

Raman spectra of diamond at high pressures

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(Received 22 April 1985)

The first-order Raman spectrum of diamond has been measured in a diamond-anvil cell up to 27 GPa. The fundamental phonon line varies linearly in pressure with a shift of $2.87 \text{ cm}^{-1}/\text{GPa}$. This line appears to be an excellent pressure-calibration standard as an alternate to the ruby pressure scale.

Diamond is optically transparent and the hardest material known to man. In recent years it has been responsible for a revolution in high-pressure techniques,¹ providing the experimenter access to static pressures in the megabar region, having an optical port on the sample with the diamond-anvil cell (DAC) technique. Theoretical interest in this substance has been kindled with considerations of the phonon spectrum, energy, stability, and phase diagram as a function of density.²⁻⁴ Oddly enough, until recently, there have been no published studies of the phonon spectra at the high pressures now available.⁵ Of particular interest are the Raman-active first- and second-order spectra. The first-order phonon line is sharp and intense and may be of utility as an alternative to the ruby pressure scale at very high pressures if it is well behaved. This may be vital for high-pressure research as recent reports of static pressures up to almost 300 GPa indicate a severe deterioration of the ruby line due to broadening, weakening, and masking by luminescence from the diamond itself.⁶ It can also be used in the analyses of the stress distribution in diamond anvils. The second-order phonon spectrum at zero pressure has sparked particular attention because of a controversial feature near its band edge.⁷ Owing to inhomogeneous broadening and its weak intensity it is much more difficult to study at high pressures. We devote this article to the first-order spectrum at room temperature.

The first-order phonon frequency has a zero-pressure value of 1332.5 cm^{-1} ; its threefold degeneracy can be lifted by nonhydrostatic pressures. The diamond anvil itself in a DAC is a poor candidate for the sample as its stress is anisotropic and nonuniform, and varies from the high value at the culet (the normal position of the sample) to zero at the diamond table. Thus to study diamond itself, a diamond sample should be placed in the gasket hole which has typical dimensions of $100\text{-}\mu\text{m}$ diameter and $10\text{-}30\text{-}\mu\text{m}$ thickness. We used (100) cut diamond plates of dimension $60 \times 60 \times 15 \mu\text{m}^3$, supplied by D. Drukker and Zn., B.V. A back-scattering geometry was employed with $5145\text{-}\text{\AA}$ excitation from an argon-ion laser. Hydrogen, argon, and xenon were used as hydrostatic media and were loaded by cryogenic techniques described elsewhere,⁸ along with a few grains of ruby to measure the pressure and pressure distribution in the medium.

The prime experimental challenge was to separate the Raman signal of the $15\text{-}\mu\text{m}$ -thick plate from that arising from the $3000\text{-}\mu\text{m}$ -thick anvils. By silver plating the back face of the plate, its Raman signal could be doubled relative to that from the anvil. A microscope objective was used to focus the laser with an approximately $30\text{-}\mu\text{m}$ depth of focus and a spot size of about $5 \mu\text{m}$. The focus could be scanned in the xy plane of the plate or in the z direction (z scan) along the

beam axis. The small focal spot allowed us to move the focus on and off the plate to compare signals arising from plate and anvil, as well as to excite individual ruby grains. The z scans were useful in studying the signal from the anvils.

In Fig. 1(a) we show the first-order phonon spectrum arising from the anvils and from the diamond plate plus anvil for a pressure of 12.8 GPa. The signal from the plate is sharp (linewidth $\sim 2 \text{ cm}^{-1}$) while that from the anvils is broad, reflecting their inhomogeneous stress distributions. For low pressures of order 3 GPa the plate signal could be

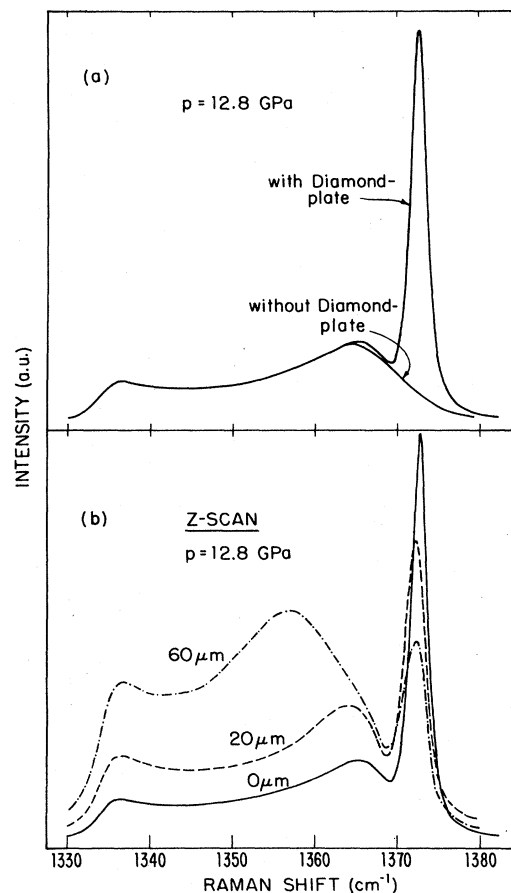


FIG. 1. (a) First-order phonon spectrum from the anvils and from the diamond plate plus anvil at 12.8 GPa and $T = 293 \text{ K}$. (b) z scan (along the beam axis) 0, 20, and $60 \mu\text{m}$ refer to the position of the focus with respect to the diamond plate.

