Pressure-induced charge transfer phase transition in crystalline $C_{60} * C_{10}H_{12}Se_4 * 2(CS_2)$ molecular complex studied by Raman spectroscopy

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Abstract

The Raman spectra of the molecular neutral state complex $C_{60} * C_{10}H_{12}Se_4 * 2(CS_2)$ [$C_{10}H_{12}Se_4$, tetramethyl-tetraselenafulvalene (TMTSF)] have been measured as a function of pressure up to 9.5 GPa at room temperature. The pressure dependence of the frequencies of almost all intramolecular phonon modes exhibits irreversible changes at 5.0 ± 0.5 GPa. These changes include splitting and softening of various modes, the most characteristic being the irreversible softening by 9 cm^{-1} of the $A_g(2)$ pentagon-pinch (PP) mode, observed upon total release of pressure. This softening is the same as in the case of the potassium-doped fullerene KC_{60}. These observations are attributed to a pressure-induced irreversible phase transition, associated with the transfer of one electron from TMTSF donor to C_{60} acceptor molecule. © 1997 Elsevier Science B.V.

1. Introduction

The family of fullerene-based compounds has been continuously growing by the synthesis of new materials and their novel properties are attracting the interest of physicists, chemists and material scientists. The parent molecule C_{60}, with its unique structure, in which the 60 carbon atoms are located on the near spherical shape of a truncated icosahedron, offers a large free volume inside it as well as a large interstitial free space in the condensed state [1]. These characteristics result in a variety of chemical properties, such as the intercalation with alkali and alkaline-earth metals. Fullerene derivatives, with stoichiometry M_3C_{60}, where M is K, Rb, Cs, Ca, etc., are conductors and demonstrate superconductivity at relatively high temperatures [2,3].

An alternative way of synthesizing conducting fullerene-based materials is to form anionic C_{60} complexes with organic donors. The synthesis of new chemical compounds of fullerenes and the study of their structure, optical properties and energy spectrum is a fast growing area in the recent years [4–7]. A subject of special interest is the study of the influence of the donor-acceptor interaction potential to the phonon and electron energy spectra of

fullerene, as well as the effect of high pressure on the interaction potential between the molecules forming the complex.

In the present work we investigate, by means of Raman spectroscopy, the pressure behavior of phonon modes of the neutral state molecular complex of fullerene $C_{60} * TMTSF * 2(CS_2)$. Our motivation is to look at the pressure-induced enhancement of the charge transfer from the donor TMTSF to the acceptor C_{60} molecule and the related changes in the phonon and electron energy spectra. The pressure dependence of the frequencies of almost all intramolecular phonon modes shows irreversible changes at 5.0 ± 0.5 GPa, associated with both softening and splitting of modes. The residual value of the softening of the $A_g(2)$ PP-mode, observed after the total release of pressure, is the same as in the case of KC_{60}. This is attributed to a charge transfer phase transition, associated with the transfer of one electron from the TMTSF to the C_{60} molecule.

2. Experiments and results

Single crystals of $C_{60} * TMTSF * 2(CS_2)$ were grown by co-crystallization, under controlled temperature increase, of 30 ml solution containing 7 mg of C_{60}, obtained by the Krätschmer method [8] (purity better than 99.9%) and 18 mg TMTSF (Aldrich, purity better than 99%) in CS_2. The crystals formed by slow evaporation (10 days) of the solvent at room temperature, were carefully washed off with dehydrated EtOH and dried in air. The typical size of the crystals was $3 \times 3 \times 2$ mm^3, their structure, determined by X-ray, is monoclinic with lattice parameters: $a = 1.5407$, $b = 1.2934$, $c = 1.2026$ nm, $\beta = 108.39°$, $V = 2.2741$ nm^3, space group C_m, $Z = 2$, $\rho_{calc} = 1.929$ g/cm^3, $R = 0.047$ [9]. The conformation of the C_{60} molecule and the distances between them are not changed significantly in comparison with the pristine C_{60} crystals. The conformation of TMTSF molecule is significantly altered and becomes non-planar [9]. For our measurements small chips of $C_{60} * TMTSF * 2(CS_2)$, cut from a single crystal, were used.

