ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ

Дубна

E17-95-426

V.L.Aksenov, Yu.A.Ossipyan*, V.S.Shakhmatov

PHASE TRANSITION IN AC_{60} ($A = K,Rb$) FULLERIDE CRYSTALS

Submitted to «Письма в ЖЭТФ»

---

*ISSP, RAS, Chernogolovka, Russia

1995

1. Introduction

From experimental investigations, e.g. [1], it is known that the phase transition (PT) from the high temperature face–centered cubic phase of the Fm$\bar{3}$m (O_h^5) symmetry to the low temperature polymeric-like phase of the Pnnm(D_{2h}^{12}) orthorhombic symmetry is observed in AC$_{60}$ (A=K,Rb) fulleride crystals.

The orthorhombic phase is characterized by shorter distances between the C$_{60}$ nearest molecules in one of the three crystalline directions which Fm$\bar{3}$m phase lattice translational vectors are directed in. This difference is on the order of 8% and is the result of a specific double bond between two of the nearest C$_{60}$ molecules. Inter–arrangement of the crystal cells of the above two phases is shown in Fig. 1.

The AC$_{60}$ compounds exhibit a number of very interesting physical properties. In the Fm$\bar{3}$m high temperature phase, these compounds demonstrate strong localization of electrons, while in the polymeric-like phase, the AC$_{60}$ compounds are quasi–one–dimensional metals. Moreover, at low temperatures the metallic state is unstable with respect to the formation of spin or charge density waves [2].

At present, investigations of the microscopic nature of PT to the orthorhombic phase are of great interest. In this connection a comparative analysis of the physical properties of PT in AC$_{60}$ and C$_{60}$ crystals is to be carried out. Note that at atmospheric pressure the orthorhombic phase is not observed in C$_{60}$ and the PT leads to a change in the symmetry from Fm$\bar{3}$m (O_h^5)→ Pa$\bar{3}$. The PT temperatures in AC$_{60}$ crystals are higher than in C$_{60}$. For example in RbC$_{60}$, T_c ~380 K and in C$_{60}$ $T_c \sim 260$ K.

In the present paper, the Landau phenomenological theory of PT to the orthorhombic phase in AC$_{60}$ (A=K,Rb) crystals is developed on the basis of symmetry analysis. The microscopic nature of the PT is discussed. By analysis of the interactions between order parameters (OP), probable PT connected changes in the subsystem of metal atoms are investigated.

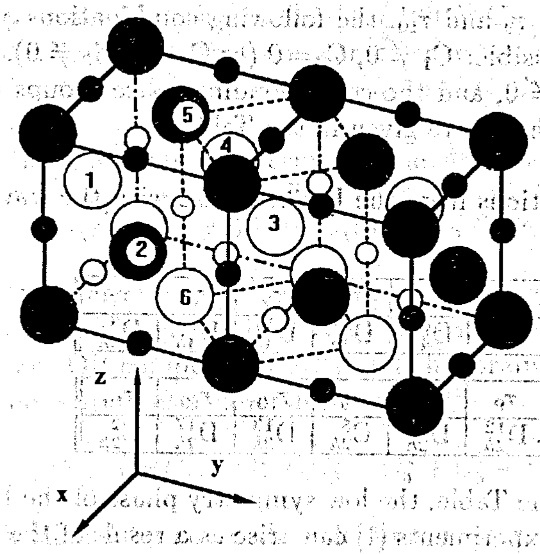

Fig. 1. Inter–arrangement of crystal cells in the Fm$\bar{3}$m and Pnnm phases. Large circles refer to C$_{60}$ molecules, smaller circles refer to metal atoms. Black circles indicate metal atoms and C$_{60}$ molecules situated on visible faces of two face–centered cubic cells in the Fm$\bar{3}$m phase. The Pnnm phase crystal cell (for the PT with the wave vector (001)) is shown by dashed lines. The C$_{60}$ molecules creating the octahedral environment for the metal atom are denoted by the numbers 1,...,6.

