopes 2.50, 2.25, and 0.60 in cm^{-1}/GPa, which compare very favorably with those estimated from the PDP based on samples *a* and *c*, i.e., 2.80, 2.26, and 0.52, respectively.

IV. THE KEATING MODEL

In the original work of Keating on the theory of third-order elastic constants[21] only three anharmonic VFF spring-constant parameters γ, δ, and ε were considered, and the six third-order elastic constants were expressed in terms of these parameters. There are, however, two terms that were not taken into account in the energy expansion considered by Keating. The corresponding spring constants are, in principle, of the same order of magnitude as δ or ε. We have included these two terms in the energy expansion and represent them by the new VFF parameters η and θ. The five-parameter model is then used to fit simultaneously our data and the existing values of the third-order elastic constants of Si.

The total energy per primitive cell is written, up to third order in angular and bond deformations, as

$$\begin{aligned} E = {} & \frac{1}{2}\frac{\alpha a^2}{4}\sum_{i\neq 1} h_{ii}^2 + \frac{1}{2}\frac{\beta a^2}{2}\sum_{i<j} h_{ij}^2 + \tfrac{1}{12}\gamma a^3 \sum_{i=1}^{4} h_{ii}^2 \\ & + \tfrac{1}{6}\delta a^3 \sum_{i<j} h_{ij}^3 + \tfrac{1}{4}\eta a^3 \sum_{i\neq j} h_{ii}^2 h_{ij} + \tfrac{1}{4}\varepsilon a^3 \sum_{i\neq j} h_{ii} h_{ij}^2 \\ & + \tfrac{1}{2}\theta a^3 \sum_{i<j} h_{ii} h_{jj} h_{ij} , \end{aligned} \tag{1}$$

where $4a$ is the crystallographic unit-cell lattice constant and

$$h_{ii} = \frac{x_i^2}{a^2} - 3, \quad h_{ij} = \frac{\mathbf{x}_i \cdot \mathbf{x}_j}{a^2} + 1 .$$

We have omitted in Eq. (1) the terms in $h_{ii}^2 h_{jj}$ (coefficient $k_{rrr'}$ in Ref. 22) since, as shown in Ref. 22, they have little effect on the fitted data. Physically, these terms imply "anharmonic crosstalk" between the lengths of contiguous bonds. We feel that the crosstalk should be small, a fact which is corroborated by the results of Ref. 22 and the satisfactory fits to anharmonic data obtained below.

This expression fulfills the requirement of translational and rotational invariance, in the same way as that of Keating. Only the bonds about one atoms are included in the first and third terms of Eq. (1), to avoid double counting on the sum over the primitive unit cell. In the remaining terms, a factor of 2 has been taken into account in order to include both atoms in the primitive cell while limiting the sum to only one atom. This procedure is correct only for the calculation involving the elastic constants and the zone-center optical-phonon frequencies.

TABLE I. Mode-Grüneisen parameter and phonon deformation potentials of Si.

	Experiment				Theory			
γ_G	0.92[a]	0.91±0.05[b]	0.98±0.06[c]	1.08±0.07[d]	0.9[e]	0.99[f]	0.70[g]	1.21[h]
p/ω_0^2	−1.25[a]	−1.49±0.07[b]		−1.85±0.06[d]	−1.63[e]	−1.67[f]	0.11[g]	−2.11[h]
q/ω_0^2	−1.87[a]	−1.97±0.09[b]		−2.31±0.06[d]	−1.89[e]	−2.13[f]	−2.03[g]	−2.57[h]
r/ω_0^2	−0.66[a]	−0.61±0.03[b]		−0.71±0.02[d]	−0.6[e]	−0.97[f]	−2.78[g]	−0.69[h]

[a]Reference 28, 6328-Å laser radiation.
[b]Reference 29, 6471-Å laser radiation.
[c]Reference 31, diamond-anvil cell.
[d]Present work.
[e]Reference 9, *ab initio* pseudopotential method.
[f]Reference 10, full potential linear muffin-tin-orbitals method (FP-LMTO).
[g]Reference 22, from fitted VFF-like parameters (see discussion, Sec. VI).
[h]Present work, from fitted VFF parameters.

