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Reversible pressure-driven nanoscale phase separation in Rb_4C_{60}

M. G. Yao, B. Sundqvist, and T. Wågberg
Department of Physics, Umeå University, 901 87 Umeå, Sweden

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We present Raman spectra for Rb_4C_{60} at pressures up to 13 GPa. Above 1 GPa we observe a phase separation of Rb_4C_{60} into Rb_6C_{60} and Rb_3C_{60}, identified by a splitting of the $A_g(2)$ mode and the appearance of characteristic Raman modes of the daughter phases. Remarkably, the phase separation is completely reversible and the sample returns to a homogeneous Rb_4C_{60} phase after pressure release. The reversibility of the phase separation suggests that the structural change is associated with small displacements of Rb ions in the unit cell, giving local differences in the charge state of the C_{60} molecules. The pressure dependence of the Raman shifts agrees well with earlier measurements. Our observation of a reversible phase separation explains several peculiar results reported earlier for Rb_4C_{60}.

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Alkali fullerides have attracted much attention in the past decade due to their interesting electronic and structural properties.[1–3] Depending on the charge transfer to the C_{60} and the size of the metal ions the alkali fullerides either remain in monomer form with weakly interacting C_{60} molecules or transform into polymerized phases with one- or two-dimensional structures.[4–7] The possibility to tune the electronic and structural properties by changes in the doping level make alkali-metal intercalated fullerenes to interesting systems, and large efforts have been made to understand their behavior.[1–11] The A_4C_{60} phases are the most complex systems and have been more difficult to explain than the A_3C_{60} and the A_6C_{60} phases, which can be understood from band models.[1,8–11] The study of intercalated fullerenes is further complicated by the fact that the thermodynamic stabilities of different phases lie very close in energy.[12] Minor differences in stoichiometry can lead to drastic changes in their properties[13] or even to phase separation, and it is important to understand the driving mechanism for such instabilities. Recently, phase separations have been studied in nominally pure phases, such as Na_2C_{60} (Ref. 14) and Cs_xC_{60} (Ref. 13, and references therein). External pressure changes the thermodynamic energy levels of alkali fullerides[15–21] and pressure studies are therefore very powerful tools to explore structural phase transitions. The narrow-gap insulator A_4C_{60} (A=K,Rb) is an especially interesting system for which a number of high-pressure studies have been reported, but where the data and interpretations by different groups are contradictory.[11,16–19] Sabouri-Dodaran *et al.*[16] reported an abrupt jump in the compressibility of Rb_4C_{60} between 0.5 GPa and 0.8 GPa, attributed to a phase transition preserving the tetragonal symmetry. A later study suggests instead a transition from tetragonal to orthorhombic symmetry above 0.4 GPa, accompanied by an orientational disorder-order transition for the C_{60} molecules.[17] Although NMR studies have indicated that Rb_4C_{60} undergoes a pressure-induced Mott insulator-metal transition at around 0.8 GPa,[18] recent resistance measurements on single-phase Rb_4C_{60} clearly showed that no such transition occurs and that Rb_4C_{60} remains semiconducting up to 2 GPa in the range 90–500 K.[11] Clearly, the data contain features which are not fully explained by current knowledge. Searching for an explanation for these peculiarities we have recently performed a high-pressure Raman study on well-characterized Rb_4C_{60}. Surprisingly, we find that a distinct and fully reversible phase separation from Rb_4C_{60} into Rb_6C_{60} and Rb_3C_{60} is induced by pressure. We show that this observation offers an explanation to all "odd" results reported for Rb_4C_{60} under pressure. Because of the similarities between heavy alkali-metal intercalated fullerides it is probable that pressure studies could lead to similar discoveries also for other systems.

