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Pressure-induced transformation in Na_4C_{60} polymer: X-ray diffraction and Raman scattering experiments

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In this article the alkali metal-intercalated two-dimensional (2D) polymer Na_4C_{60} is studied under pressure up to 41 GPa at room temperature by Raman spectroscopy and x-ray diffraction (XRD) measurements. Two transitions are identified in the studied pressure range. The first one is observed at ∼3 GPa by both diffraction and Raman scattering. A kink in the pressure slope of the cell parameters (especially along the c axis) shows the appearance of a less compressible phase. The decrease in the C_{60}-C_{60} distance and the Na-C distance, combined with the frequency softening of the Raman modes, leads to a picture of higher electron hopping. The second transition occurs at around 15 GPa, where the distinct Raman peaks of 2D-Na_4C_{60} disappear and become very broad and diffuse. New bands at 200–800 cm^{-1}, 1590 cm^{-1}, and ∼1800 cm^{-1}, exhibit similar features to those of a reported 3D-C_{60} polymeric structure. The XRD data show that the cell parameters a, b, and c deviate from their early pressure evolution and become almost pressure independent, accompanied by the formation of amorphous material. Both the evolution of the Raman features of Na_4C_{60} at pressures above 15 GPa and the Raman measurements of the samples on decompression indicate that most C_{60} molecules in the material are preserved after such a high pressure cycle. Our findings are discussed in terms of the formation of the first high-pressure intercalated C_{60} 3D-polymer structure through the random creation of new polymeric bonds between fullerene molecules.

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I. INTRODUCTION

Pristine C_{60} has a great potential to build novel structural architectures through one-, two-, or three-dimensional polymerization due to the existence of 30 double $C = C$ bonds in the molecular cage. Polymerization can be induced by different treatments such as laser irradiation, intercalation with alkali metal, or high-pressure and high-temperature conditions.[1–3] Among the C_{60} polymers, three-dimensional (3D) polymerized C_{60} structures, in which C_{60} molecules are covalently bonded to form a strong 3D network, have attracted special attention because of their exceptional mechanical properties: they can be extremely hard and have bulk moduli even larger than those of diamond.[4–9] Recently single crystal 3D polymers have been synthesized by pressurizing pristine C_{60} or two-dimensional (2D) polymeric C_{60} under pressures higher than 15 GPa at high temperatures. In the latter case it has been shown that during the 2D-to-3D conversion, when new C-C bonds are created between the layers by [3+3] cycloaddition, the orientation and arrangement of C_{60} molecules are retained and the rhombohedral (-R) or tetragonal (-T) symmetry is preserved.[10,11]

In theory by applying a uniaxial pressure of ∼20 GPa it is possible to transform the 2D-polymeric tetragonal phase of C_{60} into a 3D-polymerized fullerite expected to have a metallic character.[12] Using Raman spectroscopy, an irreversible transition to a rather disordered phase has been observed when compressing 2D R-phase C_{60} above 15 GPa, while 2D T-phase C_{60} transforms into a metastable new phase near 20 GPa.[13,14] However, no new phases were detected by *in situ* x-ray diffraction (XRD) experiments of 2D T-phase up to 40 GPa,[15] and the authors suggested that the high pressure treatment triggers a gradual destruction of C_{60} molecules above 10 GPa and thus amorphization occurs well before the hypothetical 3D polymerization. Later, Chi *et al.* compressed a 2D T-phase of C_{60} with a different space group (*Immm*) and deduced that a 3D polymer was formed above 26 GPa.[16] In this case although the C_{60} molecules underwent significant deformations above 20 GPa, the cage structure was still retained. A certain number of C atoms were found to protrude from C_{60} cages to interconnect neighboring C_{60} molecules. These results suggest that the C_{60} molecules are basically stable enough under high pressure to realize a 3D polymerization, but that the C_{60} molecules suffer high distortion at compressions high enough to move them close enough together to form sp^3 bonds. Therefore, to synthesize 3D polymers under high pressure in fullerenes it is necessary to stabilize the C_{60} molecules during compression.

Very recently, high pressure studies on intercalated fullerides A_6C_{60} (A = Rb, Cs) have shown that the intercalation of alkali metals significantly enhances the stability of the C_{60} molecules.[17,18] Cs_6C_{60} is stable up to 45 GPa, twice the amorphization pressure of pristine C_{60}, while Rb_6C_{60} shows a structural transition above 35 GPa to a 2D polymeric phase. This is probably due to the smaller ionic radius of Rb atoms compared to Cs, which allows the C_{60} cages to get close enough to polymerize under high compression. Motivated

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by these results, we envisaged that intercalating an alkali metal ion of suitable size would enable 3D polymerization under cold compression. A potential intercalated 3D fulleride, constituting an alternative to carbon clathrates of the type-I or type-II structure, may be expected to exhibit excellent mechanical properties[19] and high *Tc* due to a very high phonon-electron interaction.[20] In fact the paths for carbon clathrate synthesis appear to face serious difficulties.[21]

Motivated by these expectations, we have chosen Na_4C_{60} as a precursor to search for the synthesis of a possible intercalated cage-like carbon under high pressure. Na_4C_{60} has a unique 2D polymeric structure wherein each fullerene molecule is linked to four other neighbors by single covalent C–C bonds in a plane.[22] In order to study the structural evolution of this fullerite, *in situ* high-pressure Raman spectroscopy and synchrotron XRD were employed.

