Shock Induced Splitting of the Triply Degenerate Raman Line in Diamond

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(Received 2 September 1993)

Strain-induced symmetry changes in diamond have been observed in shock compression experiments. The experimental method utilizes time-resolved Raman spectroscopy to probe the diamond structure behind the shock front. Peak longitudinal stresses to 50 GPA were achieved by uniaxial strain loading. Strain applied along the [100] and [110] directions is predicted to partially or completely lift the triple degeneracy of the ambient Raman line. The degenerate Raman line was observed to split in accordance with the predicted behavior. The observed changes, despite the large nonhydrostatic stresses, are reversible.

PACS numbers: 62.50.+p, 78.30.Hv

Optical spectroscopy and x-ray diffraction measurements in shocked condensed materials [1], though inherently difficult to perform, can address two important scientific problems. First, they provide an insight into the atomic-molecular processes governing the shocked state. Second, because of the fast temporal nature of shock wave loading, time-resolved measurements can permit real time examination of structural and chemical changes due to well defined, large compressions. In solids, the large compressions under shock loading are also accompanied by macroscopically uniform nonhydrostatic loading which permits an examination of deformation tensor effects. In this Letter, we report the first measurements of shock induced splitting of the degenerate Raman line in diamond to demonstrate the symmetry changes in the shocked state.

The uniaxial strain state under shock loading may have a lower symmetry depending upon the initial symmetry and the loading direction. Strains and changes in crystal symmetry are expected to alter the vibrational mode frequencies and intensities due to anharmonic effects and changes in selection rules. Symmetry lowering, in particular, is expected to partially (or completely) lift any degeneracies associated with the vibrational modes. Hence, Raman measurements are well suited for exploring shock induced symmetry changes.

Diamond was selected because its large Raman cross section [2] permits time-resolved measurements (~ 10 ns) and because of its importance in many contemporary scientific investigations including static high pressure studies [3-8]. In the experiments reported here, the strain-induced symmetry changes in diamond were examined by measuring the first-order Raman spectrum of single crystals shocked along the [110] and [100] directions. Deformation along these directions is predicted to completely or partially lift the triple degeneracy of the ambient Raman line [9].

The overall configuration for performing the time-resolved Raman experiments is shown in Fig. 1. Excitation was provided by a coaxial flashlamp-pumped dye laser (pulsewidth ≈ 2.5 μs) operating at 514.5 nm. Energy delivered to the diamond sample was regulated by an aperture stop which blocked a portion of the laser light exiting the laser head. The light, coupled into an optical fiber, was incident at 45° to the sample normal. The scattered signal was collected normal to the sample surface and delivered by a second fiber to the spectrometer (SPEX 1877, 1800 gr/mm grating) where it was spatially dispersed. Subsequently, the signal was further separated from the elastic component by a Raman holographic edge filter, temporally dispersed by an image converting streak camera (Imacon 790), and intensified by a microchannel-plate image intensifier (ITT F4113). The intensifier output was lens coupled to a two-dimensional detector array (EG&G 1254 intensified Vidicon) and the digitized image displayed as intensity vs wavelength vs time on an OMA (EG&G 1460). A typical time-resolved spectrum consisted of thirty spectra recorded in sequential 10 ns intervals. Work is currently underway to achieve even higher time resolution. Further details about time-resolved Raman measurements in shock experiments may be seen in Ref. [10].

For the present set of experiments, shock waves were produced by impacting type II-*A* diamonds (2.5–3.5 mm in diameter and 0.75–1.0 mm thickness) with Pt, Ta, and Cu plates mounted on projectiles and accelerated in a single-stage light gas gun [11]. On impact, the shock

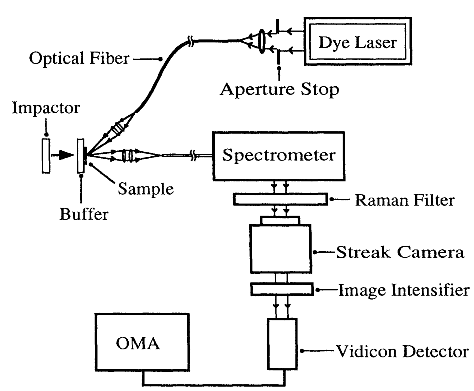

FIG. 1. Overall experimental configuration used for time-resolved Raman measurements in shock compressed diamond.

