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## The gem anvil cell: high-pressure behaviour of diamond and related materials

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### Abstract

The moissanite anvil cell has been used to study the high-pressure behaviour of diamond. The first-order Raman shift of diamond shows a strong dependence on hydrostaticity, with very different pressure dependences observed under hydrostatic and non-hydrostatic conditions. The shift of the second-order Raman band under hydrostatic pressures was determined for the first time. Sapphire has almost no peaks above  $1000\text{ cm}^{-1}$  in the Raman spectrum and no absorption in the ultraviolet range; it is therefore especially useful for studies in those spectral regions. A sapphire anvil cell was used in a study of graphite up to 24 GPa. A phase transition was found near 18 GPa, consistent with previous reports, and no peaks characteristic of diamond in the  $1330\text{ cm}^{-1}$  range were found, indicating that the phase is not diamond.

Despite the importance of diamond in high-pressure studies, it is difficult to study the compressional behaviour of diamond itself, since the signal from the anvil seriously interferes with that from the diamond sample. This is the case whenever the measured properties are close to those of diamond. Various gem anvil cells can be employed to address this issue. The highest pressures achieved to date in gem anvil cells are 58.7 GPa for moissanite anvils [1, 2], 25.8 GPa for sapphire anvils, and 16.7 GPa for cubic zirconia anvils (table 1) [3]. These gem anvil cells are suitable for work in various situations where the diamond anvil cell (DAC) cannot be used. Here, we briefly report results of several studies in this area carried out in our laboratory during the past few years.

At ambient conditions, the first-order Raman spectrum of diamond is characterized by a strong, narrow peak (FWHM in the range of  $0.6\text{ cm}^{-1}$ ) located near  $1333\text{ cm}^{-1}$ . The mode is triply degenerate with  $T_{2g}$  symmetry (Brillouin zone centre). Separation of the signal due to diamond samples from that of the anvils in DAC experiments is difficult. In principle, the use of a  $^{13}\text{C}$  DAC can solve the problem, but such anvils are not readily available [4]. Hence, we have employed the moissanite anvil cell (MAC) for such a study.

In our experiments, two kinds of pressure environment were used. With 4:1 methanol/ethanol solutions, Ar, or He as the pressure media, the sample is pressurized under

**Table 1.** Comparison of physical properties of different gem anvil materials.

	Moissanite	Sapphire	c-zirconia
Composition	SiC	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>
Impurities (mol%)	—	—	15Y <sub>2</sub> O <sub>3</sub>
Crystal structure	<i>P6<sub>3</sub>mc</i>	<i>R3C (D<sub>3d</sub><sup>6</sup>)</i>	SiC-6H Cubic
Density (g cm <sup>-3</sup> )	3.217	3.97	5.6
Hardness (Knoop)	3000	2000	1370
Hardness (Mohr)	9.25	9.0	8.5
Bulk modulus (GPa)	224; 267–335	253–255	—
Young's modulus	—	348.6	—
Melting point (°C)	2700	2105	2680
Thermal conductivity (W m <sup>-1</sup> K <sup>-1</sup> at 293 K)	140–500	35	1.8
Thermal expansion (10 <sup>-6</sup> )	2.8	7.8	10–16.6
Stable <i>T</i> (°C)			
In air	1700	1700	2400
In vacuum	2000		
Refractive index, <i>n</i>	2.648, 2.6911	1.73	2.15–2.18
Birefringence	0.043		
Dispersion	0.104		
Transparency	>425 nm	<5.5 μm	<6.9 μm
Highest <i>P</i> (GPa)	58.7	25.8	16.7
Year achieved	2001	1995	1995

hydrostatic conditions. The  $T_{2g}$  phonon measured for the diamond sample remains triply degenerate; correspondingly, the Raman peak is strong and narrow up to at least 10 GPa. The frequency of the peak shifts linearly to higher wavenumbers with pressure, as shown in figure 1. The pressure dependence of its frequency ( $d\nu/dP$ ) is  $2.96 (\pm 0.05) \text{ cm}^{-1} \text{ GPa}^{-1}$ , in good agreement with the highest previously reported value of  $2.93 \text{ cm}^{-1} \text{ GPa}^{-1}$  [5], which was measured above 10 GPa in a DAC with a He pressure medium. This  $d\nu/dP$  value is also in good agreement with theoretical first-principles results [6].