II. EXPERIMENTAL SECTION

The synthesis and sample characterization have been reported previously.[20] In brief well-mixed stoichiometric amounts of presublimed C_{60} (purity 99.98%, MTR Ltd.) and alkali metal Na (Aldrich, 99.95%) were loaded into copper or stainless steel crucibles and then annealed at elevated temperatures (350 °C) for about one month in an oxygen-free glove box. The samples were reground once every week, and the progress of the reaction was monitored by XRD and Raman spectroscopy. The final products were confirmed to be single phase Na_4C_{60} having the same structural and spectroscopic features as observed in earlier work.[22–25] The sample was loaded under protective atmosphere into a gasket in a diamond-anvil cell without any pressure transmitting medium. High-pressure and room-temperature Raman spectra were recorded using a Horiba (Jobin Yvon) HR-800 LabRAM spectrometer with double notch filtering and an air-cooled charge-coupled device detector at ENS, Lyon, or a Renishaw 1000 notch filter spectrometer at Umea, Sweden. The exciting laser beam (514.5-nm line of an Ar^+ laser) was focused down to a 2-μm spot on the sample, and the backscattered light was collected through the same objective. Laser power of 5 to 10 mW was directly measured before the high-pressure cell. The pressure was measured *in situ* before and after each measurement by using the R1 fluorescence emission of a ruby sphere placed into the gasket hole. Due to the Raman scattering from the diamond of the high-pressure cell, we did not collect data in the frequency shift region around 1332 cm^{-1} to avoid the very strong diamond peak.

Angle dispersive XRD experiments were performed at the insertion device ID27 beamline at ESRF, Grenoble. Monochromatic beams with wavelength $\lambda = 0.3738$ Å were selected by using a Si (111) monochromator and focused on the sample by using multilayer mirrors in the Kirkpatrick-Baez geometry. The focal spot size was $1 \times 1\ \mu m^2$ full width at half maximum (FWHM). The 2D-diffraction rings were recorded on a fast large-area scanning MAR345 image plate and were converted into one-dimensional (1D) diffraction patterns using the FIT2D software package.[18] The sample-to-detector distance and the image-plate tilt angles were calibrated using a silicon standard located at the sample position. Data were analyzed using the GSAS code.[26]

III. EXPERIMENTAL RESULTS

A. *In situ* Raman study up to 31 GPa

Raman spectroscopy is a powerful tool used to characterize the structure and bonding states of C_{60} molecules in pure and intercalated fullerenes. The free isolated C_{60} molecule with *Ih* symmetry exhibits ten (two Ag + eight Hg) Raman allowed modes, which are governed by strict selection rules. When the highly symmetric pristine C_{60} material is doped with the right amount of Na, the symmetry is lowered to the monoclinic Na_4C_{60} structure with space group $I2/m$ and with single polymer bonds in the (10-1) plane. This leads to a splitting of the fivefold degenerate Hg modes and the appearance of other Raman modes that were either optically silent or forbidden in the original *Ih* symmetry. In addition we observe new modes connected with the formation of the polymerized structure and the introduction of the dopant ions. A detailed analysis and assignment of the Raman modes of Na_4C_{60} at ambient conditions has been reported by Wågberg *et al.* (see Ref. 25).

We will first analyze the behavior of Na_4C_{60} below 15 GPa. In Fig. 1(a) we show the Raman spectra of Na_4C_{60} at various pressures up to 12 GPa. The initial spectrum, taken at ambient pressure, is identical to the spectra reported earlier[25] and exhibits all the typical Raman features of 2D Na_4C_{60}. The lines gradually broaden and merge as the pressure increases. Different Raman modes shift in frequency with the applied pressure at different rates, as shown in Figs. 1(b) and 1(c) where we plot the Raman modes in the frequency region 200–600 cm^{-1} as a function of pressure. The modes in this range shift to higher energy with increasing pressure, with the exception of the Raman peaks at 422 cm^{-1}, 532 cm^{-1}, and also some modes in the range 600–780 cm^{-1} (not shown in the plot), which include the $F2g(1)$, $Hg(2)$, $Hg(3)$, $Hg(4)$, $Gg(2)$, and $F1u(2)$ modes. These latter modes are either almost pressure independent or have very small negative pressure coefficients. At about 3 GPa we observe a clear change with a decrease of the pressure slope for the $Hg(1)$ and $Hg(2)$ modes and a splitting of the $Ag(1)$ mode. The "polymer fingerprint" near 950 cm^{-1} broadens considerably and becomes weak above 3 GPa. On the other hand the $Ag(2)$ pentagonal pinch mode at around 1450 cm^{-1} rapidly decreases its intensity as pressure increases and merges with the $Hg(7)$ mode into one broad peak at 2 GPa.

Finally we observe that the intensities of all Raman modes decrease significantly above 3 GPa. These results suggest that a structural, as well as an electronic, transition occurs in the material at around 3 GPa.

The 2D polymers of pure C_{60} have different behaviors under pressure in both the R- and T-phases. The "polymer fingerprint" peak(s) and the $Ag(2)$ mode survive up to 15 GPa[13,14] and undergo significant changes only above 15 GPa, where a transformation occurs in the material. These different behaviors under pressure could be related to the different polymeric configurations of 2D-Na_4C_{60} and 2D-C_{60} and to the intercalation of alkali metal Na on the C_{60} molecular vibrations, especially on the $Ag(2)$ mode, which is very sensitive to doping effects.

