

# **C<sub>60</sub> fullerene and its molecular complexes under axial and shear deformation**

**N G Spitsina<sup>1</sup>, M V Motyakin<sup>2</sup>, I V Bashkin<sup>3</sup> and K P Meletov<sup>3</sup>**

<sup>1</sup> Institute of Problems of Chemical Physics RAS, 142432 Chernogolovka, Russia

<sup>2</sup> Institute of Chemical Physics RAS, Kosygin 4, 117977 Moscow, Russia

<sup>3</sup> Institute of Solid State Physics RAS, 142432 Chernogolovka, Russia

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## **Abstract**

We have studied the pristine C<sub>60</sub> and its molecular complexes with the organic donors bis(ethylenedithio) tetrathiafulvalene (BEDT-TTF or ET) and tetramethyltetraselenafulvalene (TMTSF) by means of ESR and Raman spectroscopy at high pressure. The important changes in the ESR signal of C<sub>60</sub> were observed under axial pressure combined with shear deformation. It is shown that the treatment at an anisotropic pressure of 4 GPa results in a reduction in the symmetry of the C<sub>60</sub> molecule and the formation of radicals. Treatment of the molecular complex of (ET)<sub>2</sub>·C<sub>60</sub> at a pressure of ~4.5 GPa and a temperature of 150 °C leads to the formation of C<sub>60</sub> dimers. The Raman spectra of the molecular complex C<sub>60</sub>·TMTSF·2(CS<sub>2</sub>) were measured *in situ* at ambient temperature and pressures up to 9.5 GPa. The pressure behaviour of the Raman peaks reveals singularity at 5.0 ± 0.5 GPa related to the softening and splitting of some of the phonon modes. The residual softening of the A<sub>g</sub>(2) mode is the same as in the case of KC<sub>60</sub>, which may be an indication that the transition has a charge-transfer character, resulting in the formation of the C<sub>60</sub><sup>-1</sup> anionic state charge-transfer complex.

## **1. Introduction**

The investigation of the physical and chemical properties of fullerene C<sub>60</sub> and its derivatives at ambient and high pressure has been the main focus of research since its discovery [1–5]. The quasi-spherical structure of the C<sub>60</sub> molecule, sp<sup>2</sup>-like hybridization of molecular bonds and weak van der Waals intermolecular interaction result, in particular, in high stability towards isotropic deformation at high pressure. The phase transitions that occur under high pressure have contributed drastically to the interest in studying their origin and mechanism [2].

The important property of C<sub>60</sub> is that its derivatives of the formula MC<sub>60</sub>, where M is K, Rb, Cs, Ca etc, are conductors and reveal superconductivity at temperatures up to 39 K [3]. To date such organic compounds have been studied by varying their parameters using ‘chemical doping’ and applying high pressure. Recently, researchers from the Bell Lab (Batlogg, Shon,

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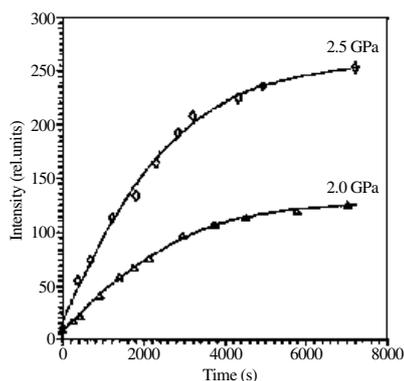
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**Figure 1.** The intensity of the ESR signal as a function of the shear deformation application time (at axial stresses of 2.0 and 2.5 GPa).

and Kloc) have demonstrated spectacular results by creating new class of low-dimensional carrier systems with ultra-high mobility, in metal-oxide semiconductor (MOS)-system on the surface of organic molecular crystals (pentacene, tetracene,  $C_{60}$ , etc). Due to the low dielectric permittivity and high effective masses of carriers in these systems, much higher  $r_s$  values can be achieved than in the Si-MOS system. Moreover, with the application of the gate voltage to the MOS structures on  $C_{60}$ , a superconductivity was observed with an electrically tunable critical temperature up to 52 K (recently increased to 117 K in a  $C_{60}$  intercalated  $CHBr_3$  compound) [6, 7].

