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1995 J. Phys.: Condens. Matter 7 L637

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LETTER TO THE EDITOR

## A micro-Raman investigation of high-pressure quenched graphite

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Received 22 August 1995, in final form 11 September 1995

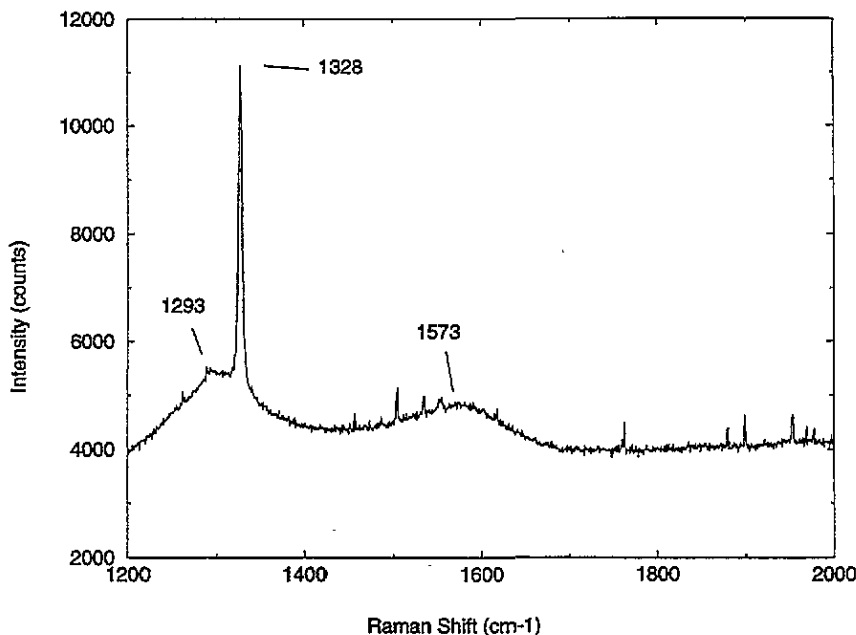
**Abstract.** Polycrystalline pyrolytic graphite was compressed in a diamond anvil cell to pressures up to 73 GPa. *In situ* Raman measurements reveal evidence of a phase transition at 15–20 GPa, consistent with earlier static high-pressure experiments on graphite. The sample was quenched by rapid downloading of the cell to ambient pressure. Micro-Raman investigation of the quenched sample reveals a broad range of previously unobserved intermediate carbon structures, sometimes coexisting with diamond. We also observe the quenching of the 'nanocrystalline' phase of graphite.

High-pressure-high-temperature studies of graphite are of fundamental scientific and technological interest. Graphite has been extensively studied under high pressure over several decades [1–7]. However, the behaviour of graphite under compression at ambient temperature is still not well understood.

Yagi and coworkers [1–3] have performed *in situ* x-ray diffraction on single-crystal graphite, and suggested the formation of hexagonal diamond (lonsdaleite) under high pressure. However, this hexagonal diamond is observed to back-transform below  $\sim 5$  GPa upon release of pressure. To date it has not been possible to quench hexagonal diamond to ambient conditions after high-pressure application at room temperature. The present studies are motivated by these considerations as well as by the desire to study changes in C–C bonding during both compression and decompression. In particular, we report the first high-resolution measurements of quenched samples using micro-Raman spectroscopy. This was achieved by removing the gasket from the high-pressure device and studying the sample with a 100 $\times$  microscope objective. Micro-Raman spectroscopy provides rapid identification of diamond (peak at 1332  $\text{cm}^{-1}$ ), graphite (1580  $\text{cm}^{-1}$ ), and nanocrystalline graphite (1600  $\text{cm}^{-1}$  and 1350  $\text{cm}^{-1}$ ). This letter also reports previously undocumented carbon structures which appear to be intermediate phases between graphite and diamond coexisting with small amounts of diamond.

Four experiments were performed on samples of polycrystalline graphite in a diamond anvil cell. An Innova-70 laser (Coherent) was used in the micro-Raman measurements, with an excitation wavelength of 514.5 nm. The detector was an OMA-Vision model 1530-P-1024S utilizing a Thompson CSF THX-31159A L-grade CCD array with 1024  $\times$  256 19  $\times$  19  $\mu\text{m}^2$  photoelements [8]. Pressure was determined via the shift of position of the fluorescence peak from a ruby chip placed in a sample volume [9]. The first three experiments utilized a synthetic blue diamond anvil with a 200  $\mu\text{m}$  central flat opposite a synthetic yellow diamond with a 300  $\mu\text{m}$  flat, and with a 50  $\mu\text{m}$  sample hole in the gasket.

