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Author(s): George Rodriguez - MST-11
Jeffrey P. Roberts - MST-11
Antoinette J. Taylor - MST-11

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DEVELOPMENT OF AN HIGH PRESSURE DIAGNOSTIC BASED ON OPTICAL RAMAN BACKSCATTER MEASUREMENTS IN DIAMOND

G. Rodriguez, J. P. Roberts, and A. J. Taylor
Los Alamos National Laboratory
Los Alamos, NM 87545 USA

ABSTRACT

High pressure diagnostics for pulsed power high energy density physics experiments require time-resolved measurements under shock loading conditions with pressures exceeding a megabar. A high pressure diagnostic based on the optical Raman spectrum in oriented crystalline diamond is discussed. By placing the diamond probe in a preferred crystallographic orientation, shock loading due to the pressure wave induces a crystal strain proportional to the applied stress. A strain induced optical frequency shift in the Raman spectrum of diamond is measured temporally with a streak camera to permit real time determination of the pressure wave amplitude. Diamond Raman should provide a first step in achieving a high pressure probe standard for shock loading conditions and large density compression studies exceeding megabar stresses.

INTRODUCTION

Interest in developing an high pressure transducer for shock loading experiments at the PEGASUS pulsed power facility has led to consideration of diamond Raman spectroscopy as a potential technique for probing pressure waves exceeding 1 Mbar. Diamond is an attractive candidate for such a probe due to its high mechanical strength, its wide use for static high pressure measurements in diamond anvil cell (DAC) technology, and its large spectroscopic Raman cross section. Static pressures above 4 Mbar have been achieved in a DAC¹, thus opening the possibility of diamond as a multi-megabar pressure probe. In a set of gas gun experiments on shock compressed diamond², optical measurement of the degeneracy splitting in the Raman spectrum has demonstrated this technique for shock pressures of up to 0.45 Mbar. It is the goal of this work to extend this technology into the multi-megabar regime using compression from the PEGASUS machine, and ultimately the ATLAS machine.³

CRYSTAL STRUCTURE AND STRAIN INDUCED SPECTRAL SPLITTINGS

The Raman effect in a crystal is due to inelastic scattering of incident photons from the lattice vibrations of the crystal. A fraction of the incident photon momentum is imparted to the phonon, and the resultant scattered photon is shifted in frequency by the amount of energy in the lattice vibration. In diamond, the Raman active vibrations correspond to the relative motion between a center atom and the four outer tetrahedral site atoms that occupy four of the eight corners in a cubic lattice unit cell. This arrangement is shown in Figure 1. The Raman shift in frequency corresponding to each of the three vibrational modes depicted below corresponds to an energy of 1332.5 cm⁻¹ and are degenerate. However, when diamond is elastically deformed, crystal strain perturbs the symmetry and either a full or a partial lifting of the degeneracy is observed in the Raman spectrum. This is manifested in the appearance of Raman lines frequency shifted from the line at 1332.5 cm⁻¹. In an hydrostatic DAC experiment, Goncharov et. al.⁴ measured a pressure dependent frequency shift of the 1332.5-cm⁻¹ Raman line of ~ 300 cm⁻¹ per Mbar for pressures up to 0.720 Mbar. In Boteler's shock loading experiment², uniaxial strain loading along the [110] crystallographic direction completely lifts the degeneracy of the 1332.5 cm⁻¹ line. Separation into three frequency components associated with the three phonon modes along [100], [010], and [001] directions is observed. The strain-induced frequency shifts in the Raman spectrum were found to agree quite well with the theoretically calculated shifts based on a models derived by Ganesan et. al.⁵ and Anastassakis et. al.⁶ In these models, the strain-induced dynamical equation of motion for the optical phonon modes has the form:

$$\overline{m}\ddot{u}_i = - \left[K_{ii}^{(0)} u_i + \sum_{klm} \frac{\partial K_{ik}}{\partial \eta_{lm}} \eta_{lm} u_k \right] \quad (1)$$