Following a procedure similar to that of Keating,[21] it is straightforward to show that the anharmonic elastic constants are given by

$$
\begin{aligned}
c_{111} &= \gamma-\delta-3\eta+9\varepsilon-3\theta \ , \\
c_{112} &= \gamma-\delta-3\eta+\varepsilon-3\theta \ , \\
c_{123} &= \gamma+3\delta-3\eta-3\varepsilon-3\theta \ , \\
c_{144} &= (1-\zeta)^2\gamma+(1+\zeta)^2\delta-(1-\zeta)(3+\zeta)\eta \\
&\quad +(1+\zeta)(3\zeta-1)\varepsilon+(5\zeta-1)(\zeta-1)\theta+c_{12}\zeta^2 \ , \\
c_{166} &= (1-\zeta)^2\gamma-(1+\zeta)^2\delta-(1-\zeta)(3+\zeta)\eta \\
&\quad +(1+\zeta)(3-\zeta)\varepsilon-(1-\zeta)(3+\zeta)\theta+c_{12}\zeta^2 \ , \\
c_{156} &= (1-\zeta)^3\gamma-3(1-\zeta)^2(1+\zeta)(\eta-\theta) \ .
\end{aligned}
\tag{2}
$$

The internal-strain parameter ζ and the elastic constants c_{ij} are related to the harmonic force constants α and β by[1]

$$
\zeta=\frac{\alpha-\beta}{\alpha+\beta} \ , \tag{3}
$$

$$
\begin{aligned}
c_{11} &= \frac{\alpha+3\beta}{4a} \ , \\
c_{12} &= \frac{\alpha-\beta}{4a} \ , \\
c_{14} &= \frac{\alpha\beta}{a(\alpha+\beta)} \ ,
\end{aligned}
\tag{4}
$$

while the zone-center optical-phonon frequency can be written as[2]

$$
\omega_0^2=\frac{8}{M}(\alpha+\beta) \ , \tag{5}
$$

where M is the mass of the Si atom. The mode-Grüneisen parameter and the phonon deformation potentials take the following form in our model,

$$
\begin{aligned}
\gamma_G &= -\frac{5\alpha-\beta+4a(3\gamma-\delta+3\eta+\varepsilon+7\theta)}{6(\alpha+\beta)} \\
\frac{r}{\omega_0^2} &= 1+\frac{4a[\gamma(1-\zeta)-(\eta-\theta)(3\zeta-1)]}{\alpha+\beta} \ , \\
\frac{p-q}{2\omega_0^2} &= 1+\frac{4a(\delta+2\varepsilon+2\theta)}{\alpha+\beta} \ .
\end{aligned}
\tag{6}
$$

The term equal to 1 on the right-hand side of Eq. (6) is a geometrical term produced by the bending of bonds and is independent of anharmonicity; the second term contains the anharmonic parameters. In the case of $p-q$ of Si, the two terms have opposite sign. For diamond the signs are the same (see Table IV below). Note that the value of r depends rather critically on the internal-strain parameter ζ.

V. FITTING PROCEDURE

The values of the VFF parameters α and β reported by Keating and Martin in Refs. 1 and 2 were obtained through the requirement of best fit to the second-order elastic constants only. However, as pointed out by Martin, these values lead to phonon frequencies ω_0 which are by 5% (15%) different from the experimental ones for Si (diamond). Since the theory provides the elastic constants and the phonon frequency in terms of α and β, we believe that more reliable values of α and β can be obtained by fitting the second-order elastic constants and the phonon frequency simultaneously.

In Table II we present the fitted values of α and β, the corresponding value of ζ for silicon and diamond, and the most reliable experimental data of the latter. Also, for comparison, we give the values of ζ which Martin deduced by fitting only the elastic constants. The values of α,β,ζ which we obtained, together with available experimental values for the second-order elastic constants, were next used as fixed parameters in the fitting of the anharmonic coefficients.