A methanol:ethanol mixture was used as a hydrostatic pressure transmitting medium within the cell in all experiments. The fourth experiment used basically the same arrangement, with the exception of the use of two 300  $\mu\text{m}$  anvils. Pressure was applied incrementally, with Raman spectra taken in between increments until a pressure of  $\sim 70$  GPa was reached. The samples were then quenched by releasing the pressure rapidly, in one continuous turn of the nut (with the exception of the first sample, where the pressure was released slowly). The gaskets were removed and the samples inspected by micro-Raman spectroscopy. The lateral resolution of the region sampled was diffraction limited with the 100 $\times$  objective and a laser spot size of  $\sim 1$   $\mu\text{m}$ .



**Figure 1.** The micro-Raman spectrum of high-pressure quenched graphite. The diamond phase ( $1328\text{ cm}^{-1}$ ) coexists with an unknown carbon phase (peak at  $1294\text{ cm}^{-1}$ ). Relative amounts varied around the area in the gasket where diamond was present.

The initial pressure of the first experiment was high (32 GPa), such that measurements of the graphite spectrum at the pressures where phase transition was later found to occur were unobtainable (these occurred at  $\sim 15$ – $20$  GPa). However, an interesting event occurred around 58 GPa, at which point our previously opaque sample began to noticeably transmit light at spots scattered throughout the sample. Later samples also showed increased transmission at higher pressures, though not as dramatically, as our first sample was the only one which was initially completely opaque. After reaching 68 GPa, pressure was decreased gradually, and transmission was observed to persist to low pressures. Micro-Raman inspection of the gasket was unfruitful in this experiment due to insufficient amounts of the sample adhering to the gasket after removal from the anvil.

The second experiment, however, yielded much information. This sample was taken to 72 GPa and quickly quenched; inspection of the gasket with a 100 $\times$  objective revealed a wealth of different types of spectrum, the most impressive of which was a sharp, strong peak at  $1328\text{ cm}^{-1}$  and a peak around  $1294\text{ cm}^{-1}$  (fwhm  $\sim 23\text{ cm}^{-1}$ ) which was ubiquitous

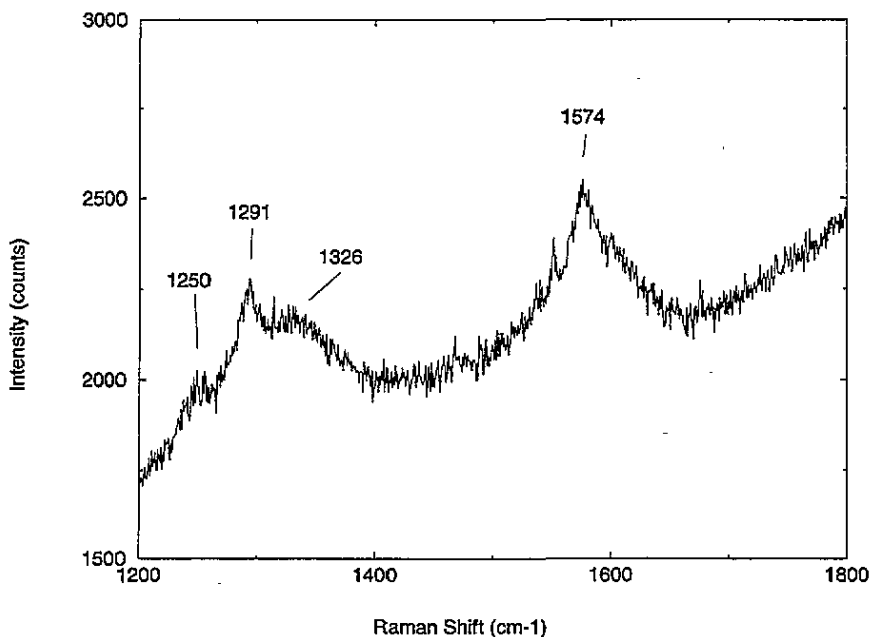


Figure 2. The micro-Raman spectrum of quenched graphite showing a different region without a sharp diamond peak at  $1328\text{ cm}^{-1}$ .

