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Pressure-induced transformation and superhard phase in fullerenes: The effect of solvent intercalation

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Abstract:

We studied the behavior of solvated and desolvated C₆₀ crystals under pressure by in situ Raman spectroscopy. The pressure-induced bonding change and structural transformation of C₆₀s are similar in the two samples, both undergoing deformation and amorphization. Nevertheless, the high pressure phases of solvated C₆₀ can indent diamond anvils while that of desolvated C₆₀s cannot. Further experiments suggest that the solvents in the solvated C₆₀ act as both spacers and bridges by forming covalent bonds with neighbors in 3D network at high pressure, and thus, a fraction of fullerenes may preserve the periodic arrangement in spite of their amorphization.

Due to its flexibility in forming sp , sp^2 , and sp^3 bonds, carbon can adopt a wide range of structures. Depending on experimental conditions, one carbon allotrope can transform into another with dramatically different electronic and mechanical properties. Thus, the conversion mechanisms between various forms of carbon have long been a topic of interest. Thanks to the strong C-C covalent bonds, many carbon phases, including both crystalline and non-crystalline forms, are found to exhibit high hardness and have important technological applications in different fields. The structures and the formation mechanisms of hard carbon phases thus have been subjected to numerous experimental [1–9] and theoretical [10,11] works.

Fullerenes are one type of important precursors for studying the phase diagram of carbon and synthesizing various hard carbon phases.[1–6] At high pressure and high temperature conditions, C_{60} may transform into 3D polymer with hardness comparable to that of cubic BN or into amorphous fullerite phases. Some amorphous phases produced show super- or ultra-hardness, such that they can even break diamonds. [2] Cold compression of C_{60} s results in an amorphization of the material above 20 GPa and no superhard phase has been observed even at higher pressures.[12–14] Recently, Wang et al. reported that compression of solvated fullerenes (C_{60} /m-xylene) produces a carbon phase composed of ordered amorphous carbon clusters (OACC).[15] Such formed OACC with a long range periodic structure is challenging the categorization of solid-state materials (including crystalline, amorphous, and quasi-crystalline phases). Moreover, this phase exhibits very high hardness and can indent diamond anvils at high pressure. However, the underlying mechanism for such huge differences in the behaviors of these formed phases and the transformation pathways are not clear. Additional information, including clarifying the roles of the solvents on the transformation of the C_{60} molecules and the nature of the amorphized cell units, is needed to establish the existence of such a transition and to identify the mechanism and the implications for the high-pressure behavior of these unique hard phases in general.

In this work, high pressure Raman spectroscopy has been used to clarify the role of the intercalated solvent on the structural evolution of C_{60} upon compression by a comparative experiment on solvated and desolvated C_{60} s crystals. Further Raman studies, laser irradiation, and transmission electron microscopy (TEM) observations on the decompressed samples are used to reveal the nature of the superhard phase at high pressure.

Solvated C_{60} single crystals were prepared on a glass substrate by evaporating a saturated C_{60} /m-xylene solution at room temperature.[15,16] The as-prepared samples contain solvent and have a hexagonal structure (P63, $a = b = 2.37$ nm and $c = 1.012$ nm). The solvent was removed by heating samples at 150° C under vacuum, transforming it into a FCC structure (here called desolvated sample). The solvated and desolvated samples were loaded separately in a diamond anvil cell (DAC) for high pressure study without using a pressure transmitting medium. High-pressure and room temperature Raman spectra were recorded using a Renishaw 1000 notch filter spectrometer equipped with 830 nm and 514 nm exciting lasers. The R_1 -line emission of a tiny ruby was used for pressure calibration. The structure of the released samples was characterized by TEM (JEOL 2200FS).

