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Pressure dependence of the first-order Raman mode in diamond

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The effect of isotropic pressure on the frequency of the fundamental Raman mode of diamond has been measured up to 40 GPa. The mode frequency increases linearly with the change in wavelength of the R_1 luminescence of ruby, which is used for pressure measurement. The mode frequency has been calculated theoretically for pressures up to 600 GPa and is found to vary sublinearly with pressure. The possibility of using the Raman mode as a pressure gauge is discussed.

I. INTRODUCTION

The development of the diamond-anvil high-pressure cell has stimulated Raman-scattering investigations of vibrational modes in covalent solids.[1] The extended hydrostatic pressure range has made possible the detection of nonlinear effects in the pressure dependence of mode frequencies. Among the group-IV elements, Si (Ref. 2) and Ge (Ref. 3) have been studied up to 12.5 and 10.5 GPa, respectively, which roughly corresponds to the stability range of the tetrahedrally coordinated phases.

In this Rapid Communication we report on Raman measurements of the fundamental zone-center mode of diamond subjected to isotropic stress in a diamond-anvil cell and on an *ab initio* theoretical calculation of the dependence of this mode on pressure.

Previous Raman studies of the fundamental zone-center mode of diamond have covered the pressure range below 2.5 GPa. The linear pressure coefficient reported by Mitra, Brafman, Daniels, and Crawford[4] (2.8 ± 0.3 cm^{-1}/GPa) agrees to within mutual experimental error with the result of Whalley, Lavergne, and Wong[5] (2.96 ± 0.11 cm^{-1}/GPa). Both experiments were performed under truly hydrostatic conditions up to 1.0 and 2.3 GPa, respectively. Parsons[6] finds a somewhat larger value (3.6 ± 0.3 cm^{-1}/GPa) in an experiment with a solid pressure medium and a pressure scale based on the optical absorption in nickel dimethylglyoxime. The hydrostatic pressure coefficient derived from uniaxial stress experiments is 3.2 ± 0.2 cm^{-1}/GPa.[7]

In the present experiment we have observed the first-order Raman mode at pressures between 15 and 40 GPa. Despite the strong Raman scattering from the diamond windows, the observation of the signal from the sample is possible above roughly 15 GPa because the change in the Raman profile of the strained anvils[8] differs sufficiently from the charge due to isotropic stress. We find that the mode frequency increases linearly with the wavelength change of the R_1 luminescence line of ruby, which serves as a pressure gauge.[9,10] The experimental detectability of a nonlinear pressure dependence of the zone-center mode frequency of diamond critically depends on the calibration of the ruby scale.

An *ab initio* pseudopotential total-energy calculation is used to find the phonon frequency as a function of volume by the frozen-phonon method as described in Ref. 11. The pressure is determined from the numerical derivative of energy with respect to volume. Results for pressures up to 600 GPa are obtained. The theoretical results show a clear sublinear dependence of the phonon frequency on pressure, and indicate that the sublinearity of the variation of the ruby-luminescence wavelength with pressure may, in fact, be somewhat greater than that determined in earlier experimental studies.[10]

II. EXPERIMENTAL PROCEDURE

Raman measurements were performed on polished diamond flats of about 60 μm in diameter and 15 μm in thickness. A single piece of the sample material was placed in the gasket hole of a diamond-anvil cell together with some ruby splinters. Solid xenon was used as the pressure medium. The final gasket thickness at the highest pressure is estimated to be at least 30 μm, so that bridging of the sample between the anvils is avoided. The Raman signal was measured in nearly backscattering geometry using a microoptical setup described elsewhere.[12] The sample crystals were oriented with the [001] axis perpendicular to their polished surface, so that this direction points along the optical axis. The diameter of the laser focus at the sample was 30 μm. Spectra were recorded with 514.6-nm excitation.

III. RESULTS AND DISCUSSION

Figure 1 shows Raman spectra of diamond measured at three different pressures. Spectra are taken from different runs with varying levels of background luminescence (not shown). Above roughly 15 GPa the sample signal starts to become observable as a peak separated in frequency from the anvil signal. For a discussion of the anvil signal under applied load we refer to Ref. 8. The observed linewidth (4.0–5.5 cm^{-1}) is a contribution from three effects: instrumental resolution (2.5–4.0 cm^{-1}, depending on spectrometer slit setting), intrinsic broadening (1.65 cm^{-1}),[13] and pos-