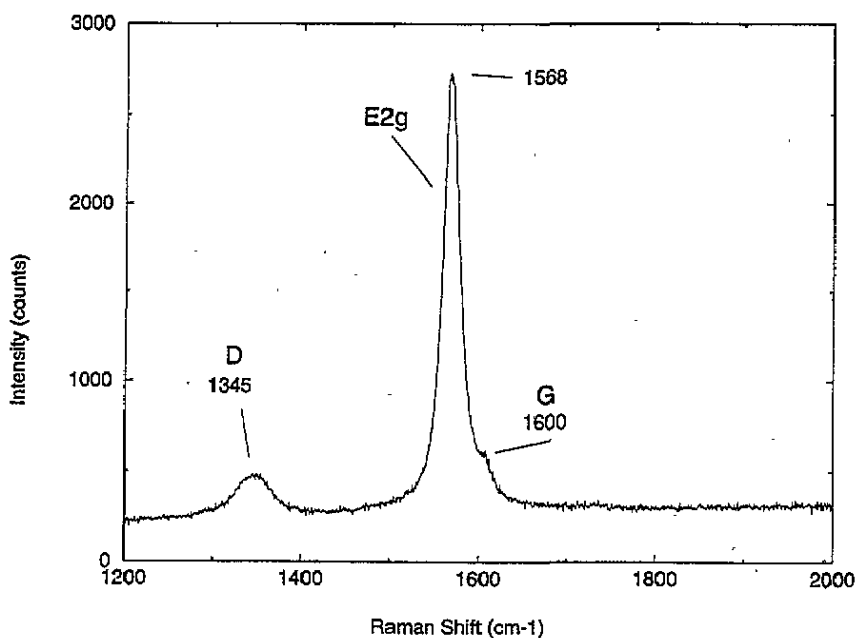


Figure 3. The spectrum of quenched nanocrystalline graphite collected from the surface of the diamond anvil.

in this and later quenched samples (figure 1). The peak at  $1328\text{ cm}^{-1}$  was present only in

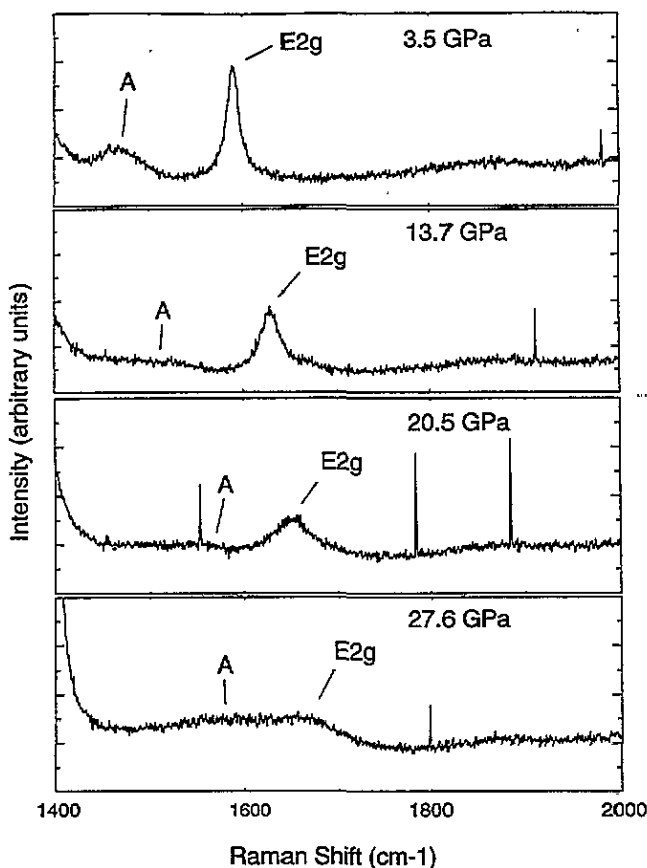


Figure 4. Micro-Raman spectra with increasing pressure showing broadening of the  $E_{2g}$  peak at high pressures. The broad feature labelled A is from the diamond anvil. The sharp spikes are the result of random noise in the detector.

a localized area of the sample  $\sim 3 \mu\text{m}$  across. The phase which gives rise to this peak is highly stable, and does not appear to be subject to the transient existence exhibited by the phase investigated by Utsumi and Yagi [2,3]. The spectra obtained from various regions of this sample exhibit features which are suggestive of those presented by Aleksandrov *et al* as 'impact diamond' with a high lonsdaleite content [4]. It should be added that the diamond peak at  $1328 \text{ cm}^{-1}$  is lower than the  $1331 \text{ cm}^{-1}$  peak from a cubic diamond crystal obtained with the same system. Localized heating caused by the laser beam or the existence of tensile strain in the sample could both account for this  $3 \text{ cm}^{-1}$  downward shift. Using the calibration of Herchen and Cappelli, we estimate the temperature which would result in such a shift in the Raman peak of diamond to be 496 K [10].

