

Reversible Pressure-Induced Amorphization in Solid C_{70} : Raman and Photoluminescence Study

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Abstract

We have studied single crystals of C_{70} by Raman scattering and photoluminescence in the pressure range from 0 to 31.1 GPa. The Raman spectrum at 31.1 GPa shows only a broad band similar to that of the amorphous carbon without any trace of the Raman lines of C_{70} . After releasing the pressure from 31.1 GPa, the Raman and the photoluminescence spectra of the recovered sample are that of the starting C_{70} crystal. These results indicate that the C_{70} molecules are stable upto 31.1 GPa and the amorphous carbon high pressure phase is reversible, in sharp contrast to the results on solid C_{60} . A qualitative explanation is suggested in terms of inter- versus intra-molecular

interactions.

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Among the many fascinating properties of fullerenes, studies on structure of C_{60} and C_{70} and their structural transformations as a function of temperature and pressure have attracted considerable attention [1]. The orientational order-disorder transition occurs at $T_c \sim 250$ K in C_{60} [2] and the transition temperature increases with pressure (~ 100 K/GPa) resulting in the room-temperature phase transition at ~ 0.4 GPa [3]. The stability of the C_{60} buckyballs at high pressures and the nature of the compressed phase have been debated extensively in the last two years [4–9]. Early x-ray diffraction experiments [4] showed a structural phase transition of cubic C_{60} to a lower symmetry phase at ~ 20 GPa under non-hydrostatic compression. Raman Spectroscopy [5,6] and optical reflectivity [6] studies showed that the solid C_{60} undergoes an irreversible transformation to an amorphous carbon phase at pressures greater than 22 GPa. Moshary *et al.* [7] reported anomalously high transparency of the irreversible high pressure phase thus suggesting the collapse of the C_{60} molecules into a new structure of carbon. However, the recent measurements [8] of optical absorption at high pressures do not find any evidence of high transparency and reconfirm the earlier conclusion of irreversible transformation of C_{60} to amorphous carbon. It has also been reported [9] that rapid, non-hydrostatic compression of solid C_{60} transforms it to cubic diamond at about 20 ± 5 GPa. Such a conversion to the cubic diamond has not been seen in hydrostatic pressure experiments [8].

Compared to C_{60} , the stability of C_{70} - the second most abundant fullerene present in the arc-processed carbon deposits, with respect to compression and the nature of the high pressure phase is relatively much less understood. The order-disorder transitions occur at ~ 276 K and 337 K [10,11]. Recent high pressure x-ray diffraction experiments [12] at room temperature reveal fcc \rightarrow rhombohedral phase transition at 0.35 GPa with fcc phase coexisting till ~ 1 GPa. On further compression beyond 18 GPa, solid C_{70} transforms to an amorphous phase. Though it has been stated [12] that the transition is irreversible, there are no results on decompression and on the pressure-cycled recovered sample.

In this paper we report our high pressure Raman and photoluminescence (PL) results on single crystals of C_{70} upto 31.1 GPa. Raman lines, characteristic of intramolecular modes

of C_{70} could be followed upto 12 GPa. The lines broaden and shift with pressure, with a characteristic change of slope at ~ 1 GPa which can be attributed to orientational ordering transition. At $P > 20$ GPa, the Raman spectra starts showing a broad band near 1650 cm^{-1} , matching very well with the high pressure phase of the amorphous carbon [13] and there are no Raman signatures corresponding to the intramolecular vibrations of the C_{70} . The most spectacular result is that the Raman spectra at 0.1 GPa in the decreasing pressure run and in the recovered sample (outside the diamond anvil cell(DAC)) are that of the starting C_{70} crystal. In addition to Raman studies, PL measurements have also been carried out as a function of pressure. The PL of the pressure-cycled sample is seen to be similar to that of the starting C_{70} sample. These results unambiguously indicate that the amorphous phase at high pressures is reversible and the C_{70} molecules are stable upto 31.1 GPa, in sharp contrast to the high pressure results on the solid C_{60} .

The mixture of C_{60} and C_{70} was prepared by the well-known contact-arc vaporization of graphite in helium atmosphere. The soxhlet extract was subjected to repeated chromatographic separation using neutral grade alumina column using toluene and hexane as eluent. Based on the UV-visible absorption, infrared and Raman spectra, the purity of C_{70} is estimated to be better than 99%. Small single crystals were grown by the temperature gradient vapour deposition method. High pressure Raman and PL experiments were carried out using 5145 \AA argon laser line (power < 5 mW before the DAC) at room temperature in a gasketed Mao-Bell type DAC with 4:1 methanol-ethanol mixture as pressure-transmitting medium. Pressure was measured by the well-known ruby fluorescence technique. The interference of the ruby fluorescence ($\sim 1.78\text{ eV}$ to 1.67 eV at ambient pressure) with the PL of the C_{70} crystal was minimised by keeping the ruby crystal (size $\sim 20\text{ }\mu\text{m}$) as far away from the sample as possible in the gasket hole (size $\sim 200\text{ }\mu\text{m}$). The spectra were recorded using a DIOR-XY spectrophotometer equipped with a liquid nitrogen cooled CCD detector as well as using a Spex Ramalog with a cooled photomultiplier tube (Burleigh C31034A). Twelve pressure runs were done reaching a maximum pressure of 31.1 GPa. The ruby fluorescence lines were seen to broaden beyond 12 GPa but were clearly resolved upto the highest pressure.