wave transits the copper buffer material and propagates into the diamond. All experimental measurements were completed prior to the arrival of edge effects. Density compression was determined from impedance matching calculations and the projectile velocity. The longitudinal and lateral stresses were determined from nonlinear elastic relations developed for diamond [12]. For very stiff materials, such as diamond, the calculation of nonvanishing stress components from finite strain analysis is expected to be in very good agreement with measured values [13]. Peak longitudinal stresses ranging between 10 to 50 GPa (approximately 1% to 4% density compression) were achieved in this manner. The large nonhydrostatic stresses achieved are a consequence of the diamond stiffness and uniaxial strain loading. At 3.5% density compression, the stress difference between longitudinal and lateral stress components approached 40 GPa. As indicated below, the diamond response was elastic at the highest stress levels in our experiments. All of the shock compression experiments were performed on single crystal diamonds, most with strain applied along the [110] crystallographic direction and some with strain applied along the [100] principal cubic axis. After each experiment a wavelength calibration was performed to ensure that the Raman shifts were correctly assigned. Further details about the experiments may be found in Ref. [12] and will be published in a comprehensive paper at a future date.

Figure 2 shows representative time-resolved spectra for shock compression experiments on [110] oriented diamonds. In this figure, the experimentally observed Raman shift (cm^{-1}) and intensity are plotted in contiguous 10 ns time intervals as the shock wave progresses into the diamond. Track 1 shows the spectrum at ambient pressure recorded immediately prior to shock wave arrival at the buffer/diamond boundary; the peak location (ω_0) is 1332.5 cm^{-1}. The shock wave has arrived at the sample at track 2 (10 ns later) and a shifted peak (ω_1) is readily seen to the right of the central peak. The large amplitude peak represents a convolution of the ambient Raman peak (ω_0) and a new peak (ω_3) induced by the strain but which is only slightly shifted from the ambient Raman peak location. As the shock wave progresses through the sample and more material is subjected to uniaxial strain, the intensity of the ω_1 peak increases accordingly. By track 6 (highlighted), the shock wave has reached the rear of the diamond and the largest intensity is displayed. The intensity of ω_1 then begins to drop as the release wave originating from the rear surface propagates through the sample; less of the sample is at peak stress. The final track in this figure shows a single Raman shifted line located at the ambient peak location ω_0, demonstrating that the diamond sample displayed a reversible or elastic response. There is also a third Raman shifted peak denoted ω_2, barely discernible in this figure, located to the right of ω_1. The peak longitudinal stress was calculated to be 45.2 GPa (3.5% density compression) for this particular experiment.

A Gaussian expression was fitted to the observed spectrum at peak longitudinal stress for each experiment. Figure 3 is an example of one such fit for the 15.2 GPa stress (1.24% density compression) experiment. The three peaks (ω_1, ω_2, and ω_3) seen in this figure exemplify the results for all shock loading experiments performed on the [110] diamond orientation and demonstrate clearly the symmetry change due to shock loading. The triply degenerate ambient Raman line (ω_0) is indicated by the vertical bar in this figure. The FWHM is about 10 cm^{-1} for the observed peaks, very close to the calculated instrumental bandwidth. Despite the large nonhydrostatic stresses achieved in this study, there was no apparent line broadening; this is to be expected because of the uniform stress state in the recording region [14]. The relative intensity of the three peaks is in accordance with the quasi-backscatter geometry and polarization calculations [12].