Below 2.86 GPa, the pressure coefficients of the plotted Raman modes are in the range 0.8–4.5 cm^{-1} GPa^{-1}. Above 2.86 GPa, the range is 0.1–2.4 cm^{-1} GPa^{-1}. These values are close to those of the Raman modes in the initial 2D-R C_{60} phase

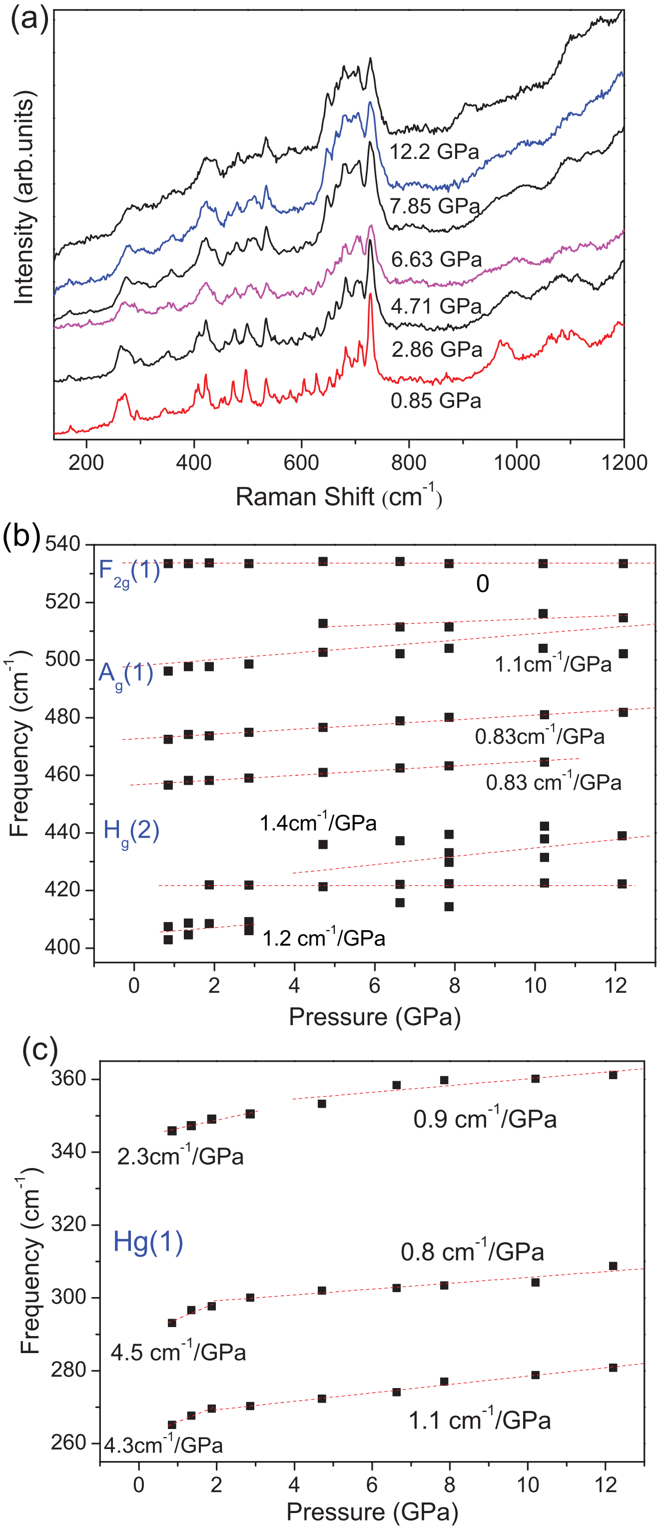

FIG. 1. (Color online) (a) Raman spectra of Na_4C_{60} at different pressures up to 12 GPa. (b) and (c) Selected Raman mode frequencies as a function of pressure (GPa).

range (~0.1–3.4 cm^{-1} GPa^{-1}).[14] Up to 12 GPa the pressure coefficients of the Raman modes in pristine C_{60} vary between −4.1 and 9.8 cm^{-1} GPa^{-1}.[1] These results are compatible with the fact that polymerized materials become less compressible as the degree of polymerization increases.

Above 15 GPa the Raman spectra become very diffuse and lose their fine structure in all frequency regions. They differ significantly from the spectra below 15 GPa and suggest the occurrence of another structural change accompanied by increasing disorder.

Some broad Raman bands are still observed at 390 cm^{-1}, 510 cm^{-1}, 680 cm^{-1}, ~1460 cm^{-1} (the pentagonal pinch mode), 1590 cm^{-1} (the graphite-like mode), and 1830 cm^{-1}. The 1830 cm^{-1} mode is at similar frequencies as the Raman peaks observed in a 3D-C_{60} polymer obtained by pressurizing a 2D polymer.[13] This mode cannot be related to the C_{60} molecular cage. It has been attributed to the ethylenic-like stretching vibration of the interfullerene bridging C-C bond when a 3D polymerization occurs.[27]

In this pressure range the Raman band at 680 cm^{-1} shows a small negative-pressure dependence of about −0.7 cm^{-1} GPa^{-1} with increasing pressure while the bands at 510 cm^{-1} and 390 cm^{-1} are almost pressure independent, having the same pressure evolution as before the transition.

For the pentagonal pinch mode at ~1460 cm^{-1} and the graphite-like mode at 1590 cm^{-1}, the pressure dependence is estimated to be about 2 ± 0.7 cm^{-1} GPa^{-1} above 15 GPa (Fig. 2), which is slightly lower than the values