We shall first discuss the Raman results. In the spectral range of 200 - 1700 cm⁻¹, we observe 20 distinct intramolecular modes at almost ambient pressure (< 0.1 GPa) with the sample in the DAC, similar to the earlier reports [14,15]. The region 1300 - 1400 cm⁻¹ is dominated by the first order Raman line of the diamond anvils at 1332 cm⁻¹. The variation of Raman lines with increase in pressure in the range 0 to 31.1 GPa are shown in Fig. 1(a) and (b). As the pressure increases, C_{70} Raman lines broaden and their intensities decrease substantially. Even the 1567 cm⁻¹ mode which is most intense at ambient pressures can be followed only upto \sim 12 GPa after which it merges with the background (see Fig. 1(a)). We find that the slopes in the pressure dependence of the peak position of Raman modes at 1567, 1516, 1470 and 1449 cm⁻¹ change at \sim 1 GPa [16], which can be related to the reported orientational ordering phase transition from fcc to rhombohedral structure observed by x-ray diffraction [12].

At high pressures (P > 20 GPa), only a broad Raman band appears between 1500 and 1900 cm⁻¹. The intensity of this band is very weak. In order to improve signal to noise ratio, these measured spectra (at P > 20 GPa) were subjected to discrete wavelet transform filtering [17]. The Raman spectrum at pressure 31.1 GPa shows a broad band peaked at 1720 cm⁻¹. This broad band is exactly similar to the corresponding high pressure Raman spectrum of the amorphous carbon which has a Raman band centered about ω = 1580 cm⁻¹ at ambient pressure and pressure derivative $d\omega/dP$ of 4.4 cm⁻¹/GPa [13]. On decrease of pressure from 31.1 GPa, the Raman measurements at 10 GPa still show a broad band at 1600 cm⁻¹ (see inset Fig. 2), implying that the amorphous phase is present upto this pressure. The most interesting result is that the Raman spectra at 0.1 GPa and that of the recovered sample outside the DAC are that of the starting C_{70} crystal wherein 20 lines are again seen in the range of 200 - 1700 cm⁻¹.

Fig. 3(a) shows the PL spectra of the C_{70} crystal in the DAC at four different pressures of 0, 0.7, 1.7 and 2.8 GPa in the increasing pressure run. The PL spectrum of the starting C_{70} crystal is similar to the one reported earlier of the C_{70} film on Si substrate [18]. The PL bands move to lower energies with increasing pressure, similar to that in C_{60} . At P > 2.8

GPa, the PL band shifts to less than 1.4 eV, the lower limit of detection in our experiments. The red-shift of the PL band with pressure (~ -0.09 eV/GPa) is mostly associated with the reduction of the band gap which, in turn, is related to the broadening of the valence and conduction bands due to pressure-induced enhancement of intermolecular interactions [19].

The PL of the sample recovered after cycling to 31.1 GPa (Fig. 3(b)) is very similar to the starting sample, except for a small blue shift of 0.1 eV. The blue shift which reflects a decrease in overlap between C_{70} orbitals can be either due to defects or clathration of the alcohol molecules in C_{70} , as seen in the case of C_{60} crystals [20]. The results shown in Fig. 2 and Fig. 3(b) unambiguously show that the amorphous phase as identified by Raman spectra at high pressures beyond 20 GPa (cf Fig. 1(b)) reverts back to the solid C_{70} on release of pressure. This is in sharp contrast to the irreversible amorphization of solid C_{60} at $P > 22$ GPa. In the case of graphite (the parent material for fullerenes), transformation to an amorphous phase occurs at 23 GPa [21] which has been reported to be reversible on decompression [6].

At this stage, we address the question if the possible quasi-hydrostatic nature of the pressure in the DAC can influence the reversible nature of the high pressure phase. Broadened linewidths and the separation (Δ) of the R_1 and R_2 ruby fluorescence lines are generally regarded as indicators of the presence of non hydrostatic stress components. In our experiments, the R_1 and R_2 lines are clearly resolved even at the highest pressure of 31.1 GPa, although their linewidths are broadened for $P > 12$ GPa. The pertinent observation in relation to our results is that in the return pressure run, the linewidth and the separation Δ for $P = 10$ GPa and 0.1 GPa remain nearly similar whereas the measured Raman spectra are drastically different. This indicates that the nature of pressure, in particular the extent of non-hydrostaticity, does not influence our main results.

