

METALLIC AND SEMICONDUCTOR BEHAVIOR OF POLYMERIZED C₆₀

*T.L.Makarova**, *A.Ya.Vul'**, *V.A.Davydov***, *L.S.Kashevarova***,
*A.V.Rakhmanina***, and *P.Scharff****

**Ioffe Physico-Technical University*

Polytekhnicheskaya 26 St.Petersburg 194021 Russia

***Vereschagin Institute of High Pressure Physics*

Troitsk, Moscow region 142092 Russia

****Technical University Clausthal*

Paul-Ernst str.4 Clausthal-Zellerfeld 38670 Germany

Introduction

Among the unique properties of fullerenes is their ability to form covalent bonds in response to some external factors. The present study was designed to follow the changes in the structure and the electrical properties of fullerite C₆₀ subjected to the pressures up to 10 GPa and the temperatures up to 1273 K.

Experimental

The samples were obtained by quasistatic compression in the Toroid high-pressure chamber described in Ref.1 The initial material was powder containing 99.9% C₆₀. Cylindrical samples pressed from the powder were inserted in the chamber, where they were compressed to a given level, heated and held isothermally at a given temperature, then cooled rapidly before removing the load This sequence of the operations results in quenching of the sample so that the carbon states obtained can be analyzed under normal conditions. Gold contacts were attached to the ends of cylindrical samples with silver paste to investigate the electrical properties of the structures. Temperature dependence of conductivity were obtained by measuring the direct current at the voltage of 100 V. The current-voltage characteristics proved to be linear in the range of 1 - 600 V. Electrical properties of the structures were independent on the reduction of oxygen pressure in the measuring chamber.

Results and Discussion

The temperature dependencies of conductivity of the pressure treated samples show Arrhenius behavior (Fig.1) being reproducible both for heating up to 500 K and for cooling. Assuming intrinsic conductivity, one can determine the band gap from the slope of the curves.

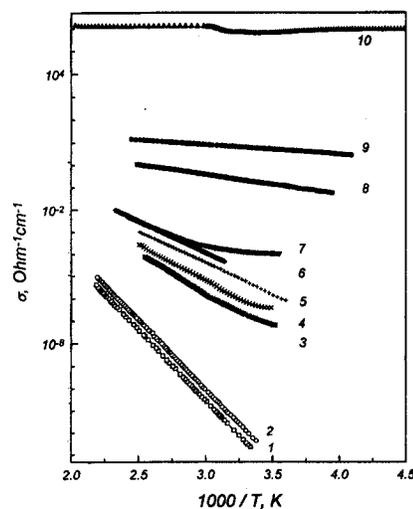


Fig.1. Temperature dependencies of conductivity of pressure-polymerized fullerenes C₆₀. The numbering of the curves corresponds to the sample number in the Table 1.

Table 1. Values of the gap (E_g), conductivity prefactor (σ_0) depending on the parameters of sample preparation: quasihydrostatic pressure (p) and temperature (T)

No	p , GPa	T , °C	E_g , eV	σ_0 , mkOhm ⁻¹ cm ⁻¹
1	8	100	2.38	$6.7 \cdot 10^8$
2	6	100	2.35	$5.1 \cdot 10^8$
3	2	100	1.50	$2.6 \cdot 10^5$
4	2	200	1.46	$1.2 \cdot 10^5$
5	2	400	1.20	$5.3 \cdot 10^4$
6	1.5	450	1.14	$1.4 \cdot 10^4$
7	2	650	1.04	$1.1 \cdot 10^4$
8	6	600	0.36	$2.0 \cdot 10^2$
9	6	700	0.08	$1.5 \cdot 10^2$
10	10	1000	-	-

The polymerization state of the samples was characterized by means of Raman spectroscopy. Some of the spectra are presented in Ref.1. Samples № 1 - № 3 do not have features due to the polymerization. The similarity of the spectrum of the sample № 3 to that of the powder makes it possible to consider this sample as a reference one. The data obtained on the samples № 1 and № 2 clearly show that compression followed by increasing in density up to 1.70 g/cm³ results in a drop in conductivity by several order of magnitude. It has been known that the treatment at the temperatures below the point of the orientational phase transition for a given pressure does not lead to polymerization. Our results show that just decrease of interatomic distances leads to the increase in the band gap instead of decrease as could be expected.