High pressure was generated using the gasketed diamond anvil cell of Mao–Bell type [10]. A 4:1 methanol-ethanol mixture was used as the pressure

transmitting medium and the ruby fluorescence technique was used for pressure calibration [11]. Raman spectra were recorded using a triple monochromator (DILOR XY-500) equipped with a CCD cryogenic detector system. The spectral width of the system was ~ 5 cm^{-1}. The 514.5 nm line of Ar$^+$ laser was used for excitation. The laser beam was focused onto a spot of ~ 15 μm in diameter using the NIKON $20 \times$ objective with flux adapter and working distance of 20 mm. The power, measured directly before the cell, was kept lower than 1.5 mW (corresponding power density $\sim 8.5 \times 10^2$ W cm^{-2}). The power density reaching the sample is still lower, by almost one order of magnitude, taking into account the reflection losses in the diamond interfaces. The spectra were recorded in the back scattering geometry using a $\lambda/4$ plate as a scrambler and an OLYMPUS microscope system for the image processing. Results from three different runs were recorded for both increasing and releasing pressure.

The Raman spectra of the $C_{60} * TMTSF * 2(CS_2)$ complex in the wavenumber range from 100 to 1700 cm^{-1} at various pressures and room temperature are illustrated in Fig. 1. At normal pressure the spectrum contains eight of the ten main modes of the C_{60} molecule, $H_g(1)$, $H_g(2)$, $A_g(1)$, $H_g(3)$, $H_g(4)$, $H_g(7)$, $A_g(2)$, $H_g(8)$ with wavenumbers: 271, 433, 494, 709, 773, 1424, 1468 and 1574 cm^{-1}, respectively. Their wavenumbers are practically the same as the corresponding modes of the pristine C_{60} crystal [12,13], the differences observed do not exceed 3 cm^{-1}, which are within the spectral width of our apparatus. In addition to these bands, there are some weak Raman bands, whose origin may be a second order scattering from the C_{60} molecule. The observed wavenumbers do not resemble those observed in TMTSF powder or TMTSF^{-1} in solution [14].

The pressure dependence of the $H_g(7)$, $A_g(2)$ and $H_g(8)$ phonon frequencies is shown in Fig. 2, while that of the $H_g(3)$ and $H_g(4)$ mode frequencies is shown in Fig. 3. The additional weak Raman band observed at $\omega = 755$ cm^{-1}, at normal pressure, is related to two-phonon scattering from the combination of $[F_{2u}(1) + G_u(1)]$ modes [15]. All modes exhibit a positive response (~ 5.2 cm^{-1}/GPa) to pressure except $H_g(3)$ and the combination mode, which exhibit a negative response in the whole pressure range under investigation. The pressure dependence
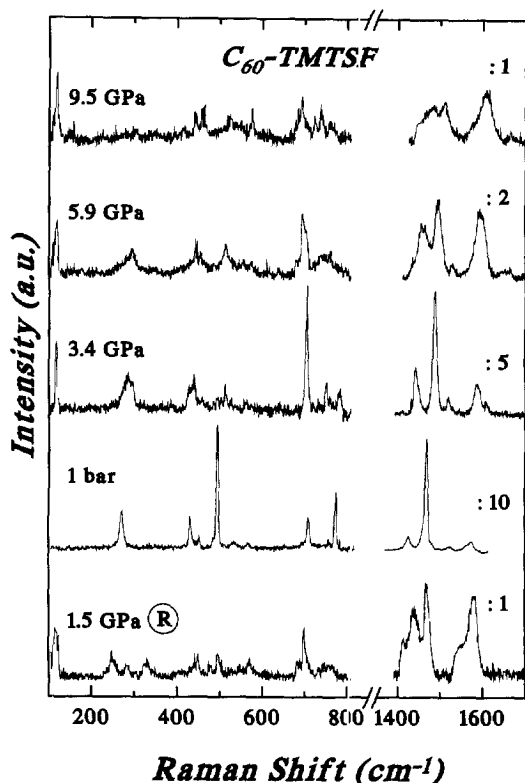
Fig. 1. Raman spectra of the $C_{60} * TMTSF * 2(CS_2)$ molecular complex at room temperature and for pressures up to 9.5 GPa. The spectrum at the bottom, marked by an R, is recorded upon pressure release.

of both modes is practically the same with values of the slopes -1.4 cm^{-1}/GPa for increasing and -0.9 cm^{-1}/GPa for releasing pressure. The wavenumber peak positions were determined by fitting Gaussian lineshapes to the experimental data. Open symbols (solid symbols) represent data recorded for increasing (decreasing) pressure. The solid lines indicate the path of increasing and the dashed lines of decreasing pressure, respectively.