Fig. 1 shows the Raman spectra of solvated and desolvated C_{60} crystals measured using an 830 nm laser in two separate experiments at ambient and high pressures. The ambient Raman spectra of both samples are similar, with 10 Raman-active modes ($2A_g$ and $8H_g$) arising from the intramolecular vibrations of C_{60} . The $A_g(2)$ mode at 1469 cm^{-1} in the solvated sample suggests a weak van der Waals interaction between solvent and C_{60} . From the recorded spectra up to 44.5 GPa, we can see that the Raman peaks of both samples show quite similar pressure evolutions, shifted and weakened with increasing pressure. As the pressure increases, the $A_g(2)$ intensity decreases while the $H_g(7)$ intensity increases, implying that the C_{60} molecules are distorted to a lower symmetry structure.[13,17] The H_g modes become broad and dominant for both samples in the spectra recorded above 20 GPa while other peaks disappear, suggesting significant deformation and amorphization of C_{60} molecules.

We further plotted the frequencies of these Raman peaks as functions of pressure. Observations were first focused on the characteristic $H_g(7)$, $A_g(2)$, and $H_g(8)$ modes (Fig. 2), which show quite similar pressure evolutions for the two samples with a clear transition indicated by a change in the slope at 2 GPa. The slope change, together with the significant intensity decrease for the Raman peaks with frequencies lower than 800 cm^{-1} (related to the breathing modes of the C_{60} cage) at ≈ 2 GPa suggest that a rotational transition of the C_{60} molecules takes place in the samples.[1,18] Besides the three modes, the plotted curves for other Raman modes of the two samples also show similar pressure evolutions but slightly different pressure coefficients. This should be caused by the slight difference in the compressibility between the two materials due to the presence of solvent in one of the lattices while the dopant has little effect on the transformation of C_{60} below 20 GPa. Above 20 GPa,

the pressure dependence of the $H_g(7)$ mode exhibits a transition and its frequency becomes almost pressure independent, which is consistent with the low compressibility of the phase formed as determined by X-ray diffraction (XRD) measurements.[15] It is worth noting that when a 514 nm laser was used for excitation the $H_g(8)$ mode became dominant above 20 GPa, instead of the $H_g(7)$ mode which dominated when the 830 nm laser was used.

It is striking that, although the spectroscopic evolutions of the two samples are similar upon compression, the mechanical properties of their high pressure phases are significantly different. The high pressure phase of the solvated sample created clear ring cracks on the diamond anvils but the desolvated sample created only a very small crack on the anvil (note that in another experiment no crack appeared) after a similar compression to 44 GPa (see Fig. 3). This indicates that the transformations of the two materials at high pressure are different due to the solvent intercalation.

To understand the transformations in the materials under pressure, we performed Raman measurements on released samples (Fig. 4). The spectrum of the solvated sample decompressed from an intermediate pressure of 20.5 GPa (at this pressure the material undergoes a transformation) clearly suggests the presence of C_{60} polymers, with Raman peaks at 950 cm^{-1} , characteristic for C_{60} polymerization, and $A_g(2)$ modes downshifted to 1464 and 1459 cm^{-1} (Fig. 4(a)). Such polymerization was not observed in solvated C_{60} released from 13 GPa in Ref. 15. This suggests that the deformation or even collapse of the C_{60} cages increases at higher pressure, which can overcome the restrictions imposed by the solvent molecules (acting as spacers) and thus allow polymerization. For the sample released from higher pressure (Fig. 4(b)), we see that all these spectra have similar Raman features, i.e., a broad and asymmetric band at $\approx 1500\text{ cm}^{-1}$ and weaker bands in the $600\text{--}750\text{ cm}^{-1}$ region, suggesting that the high pressure phase can be quenched. This is in agreement with the previous X-ray studies, from which the solvated sample preserves a hexagonal structure at pressure above 60 GPa and upon decompression, while the FCC C_{60} sample was amorphized at above 30 GPa and the amorphous phases were quenched to ambient conditions. These two broad Raman bands are generally observed in amorphized fullerite phases containing both sp^2 and sp^3 bonded carbons.[19,20] We found that, for the high frequency broad band, the most intense peak is at 1470 cm^{-1} when excited by an 830 nm laser, while it becomes 1540 cm^{-1} when using 514 nm excitation. From in situ high pressure Raman measurements, we can clearly see that the two bands at 1470 cm^{-1} and 1540 cm^{-1} evolve from the $H_g(7)$ and $H_g(8)$