A. Silicon

The third-order elastic constants of Si are known.[32] They allow us to obtain the five VFF constants used in the present model from a simultaneous fit of these third-order elastic constants, of the Grüneisen parameter, and of the phonon deformation potentials. The inverse of the squared experimental uncertainties has been used as a weighting factor in the least-squares fit. The resulting values of the VFF constants are given in Table III, together with those obtained through the same procedure with the three-parameter model of Keating, and with the values obtained from the anharmonic constants of Vanderbilt *et al.*[22] (the necessary conversion equations are

TABLE II. Harmonic force constants (in units of 10^5 dyn/cm) and internal-strain parameter for Si and diamond.

	α			β			ζ					
Si	0.49[a]	0.431[b]	0.485[c]	0.140[a]	0.134[b]	0.138[b]	0.533[a]	0.546[b]	0.56[c]	0.54[e]	0.53[f]	0.51[g]
C	1.068[a]		1.293[c]	0.821[a]		0.848[c]	0.131[a]	0.21[c]	0.125 $\pm$0.02[d]			

[a]Present work.
[b]Reference 22, see Sec. VI.
[c]Reference 2, fit to second-order elastic constants only.
[d]Reference 30, synchrotron-radiation measurements.
[e]Reference 16, x rays.
[f]Reference 9, *ab initio* pseudopotential.
[g]Reference 10, LMTO.

TABLE III. Anharmonic force constants (in 10^{12} dyn/cm^{-2}) obtained from least-squares fit as explained in the text.

	Si			Diamond	
γ	-3.50^{a}	-3.80^{b}	-3.51^{c}	-14.78^{a}	-16.7^{d}
δ	0.45^{a}	0.34^{b}	0.47^{e}	1.40^{a}	0.95^{d}
η	0.20^{a}	0.52^{b}		-2.27^{a}	
ε	-0.46^{a}	-0.52^{b}	-0.47^{c}	-6.54^{a}	-4.99^{d}
θ	-0.19^{a}	0.17^{b}		1.81^{a}	

[a]Present work.
[b]Reference 22, as deduced from Eq. (9).
[c]Reference 1.
[d]Reference 33, based on $\zeta=0.21$.

given in Sec. VI). Table IV shows the improved values (obtained from the present fit) for the anharmonic elastic constants, and the phonon deformation potentials $(p-q)/2\omega_0^2$ and r/ω_0^2, together with the experimental values and uncertainties.

B. Diamond

The complete set of third-order elastic constants of diamond is not known, and therefore the procedure applied in the case of Si had to be modified. Following the approach of Grimsditch *et al.*,[33] but with $\zeta=0.13$ (instead of $\zeta=0.21$), and with our five-parameter model, we were able to obtain a set of third-order elastic constants from the simultaneous fits of the three pressure derivatives of the elastic constants plus the three PDP's (a total of six experimental data). The expressions of the pressure derivatives of the second-order elastic constants in terms of the third-order elastic constants are[35,36]

$$\begin{aligned}
\frac{\Delta\frac{1}{2}(c_{11}-c_{12})}{\Delta P} &= -1-\frac{1}{3B}(c_{11}-c_{12}+\tfrac{1}{2}c_{111}-c_{123}) , \\
\frac{\Delta\frac{1}{2}(c_{11}+c_{12}+2c_{44})}{\Delta P} &= -1-\frac{1}{3B}(c_{11}+c_{12}+2c_{44}+\tfrac{1}{2}c_{111}+2c_{112} \\
&\quad +c_{144}+2c_{166}+\tfrac{1}{2}c_{123}) , \\
\frac{\Delta c_{44}}{\Delta P} &= -1-\frac{1}{3B}(c_{44}+c_{144}+2c_{166}) .
\end{aligned} \tag{7}$$

Table IV includes the values of the third-order elastic constants obtained in this way. These can then be used to generate values of the pressure derivatives through Eq. (7). Such values are also included in Table IV and reflect the consistency of the whole procedure.