where u_i is the i th component of the relative displacement of the two atoms per primitive unit cell, $\bar{m}$ is the reduced mass, and K_{ij} are the atomic force constants (spring constants) satisfying cubic symmetry, and η_{lm} are the individual elements of the strain tensor, η . $K_{ii}^{(0)} = \bar{m} \omega_R^2$ is the atomic force constant in the absence of strain (i.e., $\hbar \omega_R = 1332.5 \text{ cm}^{-1}$). $(\partial K_{ik} / \partial \eta_{lm}) \eta_{lm} = K_{iklm}^{(1)} \eta_{lm}$ is the change in the atomic force constant due to the applied strain, η_{lm} ; and i, k, l , and m designate x, y , or z . In cubic symmetric crystals, there are three independent elements of the tensor, $K^{(1)}$, namely: $K_{iiii}^{(1)} = \bar{m} p$, $K_{iikk}^{(1)} = \bar{m} q$, and $K_{ikik}^{(1)} = \bar{m} r$. The most accurate $\{p, q, r\}$ parameters are taken from Grimsditch⁷ and are: $p = -2.92 \omega_R^2$, $q = -1.90 \omega_R^2$, $r = -1.20 \omega_R^2$.

Figure 1. Cubic lattice cell showing tetrahedral arrangement of atoms. Arrows indicate lattice vibrations, and the unit normal vector directions $\{x_1, x_2, x_3\}$ are also shown in their corresponding Miller index directions $\{[100], [010], [001]\}$. For the unstrained crystal, the three lattice vibrations shown are degenerate with a phonon energy, $\omega_R = 1332.5 \text{ cm}^{-1}$.

From the dynamical Eq. (1) above, one obtains a secular equation with eigenvalues, λ , whose solutions yield the new frequencies, ω , of the optical phonon Raman modes in the presence of strain:

$$\begin{bmatrix} p\eta_{xx} + q(\eta_{yy} + \eta_{zz}) - \lambda & 2\eta_{xy} & 2\eta_{xz} \\ 2\eta_{xy} & p\eta_{yy} + q(\eta_{zz} + \eta_{xx}) - \lambda & 2\eta_{yz} \\ 2\eta_{xz} & 2\eta_{yz} & p\eta_{zz} + q(\eta_{xx} + \eta_{yy}) - \lambda \end{bmatrix} = 0 \quad (2)$$

where, $\lambda = \omega^2 - \omega_R^2$; ω is the strain dependent optical Raman frequency. The secular equation above, Eq. (2), is referenced to the crystallographic axes: $x=x_1=[100]$, $y=x_2=[010]$, and $z=x_3=[001]$. Applying Eq. (2) to uniaxial strain loading along the $[100]$ direction requires that $\eta=\eta_{xx}$ be the only strain tensor element. The eigenvalues of the secular equation yield: $\lambda_1=p\eta$ and $\lambda_2=\lambda_3=q\eta$. From the λ eigenvalues, the new Raman frequencies are $\omega_1=(\omega_R^2 + p\eta)^{1/2}$ and $\omega_2=\omega_3=(\omega_R^2 + q\eta)^{1/2}$. One immediately notices that only a partial lifting of the three-fold degeneracy is removed since $\omega_2=\omega_3$. Similarly, strain loading along the $[110]$ direction requires that $\eta/2=\eta_{xx}=\eta_{yy}$ and $\eta/2=\eta_{xy}$. For this case, the eigenvalues are: $\lambda_1=q\eta$, $\lambda_2=(\eta/2)(p+q+2r)$, and $\lambda_3=(\eta/2)(p+q-2r)$, and the new Raman frequencies

are: $\omega_1 = (\omega_R^2 + q\eta)^{1/2}$, $\omega_2 = [\omega_R^2 + (\eta/2)(p+q+2r)]^{1/2}$, $\omega_3 = [\omega_R^2 + (\eta/2)(p+q-2r)]^{1/2}$. Strain loading along [110] completely lifts the three-fold degeneracy.