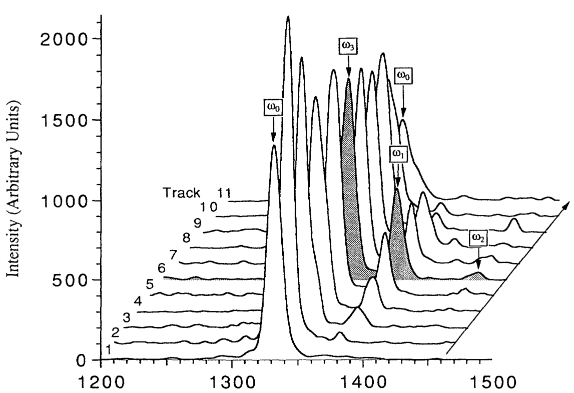

FIG. 2. Time-resolved, Raman spectra for [110] compression.

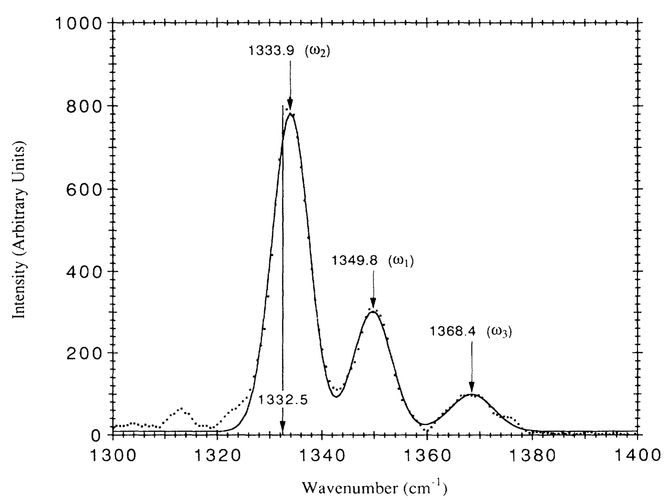

FIG. 3. Observed and fitted spectrum for [110] compression showing complete lifting of the triple degeneracy.

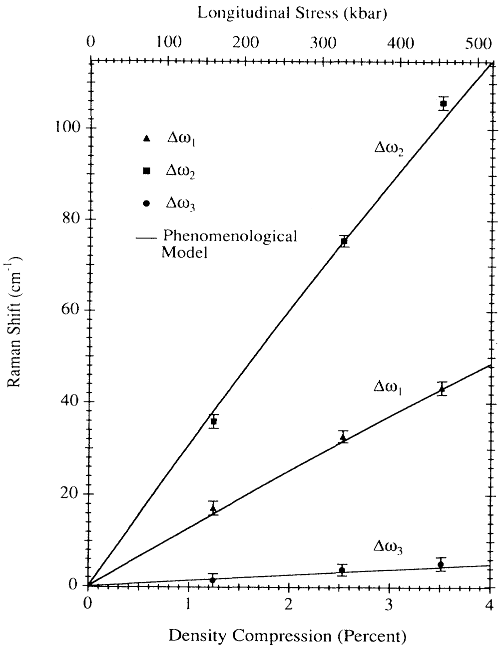

FIG. 4. Data from [110] compression experiments and fit to the phenomenological model predictions.

Fluctuations in intensity due to changes in the detector response prevented absolute intensity measurements. The three peaks observed in Fig. 3 clearly show that the triply degenerate ambient Raman frequency is completely lifted for uniaxial strain along [110], in agreement with the predictions of group theory.

Results from representative experiments performed on the [110] orientation are shown in Fig. 4. The shift from the ambient Raman line is plotted for all three peaks as a function of density compression. The longitudinal stress corresponding to the density compression, given on the bottom axis, is plotted on the top horizontal axis. The experimental values are shown as solid symbols with vertical error bars reflecting the uncertainty in the measured frequency shift. The data in Fig. 4 show that the strain-induced peaks display shifts from the ambient Raman line which increase with density compression. The solid line in this figure represents the phenomenological model predictions [12]. This model is based on the microscopic lattice theory developed by Ganesan, Maradudin, and Oitmaa [9]. It employs three fitting parameters which define the phonon deformation potentials. The frequency shift for any arbitrary deformation is described by the deformation potential response to applied strain. The application of strain along [110] lowers the cubic symmetry to orthorhombic, completely lifting the degeneracy, and permits unambiguous determination of the three fitting parameters. A full discussion, including details of the model and its predictions, will be presented at a later date.