VI. DISCUSSION AND CONCLUSIONS

The Keating model with two harmonic parameters α and β fits the elastic constants and the zone-center optical-phonon frequency at the Γ point very well, as discussed earlier (also see Table II). However, it does not fit the phonon frequency of the TA mode at the X or L point. According to the model, these frequencies depend only on β.[3] A very good fit to the TA frequency at the X point is obtained in the Vanderbilt model with six second-order VFF constants, by loading the latter with a very large weighting factor. For convenience, we give the following expressions connecting the harmonic force constants used in Refs. 1 and 2:

$$\begin{aligned}
\alpha a^2 &= 4k_{rr}+\tfrac{2}{3}k_{\theta\theta}+8k_{r\theta} , \\
\beta a^2 &= 4k_{\theta\theta} .
\end{aligned} \tag{8}$$

In order to calculate the elastic constants and the

TABLE IV. Third-order elastic constants (in 10^{12} dyn cm^{-2}), pressure derivatives of second-order elastic constants, mode-Grüneisen parameter, and phonon deformation potentials deduced from the force constants given in Tables II and III. The standard deviations for Si and diamond are 0.0035 and 0.0025, respectively.

	Si		Diamond	
c_{111}	-8.16^{a}	-8.25 ± 0.1^{b}	-73.67^{a}	
c_{112}	-4.46^{a}	-4.51 ± 0.05^{b}	-21.36^{a}	
c_{123}	-0.79^{a}	-0.64 ± 0.1^{b}	10.40^{a}	
c_{144}	-0.14^{a}	0.12 ± 0.25^{b}	1.86^{a}	
c_{166}	-3.44^{a}	-3.1 ± 0.1^{b}	-32.92^{a}	
c_{456}	-0.76^{a}	-0.64 ± 0.2^{b}	0.76^{a}	
γ_G	1.21^{a}	1.08 ± 0.06^{c}	1.06^{a}	1.06 ± 0.08^{d}
r/ω_0^2	-0.69^{a}	-0.71 ± 0.03^{c}	-1.90^{a}	-1.9 ± 0.2^{d}
$(p-q)/2\omega_0^2$	0.23^{a}	0.25 ± 0.05^{c}	-0.52^{a}	-0.52 ± 0.08^{d}
$\Delta\frac{1}{2}(c_{11}+c_{12})/\Delta p$			1.45^{a}	1.45 ± 0.7^{e}
$\Delta\frac{1}{2}(c_{11}-c_{12}+2c_{44})/\Delta p$			7.65^{a}	7.55 ± 0.7^{e}
$\Delta c_{44}/\Delta p$			2.95^{a}	3.00 ± 0.3^{e}

[a]Present work, theoretical values.
[b]Reference 32, experimental values.
[c]Present work, experimental values.
[d]Reference 33, experimental values.
[e]Reference 34, experimental values.

zone-center phonon frequencies, however, βa^2 should be replaced by an effective constant $4k_{\theta\theta}+8k_{\theta\theta^*}$ so as to include the additional VFF parameter $k_{\theta\theta^*}$ absent in the original Keating model.[1] The corresponding value of β is given in Table II. In this manner Keating's model and the one used in Ref. 22 can be shown to give results for the harmonic parameters at the zone center.

The internal-strain parameter of silicon obtained here agrees very well with the theoretical values of either Ref. 22 or that from *ab initio* calculations.[9] However, most of the experimental data suggest a larger value of ζ. Several reasons appear to be responsible for this discrepancy. It could be due to the displacement of the electron cloud and that of the core under stress. X-ray measurements can only measure the electron density, while VFF models apply to the cores. Neutron-scattering experiments under stress, sensitive only to the cores, would test the quality of old x-ray measurements and the validity of the above conjecture. Recent calculations by Labrot *et al.*[7] give two different internal-strain parameters, one for the core ($\zeta=0.54$) and one for the shell ($\zeta=0.58$). The difference, however, is not sufficient to explain the large experimental values.

The distribution of strains on the surface and in the bulk of the material is another point of concern. Cousins *et al.*[30] attribute the large values of ζ (~ 0.7) obtained in most of the experimental work for Si to a strain enhancement near the surface. It is difficult, however, to figure out how this enhancement may arise. Our piezo-Raman measurements under opaque and transparent conditions suggest that the opposite is true: smaller stress-induced phonon shifts are obtained in the former than in the latter case.