Rb_4C_{60} was synthesized by a solid-solid reaction between stoichiometric amounts of C_{60} and presynthesized Rb_6C_{60}. The synthesis and sample characterization have been reported earlier.[11] Prior to use the Rb_4C_{60} sample was sealed in a capillary under argon and heated for 5–7 days to anneal away minor inhomogeneities on the surface. The sample was loaded into a diamond-anvil cell (DAC) without any pressure transmitting medium in a glove box, using a stainless-steel gasket on a 350 μm diamond culet. The $R1$ line of a tiny ruby was used for pressure calibration. Raman experiments were carried out with a resolution of about 2 cm^{-1} at room temperature using a Renishaw 1000 grating spectrometer. As excitation source, a 514.5 nm argon-ion laser was used with a power density on the sample smaller than 5 W/cm^2. To ensure that the data were not influenced by surface inhomogeneities we made all measurements on the same 3-5 sample spots near the ruby throughout the experiment. Measurements were performed at roughly 1 GPa intervals from atmospheric pressures up to around 13 GPa, and with larger pressure spacings while decreasing pressure to atmospheric pressure.

For intercalated fullerenes, Raman spectroscopy provides information on both the structure and the charge state of the C_{60} molecules. Figure 1 shows selected Raman spectra for one sample under pressure. All characteristic Raman vibrations of Rb_4C_{60} are observed, and the assignments to the parent modes in pure C_{60} at atmospheric pressures are given by tick marks at the top. For alkali-metal intercalated C_{60} phases that remain unpolymerized the effect of alkali ion intercalation on the Raman spectrum is relatively small. The most prominent, and often the only observed, effect occurs for the pentagonal pinch $A_g(2)$ mode (the symmetric stretch mode of C=C double bonds joining two pentagons). Since charge transfer to C_{60} leads to elongation of the C=C bond it shifts the pentagonal pinch mode downward[22,23] by 6 cm^{-1}

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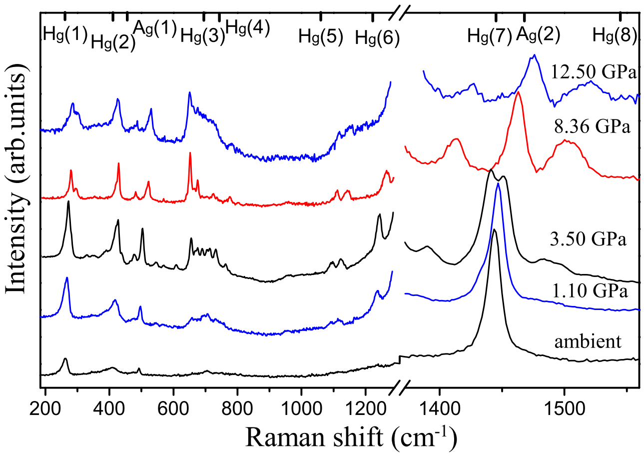

FIG. 1. (Color online) Raman spectra of a Rb_4C_{60} sample at the pressures indicated. Linear backgrounds have been removed for clarity. The break at 1300–1350 cm^{-1} is inserted to remove the Raman peak of diamond at 1333 cm^{-1}.