isolated by subtraction of the anvil contribution, whereas at higher pressures the spectral separation was adequate so that subtraction was unnecessary. In Fig. 1(b) we show the result of a z scan. Here it is clearly demonstrated that the frequency and intensity of the peak of the signal from the anvil depends strongly on the location of the focus. On the other hand, the peak from the plate only gets weaker in intensity and its frequency does not show any dependence on the position of the focus. Thus the peak of the signal from the anvils would be a very poor feature to use for a pressure calibration or standard. This is unfortunate as placing a diamond plate in a DAC complicates procedures. In Fig. 2 we show the frequency of the first-order phonon peak as a function of pressure (using the ruby-scale calibration of Mao, Bell, Shaner, and Steinberg⁹). Unfortunately, the pressure range that we achieved in these measurements was limited to just under 30 GPa. The principle limitation to increasing the pressure was contact or close proximity between the anvil culets and the plate. Using hydrogen as a pressure medium limited the pressure to about 15 GPa due to the large compressibility of H_2 . Argon became nonhydrostatic above about 12 GPa, whereas xenon maintained its hydrostaticity to much higher pressures and has a low compressibility,¹⁰ and thus was used for the high-pressure measurements. The solid line in Fig. 2 is the result of a least-squares fit, which gives a slope of $2.87 \pm 0.10 \text{ cm}^{-1}/\text{GPa}$. The mode Grüneisen parameter $\gamma_i = -\partial \ln \nu_i / \partial \ln V = (B/\nu_i)(\partial \nu_i / \partial p)$ is 0.95 ± 0.03 (with the bulk modulus $B = 442 \text{ GPa}$, Ref. 11). Our value is in good agreement with results from earlier measurements in the pressure range up to 2.4 GPa (Mitra, Brafman, Daniels, and Crawford¹² $\gamma = 0.94 \pm 0.10$; Whalley, Lavergne, and Wong¹³ $\gamma = 0.98 \pm 0.04$; Grimsditch, Anastassakis, and Cardona¹⁴ $\gamma = 1.06 \pm 0.08$; Parsons¹⁵ $\gamma = 1.19 \pm 0.09$). We believe the deviation of the two points at higher pressure from the straight line in Fig. 2 to be due to nonhydrostaticity in the xenon. This could be observed from several ruby grains in the xenon and probably arose from the proximity of the diamond plate and the anvils at high pressure.

Diamond is a prototype crystal with a special status in solid-state physics due to its simplicity and unique properties. A recent calculation about the stability of diamond predicts a transition into the $B-8$ phase at 12 Mbar.^{3,4} Another calculation found the diamond phase stable up to 23 Mbar.¹⁶ So far no calculation has been made concerning the pressure dependence of the phonon frequencies in diamond. It would be very interesting to compare our experimental results with "first-principles" calculations.

In considering the value of the diamond phonon as an alternate to the ruby scale, this transition appears to meet the criteria of sharpness and reproducibility that one would desire for a pressure scale. However, owing to the difficulty in using it, including the low-intensity signal, as compared to ruby, it may only be useful in the very-high-pressure

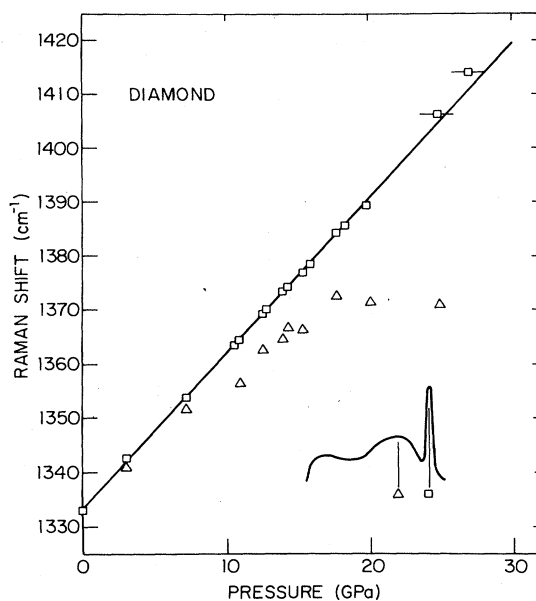


FIG. 2. Pressure dependence of the first-order phonon peak. The squares are the measured peak positions of the diamond plate; the triangles are the maxima in the diamond-anvil spectra. The solid line is a least-squares fit.

ranges. It is possible that one might use the maximum frequency of the anvil peak from a z -scan, or the extrapolation of the high-frequency wing of this line to zero amplitude; however, this requires very careful work and certainly would have a much larger uncertainty than could be attained by using a plate or grain of diamond embedded in the pressure medium. In conclusion, we find the phonon frequency as measured in a diamond sample should be a valuable high-pressure standard but experimentally difficult to implement. It would be interesting to extend these studies to higher pressures, low temperatures, and to include the two-phonon Raman-active band.

After writing this paper we received a copy of a similar work by Hanfland *et al.*¹⁷ Their experimental results agree very well with ours. In addition, theoretical calculations using the *ab initio* pseudopotential theory within the local-density-functional formalism have been carried out up to 6 Mbar. The agreement with the experiment is very good, within the expected theoretical uncertainty.

This work has been supported in part by National Science Foundation Low Temperature Physics Grant No. DMR-82-13662. One of us (H.B.) acknowledges financial assistance from IBM.

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