Shock compression experiments conducted on the [100] oriented diamond crystals permit an independent check of

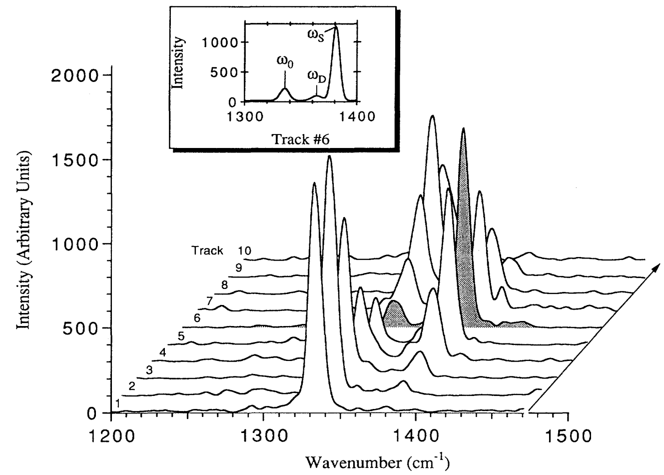

FIG. 5. Time-resolved, Raman spectra for [100] compression.

the phenomenological model. Uniaxial strain along [100] lowers the symmetry to tetragonal, partially lifting the degeneracy, and resulting in a singlet and doublet. Knowledge of the fitting parameters from the [110] data allows predictions to be made for the singlet and doublet frequency response to uniaxial strain, thus providing an independent verification of the parameter values.

Figure 5 shows representative time-resolved spectra for shock compression experiments on [100] oriented diamonds. As in Fig. 2, the observed Raman shift and intensity are plotted in contiguous 10 ns time intervals as the shock transits the material. Track 1 shows the spectrum at ambient stress (1332.5 cm^{-1}), recorded prior to wave arrival. The shock wave has arrived by track 2, where the singlet peak (ω_S) is seen to the right of the ambient peak. As the shock progresses through the sample, the ω_S peak intensity continues to rise. The much less intense doublet peak (ω_D), located on the left shoulder of the singlet, may be observed in tracks 4–8. Peak stress occurs at track 6 (highlighted), five tracks after impact. The inset in Fig. 5 shows the observed spectrum for this track. The simultaneous reduction in intensity (to near zero) of the unshifted central peak is a feature that was always present in experiments performed for this orientation. This result is to be expected since the singlet and doublet peaks are predicted to be well removed from the ambient peak at 1332.5 cm^{-1}. The peak longitudinal stress was calculated to be 27.8 GPa (2.5% compression) for the experiment shown in Fig. 5.

The phenomenological model predictions for strain applied along [100] are illustrated in Fig. 6 for density compression approaching 4%. In this figure the solid symbols represent the measured shifts of the singlet (triangles) and doublet (squares) Raman lines from the ambient position [15]. The agreement between model predictions and experiment is again very good. In a similar manner, the model may be used to predict the phonon be-

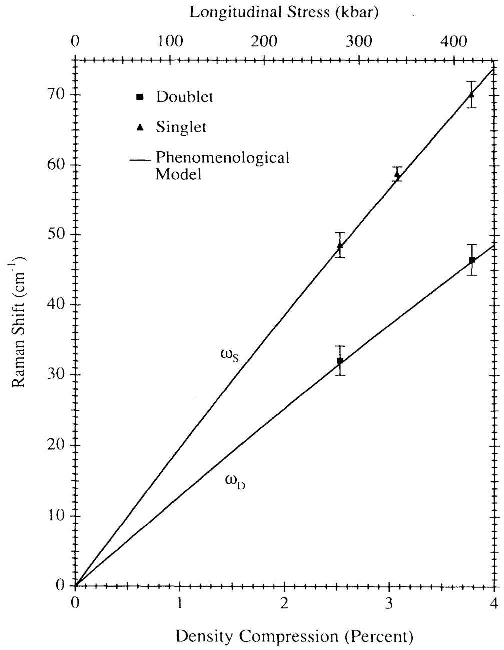

FIG. 6. Data from [100] compression experiments and comparison with phenomenological model predictions.

havior for uniaxial stress and hydrostatic stress [12]; good agreement was obtained in both cases.