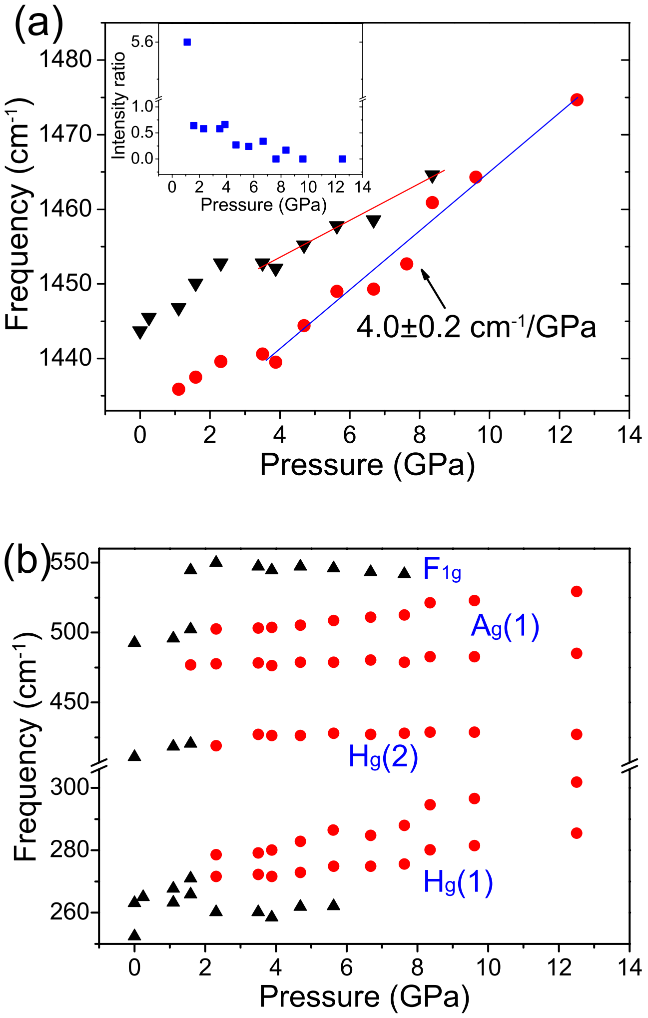

FIG. 2. (Color online) (a) Raman shifts of the $A_g(2)$ modes as a function of pressure. Inset shows the intensity ratio of the fitted $A_g(2)$ peaks from Rb_4C_{60} and Rb_6C_{60}. (b) Raman shifts of low-frequency modes as functions of pressure [corresponding pressure dependences for the $H_g(7)$ and $H_g(8)$ modes are 3.8 and 3.5 cm^{-1}/GPa, respectively]. In both figures, dots indicate Rb_6C_{60} and triangles indicate "Rb_4C_{60}."

for each electron transferred to the C_{60} molecule. At ambient pressure the position of the $A_g(2)$ mode at 1443 cm^{-1} agrees very well with a charge transfer of four electrons and also agrees well with previous studies of K_4C_{60} and Rb_4C_{60}.[22] Other modes characteristic for Rb_4C_{60} at atmospheric pressure are found at 493, 268, and 409 cm^{-1} [$A_g(1)$ radial breathing mode, $H_g(1)$, and $H_g(2)$ modes, respectively]. Most low-frequency H_g modes show a Breit–Wigner–Fano (BWF) shape due to electron-phonon coupling.[23]

Figures 2(a) and 2(b) show the pressure dependence of several Raman modes. With increasing pressure we observe not only the expected pressure-induced shifts of the Raman lines but also the gradual appearance and growth of new Raman lines that cannot be attributed to Rb_4C_{60} but rather to Rb_6C_{60} and Rb_3C_{60}. These are discussed in detail below, but as a first example we call attention to the $H_g(7)$ and $H_g(8)$ modes, known to be weak for Rb_4C_{60} but prominent in the Rb_6C_{60} spectrum.[22] The large intensity of these modes at 3.5 GPa and above strongly supports the suggested phase separation of Rb_4C_{60} into Rb_6C_{60} and Rb_3C_{60}.

Turning to the details of the Raman spectra of Rb_4C_{60} under pressure, Fig. 3 shows the $A_g(2)$ mode for increasing pressure (left) and decreasing pressure (right). In addition to the expected pressure-induced shift of the lines we observe another far more interesting effect. At 1.1 GPa a small shoulder appears around 1436 cm^{-1} and at 1.59 GPa its intensity has grown significantly. Taking into account the pressure-induced shift of the $A_g(2)$ mode, the position at 1436 cm^{-1} at 1.1 GPa corresponds to about 1432 cm^{-1} at atmospheric pressure. It is therefore plausible to attribute the appearance of this peak to the formation of Rb_6C_{60}. This interpretation is supported by the simultaneous appearance of several other Rb_6C_{60} modes in the Raman spectrum, as discussed below. The inset in Fig. 2(a) shows the ratio of the integrated intensities of the $A_g(2)$ peaks for Rb_4C_{60} and Rb_6C_{60}, and reveals that the Rb_6C_{60} fraction grows continuously up to 8 GPa, above which no traces of Rb_4C_{60} are seen in the spectra.