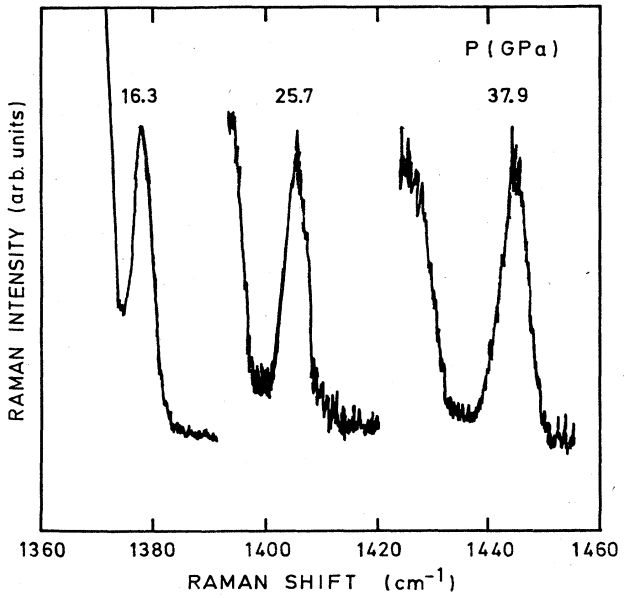

FIG. 1. First-order Raman spectra of diamond at three different pressures. The low-frequency edge is due to the Raman signal of the strained diamond windows.

sible inhomogeneous stress effects. The increase in linewidth over the value at normal pressure is less than 1 cm^{-1}, which indicates a fairly homogeneous stress distribution across the sample region illuminated by the laser.

Experimental results for the phonon frequency of the fundamental Raman mode as a function of wavelength of the R_1 luminescence of ruby are shown in Fig. 2. The solid line corresponds to the result of a least-squares fit which yields a slope of 7.94 ± 0.1 cm^{-1}/nm. The standard deviation is 1.3 cm^{-1}. The scatter of the data points about the straight line reflects the combined error in Raman and luminescence measurements. The linear coefficient is almost unchanged (8.09 ± 0.2 cm^{-1}/nm), if the zero-pressure frequency (measured value $\omega_0 = 1333.0 \pm 0.5$ cm^{-1}) is not included in the fit. Therefore, a linear relation accounts well for the experimental results over the entire pressure range.

Piermarini, Block, Barnett, and Forman[9] have calibrated the ruby-luminescence shift against the equation of state of NaCl up to pressures of 20 GPa. Using their pressure coefficient of $0.365 + 0.002$ nm/GPa for the red shift of the ruby line, the slope of the solid line in Fig. 2 converts to a linear pressure coefficient of 2.90 ± 0.05 cm^{-1}/GPa for the Raman mode frequency, in close agreement with the low-pressure results reported in Refs. 4 and 5. The corresponding mode Grüneisen parameter near normal pressure $\gamma_0 = -(d \ln\omega / d \ln V)_0$ is 0.96, if we adopt the adiabatic bulk modulus $B_0 = 442$ GPa.[14] Mao, Bell, Shaner, and Steinberg[10] have performed a calibration of the ruby scale up to 95 GPa against the equations of state of four different metals. They find evidence for a sublinear dependence of the ruby-luminescence shift on pressure. Near 40 GPa the pressure from the nonlinear ruby scale is about 4% higher compared with the linear scale. Thus, if we rely on the ruby calibration of Mao *et al.*,[10] there is experimental evidence for a weak sublinear behavior of the zone-center mode as a function of pressure.

For the present experimental configuration an additional uniaxial compressive stress component along the rotational symmetry axis of the cell is equivalent to stress in the [001]

