

**Reversible Pressure-Induced Amorphization in Solid C<sub>70</sub>: Raman and Photoluminescence Study**N. Chandrabhas, Ajay K. Sood,<sup>\*,†</sup> and D. V. S. Muthu*Department of Physics, Indian Institute of Science, Bangalore 560 012, India*

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(Received 27 December 1993; revised manuscript received 3 August 1994)

We have studied single crystals of C<sub>70</sub> 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 broadband similar to that of the amorphous carbon without any trace of the Raman lines of C<sub>70</sub>. After releasing the pressure from 31.1 GPa, the Raman and the photoluminescence spectra of the recovered sample are that of the starting C<sub>70</sub> crystal. These results indicate that the C<sub>70</sub> molecules are stable up to 31.1 GPa and the amorphous carbon high pressure phase is reversible, in sharp contrast to the results on solid C<sub>60</sub>. A qualitative explanation is suggested in terms of intermolecular versus intramolecular interactions.

PACS numbers: 61.43.-j, 61.50.Ks, 62.50.+p, 64.70.Kb

Among the many fascinating properties of fullerenes, studies on the structure of C<sub>60</sub> and C<sub>70</sub> 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<sub>60</sub> [2], and the transition temperature increases with pressure ( $\sim 100$  K/GPa), resulting in the room-temperature phase transition at  $\sim 0.4$  GPa [3]. The stability of the C<sub>60</sub> 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<sub>60</sub> to a lower symmetry phase at  $\sim 20$  GPa under nonhydrostatic compression. Raman spectroscopy [5,6] and optical reflectivity [6] studies showed that the solid C<sub>60</sub> 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<sub>60</sub> 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<sub>60</sub> to amorphous carbon. It has also been reported [9] that rapid, nonhydrostatic compression of solid C<sub>60</sub> transforms it to cubic diamond at about  $20 \pm 5$  GPa. Such a conversion to the cubic diamond has not been seen in hydrostatic pressure experiments [8].

Compared to C<sub>60</sub>, the stability of C<sub>70</sub>—the second most abundant fullerene present in the arc-processed carbon deposits—is with respect to compression and the nature of the high pressure phase relatively much less understood. The order-disorder transitions occur at  $\sim 276$  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  $\sim 1$  GPa. On further compression beyond 18 GPa, solid C<sub>70</sub> 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 Letter we report our high pressure Raman and photoluminescence (PL) results on single crystals of C<sub>70</sub> up to 31.1 GPa. Raman lines, characteristic of intramolecular modes of C<sub>70</sub> could be followed up to 12 GPa. The lines broaden and shift with pressure, with a characteristic change of slope at  $\sim 1$  GPa which can be attributed to orientational ordering transition. At  $P > 20$  GPa, the Raman spectra start showing a broad band near  $1650$  cm<sup>-1</sup>, 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<sub>70</sub>. 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 those of the starting C<sub>70</sub> 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<sub>70</sub> sample. These results unambiguously indicate that the amorphous phase at high pressures is reversible and the C<sub>70</sub> molecules are stable up to 31.1 GPa, in sharp contrast to the high pressure results on the solid C<sub>70</sub>.

The mixture of C<sub>60</sub> and C<sub>70</sub> was prepared by the well known contact-arc vaporization of graphite in helium atmosphere. The solvent 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<sub>70</sub> is estimated to be better than 99%. Small

single crystals were grown by the temperature gradient vapor deposition method. High pressure Raman and PL experiments were carried out using 5145 Å argon laser line (power < 5 mW before the DAC) at room temperature in a gasketed Mao-Bell type DAC with a 4:1 methanol-ethanol mixture as the pressure-transmitting medium. Pressure was measured by the well known ruby fluorescence technique. The interference of the ruby fluorescence ( $\sim 1.78$  to  $1.67$  eV at ambient pressure) with the PL of the  $C_{70}$  crystal was minimized by keeping the ruby crystal (size  $\sim 20$   $\mu\text{m}$ ) as far away from the sample as possible in the gasket hole (size  $\sim 20$   $\mu\text{m}$ ). The spectra were recorded using a DILOR-XY spectrophotometer equipped with a liquid nitrogen cooled charge coupled device 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 up to the highest pressure.