Near 2 GPa there is a clear change in the slope $d\nu/dp$ for most modes, especially for the former H_g modes, leading to a weaker pressure dependence. Assuming that a phase separation occurs, the change in slope should be connected with the change in compressibility at the transformation. A similar change in the pressure dependence is observed by Bellin *et al.*[24] around 1.7 GPa, although we note that our observed pressure dependences are always lower than those found in their study. Above the transition the pressure dependences of the Raman modes agree quite well with the results reported by Poloni *et al.*[20] for Rb_6C_{60}. The discrepancies between our results and those reported by Bellin *et al.* are probably related to the neon used as pressure-transmitting medium in their study. Neon rapidly intercalates in the fullerene lattice, making it less compressible.[25–27]

The existence of a phase separation is further supported by pressure-induced changes in the $H_g(1)$, $H_g(2)$, $H_g(3)$, and $H_g(4)$ Raman modes. The top spectrum in Fig. 4, obtained at a pressure of 3.5 GPa, is a clear superposition of the "pure" Rb_6C_{60} spectrum[20] (bottom curve) observed at 10.8 GPa and

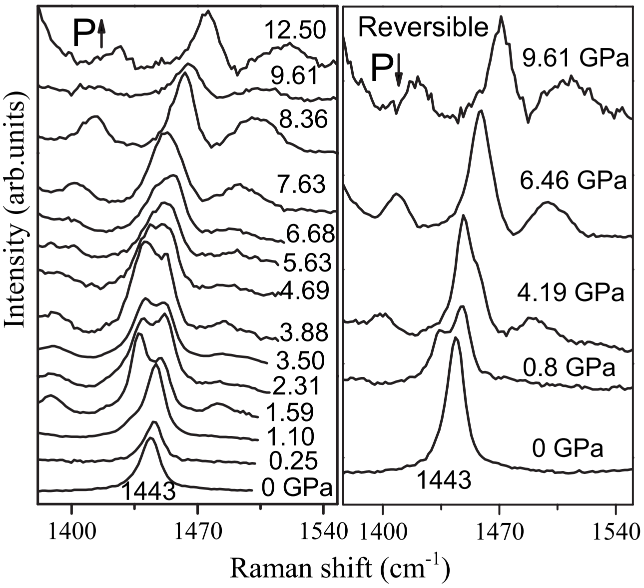

FIG. 3. The $A_g(2)$ Raman mode for Rb_4C_{60} with (left) increasing and (right) decreasing pressure; the corresponding pressure values are given in the figure.

the “pure” Rb_4C_{60} spectrum (middle curve) observed at atmospheric pressure (taking into account the positional differences due to the pressure differences). In addition to clear contributions from Rb_4C_{60} and Rb_6C_{60}, an additional mode (or modes) near 709 cm^{-1} indicates the presence of Rb_3C_{60}.[22] The assignment of modes to the latter phase is difficult because of the lack of high-pressure Raman studies, but some unassigned modes in the region 650–750 cm^{-1} probably originate from Rb_3C_{60} or some other low-Rb phase. (We stress that pure C_{60} is not observed at any pressure.) All results show unambiguously that the sample undergoes a pressure-induced phase separation from Rb_4C_{60} to Rb_6C_{60} and Rb_3C_{60}, completed around 8 GPa.