An alternative way of designing conducting fullerene-based materials is to form anionic  $C_{60}$  complexes with organic donors. The synthesis of chemical compounds of  $C_{60}$  and the study of their structure, electronic and optical properties, as well as the influence of pressure on the donor-acceptor interaction in complexes is an important area of research.

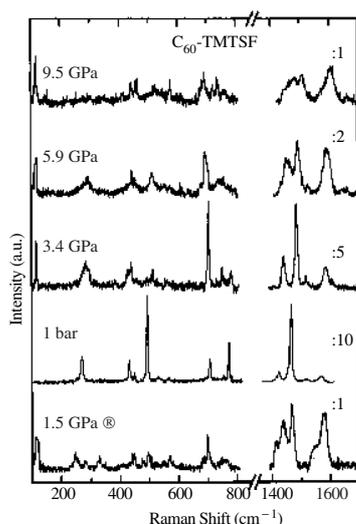
## 2. Experimental procedures and results

The ESR spectra of  $C_{60}$ , measured at room temperature and an axial pressure up to 4 GPa combined with shear deformation, are shown in figure 1. Shear deformation at a mean rate of  $1.2 \times 10^{-3} \text{ rad s}^{-1}$  was found to result in a dramatic increase in ESR absorption. The integral intensity increases proportionally to the application time of the axial stress, whereas the width of the ESR signal decreases with an increase in the application time of the shear deformation.

High pressure modifies both the crystal and electronic structures of  $C_{60}$  and results in the appearance of uncoupled electrons related to broken chemical bonds. This process is accompanied by relative change in the number of  $\sigma$ - and  $\pi$ -bonds, the appearance of local and linear defects, excitation of electrons in the conductivity band and lowering of the symmetry of  $C_{60}$  molecule. The ESR absorption may be assigned to the formed radicals. The formation of new chemical bonds is the final stage of the process and the ‘non-interacting’ fullerene cages at low pressure become ‘interacting’ at high pressures. To support this idea, we treated various molecular complexes of  $C_{60}$  at high pressure and studied the transformed materials by means of *in situ* Raman and IR spectroscopy.

We synthesized molecular complexes of  $C_{60}$  with two different TTF-type organic donors, which differ in the crystal structure and intermolecular interaction between the molecules [8, 9].

In the complex of  $(ET)_2 \cdot C_{60}$  (ET, tetrathiafulvalene) the molecules of ET and  $C_{60}$  are packed in two types of layers: those formed by ET and those form by  $C_{60}$  molecules [8]. Both types of layers are parallel to the (*bc*) plane of the crystal and uniformly alternate along *a* axis. X-ray analysis revealed that each  $C_{60}$  molecule is sandwiched between a pair of largely



**Figure 2.** Raman spectra of C<sub>60</sub>·TMTSF·2(CS<sub>2</sub>) at room temperature and various pressures. The value marked by ‘ $\textcircled{R}$ ’ is recorded upon the pressure release.

concave ET molecules and that the rotational motion of C<sub>60</sub> is quenched completely. The distances between the centres of the C<sub>60</sub> molecules in the (ET)<sub>2</sub>·C<sub>60</sub> are 10.03 Å (290 K) and 9.923 Å (150 K) (the distance between the centres of C<sub>60</sub> molecules in the fcc crystal structure is 10.02 Å). There is one shortened contact between the C<sub>60</sub> molecules in the (ET)<sub>2</sub>·C<sub>60</sub> structure: the C···C distance is 3.30(1) Å (the sum of the van der Waals radii of carbon atoms is 3.40 Å).

Thus the pressure-induced cross-linking of C<sub>60</sub> molecules in (ET)<sub>2</sub>·C<sub>60</sub> is promising because normally the charge-transfer interaction between the components of this complex is small.