The samples № 3 - № 7 were prepared at nearly the same pressure but at various temperatures. In this series of samples density grows from 1.68 to 1.80 g/cm³. Beginning at № 4, new Raman active modes appear, among them a soft mode at 118 cm⁻¹ assigned to an interball vibration, a broad band at about 960 cm⁻¹ usually attributed to the four-membered carbon ring stretch. The pentagonal pinch mode at 1469 cm⁻¹ shifts to 1459 cm⁻¹ acquiring a satellite at 1445 cm⁻¹ which can be interpreted as evidence for dimers and linear chains formation (Ref.1). During polymerization the symmetry of pristine van der Waals crystalline structure is lowered and the degenerated molecular orbitals of a separate cluster are splitted. We have observed experimentally that the band gap decreases substantially with increasing synthesis temperature, which agrees with the theoretical predictions on the increased degree of interaction between neighboring molecules. It should be emphasized that this process is followed by the decrease in conductance prefactor σ_0 pointing out that the splitting of molecular orbitals is followed by their approaching each other.

The Raman spectra of the samples № 8 - № 10 show the pentagonal pinch mode at 1464 cm⁻¹ which is peculiar to two-dimensional polymerization. Being prepared at high pressures and temperatures, the samples № 8 and № 9 have very low values of the gap, density being 1.96 - 2.02 g/cm³. The resistivity of the sample № 10 which is as dense as 2.5 g/cm³ reduces only threefold varying as $\rho = \rho_0 \cdot T^{-0.333}$ as the temperature rises from 2 to 500 K. This behavior may be explained by the quantum corrections to conductivity which are normally of minor importance and become noticeable near the point of the metal-dielectric transition.

The additional information on the sample properties comes from the electron spin resonance

(ESR) experiments. For the samples № 1 - № 8 the ESR spectrum is symmetrical, the spin concentration is about $2 \cdot 10^{18}$ s/g and the calculated g-factor is equal to those for a free electron. Although the sample № 9 behaves as a narrow-gap semiconductor, ESR spectrum is asymmetrical revealing the formation of the skin layer typical for metals (Fig.2). The asymmetry ratio for the sample № 10 grows to 3.6 and the spin concentration increases to $3.5 \cdot 10^{19}$ s/g.

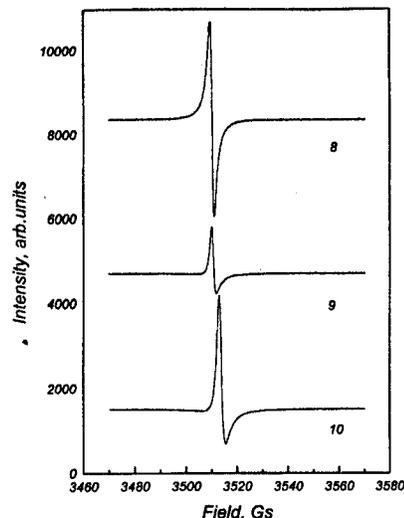


Fig.2. ESR spectra of pressure-polymerized fullerenes.

Conclusions

The pressure-induced polymerization of fullerite C₆₀ was observed to cause significant changes in the band structure and electrical conductivity. The increased degree of polymerization results in the decrease in the gap followed by the substantial increase in conductivity. The transition from semiconductor to metallic behavior was observed experimentally.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research, grant 96-02-17926. One of the authors (T.M.) is grateful to the German Department for Academic Exchanges, grant DAAD A/96/2097 which allowed her to perform measurements.

References

1. V.A.Davydov, L.S.Kashevarova, O.G.Revin, V.Agafonov, P.Dubois, R.Ceolin, H.Szwarc., *Mol.Mat.*, 1996, 7, 285.