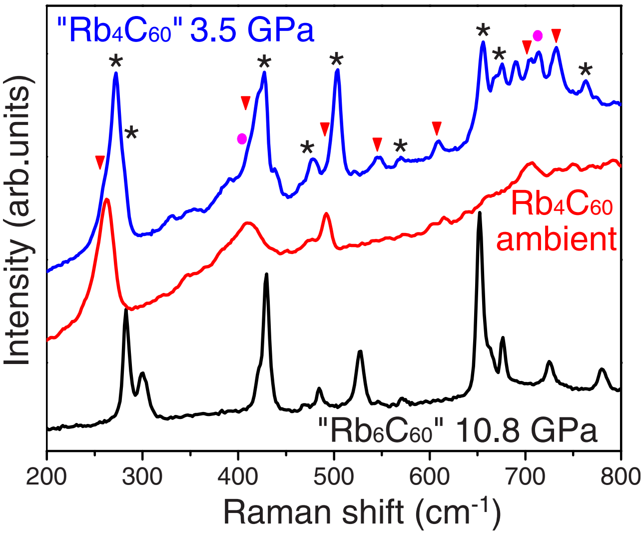

FIG. 4. (Color online) Raman spectra of our samples from 200–850 cm^{-1} at the pressure indicated. Stars, triangles, and circles indicate assignment of modes to Rb_6C_{60}, Rb_4C_{60}, and Rb_3C_{60}, respectively.

The driving mechanism for the observed phase separation of Rb_4C_{60} to Rb_6C_{60} and Rb_3C_{60} (or some other phase with a low concentration of Rb to preserve the stoichiometry) must be related to the free volume of the phases. At atmospheric pressure, the free volume of Rb_4C_{60} (547.4 Å^3) is larger than those of Rb_3C_{60} (521 Å^3) and Rb_6C_{60} (497 Å^3).[16] A simple density calculation based on the unit-cell parameters shows that a phase separation would increase the average density by ~4%, favoring a phase separation driven by the pressure-volume (pV) term in the energy. The observed Raman data, together with the fact that a phase transformation into, for example, RbC_{60} would be very difficult for thermodynamical reasons, implies that the phase separation can be described as

$$3Rb_4C_{60} \overset{\text{pressure}}{\leftrightarrow} Rb_6C_{60} + 2Rb_3C_{60}. \quad (1)$$

Remarkably, the phase separation is completely reversible. This is clearly seen in the right-hand part of Fig. 2, showing the Raman spectra of the sample at pressure release. Although there is a clear hysteresis we observe complete recovery of the Rb_4C_{60} at atmospheric pressure.

The observed phase separation explains peculiar results obtained in several earlier studies. Most of these give full support to our results but the authors have made other interpretations. High-pressure x-ray diffraction studies by Sabouri-Dodaran *et al.*[16] showed a clear trend that diffraction peaks from Rb_3C_{60} and Rb_6C_{60} grow in intensity with increasing pressure, being almost undetectable near atmospheric pressure but comparable in intensity with the Rb_4C_{60} peaks at 5 GPa, but since the initial samples were known to contain Rb_3C_{60} and Rb_6C_{60} impurities the authors did not suspect further phase separation. An abrupt jump at 0.5 GPa in their compressibility data can also be explained by the start of a phase separation into the denser mixture of Rb_6C_{60} and Rb_3C_{60}. The 4% drop in relative volume observed agrees well with the estimated densification from the transition according to Eq. (1). In a recent high-pressure Raman study of Rb_4C_{60}, a split of the $A_g(2)$ mode, similar to that found here, was observed.[24] However, this split is assigned to a deformation of the C_{60} molecules under high pressure. An important difference between their study and ours is that they observe the split at higher pressure (about 5 GPa). The main reason for this might be their use of neon as pressure transmission medium, which might stabilize the structure against a phase separation. Neon (atomic radius 1.12 Å) is smaller in size than the Rb ion (1.59 Å) and rapidly fills the voids of the C_{60} lattice.[26,27] It should thus be able to co-intercalate with Rb in the expanded Rb_4C_{60} lattice. Once inside, the small Ne atoms might impede the diffusion of Rb ions. Also, the absence of a pressure-transmitting medium in our study most likely gives rise to nonhydrostatic conditions, which are known to lower many transformation pressures.[25]

