ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ

Дубна

E14-2000-20

V.L.Aksenov, Yu.A.Ossipyan[1], L.Forro[2], S.Khasanov[1],
V.V.Chernyshev[3], V.S.Shakhmatov

FULLERENE MOLECULE STRAIN IN RbC_{60}

Submitted to «Solid State Communications»

[1]Institute of Solid State Physics RAS, Chernogolovka,
Moscow reg., Russia
[2]EPFL, Lausanne, Switzerland
[3]Lomonosov Moscow State University, Moscow, Russia

2000

In most fullerene crystals, orientational phase transitions are observed. At high temperatures, C_{60} molecules experience retarded anisotropic rotation and at the phase transition temperature, the rotation ceases and orientational ordering of C_{60} molecules takes place. In AC_{60} fullerides, where A=K, Rb, the appearance of a covalent (polymeric) bonds between nearest C_{60} molecules and strain of C_{60} molecules following the phase transition from the high symmetry phase *Fm3m* to the low symmetry phase *Pnnm* are observed [1].

In papers [2,3] a phenomenological theory of the structural phase transition in fullerides AC_{60} is constructed and a model of the orientational phase transition together with a method for the description of C_{60} molecule strain are proposed. In this article, the phonon basis suggested in paper [2] for the description of fullerene molecule strain is experimentally verified.

Structural investigations are carried out on the X-ray diffractometer with $CuK_{\alpha 1}$ radiation (λ =1.5406 Å). The spectra are recorded with the step 0.02^0 and with the fixed exposition time 30 sec. Our experimental investigations show that a polycrystalline sample of RbC_{60} contains ~13 % of pristine C_{60} fullerite.

To describe the orientational phase transition in the fulleride AC_{60} and approximately describe of anysotropically rotating C_{60} molecules in the high symmetry phase *Fm3m*, it is necessary to introduce 12 discrete orientational states for each rotating C_{60}. Therefore, the number of phonon degrees of freedom for a rotating C_{60} molecule is equal to 12×60×3=2160, where 12 is the number of the orientational states of the rotating molecule C_{60}, 60 is the number of carbon atoms in the C_{60} molecule, 3 is the number of possible atomic displacements.

The basic phonon functions describing the molecule strain of C_{60} are

$$\frac{1}{2}[u_y(i_1)+u_y(i_2)-u_y(i_3)-u_y(i_4)], \tag{1}$$

$$\frac{1}{2}[-u_z(i_1)+u_z(i_2)-u_z(i_3)+u_z(i_4)], \tag{2}$$

$$\frac{1}{2}[u_x(i_1)-u_x(i_2)+u_x(i_3)-u_x(i_4)], \tag{3}$$

where i_1=1,...,16 denote nonequivalent carbon atoms of the C_{60} molecule in the *Pnnm* phase except carbon atoms with numbers 15 and 16 (see Fig. 1).