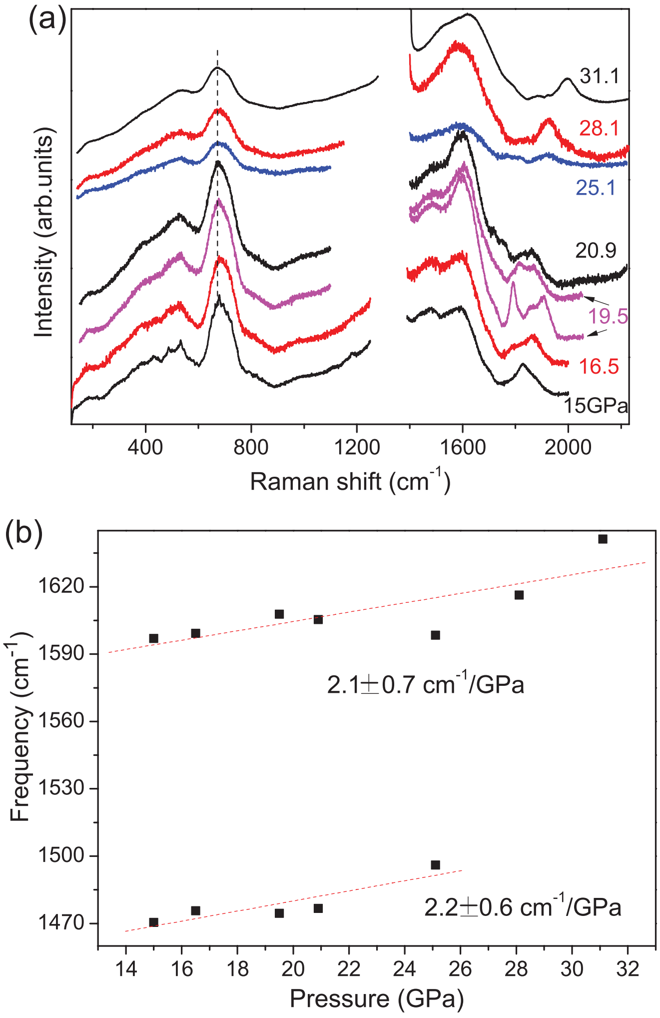

FIG. 2. (Color online) (a) The Raman spectra of Na_4C_{60} at pressures above 15 GPa; (b) the observed frequencies of the 1460 and 1590 cm^{-1} Raman lines versus pressure.

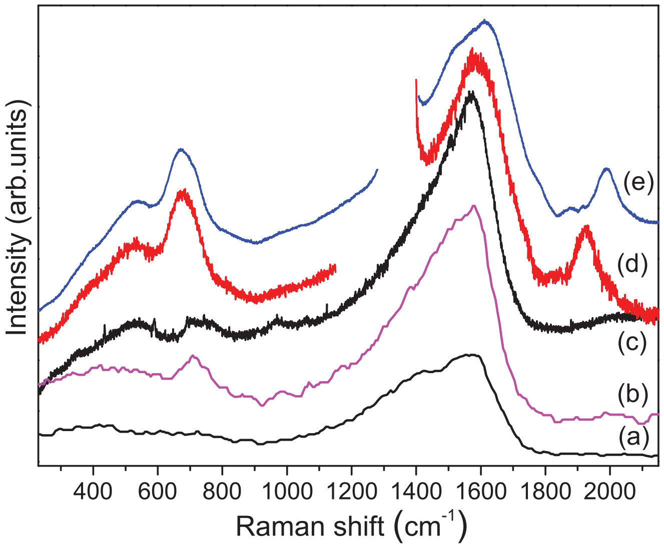

FIG. 3. (Color online) Comparison between the Raman spectra of (a) superhard C_{60} phase from 870 K and 9 GPa and (b) from 670 K and 9 GPa.[9] (c) Single-crystal 3D-C_{60} structure,[10] (d) Na_4C_{60} at 25.1 GPa, and (e) at 31.1 GPa from this work.

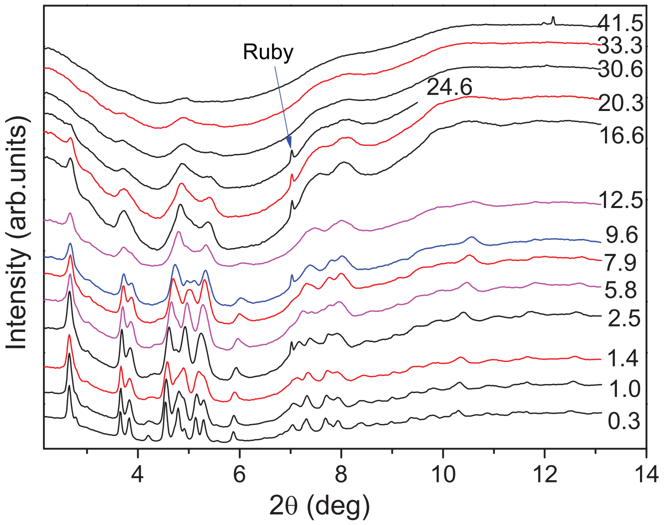

FIG. 4. (Color online) Selected XRD patterns of Na_4C_{60} under pressure up to 41.5 GPa.

3.3–4.3 cm^{-1} GPa^{-1} reported for these two bands in the R-phase of C_{60}. This could be related to the fact that Na_4C_{60} is less compressible than R-C_{60} due to the occupation of the voids in the interlayer space by Na atoms.

The relative intensities of these two bands also change with increasing pressure. At the transition pressure of 15 GPa, their intensities are almost the same. With increasing pressure, the intensity of the peak at ∼1460 cm^{-1} decreases gradually, and at pressures higher than 25 GPa the two bands up-shift and merge to a much broader and asymmetric band with its highest intensity peak at ∼1600 cm^{-1}. However, at pressures higher than 31 GPa the intensity of the low-frequency shoulder of the 1600 cm^{-1} band increases again, which gives rise to the appearance of a doublet in the Raman spectrum. It is interesting to note that the gradual evolution of these two bands under pressure is similar to the changes of the two corresponding Raman bands of the superhard phase 3D-C_{60} quenched at 9 GPa and different temperatures (see Ref. 9 and the Raman changes from 620–670 K, 670–870 K, and 870–1270 K in Fig. 3). Our high pressure phase of Na_4C_{60} has some resemblance to such a 3D, randomly linked superhard phase of C_{60}. Thus, the high pressure Raman spectra show Raman features characteristic of both sp^2 and sp^3 bonds. One possible explanation is that beyond 15 GPa, the gradual formation of a 3D network by new out-of-plane covalent bonds between fullerene molecules with increasing pressure leads to a smearing of the Raman bands. In such a state the molecules in fullerite are no longer strictly the characteristic structural elements because they are covalently bonded to form a 3D random network.