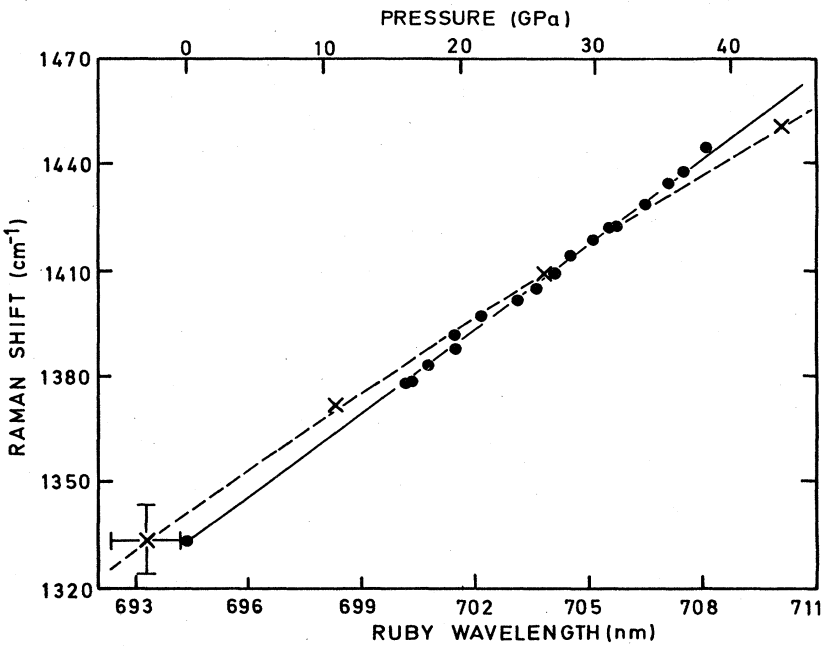

FIG. 2. Measured (●) and calculated (×) Raman shift of the diamond zone-center optical phonon plotted against pressure-induced wavelength shift of the R_1-luminescence line of ruby and against calculated pressure, respectively. The relation between the R_1-line wavelength and the pressure axis is chosen according to the linear ruby calibration (Ref. 9). Error bars indicate the estimated uncertainty in the theoretical results (see text). The dashed line is a guide to the eye.

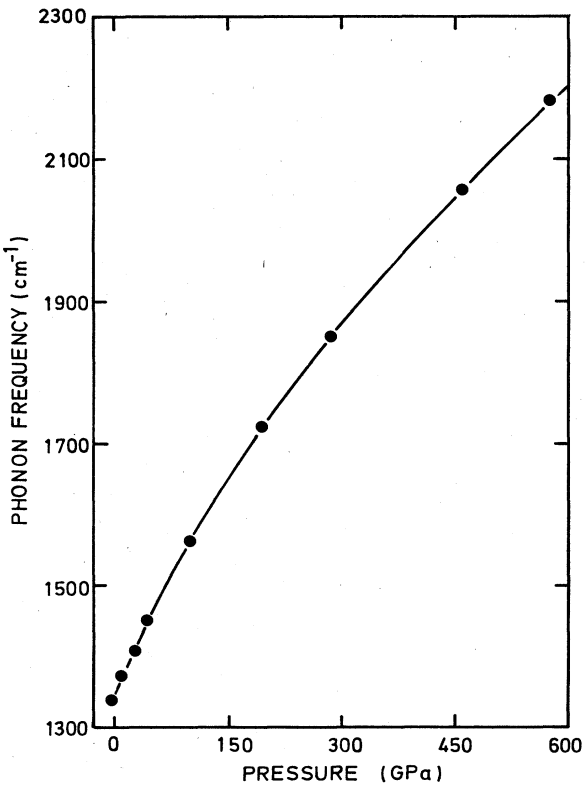

FIG. 3. Calculated frequency of the diamond zone-center optical phonon plotted against calculated pressure in the range 0–600 GPa.

direction of the sample, which splits the threefold degenerate zone-center mode of diamond into a singlet and a doublet. In the backscattering geometry one observes only the singlet mode (see Ref. 8 and literature cited therein), which lies higher in frequency ($\cong 0.5$ cm^{-1}/GPa of uniaxial stress[7]) compared with a truly hydrostatic situation. It is believed that the unaxial stress, which can be sustained by the xenon pressure medium under an average pressure of 40 GPa, is below 1 GPa. Therefore, a possible systematic error in the experimental data due to uniaxial stress effects is considered to be negligible.

In the theoretical calculation, the pressure at a given volume is determined as minus the average numerical energy derivative with respect to volume between 0.9995 and 1.0005 of a given volume with zero frozen-phonon amplitude. Because the pressure is calculated from energy differences, the numerical errors involved give an absolute uncertainty in pressure which is constant over the entire range of pressures calculated. The uncertainty in pressure arises from several aspects of the calculation, most notably, local-density-functional theory (and within that approximation, which form of the exchange-correlation-energy function is used), the incompleteness of the set of Gaussian basis functions used in describing the wave functions, and the fact that, following the scheme of Ref. 11, we do not minimize the total energy at each individual volume with respect to the decays of the Gaussian basis functions. These errors are all of the same order of magnitude, and the total uncertainty in the calculated pressure at a given volume in the range considered is estimated to be less than 3 GPa. It is important to note that the relative accuracy in the calculated pressure is better at higher pressures. This is in contrast to the experimental measurement of pressure, where the accuracy is highest at low pressure.