We shall first discuss the Raman results. In the spectral range of  $200$ – $1700$   $\text{cm}^{-1}$ , 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  $1300$ – $1400$   $\text{cm}^{-1}$  is dominated by the first order Raman line of the diamond anvils at  $1332$   $\text{cm}^{-1}$ . The variation of Raman lines with an increase in pressure in the range  $0$ – $31.1$  GPa is shown in Figs. 1(a) and 1(b). As the pressure increases,  $C_{70}$  Raman lines broaden, and their intensities decrease substantially. Even the  $1567$   $\text{cm}^{-1}$  mode, which is most intense at ambient pressures, can be followed only up to  $\sim 12$  GPa, above 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  $1449$   $\text{cm}^{-1}$  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  $1900$   $\text{cm}^{-1}$ . 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  $1720$   $\text{cm}^{-1}$ . This broad band is exactly similar to the corresponding high pressure Raman spectrum of the amorphous carbon which has a Raman band centered about  $\omega = 1580$   $\text{cm}^{-1}$  at ambient pressure and pressure derivative  $d\omega/dP$  of  $4.4$   $\text{cm}^{-1}/\text{GPa}$  [13]. On the decrease of pressure from 31.1 GPa, the Raman measurements at 10 GPa still show a broadband at  $1600$   $\text{cm}^{-1}$  (see inset in Fig. 2), implying that the amorphous phase is present up to 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  $200$ – $1700$   $\text{cm}^{-1}$ .

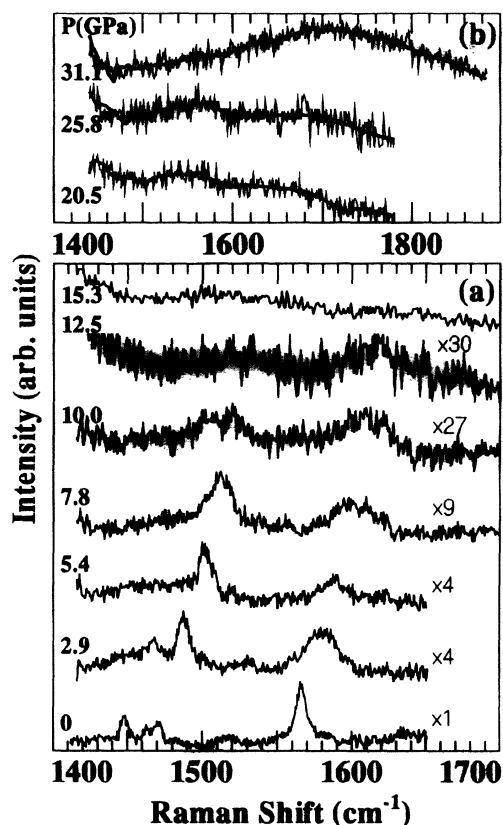


FIG. 1. (a) Raman spectra in the range  $1400$ – $1700$   $\text{cm}^{-1}$  at different pressures up to  $15.3$  GPa in the increasing pressure cycle. Magnification factors are indicated. (b) Raman spectra in the spectral range  $1400$ – $1900$   $\text{cm}^{-1}$  at higher pressures. The thick solid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

Figure 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 redshift of the PL band with pressure ( $\sim -0.09$  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 blueshift of  $0.1$  eV. The blueshift 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 Figs. 2 and 3(b) unambiguously show that the amorphous phase as identified by Raman spectra at high pressures beyond  $20$  GPa [cf. Fig. 1(b)]