In Fig. 3 we compare our Raman spectra at 25 GPa and 31 GPa with the spectrum of single crystal 3D C_{60} polymer [from Yamanaka] and other 3D C_{60} fullerites reported in the literature.[9,10] We see that all these Raman spectra have similar features, i.e., the broad and asymmetric band at ∼1600 cm^{-1} and the weaker bands in the 200–800 cm^{-1} region. The broad and asymmetric band at ∼1600 cm^{-1} is related to the presence of both sp^2 and sp^3 bonds in the fullerite samples and can be attributed to either a 3D polymer or an amorphous carbon phase.[4,6,9,28,29]

Two differences between our spectra and those found by others should be pointed out. First the bands at 400–800 cm^{-1} in our case are stronger than both those of the single crystal 3D C_{60} polymer (from Yamanaka) and of the other superhard fullerite phases[9,10] with sp^3 bonds randomly distributed in the 3D structure. In our sample these bands preserve some of the Raman futures of the initial fullerite and are still intense at the highest pressure, indicating that the vibrations in most of the C_{60} molecular cages are preserved up to at least 31 GPa. This is consistent with the already observed tendency by which intercalation stabilizes the C_{60} molecules to higher pressures and also with the observed reversibility of the amorphization transition after decompression (see Sec. III).

In our spectra we observe an additional Raman peak at ∼1800 cm^{-1} (see Fig. 3). This peak is present already at low pressure with very low intensity. It increases in intensity with increasing pressure and shows some splitting at pressures higher than 12 GPa. The amount of splitting is somewhat random depending on the sample spot (all other Raman modes show a spatially uniform response over the surface of the sample). A recent theoretical calculation shows that the stretching modes of ethylenic-like bonds in 3D-polymerized structures should occur in the 1700–1800 cm^{-1} frequency region depending on the type of polymerization in the 3D structure.[27] Because the intensity of the ∼1800 cm^{-1} band increases with pressure in our study, it is possible that the amount of sp^3 interfullerene bonding increases in the sample with pressure, and that the random appearance of splitting likely indicates a random 3D polymerization in the structure.

B. *In situ* XRD synchrotron compression study up to 41 GPa

The XRD patterns obtained when pressurizing Na_4C_{60} up to 41 GPa are shown in Fig. 4. The low-pressure XRD patterns exhibit the known diffraction peaks characteristic of

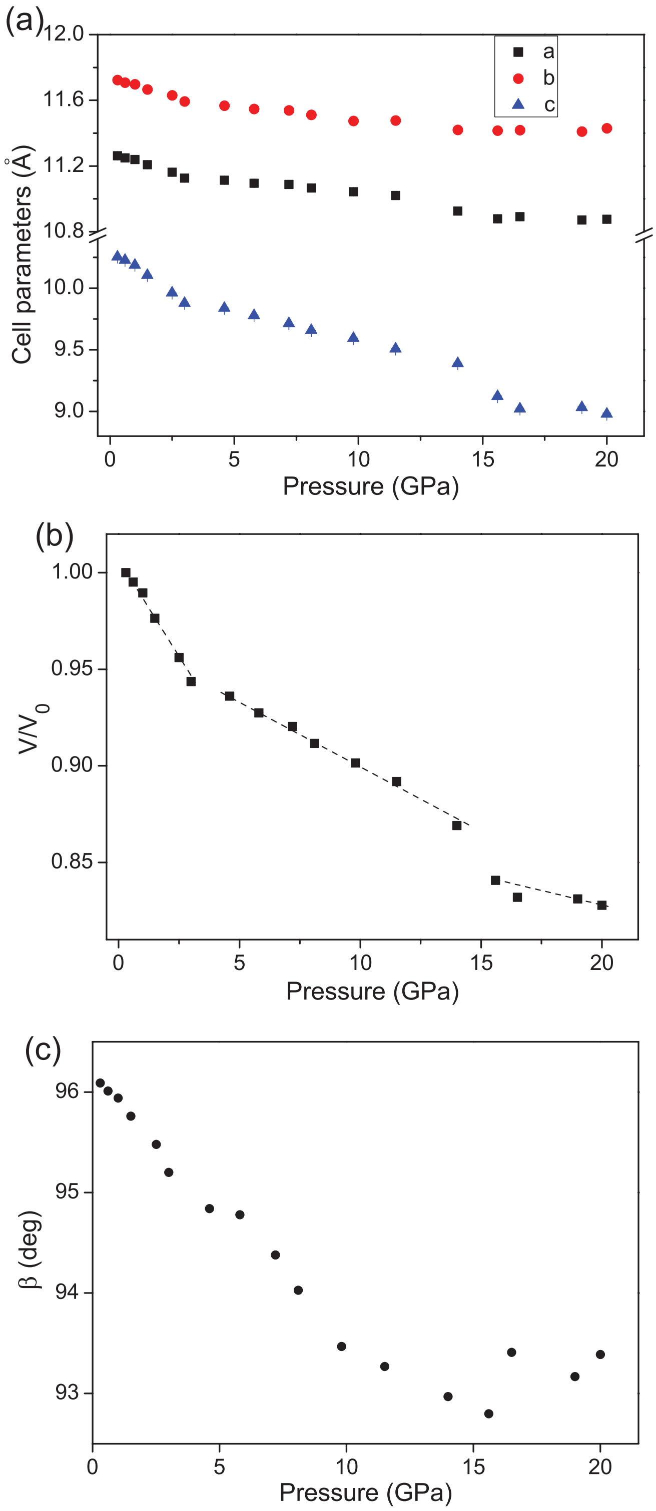

FIG. 5. (Color online) (a) and (b) Relative cell parameters of 2D Na_4C_{60} versus pressure up to 20 GPa. Significant changes of the compressibility are observed between 2.5 and 5 GPa and again at ∼15 GPa. (c) Variation of the angle β with pressure.

