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Effect of uniaxial stress on the zone-center optical phonon of diamond

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The effect of uniaxial stress along [001] and [111] on the zone-center optical phonon of diamond has been studied, and the corresponding deformation potentials determined. The results are interpreted in terms of a valence-field-force model. A fit to the theory of our experimental results and the measured variation of the elastic constants under hydrostatic stress, a total of six data with three adjustable parameters, allows all the third-order elastic constants to be determined.

I. INTRODUCTION

The first-order Raman spectrum of diamond was first observed by Ramaswamy.[1] The advent of neutron-diffraction techniques which made it possible to determine the complete phonon dispersion relations of this material,[2] spurred renewed interest in its lattice dynamics. Solin and Ramdas published in 1970 a detailed investigation of the second-order Raman spectrum of diamond[3] which was followed by considerable controversy concerning the possible existence of two-phonon bound states.[4-6] A precise determination of the first-order scattering cross section was recently performed by Grimsditch and Ramdas[7] while Calleja *et al.* investigated the dependence of the scattering cross section on the laser frequency.[8]

The frequency of first-order Raman lines can usually be determined with an accuracy considerably greater than that obtained with other techniques, in particular neutron diffraction. Thus, Raman spectroscopy is very appropriate for the investigation of the effect of relatively weak external perturbations (e.g., stress, temperature, doping) on the lattice dynamics. The method has been extensively used for the investigation of the effect of hydrostatic pressure on phonon frequencies,[9-11] and has received renewed interest as a result of the development of the diamond anvil cell[12] which enables Raman measurements to be performed to hydrostatic pressures up to ~200 kbar. Raman scattering can also be used to study the effect of a uniaxial stress on phonons.[13-17] This work yields the hydrostatic mode Grüneisen parameters and additional "uniaxial" anharmonicity constants. The interpretation of the observed shifts and splittings is first done phenomenologically by means of a group theoretical analysis. Furthermore, it is usually possible to extract from the data model anharmonicity parameters which can be compared with those obtained from an analysis of the third-order elastic constants.[17,18]

In this paper we present measurements of the effect of uniaxial stress along both [001] and [111] on the first-order Raman phonon of diamond. The results are analyzed with a three-parameter valence-field-force model[18] which can also be used to calculate the third-order elastic constants for which only incomplete data exist.[19]

II. EXPERIMENTAL DETAILS

The Raman-scattering measurements were taken in a right-angle scattering geometry with 500 mW of 4880-Å radiation from an Ar^+ ion laser, using a Jarrell Ash double monochromator and conventional photon counting techniques. The samples, obtained from D. Drukker and Sohn, Amsterdam, were parallelepipeds of typical dimensions $6 \times 1.4 \times 1.4$ mm with either of two orientations: (a) all cubic faces x, y, z parallel to $\langle 100 \rangle$; and (b) $\vec{\mathrm{x}}' \parallel [111]$, $\vec{\mathrm{y}}' \parallel [1\bar{1}0]$, $\vec{\mathrm{z}}' \parallel [11\bar{2}]$, x' being the long axis. Stresses were applied along either [100] or [111]; in both cases the zone-center optical phonon splits into a doublet and a singlet that can be identified by their polarization characteristics. Stresses of up to 10 kbar were applied using the stress apparatus described in Ref. 20. Because the splitting of the line at these stresses is not sufficient to resolve the singlet and the doublet completely, we used polarization techniques to study each component independently. The measurements were made at room temperature, since very little is gained in terms of line sharpening at low temperatures: the linewidth is 1.65 cm^{-1} at 300 °K and 1.48 cm^{-1} at both 79 and 15 °K.[3]

III. THEORY

The theory of the effect of stress on the zone-center phonons of a cubic material (piezo-Raman spectroscopy) is well known and only a summary will be given here. Since two different notations are currently being used to describe the shift and splittings of the lines, for the sake of completeness, the relation between both notations will be given. The behavior of a triply degenerate phonon in a cubic crystal under a small stress can be described by three parameters; the constants p, q, r,[13,21] or a, b, c,[22] are simply related to the behavior of the phonon under hydrostatic strain or pure shear strains along [001] or [111] as described by the following tensors:

$$\text{Hydrostatic } \underline{\epsilon} = \epsilon \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} , \tag{1}$$

$$[001] \text{ pure shear } \underline{\epsilon} = \epsilon \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix} , \tag{2}$$

and

$$[111] \text{ pure shear } \underline{\epsilon} = \epsilon \begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix} . \tag{3}$$

The shift of the line under hydrostatic stress $\Delta\omega_H$ is then given by

$$\Delta\omega_H = -3\omega_0 \gamma \epsilon = [(p+2q)\epsilon/2\omega_0] = (a+2b)\epsilon , \tag{4}$$

where γ is the mode Grüneisen parameter.[9]

The splitting under [001] shear $\Delta\omega_{[001]}$ is

$$\Delta\omega_{[001]} = [3(p-q)\epsilon/2\omega_0] = 3(a-b)\epsilon , \tag{5}$$

while the splitting under [111] shear $\Delta\omega_{[111]}$ is

$$\Delta\omega_{[111]} = (3r/\omega_0)\epsilon = 6c\epsilon , \tag{6}$$

where ω_0 is the frequency of the particular phonon in question. For a pure shear (traceless) stress the centroid of the singlet and the doublet does not change; i.e., the splitting of the singlet is twice that of the doublet and opposite in sign.