Our results also help to explain the much debated insulator-metal transition reported[18] for Rb_4C_{60}. The appearance of a metallic Rb_3C_{60} phase during the phase separation should indeed be interpreted as an insulator-metal transition. Direct support for the appearance of Rb_3C_{60} was found in our recent resistivity study of Rb_4C_{60} under pressure, in which we observed an increasing, but reversible, contribution from a metallic phase in the data above 0.4 GPa. Although initially discussed in terms of a phase separation, this explanation was discarded as unlikely because of the observed reversibility, and because the study only extended to 2 GPa Rb_3C_{60} never dominated the measured conductivity.[11]

Our results thus explain many strange results observed earlier. However, how can we explain the full reversibility of the phase separation? A pressure-induced phase separation would be expected to result in metastable phases that are retained when returning to atmospheric pressure. The reversibility can only be explained by a structural transformation of very local character. We thus propose that only minor displacements of the Rb ions occur, turning the Rb_4C_{60} structure into a lamellar structure consisting of Rb_3C_{60} and Rb_6C_{60}. *Ab initio* calculations[16] show that a tangential movement of a certain group of Rb ions in Rb_4C_{60} is activated at 0.5 GPa. The octahedral voids in Rb_4C_{60} and Rb_6C_{60} contain two and four Rb ions, respectively, and a possible model for the separation process is that two Rb ions, one from each of two adjacent octahedral sites, jump into a third site to fill this completely, converting the homogeneous Rb_4C_{60} lattice into a lamellar structure consisting of Rb_6C_{60} planes separated by double Rb_3C_{60} layers. The formation of such local nanoscale lamellar substructures could explain why the phase transition is not identified by x-ray diffraction. This type of structure should give relatively broad diffraction peaks that are difficult to observe, and the peaks observed by Sabouri-Dodaran[16] above the phase transformation pressure are significantly broader for the Rb_3C_{60} and Rb_6C_{60} phases than those for Rb_4C_{60}. Raman spectroscopy, on the other hand, probes the local charge transfer to the C_{60} molecules and is thus more sensitive to local structural differences. In this case however the scarcity of strong signals from Rb_3C_{60} is probably related to a combination of lower Raman-scattering cross section because of its metallic properties, broad Raman modes due to electron-phonon coupling, and the small differences between the positions of the Raman modes of Rb_4C_{60} and Rb_3C_{60}.

The diffusion of alkali-metal ions in fulleride structures and the subsequent formation of local "nanostructures" is already a well-discussed subject. Klupp *et al.*[14] suggested that the room-temperature Na_2C_{60} "phase" consists of insulating C_{60} and metallic Na_2C_{60} regions, each $\sim 3-10$ nm in size. Upon heating to $T \sim 460$ K, this nanosegregation is thought to disappear, presumably mediated by jump diffusion of sodium ions.[14]

To summarize, Raman spectroscopy has identified a phase separation of Rb_4C_{60} into Rb_3C_{60} and Rb_6C_{60} under pressure, starting around 1.1 GPa. Remarkably, the phase separation is completely reversible and the sample returns to homogeneous Rb_4C_{60} at atmospheric pressure. Based on the reversible nature of the phase transformation, and on thermodynamic reasons, we suggest that it occurs by very local displacement of Rb ions leading to the formation of a lamellar structure of Rb_6C_{60} and Rb_3C_{60}. Whatever the final structure, our observed phase separation gives an explanation for many "odd" unexpected results reported earlier for Rb_4C_{60}. We believe that studies of similar alkali-metal-doped structures will reveal similar effects.

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