The third experiment was taken to 70 GPa and quenched by rapid downloading. Sample remnants in the gasket hole and the surface as well as those collected from the surface of the diamond anvil were inspected with the  $100\times$  objective. Spectra obtained from the surface of the gasket yielded the same feature around  $1293 \text{ cm}^{-1}$ , almost to the exclusion of the graphite 'G' band. Spectra obtained from the gasket hole showed a wide variety of structures, and a representative example is shown in figure 2. The wide 'D' band shows three peaks, at  $1250$ ,  $1291$  and  $1326 \text{ cm}^{-1}$ . Remnants collected from the surface of the

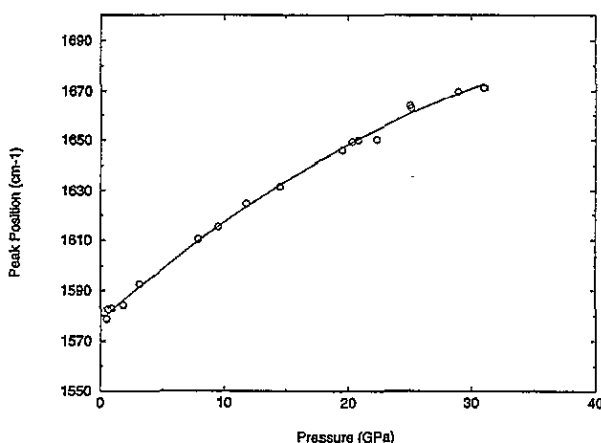


Figure 5. The pressure variation of the Raman frequency of graphite to 30 GPa. The solid curve is a quadratic fit to the data.

anvil clearly showed the 'D' band characteristic of nanocrystalline graphite at  $1345\text{ cm}^{-1}$  (figure 3).

The fourth experiment was taken to 62 GPa, and the remnants again transferred from the anvil to the glass slide. Small features corresponding to the  $1328\text{ cm}^{-1}$  and  $1294\text{ cm}^{-1}$  peaks were observed, but with substantially weaker intensity than those from the previous samples.

*In situ* measurements of the width and position of the graphite Raman peak ( $1580\text{ cm}^{-1}$  at ambient pressure) showed sudden broadening at between 15 and 20 GPa in all experiments (figure 4), indicating a reordering of the graphite structure, and in agreement with the experiments of Aleksandrov *et al* [4] and Hanfland *et al* [5]. We attribute the broad peak at  $1480\text{ cm}^{-1}$  in figure 4 to a defect in the diamond anvil [11] rather than a part of the sample. The graphite Raman mode ( $E_{2g}$ ) peak position was obtained by fitting a Lorentzian line shape to the observed peak. A polynomial fit to the peak position versus pressure data yielded the following quadratic relation:

$$\Delta\nu = -0.0408P^2 + 4.32P + 1580 \text{ (valid to } \sim 30 \text{ GPa) (figure 5)}$$

where  $\Delta\nu$  is the Raman shift in  $\text{cm}^{-1}$  and  $P$  is the pressure in GPa. Similar sublinear dependence on pressure has been observed previously [4, 5].

An additional experiment was run using pyrolytic rather than polycrystalline graphite, and was taken to 67 GPa. The behaviour of the observed spectra with increasing pressure was not sufficiently different from that of the polycrystalline sample. The quenched sample also revealed nanocrystalline features in the spectrum at  $1348\text{ cm}^{-1}$ .

We offer the following conclusions.

(i) We observe the quenching of nanocrystalline graphite following the rapid decompression of polycrystalline and pyrolytic graphite under high pressure at ambient temperature.

(ii) In addition to nanocrystalline graphite, we observe a variety of intermediate structures, most notably demonstrated by the bands at  $1294\text{ cm}^{-1}$  and  $1250\text{ cm}^{-1}$ . Further theoretical calculations are needed to understand the three-dimensional structure responsible for these bands.

(iii) We have observed quenching of the diamond phase following compression of polycrystalline graphite.

Trent Schindler acknowledges the support of the Research Experiences for Undergraduate (REU) supplement to DMR-9296212 from the National Science Foundation (NSF). Y K Vohra acknowledges the support of the Metals Program, NSF grant DMR-9403832.

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