Table III shows the third-order VFF constants of Si and diamond obtained from our five-anharmonic-parameter model. It is interesting to realize that the constants γ, δ, and ε of Si are in very good agreement with those derived by Keating. This indicates that the two new constants introduced here η and θ, do not contribute much to the third-order elastic constants, a fact which may explain why they were not considered by Keating. From the expressions of the third-order elastic constants [Eq. (2)], we realize that the numerical coefficients of η and θ are always the same, except for those of c_{144}; furthermore, the fits yield values of η and θ of the same order and with opposite sign. These new parameters, however, contribute strongly to the phonon deformation potentials p, q, and r, and must be taken into account if a reasonable fit to them and the elastic constants is desired.

The relationships between our five anharmonic parameters and the corresponding ones of Ref. 22 are

$$\begin{aligned}
\gamma a^3 &= 2k_{rrr}+6k_{rr\theta}+k_{r\theta\theta}+\tfrac{1}{18}k_{\theta\theta\theta}\ , \\
\delta a^3 &= 2k_{\theta\theta\theta}\ , \\
\eta a^3 &= 4k_{rr\theta}+\tfrac{4}{3}k_{r\theta\theta}+\tfrac{1}{9}k_{\theta\theta\theta}\ , \\
\varepsilon a^3 &= 4k_{r\theta\theta}+\tfrac{2}{3}k_{\theta\theta\theta}\ , \\
\theta a^3 &= \tfrac{4}{3}k_{r\theta\theta}+\tfrac{1}{9}k_{\theta\theta\theta}+4k_{rr'\theta}\ .
\end{aligned} \tag{9}$$

The values of γ, δ, and ε obtained in Ref. 22 for Si are rather similar to ours, our η is half that of Ref. 22. In the case of θ, however, the magnitude is the same, but the sign is the opposite. If we set $k_{rr'\theta}=0$, the resulting value of θ (-0.193) is in near coincidence with ours. However, $k_{rr'\theta}/a^3=0.0897\times10^{12}$ dyn/cm^2 is overweighted in Ref. 22. This large value of $k_{rr'\theta}$ and also its large coefficients listed in Ref. 22 in the expressions of p, q, and r, produce large differences between the experimental values of p, q, and r and the theoretical ones found in Ref. 22 (see Table I). The large value of $k_{rr'\theta}$ in Ref. 22 originates from the large weight given to the anomalous Grüneisen parameter and other deformation potentials of the TA(X) phonon as compared to those of the zone-center phonon. We believe this procedure involves an intrinsic inconsistency: In order to fit the harmonic TA(X)-phonon energies and the complete dispersion relations of the TA modes along (100), four VFF parameters were introduced in Ref. 22 in addition to those which correspond to α and β. The anharmonic part of the energy, however, was restricted to contributions which correspond *solely* to anharmonicities in α and β. Hence we have the poor fit of p, q, and r, as a result of the emphasis (large weight) on fitting the anharmonic properties at the X point. Our internally consistent approach has been to fit only anharmonic properties at the zone center with anharmonicities in the parameters α and β, which, by themselves, give an excellent fit to the harmonic properties at the zone center.

There are still two points concerning the present experiment that should be commented on. First, the available experimental values for the complete set of third-order elastic constants of Si have been measured at room temperature, while the piezo-Raman data were taken at liquid-N_2 temperature. The variation of c_{ijk} with temperature may be significant.[37] Thus a consistent set of experimental data, taken all at low temperatures, would probably lead to a better fit with the five VFF parameters. Secondly, as our measurements were carried out at 110 K, there were no traces of indirect-band-gap luminescence at zero stress in the region from 5 to 2000 cm^{-1}. At stresses over 0.5 GPa, however, strong emission appeared in the region $\gtrsim 700$ cm^{-1} below the Nd-YAG excitation line. The peak position, strength, and band shape of this rather broad luminescence band appeared to depend critically on the amount of stress applied and the temperature of the sample. A detailed account of this investigation is now in preparation.[38]

In conclusion, we have measured the shift of the Raman-active phonon of Si under uniaxial stress with a Nd-YAG laser. Because of the transparency of the material to this radiation, we believe we have obtained a set of phonon deformation potentials p, q, and r representative of the bulk material. For the analysis of the results, we have used the anharmonic VFF Keating model with two additional anharmonic parameters. These two parameters have been shown to have important contributions to p, q, and r. In view of the good results obtained for Si, the model has been used to reanalyze available data for diamond and to obtain a complete set of third-order elastic constants unavailable from independent experiments.

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