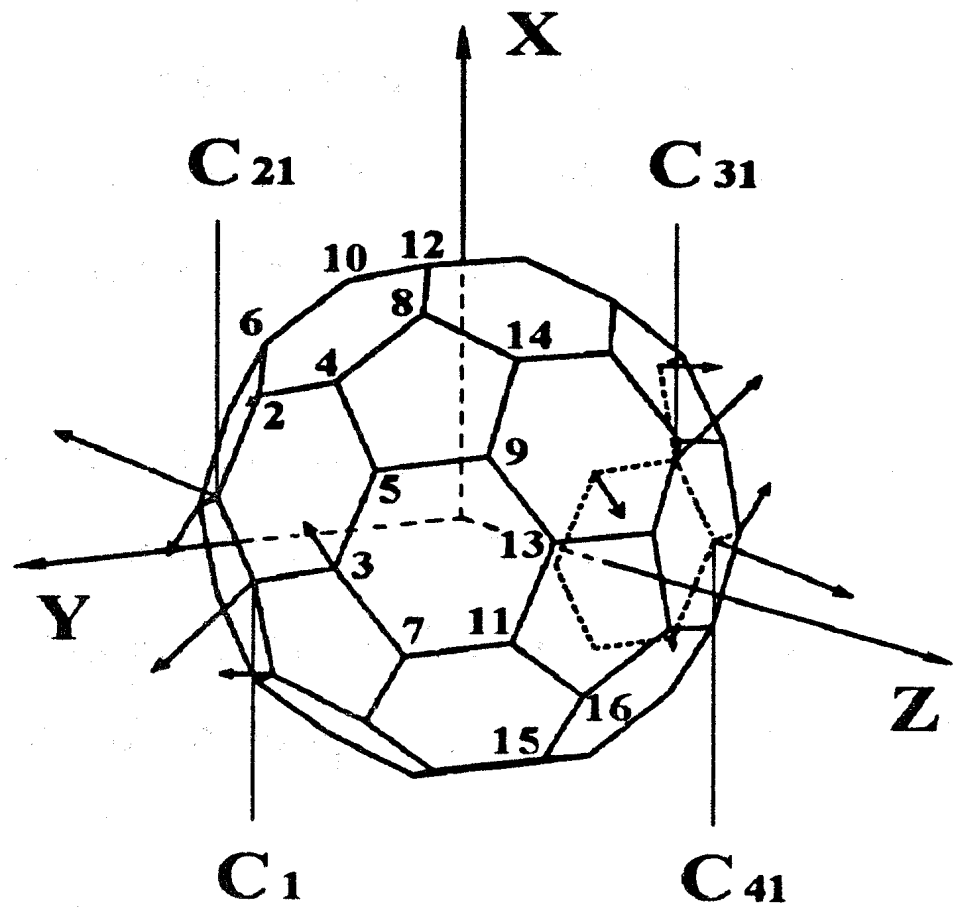

*Fig.*1. Deformational displacements of carbon atoms C1, C21, C31 and C41 of a C_{60} molecule in the *Pnnm* phase. The directions of atomic displacements are shown by arrows. The length of the arrow is increased five times in comparison with a real value [1] normalized to the size of the C_{60} molecule.

For those two atoms the basic functions are

$$\frac{1}{\sqrt{2}}[-u_z(i_1)+u_z(i_2)], \tag{4}$$

$$\frac{1}{\sqrt{2}}[u_x(i_1)-u_x(i_2)]. \tag{5}$$

In equations (1-5), $u_\alpha(i)$ is the unit displacement of an i-th atom in the crystalline α direction. Atom i_1 is connected with atom i_2 by the rotation at 180^0 about the two-fold symmetry axis parallel to the crystalline Y direction, i_3 and i_4 are defined from atoms i_1 and i_2, respectively, using inversion.

For example, the displacements of the carbon atoms C1, C21, C31 and C41 in Fig. 1 are written as:

$$\frac{1}{2}[u_y(C1)+u_y(C21)-u_y(C31)-u_y(C41)], \quad (6)$$

$$\frac{1}{2}[-u_z(C1)+u_z(C21)-u_z(C31)+u_z(C41)], \quad (7)$$

$$\frac{1}{2}[u_x(C1)-u_x(C21)+u_x(C31)-u_x(C41). \quad (8)$$

The basic function (6) describes the stretching of the C_{60} molecule in the polymeric direction and the functions (7) and (8) illustrate an increase in the covalent bond length between two carbon atoms, C1 and C21 (C31 and C41), belonging to the same molecule and participating in the formation of a polymeric bond. Such displacements are completely consistent with experimental observations [1].

It follows from the analysis of basic functions (1) - (5) that the number of phonon basic functions is equal to $3\times14 + 2\times2=46$, and the strained C_{60} molecule as a whole can experience slight rotation about a two-fold axis which coincides with the direction of the polymeric bond in the crystal (the rotation of the C_{60} molecule as a whole can be constructed from basic functions (2) - (5)). Thus, the strategy of fitting the experimental data should be the following. First, the orientation of an ideal molecule C_{60} in the low symmetry phase should be determined (as it is done, for example, in paper [1]). Then, positions of all carbon atoms in a strained C_{60} molecule are found (in paper [1] only most statistically significant displacements of three atoms, C1, C2 and C3, are determined). Finally it is necessary to subtract from them atomic displacements connected with rotation of the molecule as a whole. Only in such way it is possible to determine true displacements of carbon atoms connected with molecule strain.

In Fig. 2, the X-ray diffraction spectrum of powder RbC_{60} recorded at ambient temperature is shown. The fitting of the spectrum is made by the Rietveld method using a modernized MRIA program [4]. To describe the shape of diffraction peaks, the pseudo-Voigt function [5] is used. For the fitting of the diffraction spectrum in the phase *Pnmn* the following models are used: (A) 'freely rotating' C_{60} molecule; (B) ideal C_{60} molecule with a two-fold symmetry axis directed along the polymeric bond in a RbC_{60} crystal (lattice parameter in this direction is 9.100 Å) and rotation of the molecule around that direction at ~45^0; (C) the same as in (B) but with an additional fitting of the position of

the carbon atom most strongly displaced (atom C1 in paper [1]); (D) the same as in (C) but with an additional fitting of the positions of two carbon atoms (atoms C2 and C3 in paper [1]); (E) the same as in (B) but with fitting of coordinates of all independent carbon atoms in the molecule C_{60} (with some weak restrictions for chemical bond lengths).