modes, respectively. This is important evidence for the preservation of fullerenes or fullerene-like fragments, consisting of hexagonal and pentagonal carbon rings, in the high pressure phase and in the quenched sample released from 44 GPa. Since the H_g modes are related to bending vibrations of C-C bonds in C_{60} molecules,[17] the broadening of the H_g bands suggests an amorphization of the C_{60} molecules under pressure, while the frequency shift of the H_g modes in the released sample compared with those of the pristine sample is likely due to the covalent bonds formed in the collapsed fragments. Furthermore, in the spectra of the released solvated sample we observe an additional Raman peak at $\approx 1800\text{ cm}^{-1}$, which probably suggests that the released solvated sample has a structure richer in sp^3 carbon.[20]

Remarkably, the Raman spectrum of this sp^3 -bond rich phase is changed significantly after laser irradiation ($\approx 20\text{mW}$) during the Raman measurement (Fig. 4(b)). The two broad bands in the regions $600\text{--}750\text{ cm}^{-1}$ and $1000\text{ to }1750\text{ cm}^{-1}$ disappear and two new bands at 1321 cm^{-1} and 1598 cm^{-1} appear after irradiation. The latter two bands are the typical D- and G-bands observed in sp^2 -like amorphous carbon.[21,22] The G band is a doubly degenerate phonon mode (E_{2g} symmetry) at the Brillouin zone center that is Raman active for sp^2 carbon networks. The presence of a G band suggests that the sample contains sp^2 carbon networks. The broad D band with a large full width at half maximum (FWHM) of $\approx 200\text{ cm}^{-1}$ is generally considered to be created by a distribution of clusters with different dimensions and orders in amorphous phases.[21,22] The results suggest that the released amorphous fullerene phase is depolymerized into sp^2 carbon rich amorphous carbon clusters. This is different from that of the 3D polymerized C_{60} s resulting from cold compressing a 2D C_{60} precursor, for which free C_{60} molecules are recovered after laser irradiation.[3]

We further used high resolution TEM (HRTEM) to study the detailed structure of the released samples. Our observations show that the decompressed C_{60}/m -xylene contains both ordered phases and a number of amorphous areas (see Fig. 5(a)). Selected area electron diffraction (SAED) shows that the diffracted spots from the ordered area can be indexed in a hexagonal structure (Fig. 5(b)). Moreover, from our TEM images, we can see that the individual cell units in the lattice fringe are hard to distinguish, probably reflecting the amorphous character of the cell units (such as molecular deformation/collapse or highly bonded with neighbors). Besides this, in a small number of ordered areas, the cell units in the lattice keep the profile similar to that of the pristine C_{60} molecules. These results suggest that a large fraction of the

C₆₀ molecules are amorphized and only a small fraction are still intact after such high pressure compression, in agreement with our Raman results. The desolvated sample decompressed from 44.5 GPa is found to contain amorphous phases and small amount of ordered phase (Fig. 5(c)). Several very weak diffracted spots appear in the SAED pattern and can be indexed by a FCC structure (Fig. 5(d)). This is consistent with the X-ray diffraction measurements in previous work.[14] The results also indicate that the solvent plays role in preserving more ordered phase in the released solvated sample.