2. Symmetry analysis

According to experimental data [1], the Fm$\bar{3}$m → Pnnm PT leads to a doubling of the primitive cell volume in the Fm$\bar{3}$m high temperature phase. Hence, this PT is connected with one of the following wave vectors on the Brillouin zone boundary: (100), (010) or (001). These wave vectors form a single wave vector star, k_{10}, in the Fm$\bar{3}$m phase [3].

To be specific, let us consider a PT with the wave vector (001), i.e. a PT to one of three ray domains (see Table). In one–dimensional irreducible representations (IR), $\tau_1,...,\tau_8$, OP has one component and in two–dimensional IR, τ_9 and τ_{10}, the following combinations of the OP components are possible: $C_1 \neq 0$, $C_2 = 0$ (or $C_1 = 0$, $C_2 \neq 0$), $C_1 = C_2 \neq 0$ and $C_1 \neq C_2 \neq 0$, and the corresponding space groups (SG) of the low symmetry phases are given in the Table.

Table. Phase transitions from the Fm$\bar{3}$m phase with the wave vector (001).

IR	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_7
SG	D^1_{4h}	D^4_{4h}	D^6_{4h}	D^7_{4h}	D^{14}_{4h}	D^{15}_{4h}	D^9_{4h}

IR	τ_8	τ_9	τ_9	τ_9	τ_{10}	τ_{10}	τ_{10}
SG	D^{12}_{4h}	D^{12}_{2h}	D^{18}_{2h}	C^5_{2h}	D^{13}_{2h}	D^{17}_{2h}	C^2_{2h}

As it is seen from the Table, the low symmetry phase of the Pnnm (D^{12}_{2h}) SG observed in experiments [1] can arise as a result of the $C_1 \neq 0$, $C_2 = 0$ (or $C_1 = 0$, $C_2 \neq 0$) type condensation for OP of the τ_9 symmetry. Note that OP of the τ_9 symmetry [4] and another type of condensation, namely the $C_1 = C_2 = C_3 = C_4 = C_5 = C_6 \neq 0$ type, leads to the Fm$\bar{3}$m → Pa$\bar{3}$ symmetry change in the C_{60} crystal.

Thus, PT in the C_{60} crystal is connected with all three rays of the $\mathbf{k}_{10}$ wave vector star and PT in AC_{60} goes along one of the three rays of the same wave vector star.

The phenomenological theory of PT in C_{60} crystals was developed in a number of papers (see, for example, [5,6]). The free energy expansion can be written as

$$F_1 = F_c + F_{ce} + F_e. \tag{1}$$

The F_c term describes the orientational degrees of freedom of C_{60} molecules:

$$\begin{aligned} F_c = \; & A \sum_i C_i^2 + B(C_1C_3C_6 + C_1C_4C_5 + C_2C_3C_5 + C_2C_4C_6) + \\ & D_1 \; (\sum_i C_i^2)^2 + D_2 \sum_i C_i^4 + \ldots, \end{aligned} \tag{2}$$

where $A = \alpha(T - T_c)$, $\alpha > 0$, B, D_i are the phenomenological constants in the PT theory, $\{C_i\}$, i=1,...,6 – is the six–fold OP. The C_1 and C_2 components have the wave vector (001); C_3, C_4 – (100) and C_5, C_6 – (010). Note here, that one can rewrite the cubic terms in (2) using a unitary transformation in the form $C'_1C'_3C'_5 + C'_2C'_4C'_6$ presented in [5].