The combinations $(p-q)/2\omega_0^2$, r/ω_0^2, and the Grüneisen constant $\gamma = -(p+2q)/6\omega_0^2$ have been calculated[18] in terms of anharmonic valence-field force-constants as given in Refs. 18, 23, and 24. The results are

$$\gamma = -[5\alpha - \beta + a_0(3\overline{\gamma} - \overline{\delta} + \overline{\epsilon})]/6(\alpha+\beta) \tag{7}$$

$$r/\omega_0^2 = 1 + [a_0 \overline{\gamma}(1-\zeta)]/(\alpha+\beta) \tag{8}$$

and

$$(p-q)/2\omega_0^2 = 1 + a_0(\overline{\delta} + 2\overline{\epsilon})/(\alpha+\beta) , \tag{9}$$

where α and β are the harmonic bond-stretching and bond-bending constants, respectively, $\overline{\gamma}$ is an anharmonic bond-stretching constant, $\overline{\delta}$ is an anharmonic bond-bending constant, and $\overline{\epsilon}$ represents changes in the bond-bending constant produced by bond stretching. Also, in Eqs. (7)–(9), a_0 is the lattice parameter (3.567 Å for diamond), and ζ is the Goroff-Kleinman internal-strain parameter. From Ref. 23, $\alpha = 1.29$, $\beta = 0.85$ (in units of 10^5 dyn/cm), and $\zeta = 0.21$. The constants $\overline{\gamma}$, $\overline{\delta}$, and $\overline{\epsilon}$ are also related to the third order elastic constants (c_{ijk}) by the following equations[24]:

$$\begin{aligned} c_{111} &= \overline{\gamma} - \overline{\delta} + 9\overline{\epsilon} , \\ c_{112} &= \overline{\gamma} - \overline{\delta} + \overline{\epsilon} , \\ c_{123} &= \overline{\gamma} + 3\overline{\delta} - 3\overline{\epsilon} , \\ c_{144} &= \overline{\gamma}(1-\zeta)^2 + \overline{\delta}(1+\zeta)^2 + \overline{\epsilon}(1+\zeta)(3\zeta-1) + c_{12}\zeta^2 , \\ c_{166} &= \overline{\gamma}(1-\zeta)^2 - \overline{\delta}(1+\zeta)^2 + \overline{\epsilon}(1+\zeta)(3-\zeta) + c_{12}\zeta^2 , \\ c_{456} &= \overline{\gamma}(1-\zeta)^3 . \end{aligned} \tag{10}$$

In the case of Si, Ge, GaAs, and InSb where the c_{ijk}'s are known, Eqs. (7)–(9) yield values of γ, r, and $p-q$ in reasonable agreement with the experimental results.[18] In the case of diamond, however, only the three combinations[19] of c_{ijk}'s which correspond to the pressure dependence of the elastic constants c_{11}, c_{12}, and c_{44} are known. While these suffice in principle to determine $\overline{\gamma}$, $\overline{\delta}$, and $\overline{\epsilon}$, the experimental errors in the pressure derivatives of c_{11}, c_{12}, and c_{44} and the dependence of such derivatives on $\overline{\gamma}$, $\overline{\delta}$, and $\overline{\epsilon}$ is such that large margins of error result for these anharmonic parameters so determined. For this reason we have chosen to fit *simultaneously* the optical-phonon deformation potentials of Eqs. (7)–(9) and the pressure dependence of c_{11}, c_{12}, and c_{44} so as to minimize the sum of the standard deviations. The details of this fit will be given in Sec. IV.

IV. RESULTS AND INTERPRETATION

In Figs. 1 and 2 we present the results obtained for the position (in cm^{-1}) of the singlet S and doub-

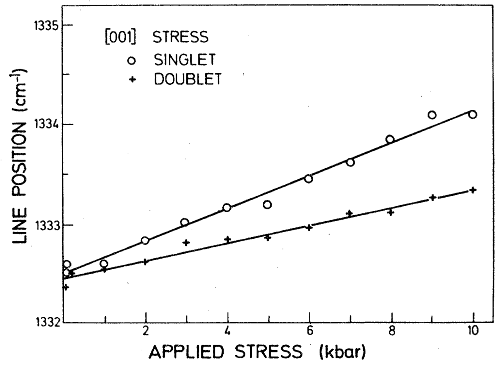

FIG. 1. Stress dependence of the frequencies of the Raman phonons of diamond under a compressive force along [001] at room temperature. The solid lines are least-squares fits used to extract the parameters of Eq. (11).