When pressure increases, in the region of 5.0 ± 0.5 GPa, the $A_g(2)$ PP-mode softens, whereas the $H_g(7)$ mode hardens considerably (Fig. 2). Upon pressure release no such peculiarities in this pressure region, or in the rest pressure range are observed. All these changes are irreversible. The slopes of the pressure dependencies for $A_g(2)$ and $H_g(7)$ modes are practically the same before and after 5.0 GPa, both for increasing and releasing pressure and are equal to 5.2

cm^{-1}/GPa. The value of the residual softening of the PP-mode, after total release of pressure, is about 9 cm^{-1}. The residual hardening of the $H_g(7)$ mode is of the same value, whereas the softening of the $H_g(8)$ mode is approximately two times smaller. The pressure dependence of the $H_g(3)$, $H_g(4)$ and the combination mode frequencies (Fig. 3) shows drastic changes in the same pressure region (5.0 ± 0.5 GPa): all frequencies decrease abruptly. This change is irreversible. Their pressure dependencies for increasing and releasing pressure differ considerably at pressures below 5.0 GPa (above 5.0 GPa these dependencies are the same). In addition, the $H_g(4)$ splits in two modes upon releasing pressure below 5.0 GPa. All three modes, upon total release of pressure, exhibit a residual softening equal to 9 cm^{-1} for the $H_g(3)$ and the two-phonon combination $[F_{2u}(1) + G_u(1)]$ modes, while for the two components resulting from the splitting of the $H_g(4)$ mode,
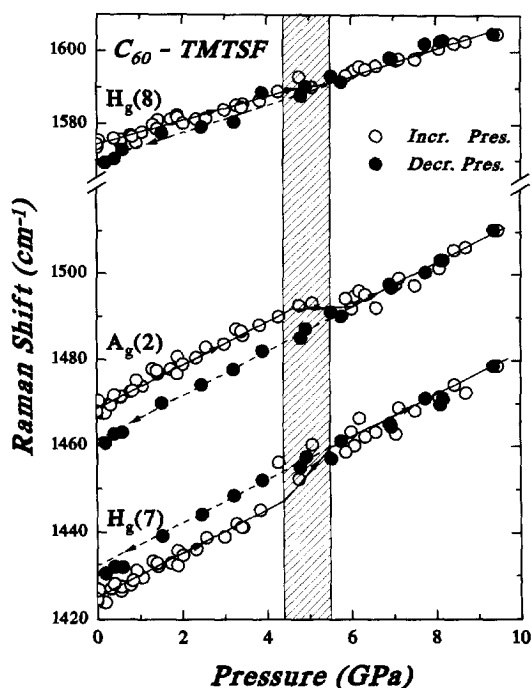

Fig. 2. Pressure dependence of the $H_g(7)$, $A_g(2)$ and $H_g(8)$ intramolecular phonon frequencies. Open (solid) symbols correspond to data taken in three pressure runs for increasing (decreasing) pressure. Solid lines (dashed lines) are guides to the eye for increasing (decreasing) pressure. The shaded area shows the pressure region of the phase transition.
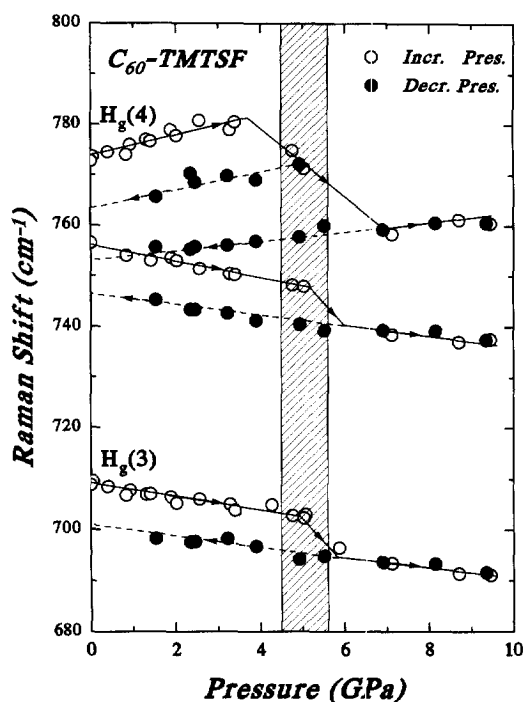
Fig. 3. Pressure dependence of the $H_g(3)$, $H_g(4)$ and the two-phonon $[F_{2u}(1)+G_u(1)]$ intramolecular phonon frequencies. Open (solid) symbols correspond to data taken in three pressure runs for increasing (decreasing) pressure. Solid lines (dashed lines) are guides to the eye for increasing (decreasing) pressure. The shaded area shows the pressure region of the phase transition.