For cubic symmetry crystals, the elastic energy has the form [7]:

$$F_e = \lambda_{11}(e_1^2 + e_2^2 + e_3^2) + \lambda_{12}(e_1e_2 + e_1e_3 + e_2e_3) + \lambda_{44}(e_4^2 + e_5^2 + e_6^2), \tag{3}$$

where λ_{ij} are the elastic constants and e_i are the spontaneous strain tensor components, all in Voigt notations. Interaction between the primary OP components $\{C_i\}$ and the strain tensor components $\{e_i\}$ can be written as follows [6]:

$$F_{ce} = \gamma(C_1^2 + C_2^2 + C_3^2 + C_4^2 + C_5^2 + C_6^2)(e_1 + e_2 + e_3). \tag{4}$$

It should be noted that the above interaction (4) is sufficient for the description of spontaneous crystal cell strains in C_{60} following PT with the $C_1 = C_2 = C_3 = C_4 = C_5 = C_6 \neq 0$ condensation, but is completely insufficient for describing of PT in AC_{60} having the $C_1 \neq 0$, $C_2 = 0$ (or $C_2 \neq 0$, $C_1 = 0$), $C_3 = C_4 = C_5 = C_6 = 0$ condensation. In the latter case, additional interactions between OP components and spontaneous strain tensor components, which transform according to the same IR, take place.

So the two quantities, $\sqrt{3}(C_3^2 + C_4^2 - C_5^2 - C_6^2)$ and $2C_1^2 + 2C_2^2 - C_3^2 - C_4^2 - C_5^2 - C_6^2$, transform according to the two–dimensional E_g IR with the wave vector $\mathbf{k}$=0:

$$E_g \sim \begin{array}{l} \sqrt{3}(C_3^2 + C_4^2 - C_5^2 - C_6^2) \\ 2C_1^2 + 2C_2^2 - C_3^2 - C_4^2 - C_5^2 - C_6^2, \end{array} \tag{5}$$

and the three quantities, $C_1^2 - C_2^2$, $C_3^2 - C_4^2$, $C_5^2 - C_6^2$, transform according to the F_{2g} IR also with the wave vector $\mathbf{k}$=0:

$$F_{2g} \sim \begin{array}{l} C_1^2 - C_2^2 \\ C_3^2 - C_4^2 \\ C_5^2 - C_6^2. \end{array} \tag{6}$$

In a similar manner, the two quantities, $\sqrt{3}(e_1 - e_2)$, $e_1 + e_2 - 2e_3$, transform according to the E_g IR and the three quantities, e_6, e_4, e_5, transform according to the F_{2g} IR. Note here that the quantities e_6, e_4 and e_5 can be rewriten in full notation as e_{xy}, e_{yz} and e_{xz}, respectively. Thus, one obtains the following additional interactions:

$$\begin{aligned} F'_{ce} = \quad & \gamma'_1\,[3(C_3^2 + C_4^2 - C_5^2 - C_6^2)(e_1 - e_2) + \\ & (2C_1^2 + 2C_2^2 - C_3^2 - C_4^2 - C_5^2 - C_6^2)(e_1 + e_2 - 2e_3)] + \\ & \gamma'_2\,[(C_1^2 - C_2^2)e_6 + (C_3^2 - C_4^2)e_4 + (C_5^2 - C_6^2)e_5]. \qquad (7) \end{aligned}$$

Note that the above mentioned unitary transformation of OP components $\{C_i\}$ will lead to substitution of only $C_1^2 - C_2^2$, $C_3^2 - C_4^2$, $C_5^2 - C_6^2$, which transform according to the F_{2g} IR by C_1C_2, C_3C_4, C_5C_6.

Interactions (4) and (7) allow us to give a complete description of spontaneous crystal cell strains following PT with the $C_1 \neq 0$, $C_2 = C_3 = C_4 = C_5 = C_6 = 0$ condensation of OP components.

In addition to a different type of OP condensation, PT in AC_{60} fullerides differ from the PT in C_{60} by the presence of a subsystem of alkali metal atoms in AC_{60}. This subsystem of alkali metal atoms has a number of degrees of freedom which can have the E_g, F_{2g} (wave vector k=0) or τ_9 (k_{10} wave vector star) symmetry.