2D Na_4C_{60},[22,30] and they can be well fitted by a body-centered monoclinic structure with space group $I2/m$. The diffraction patterns gradually change as the pressure increases. The most eye-catching features are a first structural change at around 2.5 GPa and another transition, accompanied by a strong enhancement of background, starting at 12.5 GPa. After 30 GPa the peaks become increasingly broader, and at 41 GPa almost no signs of crystallinity can be detected.

The pressure dependence of the relative lattice parameters (a, b, c, V/V_0) and of the angle β up to 20 GPa are shown in Figs. 5(a)–5(c). As observed by Kubozono *et al.*,[30] the lattice of Na_4C_{60} is much more compressible in the c direction than in the a and b directions. For other fullerene polymers a strong anisotropy in the compressibility can be easily rationalized in terms of compression along, or perpendicular to, covalent intermolecular bonds.[1,4] However, in Na_4C_{60} no such bonds are parallel to the lattice axes, and the anisotropy instead correlates well with the distances between nearest-neighbor Na ions, which is about twice as large in the c direction as in the a and b directions. The weaker Na-Na repulsion along the c direction thus makes c the most compressible axis.[30]

In Fig. 5(a) we see that between 2.5 and 5 GPa, and again between 14 and 15.6 GPa, the slopes of all three cell parameters (and especially the c parameter), and thus the compressibility of the material, change. These changes confirm the occurrence of two structural transformations in the material in the studied pressure range.

The first phase transition between 2.5 and 5 GPa preserves the monoclinic unit cell symmetry and is probably due to displacements of the Na ions in the unit cell. The second phase transition at around 15 GPa is accompanied by a structural change towards a body-centered pseudo-tetragonal (bct) structure (β approaches 90°) and by the formation of amorphous material (indicated by the increase of the background in the x-ray patterns).

The angle β decreases linearly up to 15 GPa. This corresponds to the fact that the center-to-center C_{60}-C_{60} distances in the (101) plane, dominated by the van der Waals interactions, decrease as pressure increases. However, polymer C-C contact in the (101) plane obtained through a structural phase transition from a 2D polymer to an isotropic 3D bct polymer phase would require $\beta = 90^\circ$. The fact that β cannot reach 90° at 15 GPa or at higher pressure precludes the formation of short C-C contact and consequently of a 3D bct polymer phase.

Above the transition at 15 GPa the cell parameters a and b are almost pressure independent, while the parameter c shows a step decrease in value and thereafter stays almost pressure independent.

The pressure dependence of the relative volume of Na_4C_{60} is presented in Fig. 5(b). At the first structural transformation the step change in volume is very small, but there is a sharp decrease in compressibility. A comparison with the data in Fig. 9 of Kubozono *et al.* (Ref. 30) shows that the same transition occurred in their sample near 3.5 GPa, but due to the limited resolution and pressure range in their experiment, it was not detected. At the second transition there is a clear drop in the volume by about 2.5%. At higher pressures the material exhibits a much smaller compressibility, indicating that a highly incompressible phase is formed.

The average bulk moduli calculated from linear fits to the data are 51 (±2) GPa for the ambient pressure phase, 135 (±4) GPa for the second phase, and 600 (±100) GPa for the third phase above 15 GPa. Kubozono *et al.* [30] obtained an initial bulk modulus $B_0 = 52$ GPa by fitting Murnaghan's equation of state to their data. However, their fit actually extended to

5.3 GPa, i.e., well into the much harder (less compressible) high-pressure phase. In view of this the agreement with our data is surprisingly good.

The compression data obtained above 15 GPa show strong indications of polymerization between the layers and the formation of a 3D highly incompressible phase with mixed sp^2-sp^3 character (also confirmed by the Raman measurements). This transition is accompanied by a large increase in background intensity, which is probably associated with the breaking of some intramolecular bonds while forming new out-of-plane intermolecular covalent bonds, as also occurs in the polymerization of C_{60}.

C. XRD and Raman results from decompression

To study the reversibility of different phases at ambient conditions, the sample was compressed and decompressed in subsequent pressure cycles. Compressing Na_4C_{60} to 13 GPa and than decompressing to low pressure results in a complete recovery of the sample (compare the Raman spectra in Fig. 6), indicating the reversibility of the second phase. After decompressing the sample from 31 GPa to ambient conditions, we observe that the majority of the Raman modes are recovered at low pressure, although they show some hysteresis. The hysteresis could be related to the transformation of the material under high pressure and to the further polymerization of fullerene molecules mixed to the amorphous material. Residual compressive stress might still be present upon pressure release. The exposure of the decompressed samples to air leads to the appearance of strong Raman signals characteristic of C_{60} molecules. This is due to the oxidation of the alkali metal in the samples and therefore to the depolymerization of the structure. The fullerene molecules in Na_4C_{60} are not damaged even after treatment at the very high pressure of 31 GPa. Finally decompressing the material from 36 GPa and 41 GPa, we observe by Raman spectroscopy that a fraction of C_{60} molecules remains intact after such high pressure, even though the XRD results show that the lattice is disordered (Fig. 7).