In the C<sub>60</sub>·TMTSF·2(CS<sub>2</sub>) (TMTSF, tetramethyltetraselenafulvalene) the molecules of TMTSF, C<sub>60</sub> and CS<sub>2</sub> are assembled in homomolecular layers of TMTSF molecules and heteromolecular layers formed by C<sub>60</sub> and CS<sub>2</sub> molecules [9]. Both types of layers are parallel to the (*ab*) crystal plane and uniformly alternate along the *c*-axis. Four fullerene molecules, forming a quasi-square configuration, surround a C<sub>60</sub> molecule in a heteromolecular layer and eight CS<sub>2</sub> molecules, forming a quasi-square prism, are inscribed in this ‘fullerene square’. The distance between the centres of C<sub>60</sub> molecules is 10.06 Å. No shortened contacts are found between the molecules of the C<sub>60</sub>·TMTSF·2(CS<sub>2</sub>) arranged in either homomolecular or heteromolecular layers. Shortened contacts occur between the C<sub>60</sub> and TMTSF molecules belonging to adjacent layers. In this case, each TMTSF molecule is linked to two C<sub>60</sub> molecules from adjacent layers. As a result, the stack of layers is cross-linked by zigzag chains along the *c*-axis.

High-pressure experiments were performed in a ‘toroid’-type cell and a wedge-type cubic anvil quase-hydrostatic pressure apparatus. Polycrystalline ET<sub>2</sub>C<sub>60</sub> samples loaded in a high-pressure assemblies were treated at ~5 GPa and 150 °C. After treatment the samples were recovered to ambient conditions and characterized by IR absorption spectroscopy.

*In situ* Raman measurements at high pressure were performed using a Mao–Bell-type gasketed diamond anvil cell. The 4:1 methanol–ethanol mixture was used as a pressure-transmitting medium and the ruby fluorescence technique was used for the pressure calibration.

The IR-absorption spectra of pristine C<sub>60</sub>, ET and ET<sub>2</sub>C<sub>60</sub> complex before and after squeezing were measured in the KBr pellet at ambient temperature. The peaks related to ET were not changed by pressurization, while those related to C<sub>60</sub> exhibit notable changes: the

intensities of four main peaks decrease relatively to features in the 550–850  $\text{cm}^{-1}$  region. The IR spectrum of the samples, obtained by the removal of ET after treatment with dichloroethane solvent, is similar to that of dimerized  $\text{C}_{60}$  [10]. Thus, the dimers or oligomers of  $\text{C}_{60}$  can be formed by the pressure treatment.

TMTSF donor and  $\text{C}_{60}$  acceptor molecules of the Raman spectra of the  $\text{C}_{60}\cdot\text{TMTSF}\cdot 2(\text{CS}_2)$  complex at ambient temperature and various pressures are illustrated in figure 2. The pressure dependence of almost all modes exhibits a positive response, except for two modes that have a negative response. The distinct change in the pressure dependence takes place at 5 GPa and this effect is irreversible. This peculiarity is associated with pressure-induced softening of almost all phonon modes, related to the charge transfer between the complex. During the phase transition, a transfer of one electron from TMTSF to the  $\text{C}_{60}$  molecule takes place forming a new anionic state  $\text{C}_{60}^{-1}$  charge-transfer complex. The transformation is irreversible and the residual softening of the  $\text{A}_g(2)$  mode observed upon the total release of the pressure is in complete analogy to the case of  $\text{KC}_{60}$ .

### 3. Conclusion

Changes in the ESR signal of the fullerene  $\text{C}_{60}$  induced by pressure and shear deformation were observed. It was shown that an anisotropic pressure of up to 4 GPa through shear deformation transforms reduce the symmetry of  $\text{C}_{60}$  molecules, including radical formations.

The  $\text{C}_{60}$  dimer was synthesized by the high-pressure treatment of the molecular complex of  $(\text{ET})_2\cdot\text{C}_{60}$ .

The *in situ* Raman spectra of the molecular complex  $\text{C}_{60}\cdot\text{TMTSF}\cdot 2(\text{CS}_2)$  were measured as a function of pressure up to 9.5 GPa at ambient temperature.

We indicate that a pressure-induced phase transition has a charge-transfer character, resulting in the formation of the  $\text{C}_{60}^{-1}$  anionic state charge-transfer complex.

Using a high-pressure treatment of different structures of molecular complexes of  $\text{C}_{60}$  with organic donors, it is possible to design fullerene-containing compounds with low-symmetry (e.g. polymers and fullerenes with complete charge transfer).

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