Now that the relation between Raman frequency shift and crystal strain has been shown, a correlation between stress and strain is established. For density compressions beyond a few percent (which is expected for PEGASUS and ATLAS experimental conditions), a nonlinear elastic stress-strain relation is used to describe the mechanical response of diamond. Adopting the formalism of Nielsen⁸, the Cauchy stress tensor, σ_{ij} , is related to the strain tensor, η , by (for uniaxial strain):

$$\sigma_{ij} = (\rho_o/\rho) [c_{ijkl} \eta_{kl} + c_{ijklmn} \eta_{kl} \eta_{mn}] \quad (3)$$

where, c_{ijkl} and c_{ijklmn} are the second and third order elastic constants, respectively; ρ is the mass density of diamond with $\rho_o = 3.515 \text{ g/cm}^3$. A final equation relating the density ratio to the strain is also used⁹:

$$(\rho_o/\rho)^2 = |\delta_{ij} + 2\eta_{ij}| \quad (4)$$

Using the Eqs. (2), (3), (4), the second-order elastic constants¹⁰, and the third-order elastic constants¹¹, we can compute the stresses and the strain-induced frequency shifts of the Raman spectrum versus density compression, $(\rho/\rho_o - 1)$, for strain loading along a particular crystallographic axis. Figure 2 shows the computed stresses for strain loading along [100] and [110] directions. Figure 3 demonstrates that shifts as large as $\sim 200 \text{ cm}^{-1}$ ($\sim 6.4 \text{ nm}$) are expected for stress loads of about 1 Mbar. This is well within the experimental spectral resolution of simple spectrometers. In addition, the calculated splittings of the triply degenerate 1332.5 cm^{-1} line are also well separated by several nm at 1 Mbar.

Figure 2. The calculated stress versus percent density compression for strain loading along (a) [100] and (b) [110] directions. The stresses, σ_{yy} and σ_{zz} , are equal for [100] loading.

Figure 3. The calculated frequency (wavelength) shift in the Raman spectrum diamond versus percent density compression (stress) for strain loading along (a) [100] and (b) [110] directions. The shift, $\Delta\omega_i$, is measured with respect to the normal unstrained Raman frequency at $\omega_R = 1332.5 \text{ cm}^{-1}$ (i.e., $\Delta\omega_i = |\omega_i - \omega_R|$). Strain loading along [100] shows only a partial lifting of the three-fold degeneracy, while strain loading along the [110] direction shows a full lifting of the degeneracy into three distinct Raman lines.

PRELIMINARY EXPERIMENTS

Initial experiments were performed at ambient conditions in order to optimize the laser light delivery system; diamond crystal size and orientation; signal detection, recovery, and recording. A simple schematic of the experimental setup is shown in Figure 4. Due to the low efficiency of the Raman scattering process, a pulsed laser capable of delivering 20 kW of peak power in a 1 μsec pulse was developed. The excitation laser is a double cavity Nd:YLF laser at a wavelength of 527 nm capable of delivering two 500 ns pulses each with a pulse energy of 10 mJ. Laser light is then launched along a 50-meter fused-silica 550- μm -core multimode fiber. The long fiber delivery system is used in order to isolate the laser and detection electronics from electromagnetic noise generated by the PEGASUS machine. A 4-mm tall by 3-mm diameter Type IIA diamond crystal, oriented at [100] or [110], is placed at the output of the delivery laser fiber. The diamond sample is oriented such that the expected shock travels along the [100] or [110] direction. The shock speed in diamond is $\sim 18 \text{ mm}/\mu\text{sec}$, so a 4-mm-long sample should have a transit time of $\sim 220 \text{ nsec}$.