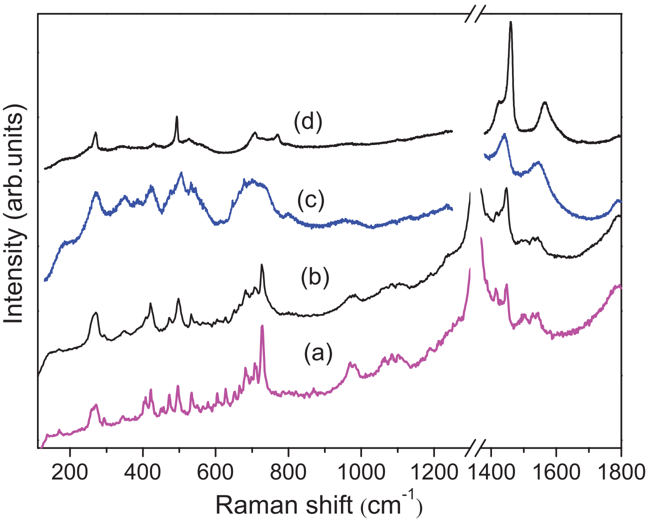

FIG. 6. (Color online) Raman spectra of Na_4C_{60} (a) at 0.8 GPa upon compression, (b) at 0.8 GPa after decompression from 13 GPa, (c) at 1.6 GPa after decompression from 31 GPa, and (d) ambient-pressure Raman spectra of Na_4C_{60} exposed to air after release from 31 GPa.

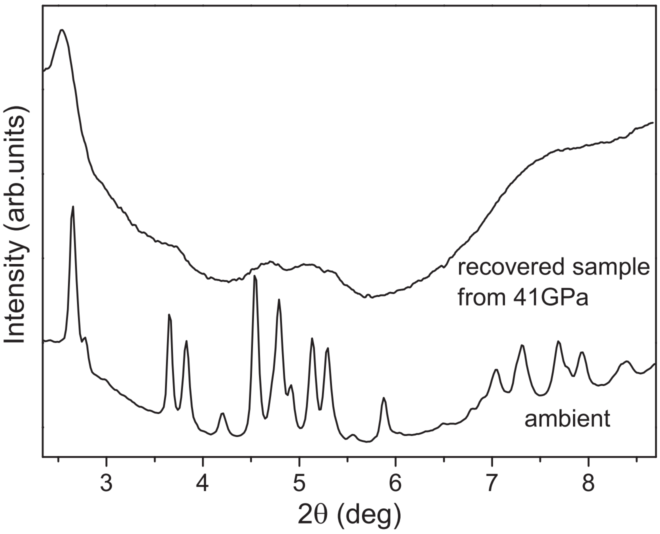

FIG. 7. XRD pattern of Na_4C_{60} at ambient pressure and after decompression from 41 GPa.

IV. DISCUSSION AND CONCLUSIONS

Both XRD and Raman measurements clearly suggest that Na_4C_{60} undergoes two structural transitions in the pressure range studied. The first transition occurs at ~3 GPa. It is evidenced by a change in the pressure slope of the frequency for some intramolecular Raman modes and the obvious attenuation of the intensity of those vibration modes around 3 GPa. The faster decrease in the intensity of the Raman modes at this pressure, compared to other pure 2D C_{60}, indicates that the attenuation of the Raman modes could be related to the higher electron-phonon coupling interaction in Na_4C_{60}. This result is consistent with the XRD analysis and the trend of a, b, and c parameters under pressure. In particular the c parameter decreases very fast below 3 GPa. It shows smaller pressure dependence above 3 GPa. The decrease in the C_{60}-C_{60} and the Na-C distances, combined with the frequency softening of the Hg(1), Ag(1), and Hg(2) modes, suggests higher electron hopping in this range of pressures.

The second transition takes place at around 15 GPa. Moving above this pressure, the Raman spectra exhibit increasingly stronger carbon sp^3 bonding. Such Raman features could be due either to the formation of a 3D polymeric structure or to the amorphization (collapse) of C_{60} molecules in the samples.[4,6,9,27,28] The latter scenario appears less probable since we observe a gradual recovery of the C_{60} features in the Raman spectrum as pressure decreases from 31 GPa. The very intense Raman bands from C_{60} molecules in the range of 200–800 cm^{-1} in the high pressure region up to 31 GPa and the appearance of strong Raman signals of C_{60} after exposing the decompressed sample to air are further evidence for the high stability of the C_{60} molecules during and after high pressure compression/decompression cycles. The high stability of C_{60} molecules in Na_4C_{60} (to at least 31 GPa) is probably associated with the intercalation of Na. Such an enhanced stability has also been observed in the alkali metal intercalated fullerides Rb_6C_{60} and Cs_6C_{60}, where the C_{60} molecules are preserved at pressures higher than 40 GPa.[17,18] Therefore, we conclude that the significant change of the Raman features observed above 15 GPa should be related to an increase of the sp^3 (intermolecular) bonding fraction in the Na_4C_{60} sample. Theoretical calculations indicate[31] that the intermolecular interaction increases with increasing pressure, and at some critical intermolecular distance an sp^3-hybridized covalent C-C bond may be formed. The fact that the C $2p_2$-like orbital tends to point radially outward from the surface of the C_{60} cage would facilitate this sp^3 bond formation.[31] In our experiments the C_{60} molecules are stable up to very high pressure (at least 41 GPa). The XRD data show that the volume of the cell exhibits an obvious drop at around 15 GPa and thereafter becomes almost pressure independent. This indicates that the distance between the polymerized planes becomes small enough to enable further intermolecular bonds between the C_{60} molecules, forming a highly incompressible phase. This agrees well with the increase of sp^3 bonding indicated by the Raman measurements. The small interplanar distance is made possible by the small ionic radius of Na^+ ($\sim$0.98Å), which is substantially smaller than the average tetrahedral site radius 1.16 Å. A similar abrupt drop in the interlayer distance (c axis) at the transition pressure ($\sim$20 GPa) was observed in an experiment with cold compression of a 2D-T C_{60} phase, in which a 3D polymerization in the sample was proposed.[16] Thus, we suggest that the 3D polymerization in these samples and in our samples takes place by similar mechanisms. It is proposed that the 2D polymer layers are preserved in both cases (no obvious transition in the pressure dependence for the a axis) even after the 3D polymerization occurs, and that the 3D polymer structure is formed by creating new C-C bonds between the 2D polymer layers by [3+3] cycloaddition. However, in our material a displacement/movement of the intercalated Na atoms may occur under compression (as was observed for Rb ions in Rb_4C_{60} under pressure[32]), which could result in some disorder and subsequently affect the C atoms on the C_{60} cage involved in the creation of new C-C bonds during 3D polymerization. This could result in a random 3D polymer bonding in the sample.