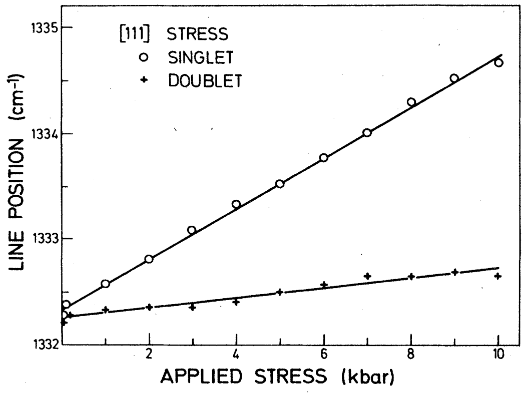

FIG. 2. Stress dependence of the frequencies of the Raman phonons of diamond under a compressive force along [111] at room temperature. The solid lines are least-squares fits used to extract the parameters of Eq. (11).

let *D* components of the zone-center optical phonon of diamond as a function of compressive uniaxial stress along [001] and [111], respectively. The full lines are least-squares fits to the experimental data. The results of five such runs yield the following averages:

$$\Delta\omega_H = 0.32 \pm 0.02\ \text{cm}^{-1}/\text{kbar}\,,$$
$$\Delta\omega_{[111]} = 0.22 \pm 0.02\ \text{cm}^{-1}/\text{kbar}\,, \qquad (11)$$
$$\Delta\omega_{[001]} = 0.073 \pm 0.010\ \text{cm}^{-1}/\text{kbar}\,.$$

Using the expressions given in Refs. 14 and 22 for the positions of the singlet and doublet as a function applied stress [also contained in Eqs. (4)–(6)] we obtain the results given in Table I. Our value of the Grüneisen parameter compares well with previous results from Refs. 9, 11, and 25 which are also given in Table I.

Following the procedure given in Ref. 26 and using the results of Ref. 19 we have calculated the following combinations of third-order elastic constants[26] which are related to the pressure derivatives of c_{11}, $\frac{1}{2}(c_{11}+c_{12}+2c_{44})$, and c_{44}:

$$\tfrac{1}{4}(c_{111}-c_{123}) = -\bar{\delta} + 3\bar{\epsilon}\,,$$
$$c_{144}+2c_{166} = 1.87\bar{\gamma} - 1.46\bar{\delta} + 6.30\bar{\epsilon}\,, \qquad (12)$$
$$\tfrac{1}{2}c_{111}+2c_{112}+c_{144}+2c_{166}+\tfrac{1}{2}c_{123} = 4.87\bar{\gamma} - 2.46\bar{\delta} + 11.3\bar{\epsilon}\,.$$

We have included in Eq. (12) the expressions for these combinations of third-order elastic constants as a function of $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\epsilon}$, as obtained from Eqs. (10). The experimental values of these combinations are given in Table I together with the values obtained from the best fit (minimum standard deviation) with $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\epsilon}$ to the experimental entries in the six rows of Table I. This best fit yields (in 10^{12} dyn/cm^2) $\bar{\gamma} = -16.7$, $\bar{\delta} = 0.95$, and $\bar{\epsilon} = -4.99$. We feel that the agreement of the results of the fit with the experimental values is good. It is also satisfying to note that the theory explains the change in sign of $(p-q)$ as compared to silicon or germanium.[14] This reversal in sign is due to a dominance of the anharmonic terms $a_0(\bar{\delta}+2\bar{\epsilon})/(\alpha+\beta)$ over the purely geometric term represented by the summand 1 in Eq. (9) which, in turn, is due purely to the bending of the bonds. Because of the good agreement obtained, it is justified to calculate the c_{ijk}'s as given by Eqs. (10) using the values obtained for $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\epsilon}$. The results which do not

TABLE I. Mode Grüneisen parameter γ and anharmonicity parameters $(p-q)/2\omega_0^2$ and r/ω_0^2 for diamond, together with the linear combinations of anharmonicity parameters $\bar{\delta}$, $\bar{\epsilon}$, and $\bar{\gamma}$ determined from Ref. 19 and from a best fit to all of the experimental data of this table. The units of $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\epsilon}$ are 10^{12} dyn/cm^2.

	Present study	Previous determinations	Best fit
γ	1.06 ± 0.08	0.94 ± 0.1[a] 1.19 ± 0.09[b] 0.98 ± 0.04[c]	1.12
$(p-q)/2\omega_0^2$	-0.52 ± 0.08	···	-0.51
r/ω_0^2	-1.9 ± 0.2	···	-1.20
$-\bar{\delta}+3\bar{\epsilon}$	···	-18.3[d]	-15.9
$1.87\bar{\gamma}-1.46\bar{\delta}+6.30\bar{\epsilon}$	···	-58.3[d]	-64.1
$4.87\bar{\gamma}-2.46\bar{\delta}+11.3\bar{\epsilon}$	···	-123.5[d]	-140

[a] Reference 9.
[b] Reference 11.
[c] Reference 25.
[d] Reference 19.

TABLE II. Third-order elastic constants of diamond (units: 10^{12} dyn/cm^2) calculated with Eqs. (10) with the values of $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\epsilon}$ obtained from a best fit to the experimental data of Table I.

c_{111}	c_{112}	c_{123}	c_{144}	c_{166}	c_{456}
−62.6	−22.6	+1.12	−6.74	−28.6	−8.23

seem to have been separately determined by experiment, are given in Table II.

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