this residual softening is equal to 18 cm^{-1} and 9 cm^{-1}, respectively. From these results it is obvious that in the pressure range 5.0 ± 0.5 GPa (shaded area in Figs. 2 and 3) take place changes in the pressure dependence of phonon modes and these effects are irreversible.

3. Discussion

The Raman spectrum of $C_{60} * TMTSF * 2(CS_2)$ at normal pressure is close to that of the pristine C_{60} crystal. The main Raman frequencies of the intramolecular phonon modes of the C_{60} molecule, within the $C_{60} * TMTSF * 2(CS_2)$ complex, practically coincide with those of the pristine C_{60} crystal. This is a manifestation that there are no significant changes of the conformation of the C_{60} molecule in the $C_{60} * TMTSF * 2(CS_2)$ complex with respect to the

pristine C_{60} crystal. This is an indication that the distances between the C_{60} molecules within the complex are close to those in the pristine C_{60} crystal. These qualitative estimations are in accordance with the results of the X-ray study of the crystal structure of the $C_{60} * TMTSF * 2(CS_2)$ [9]. A number of relatively weak Raman bands observed in the spectrum, are similar to those observed in the Raman spectrum of pristine C_{60} crystal. These modes may be associated with second order two-phonon scattering or silent modes of C_{60}. There is no indication that some of those weak Raman peaks may have their origin in intramolecular phonon modes of the TMTSF molecule or $TMTSF^{-1}$ ion [14].

The pressure dependence of the intramolecular phonon frequencies of the $C_{60} * TMTSF * 2(CS_2)$ in the initial pressure region 0–3.0 GPa differs essentially from that of the pristine C_{60} crystal. In the pristine C_{60} crystal the $A_g(2)$ PP-mode, as well as other intramolecular modes, exhibit a considerable softening in the pressure region 0–0.4 GPa [16,17]. This was explained as the manifestation of the pressure-induced orientational ordering phase transition from the face centered cubic to the simple cubic crystal structure. At normal pressure this transition takes place at 250 K [18] and the transition temperature increases with pressure [19]. The final stage of the pressure-induced orientational ordering takes place at a pressure of 2.4 GPa, where fullerite transforms to a phase with complete freeze out of the jumps of the C_{60} molecules between the two equilibrium orientational positions in the simple cubic structure [20]. These characteristics in the pressure dependence do not show up in the spectrum of $C_{60} * TMTSF * 2(CS_2)$. This is compatible with the X-ray scattering data, indicating that the C_{60} molecules in the $C_{60} * TMTSF * 2(CS_2)$ complex are orientationally ordered at room temperature and normal pressure.

The most interesting features of the pressure dependence of the phonon modes of $C_{60} * TMTSF * 2(CS_2)$ are the prominent changes at 5.0 ± 0.5 GPa, associated with the softening of all phonon modes and the splitting of some of them. These changes are irreversible and the residual softening, observed in the recovered material upon total release of pressure, varies from 5 up to 18 cm^{-1} for the various modes. The softening of several intra-

molecular phonons of pristine C_{60}, mainly of the $A_g(2)$ PP-mode, observed under various degrees of illumination [21,22], is reversible under conditions of low illumination and has been associated with the creation of the triplet excited states [21]. However, under more intense illumination this softening of the PP-mode becomes irreversible and has been associated with the photodimerization of the C_{60} molecules taking place only in the orientationally disordered phase [22]. Similar irreversible softening of the PP-mode has also been observed in high pressure and temperature polymerized C_{60} samples [23]. It must be emphasized that the photodimerization of C_{60} molecules within the $C_{60} * TMTSF * 2(CS_2)$ complex and consequently the irreversible softening of the PP-mode is not possible because of the total orientational order of the C_{60} molecules in the structure of the complex at normal conditions [9].