We can attempt to rationalise the pressure behaviour seen in C_{70} in comparison with those observed earlier in C_{60} [6] and graphite [21,6] based on intramolecular distances and steric constraints [22]. It must be remarked that pressure-induced amorphization is also seen in other molecular crystals like SiO_2 [23], AlPO_4 [24] and LiCsSO_4 [25]. Some of these

systems like SiO_2 retain their amorphous nature on pressure release whereas other like AlPO_4 and LiCsSO_4 recrystallise. In this picture pressure reduces the nearest neighbour distance between the molecules and below a limiting distance, the intermolecular interactions can become comparable to intramolecular interactions themselves, resulting in the distortion of the molecular units and the formation of a new phase having different bonding and structure.

The nearest carbon-carbon distance between the neighbouring bucky balls is $d_{C-C} = d_{n-n} - \sigma$, where d_{n-n} is the nearest neighbour distance between the centres of the molecules and σ is the relevant molecular dimension. The C_{60} molecules are spherical with $\sigma = 7.06 \text{ \AA}$ [2]. The C_{70} molecules, on the other hand are ellipsoidal [26] with long axis of 7.916 \AA and short-axis of 7.092 \AA and are oriented in the high pressure rhombohedral phase ($P > 1 \text{ GPa}$) with the long axis along the [111] direction and therefore, in the close packing (110) plane, $\sigma = 7.092 \text{ \AA}$. The pressure dependence of d_{C-C} , related to d_{n-n} has been obtained from the Murnaghan equation of state [27] using the known bulk modulus and its pressure-derivative [4,12,28]. For C_{60} solid, d_{C-C} reduces from 3.04 \AA ($P = 0$) to 1.89 \AA at 22 GPa whereas for C_{70} solid it decreases from 3.39 \AA ($P = 0$) to only about 2.67 \AA at 20 GPa . In graphite, interlayer separation along the c-axis (equivalent to d_{C-C}) reduces from 3.35 \AA ($P = 0$) to 2.76 \AA at 23 GPa . The decrease of d_{C-C} is steeper in C_{60} than that of C_{70} and graphite. Theoretical calculations in C_{60} indicate [29] that as d_{C-C} decreases, the intermolecular interaction, which is van-der Waal type at ambient pressure, acquires some covalent character with an associated partial conversion from sp^2 to sp^3 hybridization. When the fraction of sp^3 bonds increases at high pressures, the structure can be close to amorphous carbon which is characterised by the presence of $\sim 15\%$ sp^3 bonding [30]. A similar mechanism could account for the amorphisation of C_{70} with pressure. The question of reversibility of the high pressure phase on decompression should be related to the relative strengths of the inter- versus intramolecular interactions. If the latter is sufficiently stronger, the molecules will not be permanently distorted/destroyed and the high pressure amorphous phase will be reversible on decompression. This seems to be the case in solid C_{70} where the contact intermolecular distance ($d_{C-C} = 2.67 \text{ \AA}$ at 20 GPa) is much larger than in the

high pressure phase of the C_{60} ($d_{C-C} = 1.89 \text{ \AA}$ at 22 GPa). While we have provided a qualitative explanation as to why reversible transition is observed in C_{70} in contrast to C_{60} , the present results should motivate detailed molecular dynamics simulation to understand the high pressure phase of C_{70} . It will be worthwhile to extend the measurements to higher pressures to explore the possibility of irreversible transformations, if any, in C_{70} .

In conclusion, we have shown that the high pressure phase of the solid C_{70} has Raman signatures of the amorphous carbon. The amorphous phase reverts to the crystalline C_{70} on decompression as evident by the Raman lines associated with the intramolecular vibrations of C_{70} and the PL, implying that the C_{70} molecules are stable upto 31.1 GPa. Our experiments also suggest a need to do careful high pressure x-ray diffraction experiments with particular emphasis on the decreasing pressure cycle and the pressure-cycled recovered samples. Further, high pressure experiments on higher fullerenes will be interesting to see if solid C_{70} is unique in its ability to withstand pressure without irreversible transformation. The present experiments on C_{70} , in conjunction with those in C_{60} and graphite should help to obtain an understanding of the nature of C-C interactions and the relative stability of different forms of carbon.

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FIGURES

FIG. 1. (a) Raman spectra in the range of $1400 - 1700 \text{ cm}^{-1}$ at different pressures upto 15.3 GPa in the increasing pressure cycle. Magnification factors are indicated. (b) Raman spectra in the spectral range $1400 - 1900 \text{ cm}^{-1}$ at higher pressures. The thick solid lines are the wavelet transforms of the corresponding recorded spectra, shown by thin lines.

FIG. 2. Raman spectra of C_{70} cycled to 31.1 GPa during the decreasing pressure run. The inset shows the spectra at 10 GPa and 0.1 GPa, note that the full spectrum of the recovered sample shows all the characteristic Raman lines of the starting C_{70} sample.

FIG. 3. Photoluminescence spectra (a) at four typical pressures in the increasing pressure cycle and (b) of the recovered sample after cycling to 31.1 GPa, simultaneously recorded with Raman spectrum shown in Fig. 2 ($P = 0$ (Recovered)). Asterisks in top curve of (a) mark the contributions from the ruby fluorescence.