Also, since rotation of molecules is impossible in the initial 2D polymeric Na_4C_{60}, due to the presence of covalent polymer bonds between the C_{60} molecules, we suggest that the formation of new bonds in Na_4C_{60} at high pressure takes place in a random way. As a result, the new high-pressure phase exhibits a high degree of disorder characterized by random out-of-plane polymerization. The known high pressure induced deformation of the C_{60} molecule due to the coulombic interaction in intercalated fullerites[33] could also participate to the structure disorder. The structure can be close to that of amorphous carbon, which is characterized by the presence of $\sim$15% sp^3 bonding.[34] Our observations of increased XRD background, decreased peak intensity, and the broadening of the diffracted peaks (Figs. 4 and 7) are consistent with this conclusion.

Although Chi *et al.*[16] observe a reasonably well-ordered 3D polymer structure formed by interconnecting 2D layers, randomly linked 3D polymeric structures have also often been proposed to exist in pure C_{60}.[4] In these structures the orientation and structural arrangement of C_{60} molecules in the original 2D layers are usually assumed to be preserved during and after the 2D-to-3D conversion. For example a C_{60} sample treated at 13 GPa with short-time heating at 830 K was found by XRD to be amorphous but had a high hardness of 45 GPa.[35] Meletov *et al.* proposed that compressing a 2D R-phase C_{60} sample to above 15 GPa gave a probable 3D polymeric structure with a network of random 3D links between the original layers,[14] and it has also been reported that compression of the 2D orthorhombic C_{60} polymer phase at 15 GPa and 550 °C produces a 3D phase by forming new C-C bonds between the original polymer layers by [3+3] cycloaddition.[10,11] However, in an earlier high pressure XRD study on a 2D T-phase C_{60} up to 40 GPa by Léger *et al.*,[15] only a gradual destruction of C_{60} molecules was observed above 10 GPa, and the sample became amorphous well before the hypothetical 3D polymerization. This difference has been explained by the initial structure of the precursor (different space groups, $Immm$ in Ref. 16 and $P4_2/mmc$ in Ref. 15) and the pressure conditions.[16] All these studies, however, show that the new phases produced consist of intact C_{60} molecules, although the structure may be metastable, such that C_{60} molecules can be released by explosive transformation under laser light,[36] for instance. The observed stability of the C_{60} molecules in our work, probably due to the presence of the intercalated Na ions, is thus favorable for the formation of 3D structures at high pressure by room temperature compression.

The reversibility of the high pressure phase of Na_4C_{60} when released from 31 GPa also indicates the metastable nature of the transformed phase. Such reversibility (metastability) of doped polymerized phases formed at high pressure could be associated with the formation of nanocrystalline domains[37] linked to the well-known frustration mechanism of polymerization in fullerenes. A similar reversibility of the pressure-induced polymerization has also been reported in other intercalated fullerides.[18,38–40]

From another point of view the covalent 3D network in such C_{60} polymers, containing carbon cages, can be seen as carbon analogs of silicon clathrate compounds. Recently, the barium-containing silicon clathrate compound Ba_8Si_{46}, isotypic with the type-I gas (G) hydrate $Gx\text{-}(H_2O)_{46}$, has been proved to be a superconductor with a transition temperature (T_c) of 8.0 K.[41] It could, therefore, be speculated that the 3D Na_4C_{60} phase observed in our experiments might possess a structure similar to that of such compounds but composed of carbon instead of silicon. This should result in a much larger phonon-electron interaction, and thus a higher T_c should be expected.[42] The proposed intercalated 3D network of polymerized C_{60} appears to be a promising candidate for such carbon clathrate structures.

V. CONCLUSIONS

In summary the alkali-metal intercalated 2D polymer Na_4C_{60} has been studied by Raman spectroscopy and XRD measurements up to 41 GPa. Two transitions have been observed in the pressure range studied. The first was observed at $\sim$3 GPa, where a rapid decrease in the cell parameters, mainly along the c axis, ends with the formation of a less compressible structure. At this pressure, corresponding changes in the pressure behavior of the intramolecular modes *Hg*(1) and *Hg*(2) and a decrease in intensity of all Raman modes have also been observed. The change (decrease) in both the C_{60}-C_{60} distance and the Na-C distances, combined with the frequency softening of the Raman modes, leads to a picture of higher electron hopping in this range of pressure.

The second transition occurs above 15 GPa and can be considered as an isostructural volume collapse transition, at which the distinct Raman peaks disappear and become very broad and diffuse, exhibiting Raman features similar to those of 3D polymeric structures. XRD data show that the material becomes much less compressible and more disordered. The evolution of the Raman spectra at pressures above 15 GPa shows the presence of strong Raman signal from C_{60} molecules. Most of C_{60} molecules are preserved after releasing the pressure, indicating that the high pressure phase above 15 GPa contains mainly intact C_{60} fullerene molecules. This transformation is reversible.

All these effects are consistent and can be understood in terms of the formation of a 3D structure in Na_4C_{60} through random linking by 3D covalent bonds between molecules belonging to adjacent 2D polymer sheets of the initial monoclinic phase.

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