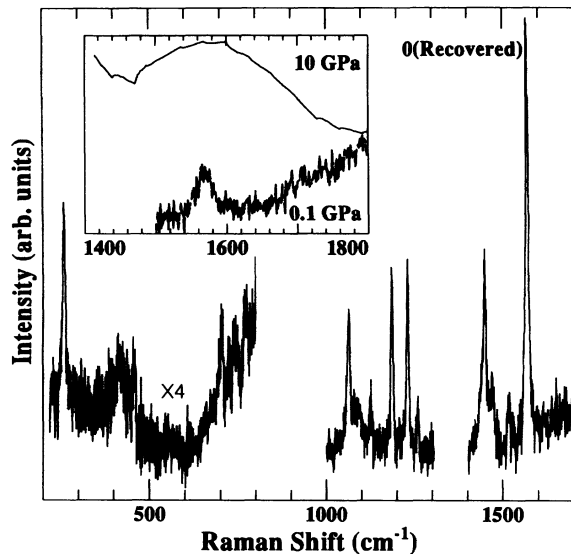


FIG. 2. Raman spectra of  $C_{70}$  cycled to 31.1 GPa during the decreasing pressure run. The inset shows the spectra at 10 and 0.1 GPa; note that the full spectrum of the recovered sample shows all the characteristic Raman lines of the starting  $C_{70}$  sample.

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].

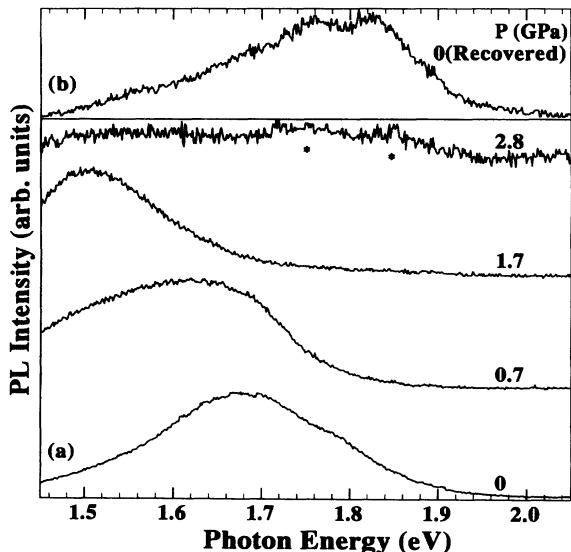


FIG. 3. Photoluminescence spectra (a) at four typical pressures in the increasing pressure cycle and (b) of the recovered sample after cycling to 31.1 GPa, simultaneously recorded with Raman spectrum shown in Fig. 2 [ $P = 0$  (Recovered)]. Asterisks in top curve of (a) mark the contributions from the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

At this stage, we address the question if the possible quasihydrostatic nature of the pressure in the DAC can influence the reversible nature of the high pressure phase. Broadened linewidths and the separation ( $\Delta$ ) of the  $R_1$  and  $R_2$  ruby fluorescence lines are generally regarded as indicators of the presence of nonhydrostatic 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  $\Delta$  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 nonhydrostaticity, does not influence our main results.

We can attempt to rationalize the pressure behavior seen in  $C_{70}$  in comparison with those observed earlier in  $C_{60}$  [6] and graphite [6,21] 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 others like  $AlPO_4$  and  $LiCsSO_4$  recrystallize. In this picture pressure reduces the nearest neighbor 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 neighboring buckyballs is  $d_{C-C} = d_{n-n} - \sigma$ , where  $d_{n-n}$  is the nearest neighbor distance between the centers of the molecules and  $\sigma$  is the relevant molecular dimension. The  $C_{60}$  molecules are spherical with  $\sigma = 7.06$  Å [2]. The  $C_{70}$  molecules, on the other hand, are ellipsoidal [26] with a long axis of 7.916 Å and a short axis of 7.092 Å and are oriented in the high pressure rhombohedral phase ( $P > 1$  GPa) with the long axis along the [111] direction and, therefore, in the close packing (110) plane,  $\sigma = 7.092$  Å. 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 Å ( $P = 0$ ) to 1.89 Å at 22 GPa, whereas for  $C_{70}$  solid it decreases from 3.39 Å ( $P = 0$ ) to only about 2.67 Å at 20 GPa. In graphite, interlayer separation along the  $c$  axis (equivalent to  $d_{C-C}$ ) reduces from 3.35 Å ( $P = 0$ ) to 2.76 Å 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

characterized by the presence of  $\sim 15\%$   $sp^3$  bonding [30]. A similar mechanism could account for the amorphization 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 intermolecular versus intramolecular interactions. If the latter is sufficiently stronger, the molecules will not be permanently distorted and/or 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 the Raman signatures of 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 up to 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.

One of us (A. K. S.) thanks the Department of Science and Technology for financial support.

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