The reversible softening of the PP-mode of crystalline C_{60}, induced by laser irradiation, has been studied in relation to the sample overheating in the laser spot [24]. It has been found that the temperature increases considerably in the laser spot with laser power density and that for constant power density the temperature in the center of the spot depends almost linearly on the spot diameter [24]. That means the smaller the spot size the higher the laser power density needed to reach the same overheating temperature. In our experiments, within the DAC, the laser spot diameter (according to the microscope objective manufacturer) on the sample is ~ 15 μm, which is at least 10^{-2} smaller than the transverse spot size used in Ref. [22], therefore, we can afford two orders of magnitude higher laser power density and still fulfil the same criteria for sample overheating set in Ref. [22]. Indeed, the laser power density used in our experiments, measured before the cell is two orders of magnitude higher, taking into account the losses in the cell interfaces (~ one order of magnitude), the power density reaching the sample in the cell is considerably smaller. In addition, we always checked, in our experiments, the Raman spectrum of the complex at normal pressure under the laser power density used and the molecular modes of C_{60} were always close to those in Ref. [22], making sure that no overheating effects are observed.

The softening of the intramolecular modes of C_{60} has been observed in the intercalated C_{60} compounds

$M6C_{60}$, M = K, Rb, Cs [25]. In this case the frequencies of the Raman active modes are insensitive to the M atom and therefore to the lattice expansion caused by doping with alkali-metal atoms with larger ionic radii. This softening has been attributed to the elongation of the intramolecular bond lengths induced by charge transfer from alkali metal atoms to the C_{60} molecule and the resulting softening of the force constants [25]. The softening of the $A_g(2)$ PP-mode in this case is equal to 37.5 cm^{-1} for all studied compounds. Winter and Kuzmany [26] have studied the softening of the PP-mode for the K_xC_{60} series of compounds with x varying from 0 up to 6. The main result of their study is that the PP-mode softens almost linearly with increasing x and, consequently, the charge transfer from K to C_{60} molecule. They have found, in particular, that in the case of the KC_{60} compound the softening of PP-mode is equal to ~ 9 cm^{-1}.

The pressure-induced softening of phonon modes in the $C_{60} * TMTSF * 2(CS_2)$ molecular complex may be associated with the charge transfer between the TMTSF donor and C_{60} acceptor molecules. At normal pressure the Van der Waals type interaction between donor and acceptor molecules is too weak and they form the neutral state molecular complex with weak charge transfer. The gradual reduction of the intermolecular donor–acceptor distances and the enhancement of the interaction between them at higher pressures, results in the charge-transfer phase transition, taking place in the region 5.0 ± 0.5 GPa. During the phase transition a transfer of one electron from TMTSF to C_{60} molecule takes place forming a new anion state C_{60}^{-1} charge-transfer complex. As a result of this, the transformation of the material becomes irreversible and the PP-mode exhibits a residual softening by 9 cm^{-1}, observed upon total release of pressure, in complete analogy to the case of KC_{60} [26]. Similar studies [27] have shown that pressure can induce neutral to ionic state phase transition in the case of the tetrathiofulvalene-haloquinone mixed stack charge transfer crystal.

In conclusion, the pressure dependence of the frequencies of the intramolecular phonon modes of the neutral state molecular complex $C_{60} * TMTSF * 2(CS_2)$ shows a softening of all phonon modes and a splitting of some of them at 5.0 ± 0.5 GPa. These changes are associated with an

irreversible pressure-induced phase transition. The residual softening of the $A_g(2)$ PP-mode, upon total pressure realease, is equal to ~ 9 cm^{-1} and is the same as in the case of potassium doped fullerene KC_{60}. This is, in our opinion, a strong indication that this pressure-induced phase transition has a charge-transfer character, resulting in the formation of the C_{60}^{-1} anion state charge-transfer molecular complex.

Acknowledgements

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