

# PRODUCTION AND INVESTIGATION OF FULLERITE C<sub>60</sub> INTERCALATED WITH SMALL MOLECULES

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## Introduction

It is well known that fullerene C<sub>60</sub> can exist as a gas (at temperature  $\geq 450$  °C) or solid. Liquid phase for C<sub>60</sub> was not established still now. At normal conditions C<sub>60</sub> molecules form fullerite – solid state of fullerene. The fullerite can be amorphous or crystalline. Transitions between amorphous and crystalline states are not possible as a rule. It is related with low temperature of C<sub>60</sub> sublimation ( $\sim 450$  °C). Ratio between amorphous and crystalline parts of solid C<sub>60</sub> formed in process of its production.

C<sub>60</sub> molecules are crystallized in face-centered cubic (*fcc*) lattice. Van der Waals forces bond molecules in fullerite. One octahedral ( $R_{oh} = 2.06$  Å) and two tetrahedral ( $R_{th} = 1.13$  Å) sites per one C<sub>60</sub> are in *fcc* lattice [1]. Small molecules can be placed in octahedral sites of fullerite if its van der Waals diameters are not substantial higher than the diameter of the site. Distance between the center of C<sub>60</sub> molecules is increased then the sites are occupied.

We find new method of fullerite doping [2] in process of its salting out from solution in organic solvent [3]. Such doping can be performed at room or lower temperature. By this method were obtained fullerites C<sub>60</sub> intercalated with Ar [4], CH<sub>4</sub> [5], CH<sub>2</sub>F<sub>2</sub> [6-7] and O<sub>2</sub> [1, 8, 9]. The main peculiarity of our samples is more high stability in compare with that of same samples obtained by means of hot pressing [10]. High stability of our samples is connecting with its more large crystalline size.

New data on the properties of our fullerites, which were obtained in last two years, are present in my report.

## Ar<sub>x</sub>C<sub>60</sub>

Fullerite with composition Ar<sub>x</sub>C<sub>60</sub> ( $0.60 < x < 0.75$ ) was obtained in accordance with [2] from solvents saturated with argon gas. It was established that constant  $a_0$  for *fcc* lattice is equal to 1.422 nm and temperature of the phase transition from *fcc* (Fm3m) lattice to a simple cubic (*sc* or Pa3) lattice is equal to  $-26$  °C. These values differ substantial from the same values for

clean fullerite (1.416 nm and  $-13$  °C correspondently). Heating of Ar<sub>x</sub>C<sub>60</sub> leads to loss of argon and returns to the structure that is characteristic for clean fullerite.

## (CH<sub>2</sub>F<sub>2</sub>)<sub>x</sub>C<sub>60</sub>

Fullerite C<sub>60</sub> with intercalated CH<sub>2</sub>F<sub>2</sub> (Freon-32) was prepared for the first time. The sample was studied by elemental analysis, X-ray powder diffraction, mass spectrometry, and IR spectroscopy. The composition of the sample was found to be (CH<sub>2</sub>F<sub>2</sub>)C<sub>60</sub>. The sample had a *fcc* lattice with  $a_0 = 1.4284$  nm that is much larger than that for pure fullerite. The gas released from the sample during heating in a vacuum to 450° C largely consisted of initial Freon (mass spectrometry data); no Freon destruction products were observed at this temperature. The C–F stretching vibration frequency (1058 cm<sup>-1</sup>) was shifted in (CH<sub>2</sub>F<sub>2</sub>)C<sub>60</sub> by 30 cm<sup>-1</sup> toward lower wave numbers compared with the gas phase. The absorption bands at 1182 and 1428 cm<sup>-1</sup> (IR active modes ( $F_{1u}$ ) of high-symmetry ( $I_h$ ) C<sub>60</sub> molecules) did not change their positions in the intercalate.

## (O<sub>2</sub>)<sub>x</sub>C<sub>60</sub>

For fullerite C<sub>60</sub> with intercalated oxygen, a sharp (by three orders of magnitude) increase in the intensity of the EPR signal with a *g*-factor of 2.0024 was observed at  $\sim 200$ ° C. The conclusion was drawn that the products of oxygen interaction with fullerene rather than the concentration of oxygen in the sample determined the intensity of the EPR signal.

Processes inside of (O<sub>2</sub>)<sub>x</sub>C<sub>60</sub> induced by the heating are also analyzed using mass-spectrometry, thermogravimetry, differential scanning calorimetry, and so on. It was found that the primary product at heating temperatures below 100° C is oxygen. At higher heating temperatures up to 200° C, carbon oxides CO and CO<sub>2</sub> were also observed. Our DSC measurements showed an intense peak at +193° C that indicates a rather unusual interaction of fullerite with intercalated oxygen. Enthalpy of the phase transition from *fcc* lattice to *sc* lattice is found to decrease by 23% as a

result of heating of fullerite samples up to 300 °C in the dry argon atmosphere. This finding can be explained by the formation of oxygen containing products of C<sub>60</sub> that exhibit no free rotation inside the crystalline fullerite. In order to gain insight in possible oxidation mechanisms, density functional theory computations were performed for the C<sub>58</sub>O<sub>n</sub> (n=0-4) and C<sub>59</sub>O<sub>m</sub> (m=0-2) species. Total energies of the optimized states are used for estimating the energetic of different oxidation channels. The lowest total energy states of C<sub>59</sub> and C<sub>58</sub>O<sub>3</sub> are found to be triplets. Thus, these states may contribute to the ESR intensity as well as to be a source of paramagnetism observed previously in C<sub>60</sub> fullerite irradiated by oxygen.

#### Fullerite C<sub>60</sub> intercalated with isopropyl alcohol

A highly defect fullerite was obtained by adding of isopropyl alcohol (IPA) in the solution of C<sub>60</sub> in 1,2-dichlorobenzene (DCB) [11]. It was shown that molecules of IPA and DCB are placed in the large size defects. At heating up to 200 °C IPA molecules are evolved from the fullerite, and acetone molecules are evolved at more high temperature (200-350 °C). Products of DCB thermal decomposition are not established at all temperature intervals. Quantum chemistry calculation of possible products of reaction between IPS and C<sub>60</sub> were performed. New data on properties of such highly defect fullerite were obtained by means of transmittance electron microscopy, powder pattern, mass spectrometry and infrared spectroscopy. One of possible mechanism of transformation of IPS to acetone in intrinsic pores of the fullerite was proposed.

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