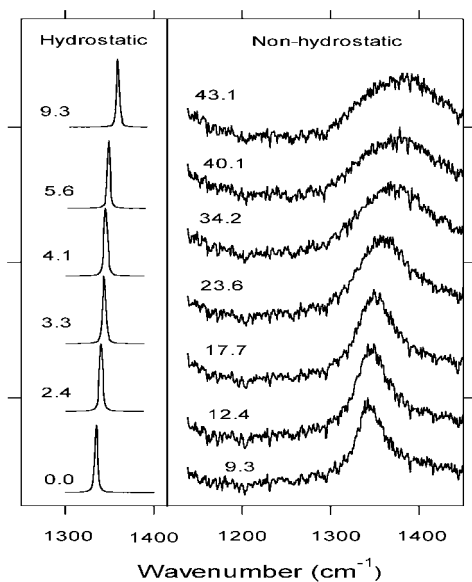
The situation is changed, however, when the pressure is applied under non-hydrostatic conditions. In this case, the sample (4 μm size diamond powder) and the pressure marker (1 μm size ruby powder) were spread on the surface of a T301 stainless steel gasket between two moissanite anvils without a pressure medium, and the non-hydrostatic pressure produced when the anvils were squeezed together. The degeneracy of the  $T_{2g}$  phonon is partially or completely lifted. The first-order Raman peak from diamond becomes weak and broad, and under higher pressure even broader (its FWHM is in the range of 18–121  $\text{cm}^{-1}$ , depending on the actual pressure applied). The result is quite consistent in different sample configurations. The frequency of the observed Raman peak also increases with pressure as shown in figure 2. Up to 43 GPa, the pressure shift can be fitted to a linear relation:

$$\nu_d (\text{cm}^{-1}) = 1334.5 + 1.023 P (\text{GPa})$$

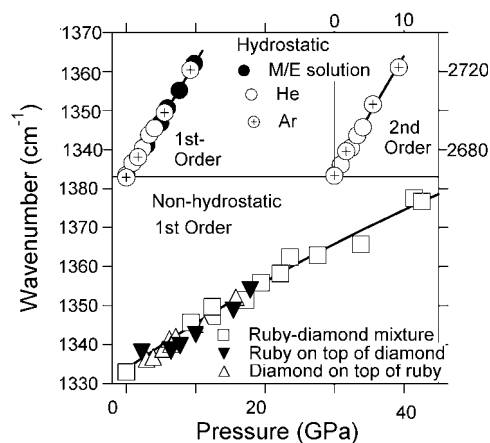
or a second-degree polynomial:

$$\nu_d = 1332.6 + 1.294 P - 0.0062 P^2 (\text{GPa}).$$

The differences between  $d\nu/dP$  in various pressure environments indicate that previously reported lower values [4, 7, 8] either show contamination by spectra of the DACs or are caused by various degrees of non-hydrostaticity in the sample. Additional structure in the broadened peak can be observed in the high-frequency tail of the band [9].



**Figure 1.** The first-order Raman peak observed at high pressures under hydrostatic (left) and non-hydrostatic conditions (right). Under hydrostatic conditions, the FWHM is in the region of  $0.7 \text{ cm}^{-1}$ , whereas under non-hydrostatic conditions the FWHM ranges from 18 to  $121 \text{ cm}^{-1}$ .