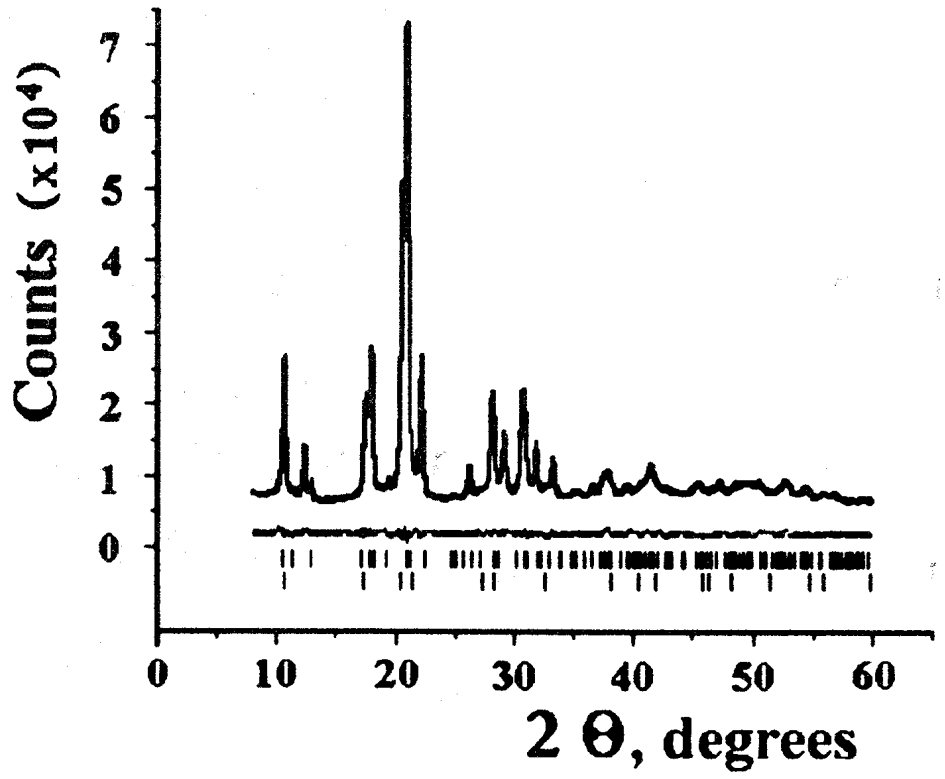

*Fig.*2. The X-ray diffraction spectrum of RbC_{60} (and ~13 % of pristine C_{60}) at 300 K.

The R-factors obtained for the models A-E are summarized in Table 1. The atomic coordinates determined in the E model for the X-ray data are shown in Table 2.

Table 1. The fitting results by different models for RbC_{60} at 300 K. $R_b = \Sigma \mid I_{obs} - I_{calc} \mid / \Sigma \mid I_{obs} - Background \mid$, $R_p = \Sigma \mid I_{obs} - I_{calc} \mid / \Sigma I_{obs}$. The sum is over all points in the spectrum.

Model*	χ^2	R_b, %	R_p, %
A	31.8	15.0	4.3
B	20.0	10.3	3.2
C	11.5	9.0	2.6
D	9.8	8.3	2.4
E	4.2	5.6	1.6

*- The A-E models are described in the text.

Table 2. The structural parameters of RbC_{60} obtained by Rietveld fitting of the X-ray spectrum at 300 K. The Debay-Waller factor of carbon is $U(C)_{iso}$=0.009 Å^2. For rubidium $U(Rb)_{iso}$=0.021(1) Å^2 and the occupancy factor is 0.90(1). The parameters of the crystalline lattice are a=14.217(4) Å, b=9.100(3) Å and c=10.113(3) Å.

Atom	Coordinates		
	X/a	Y/b	Z/c
C1	-0.040(1)	0.407(1)	0.052(1)
C2	0.122(1)	0.339(1)	-0.026(2)
C3	-0.006(2)	0.329(1)	0.181(1)
C4	0.153(1)	0.293(2)	0.097(2)
C5	0.087(1)	0.296(2)	0.206(1)
C6	0.155(1)	0.251(2)	-0.137(1)
C7	-0.077(1)	0.264(2)	0.249(2)
C8	0.209(1)	0.157(2)	0.108(1)
C9	0.103(1)	0.158(2)	0.290(2)
C10	0.217(1)	0.133(2)	-0.118(2)
C11	-0.073(1)	0.128(2)	0.320(1)
C12	0.240(1)	0.077(1)	0.002(2)
C13	0.023(1)	0.065(1)	0.329(1)
C14	0.172(1)	0.080(1)	0.221(1)
C15	-0.218(1)	0.000(1)	0.199(1)
C16	-0.131(2)	0.000(1)	0.283(2)

Table 3. The deformation displacements of carbon atoms determined in the framework of the model E.