The same numerical factors which cause uncertainty in the calculated pressure also give rise to an uncertainty of approximately 10 cm^{-1} in the theoretically determined phonon frequency. Furthermore, there is a systematic overestimation of the phonon frequency from the frozen-phonon technique due to renormalization of the phonon frequency by anharmonic effects. This systematic error has been estimated[15] to be of the order of 10 cm^{-1} for this phonon mode.

Theoretical results for the phonon frequency as a function of pressure are included in Fig. 2. The calculated and experimental phonon frequencies agree within mutual error bounds in the range of experimental data. Because of the relatively large uncertainty in the theoretical results, this agreement is true whether one adopts the linear pressure scale from Piermarini, Block, Barnett, and Forman[9] or the sublinear scale of Mao *et al.*[10] However, if we consider the full theoretical curve[16] in the range 0–600 GPa in Fig. 3, we see a clear sublinear dependence of the phonon frequency on pressure.[17] In the light of the experimental data, this gives a strong indication of a sublinear dependence of the ruby R_1 luminescence on pressure in the range 0–40 GPa which may be greater than that found by Mao *et al.*[10]

IV. CONCLUSIONS

In conclusion, we have observed the shift of the zone-center Raman mode of diamond under isotropic stress in a gasketed diamond-anvil cell. The linear pressure coefficient is in close agreement with results[4,5] obtained in the low-pressure range. We find experimental evidence for a weak sublinear pressure dependence, if we adopt the nonlinear ruby pressure scale.[10] This sublinearity is stronger in the theoretical calculation. From the phonon frequency dependence on pressure calculated here, we believe it is now possible to determine pressures from the zone-center Raman mode in diamond with an accuracy of at least ± 10 GPa in the range of 0–600 GPa when the uncertainties of both frequency and pressure as a function of volume are taken into account. While this level of accuracy is not useful for pressures less than 50 GPa, where other methods are more accurate, for higher pressures it offers the best scale of pressure determination yet available.

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[1]B. A. Weinstein and R. Zallen, in *Light Scattering in Solids IV,* edited by M. Cardona and G. Güntherodt, Topics in Applied Physics, Vol. 54 (Springer, Berlin, 1984), p. 463.

[2]B. A. Weinstein and G. J. Piermarini, Phys. Rev. B **12**, 1172 (1975).

[3]D. Olego and M. Cardona, Phys. Rev. B **25**, 1151 (1982).

[4]S. S. Mitra, O. Brafman, W. B. Daniels, and R. K. Crawford, Phys. Rev. **186**, 942 (1969).

[5]E. Whalley, A. Lavergne, and P. Wong, Rev. Sci. Instrum. **47**, 845 (1976).

[6]B. J. Parsons, Proc. R. Soc. London, Ser. A **352**, 397 (1977).

[7]M. H. Grimsditch, E. Anastassakis, and M. Cardona, Phys. Rev. B **18**, 901 (1978).

[8]M. Hanfland and K. Syassen, J. Appl. Phys. (to be published).

[9]G. J. Piermarini, S. Block, J. D. Barnett, and A. Forman, J. Appl. Phys. **46**, 2774 (1975).

[10]H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[11]J. R. Chelikowsky and S. G. Louie, Phys. Rev. B **29**, 3470 (1984).

[12]K. Syassen and R. Sonnenschein, Rev. Sci. Instrum. **53**, 644 (1982).

[13]S. A. Solin and A. K. Ramdas, Phys. Rev. B **1**, 1687 (1970).

[14]M. H. Grimsditch and A. K. Ramdas, Phys. Rev. B **11**, 3139 (1975).

[15]D. Vanderbilt, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **53**, 1477 (1984).

[16]The phonon frequencies are calculated using an s and p Gaussian orbital basis for pressures below 400 GPa; d-like orbitals are included for pressures between 400 and 600 GPa, because of the increased d character of the valence electrons at compressed volumes. In the lower-pressure region, tests show that the inclusion of d basis functions gives rise only to changes within the uncertainties indicated.

[17]Within the estimated uncertainties and over the range 0–600 GPa, the calculated dependence of pressure P on phonon frequency ω may be represented by a Birch-type expression $P=1.5a(X^7-X^5)[1-b(X^2-1)]$, where $X=(\omega/\omega_0)^{1/3}$. The parameters are $\omega_0=1341\ \mathrm{cm}^{-1}$, $a=480$ GPa, and $b=0.118$.