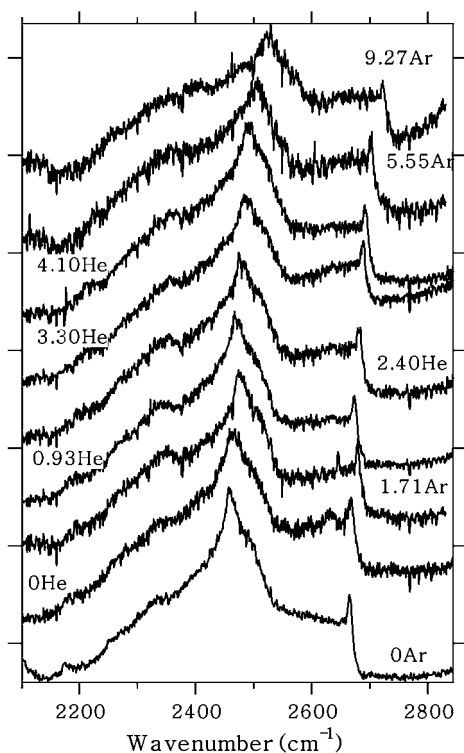


**Figure 2.** The frequency shift of the Raman peaks of diamond under pressure. Bottom panel: the first-order Raman shift under non-hydrostatic conditions ( $dv/dP = 1.0$ ). Upper panel: the Raman shift of the first- and second-order phonons ( $dv/dP = 2.95$  and  $6.04$ ) under hydrostatic conditions.

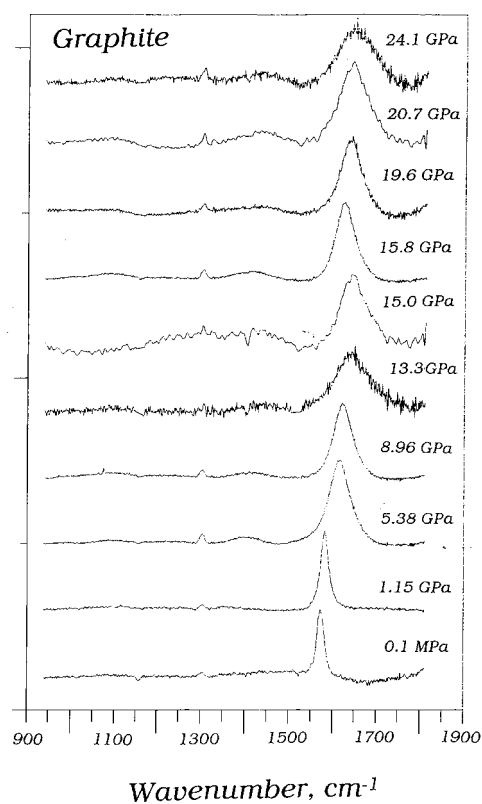
The weak second-order Raman peaks of diamond contain detailed information on the phonon band structure. Its high-pressure behaviour is interesting. However, clear observation of the structure in the second-order Raman peaks at high pressures is very difficult in a DAC. Here the MAC is again useful. Figure 3 shows the second-order spectra of diamond up to 10 GPa under hydrostatic conditions in either a He or Ar pressure medium in a MAC. The small, sharp peak located at the highest frequency in the second-order Raman peaks (see figure 3) is almost twice that of the stronger lower-frequency peak and is considered the principal overtone of the first-order Raman mode at the Brillouin zone centre. The pressure dependence ( $6.04 \pm 0.18 \text{ cm}^{-1} \text{ GPa}^{-1}$ ) is almost exactly doubled for the first-order peak ( $2.95 \pm 0.05$ ) as shown in figure 2.

Graphite transformed to a high-pressure phase around 18 GPa at room temperature, and one experiment confirmed by means of both optical microscopy and x-ray diffraction [10] that graphite transformed to hexagonal diamond (lonsdaleite). Using sapphire anvils, we placed graphite powder in a sample hole of a T301 gasket, and pressurized the sample up to 24.4 GPa. Raman measurement, as shown in figure 4, confirmed that a high-pressure phase does appear, but no bands are observed in the  $1300 \text{ cm}^{-1}$  region characteristic of hexagonal (lonsdaleite) and cubic diamond [6]. Therefore, the sample is still a diamond-like phase (i.e., not diamond). Whether the discrepancy between our results and those of [10] is due to the starting material or the pressure environment remains to be determined.

Raman studies with the gem anvil cell are also useful for other materials such as  $\text{D}_2\text{O}$ , where the spectrum is normally obscured by the second-order peaks of diamond [3].



**Figure 3.** The second-order Raman peaks of diamond at various pressures up to 10 GPa observed in a MAC in either a He or Ar medium.



**Figure 4.** Raman spectra of graphite up to 24 GPa in a sapphire anvil cell.

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