Atom	ΔX, Å	ΔY, Å	ΔZ, Å
C1	-0.10	0.23	0.01
C2	-0.09	0.06	-0.01
C3	0.01	-0.03	-0.01
C4	-0.01	0.07	-0.04
C5	0.04	0.10	-0.01
C6	-0.09	-0.02	0.03
C7	0.13	0.10	0.12
C8	-0.05	0.01	-0.10
C9	0.03	0.02	0.02
C10	-0.01	0.04	0.07
C11	-0.03	-0.01	0.05
C12	-0.06	-0.03	-0.05
C13	-0.03	-0.13	-0.12
C14	-0.11	0.03	-0.12
C15	-0.23	0.00	-0.07
C16	-0.02	0.00	-0.17

In Table 3 deformation displacements (in Angstroms) of carbon atoms in the C_{60} molecule obtained by the proposed method are given. The rotation angle of the C_{60} molecule about a two-fold symmetry axis coinciding with the polymeric direction in the crystal is $47.0(3)^0$ (see also paper [2]).

Thus, on the basis of the symmetry theory [2,3] of fullerene molecule strain at the orientational phase transition in AC_{60} crystals it is possible to obtain deformational

displacements of carbon atoms in the C_{60} molecule in diffraction experiments. Double bond lengths of strained C_{60} molecule range from 1.37 Å to 1.55 Å and single bonds lie in the interval from 1.18 Å to 1.59 Å. The length of a broken double bond in the molecule is 1.55(2) Å and the distance between the carbon atoms of two nearest molecules is equal to 1.69(1) Å.

Acknowledgements. The reported work has been performed under the auspices of the State Scientific and Technical Program «Fullerenes and Atomic Clusters», N20002, with the support of INTAS-RFFI grant 95-0639.

References

1. P.W. Stephens, G. Bortel, G. Faigel, M. Tegze, A. Janossy, S. Pekker, G. Oszlanyi, L. Forro. *Nature*, **370**, 636 (1994).
2. V.L. Aksenov, Yu.A. Ossipyan, V.S. Shakhmatov. *JETP Letters*, **64**, 120 (1996).
3. V.L. Aksenov, Yu.A. Ossipyan, V.S. Shakhmatov. *JETP*, **86**, 591 (1998).
4. V.B. Zlokazov, V.V. Chernyshev. *Journ. Appl. Crystallogr.*, **25**, 447 (1992).
5. H. Toraya. *Journ. Appl. Crystallogr.* **19**, 440 (1986).

Received by Publishing Department
on February 10, 2000.

SUBJECT CATEGORIES
OF THE JINR PUBLICATIONS

Index	Subject
1.	High energy experimental physics
2.	High energy theoretical physics
3.	Low energy experimental physics
4.	Low energy theoretical physics
5.	Mathematics
6.	Nuclear spectroscopy and radiochemistry
7.	Heavy ion physics
8.	Cryogenics
9.	Accelerators
10.	Automatization of data processing
11.	Computing mathematics and technique
12.	Chemistry
13.	Experimental techniques and methods
14.	Solid state physics. Liquids
15.	Experimental physics of nuclear reactions at low energies
16.	Health physics. Shieldings
17.	Theory of condensed matter
18.	Applied researches
19.	Biophysics

Аксенов В.Л. и др. E14-2000-20
Деформация молекулы фуллерена в RbC_{60}

Методом дифракции рентгеновских лучей впервые определены деформационные смещения атомов углерода в молекуле C_{60} фуллерида RbC_{60} в фазе *Pnnm*. Длина полимерной связи между атомами углерода двух ближайших молекул C_{60} равна 1,69(1) Å, а угол вращения молекулы относительно направления полимерной связи — $47{,}0(3)^0$.

Работа выполнена в Лаборатории нейтронной физики им. И.М.Франка ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна, 2000

Aksenov V.L. et al. E14-2000-20
Fullerene Molecule Strain in RbC_{60}

Strain displacements of carbon atoms in a C_{60} molecule in the *Pnnm* phase of the RbC_{60} fulleride are first determined by X-ray diffraction. The measurements show that the polymeric bond length between carbon atoms of two nearest molecules C_{60} is equal to 1.69(1) Å, the rotation angle of the molecule about the polymeric direction is $47.0(3)^0$.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

Preprint of the Joint Institute for Nuclear Research. Dubna, 2000