Let us now discuss the formation mechanism for the superhard phase in the solvated C₆₀. From Ref. [15], we learn that the transition pressure for sp² C into all sp³ C is above 26 GPa in solvated C₆₀. Such bonding change is probably concomitant with the polymerization of C₆₀-C₆₀ and C₆₀-solvent. The former is evidenced by the Raman measurement of our sample released from 20 GPa (Fig. 4(a)). Note that in the solvated sample about 10% sp² carbon is from the p-aromatic rings of m-xylene. This part should also transform into sp³ carbon by covalent bonding with highly compressed or collapsed C₆₀, which is reasonable since p-aromatic rings of the solvent have high chemical affinity to the fullerene. Subsequently, m-xylene acts as a bridge and also spacer to stabilize the periodic structure of the high pressure phase. In this case, part of the amorphized C₆₀ molecules can still be preserved in a periodic arrangement so that the crystalline diffraction of solvated C₆₀ persists even up to 60 GPa.[15] Such almost completely covalently bonded carbon in a 3D network, formed by the polymerization of highly deformed or collapsed C₆₀ units at high pressure, has extremely good mechanical properties and may indent the diamond anvils. The sp²-sp³ transition is partially reversible upon decompression[15] and thus the pristine hexagonal structure is recovered in the released sample. A similar reversible 3D polymerization has also been observed in Na₄C₆₀ under pressure, while in that case Na-C ionic bonds were formed and no superhard phase occurred in spite of very low compressibility of the high pressure phase.[20] In addition, our Raman measurements suggest that desolvated C₆₀s undergo similar bonding change to that of solvated C₆₀s upon compression. However, for desolvated C₆₀s crystals, the highly deformed and collapsed C₆₀ molecules may diffuse and merge with neighboring amorphized fragments when a spacer is absent. Thus, the formation of amorphous carbon and dislocation of remaining C₆₀s in the lattice lead to a disordered phase at high pressure and subsequently result in a low mechanical strength in the material. In fact, FCC C₆₀ crystals are already destroyed and amorphized above 30 GPa.[13,14]

In summary, we show that the intercalated solvent (m-xylene) has little effect on C_{60} transformations, while it plays an important role as a bridge and spacer to preserve the stability of deformed or amorphized C_{60} molecules and allow their polymerization at higher pressure. The high pressure phases of solvated C_{60} are polymeric structures composed of amorphized fullerene and small amounts of intact C_{60} s, which are kept in position by the solvent molecules in the lattice. Thus, a fraction of the fullerenes may preserve the periodic arrangement in spite of their amorphization. Such polymeric carbon forming a 3D network is superhard. The released sample contains both ordered and a number of disordered phases, while laser irradiation reveals that it is mainly composed of amorphous carbon. The results present useful insight into this type of hybrid superhard materials.

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Figure Captions:

FIG. 1. Raman spectra of solvated C₆₀/m-xylene crystals (black) and desolvated crystals at selected pressures.

FIG. 2. Pressure dependence of the characteristic H_g(7), A_g(2), and H_g(8) modes for the solvated (square) and desolvated (triangle) samples.

FIG. 3. Optical pictures of the diamond anvils after pressure cycles to 44.5 GPa and 44 GPa, respectively, for (I) solvated C₆₀ creating a ring crack and (II) desolvated C₆₀ giving a small crack (see arrow). Both culets are 300 μm in diameter.

FIG. 4. (a) Raman spectra of solvated C₆₀ crystals released from 20.5 GPa. Inset shows the Lorentzian fit to the A_g(2) modes; (b) Raman spectra of (I) desolvated C₆₀ released from 44.5 GPa; (II) solvated C₆₀ released from 44 GPa; (III) solvated C₆₀ released from 35 GPa; and (IV) released solvated C₆₀ after laser irradiation. The excitation laser used had a wavelength of 830 nm.

FIG. 5. HRTEM images of decompressed solvated C₆₀, (a) the areas contain order and amorphous phases; (b) SAED pattern from the ordered areas. The structure can be well indexed by a hexagonal structure with calculated d-spacings of 0.89–0.92 nm for the (011) plane and 0.77–0.79 nm for the (120)/(111) plane (not shown), as well as d-spacings with low plane index in the range of 0.4–0.5 nm. A weak and broad diffracted ring with the corresponding d value of around 0.4 nm that are usually from disorder also appears in the recorded patterns, in good agreement with the XRD measurements in Ref. [15]. (c) HRTEM images and (d) SAED of the decompressed de-solvated C₆₀. The obtained d-spacings of 0.65–0.7 nm and 0.45–0.5 nm (not shown) from SAED can be assigned to (002) and (022) planes in a FCC structure, respectively.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5