Figure 4 Experimental Apparatus

The backscatter Raman signal is recovered with a second large diameter fused silica 50-meter fiber (950 μm core) placed in close proximity to the diamond sample. Under ambient conditions, Raman light scattered from the diamond occurs at a frequency shifted by 1332.5 cm^{-1} from the laser frequency. For 527 nm laser light, the Raman scattered light is at 565.5 nm. The signal recovery fiber then delivers the Raman scattered light to a 527-nm holographic notch filter, and then to an f/1.8 Raman spectrometer for color separation. The spectrometer dispersion is 3.1 nm/mm. Coupled to the spectrometer is a 40-mm visible streak camera with a 40-mm gated microchannel plate. Readout of the streak camera is done with a 1:1 fiber-optic-coupled Photometrics 300 Series silicon CCD camera. The CCD camera has an effective area of 23.3 mm x 23.6 mm, and an array size of 1012 x 1024 pixels. In order to best preserve the spectral resolution of the overall system, 1:1 imaging is done from the spectrometer output to the CCD readout. Figure 5 displays a sample single-shot streak data set recorded by the CCD read-out camera.

Figure 5. Single-shot time-resolved streak image of diamond Raman signal at 565.5 nm at ambient conditions for [100] orientation. Additional signal between 530 nm and 550 nm is due to Raman scattering from the fused silica fiber delivery system. Excitation laser scatter about 527 nm is also observed. The successive row of dots at ~ 532 nm corresponds to timing marks each separated by ~ 100 nsec.

Figure 6 shows the spectrum and temporal history profile of the diamond Raman streak image. In Figure 6(a) the temporal profile from the streak image demonstrates that the maximum shock measurement time window is dictated by the excitation laser pulse width of $\sim 1.3\text{ }\mu\text{sec}$. The double-pulse structure in Figure 6(a) is also a direct consequence of the double pulse excitation laser used in these experiments. In Figure 6(b) we see that there is a large contribution in spectral signal between 530 nm and 560 nm. This is attributed to Raman scattering from 50-meter-long the fused-silica fiber. Diamond Raman measurements without the optical fiber delivery system showed no signal in the 530 nm - 560 nm region. Inspection of the spectral signal at 565.5 nm shows a narrow line-like spectrum which is characteristic of the diamond Raman line under ambient conditions. A linewidth measurement is not possible with our system since the overall spectral resolution of the system is $\sim 0.2\text{ nm/pixel}$. This resolution should make low pressure shifts difficult, but a shift of several nm is expected for pressures above 0.5 Mbar, well within the system spectral resolution. It is expected that under the current configuration, pressure shifts of 0.1-0.2 Mbar should be the lower detectable limit. Smaller pressure shifts can be made by choosing a spectrometer with higher dispersion.

Figure 6. Graphs of the recorded (a) temporal profile and (b) spectrum of the streaked diamond Raman image of Figure 5 under ambient conditions for [100] diamond. The temporal profile follows the excitation laser temporal profile, and has an overall FWHM of 1.3 μsec . The spectrum shown in (b) shows the triply degenerate Raman line at $\sim 565.5 \text{ nm}$. Under a shock loading experiment, the 1332.5 cm^{-1} will simultaneously split and shift in wavelength according to the results graphed in Figure 3.

FUTURE DEVELOPMENT

Initial fielding of this diagnostic will be on Rayleigh-Taylor Mix experiments¹² on PEGASUS where pressure pulses of $\sim 0.8 \text{ Mbar}$ are expected. By appropriate placing of the diamond sample in the load, and by correct timing of the excitation laser relative to the start of current on the machine, a shock wave traveling axially along the center (radius=0) of the machine should produce conditions necessary to observe the discussed shifts and splittings in the diamond Raman spectrum. Based on the results, and the refinement of the diagnostic on these initial shock experiments, appropriate experiments with multi-Mbar conditions will be performed.

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