In conclusion, we have presented the results of time-resolved, Raman spectroscopy performed during shock compression of diamond single crystals oriented along the [110] and [100] directions. Peak longitudinal stresses approaching 50 GPa, along with strongly nonhydrostatic but uniform stress states, were achieved using plate impact experiments utilizing uniaxial strain loading. The Raman measurements allowed explicit determination of the strain-induced symmetry changes. Spectra acquired for uniaxial strain along [110] show three distinct Raman shifted peaks, demonstrating a complete lifting of the triply degenerate first-order Raman line. This observation is consistent with a reduction in symmetry from cubic to orthorhombic. Spectra recorded for uniaxial strain along [100] show two Raman shifted peaks, corresponding to singlet and doublet lines, demonstrating a partial lifting of the degeneracy. A cubic to tetragonal reduction in symmetry is indicated by these observations. The reversible nature of the splitting and shifts upon shock unloading shows that the diamond samples display an elastic response over the stress range examined. The present results provide powerful insights into the nature of the shock-compressed state and are expected to stimulate further work on real time examination of structural changes in shocked solids.

A phenomenological model used to predict the strain-induced frequency response has been demonstrated to provide very good agreement with experiment for the compression range considered here. Further details of this model and a comparison of the present work with reported Raman shifts under uniaxial [16] and hydrostatic [3–8] stress loading of diamond will be presented in a future paper.

The authors wish to thank Paul Bellamy, Dave Savage, and Kurt Zimmerman for operating the gas gun and for their technical assistance during the course of this work. Gerry Pangilinan is thanked for many discussions during the course of this work and for a careful reading of the manuscript.

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[1] Y. M. Gupta, in *Shock Compression of Condensed Matter—1991*, edited by S. C. Schmidt, R. D. Dick, J. W. Forbes, and D. G. Tasker (North-Holland, Amsterdam, 1992), p. 15.

[2] M. Cardona, in *Light Scattering in Solids II*, edited by M. Cardona and G. Guntherodt, Topics in Applied Physics Vol. 50 (Springer-Verlag, Berlin, 1982).

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

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

[5] A. Tardieu, F. Cansell, and J. P. Petitet, J. Appl. Phys. **68**, 3243 (1990).

[6] H. Boppart, J. van Straaten, and I. F. Silvera, Phys. Rev. B **32**, 1423 (1985).

[7] M. Hanfland, K. Syassen, S. Fahy, S. G. Louie, and M. L. Cohen, Phys. Rev. B **31**, 6896 (1985).

[8] A. F. Goncharov, I. N. Makarenko, and S. M. Stishov, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 150 (1985) [JETP Lett. **41**, 184 (1985)].

[9] S. Ganesan, A. A. Maradudin, and J. Oitmaa, Ann. Phys. (N.Y.) **56**, 556 (1970).

[10] R. L. Gustavsen and Y. M. Gupta (to be published).

[11] G. R. Fowles, G. E. Duvall, J. Asay, P. Bellamy, F. Feistmann, D. Grady, T. Michaels, and R. Mitchell, Rev. Sci. Instrum. **41**, 984 (1970).

[12] J. M. Boteler, Ph.D. thesis, Washington State University, 1993 (unpublished).

[13] P. D. Horn and Y. M. Gupta, Phys. Rev. B **39**, 973 (1989).

[14] The ability to achieve large nonhydrostatic but uniform stress states for times of interest is an important attribute to shock wave experiments. See Ref. [1] for further discussion of this issue.

[15] Note that the intensity was not sufficient to satisfactorily resolve the doublet for the 340 kbar experiment.

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