Let us denote the secondary OP with the degrees of freedom of the E_g, F_{2g} and τ_9 symmetries as $\{\theta_i\}$, i=1,2, $\{\eta_i\}$, i=1,2,3 and $\{\xi_i\}$, i=1,...,6, respectively. In full analogy with interactions (7), one can write

$$\begin{aligned} F_{c\theta,c\eta} = \quad & \beta_1\,[\sqrt{3}(C_3^2 + C_4^2 - C_5^2 - C_6^2)\theta_1 + \\ & (2C_1^2 + 2C_2^2 - C_3^2 - C_4^2 - C_5^2 - C_6^2)\theta_2] + \\ & \beta_2\,[(C_1^2 - C_2^2)\eta_1 + (C_3^2 - C_4^2)\eta_2 + (C_5^2 - C_6^2)\eta_3]. \qquad (8) \end{aligned}$$

Secondary OP $\{\xi_i\}$ and primary OP $\{C_i\}$ have the same symmetry and therefore interact linearly with each other:

$$F_{c\xi} = \beta_3(C_1\xi_1 + \dots + C_6\xi_6). \qquad (9)$$

By adding quadratic terms to all of the introduced secondary OP defined above:

$$F_{\theta,\eta,\xi} = \delta_1(\theta_1^2 + \theta_2^2) + \delta_2(\eta_1^2 + \eta_2^2 + \eta_3^2) + \delta_3(\xi_1^2 + \dots + \xi_6^2), \qquad (10)$$

we obtain the free energy expansion which describes the PT in AC_{60} crystals as:

$$F = F_1 + F'_{ce} + F_{c\xi} + F_{c\theta,c\eta} + F_{\theta,\eta,\xi}. \qquad (11)$$

3. Subsystem of alkali metal atoms

Let us discuss PT in AC_{60} crystals. In analogy with the PT in the C_{60} crystal, one can assume that the primary OP $\{C_i\}$ describes the orientational ordering of rotational axes in C_{60} molecules. Secondary OP $\{\theta_i\}$, $\{\eta_i\}$ and $\{\xi_i\}$ describe changes in the metal atom subsystem.

In the case primary OP condensation of the type $C_1 \neq 0$, $C_2 = C_3 = C_4 = C_5 = C_6 = 0$, interactions (4),(7-10) lead to condensation of the following secondary OP $\xi_1 \neq 0$, $\theta_2 \neq 0$, $\eta_1 \neq 0$ as well as different spontaneous strain tensor components.

Let us consider crystal cell strains. Similar to the PT in C_{60}, interaction (4) leads to the appearance of non-zero components $e_1 = e_2 = e_3 \neq 0$, which do not affect the cubic symmetry of the crystal lattice. Then, as is seen from (7), additional deformation of the type $e_1 = e_2 = -2e_3 \neq 0$ and $e_6 \neq 0$ arises. The former reduces the crystal lattice symmetry to tetragonal and the latter shear deformation $e_6 \neq 0$ establishes the orthorhombic symmetry of the crystal lattice as it should be for the primary condensation OP leading to the PT from $Fm\bar{3}m\ (O_h^5) \rightarrow Pnnm\ (D_{2h}^{12})$. Note that namely the shear deformation component $e_6 \neq 0$ leads to strong stress type crystal cell deformation in the [110] or [–110] directions and correspondingly to shorter distances between the nearest C_{60} molecules in these crystal directions.

Remember that symmetry analysis was made for the wave vector (001). For the wave vector (100), shorter distances between the nearest molecules of C_{60} take place in the directions [011] or [0–11], and for the (010) vector in the [101] or [–101] directions.

So, the free energy expansion (11) describes the experimental data [1], namely, the symmetry of the low temperature phase and crystal cell strains.

Below we consider changes in the subsystem of alkali metal atoms connected with PT. At present, experimental data about the behavior of the subsystem of metal atoms at PT are absent. Therefore, all conclusions about structural changes following PT are the model predictions which should be verified in further diffraction experiments.

From experimental data [1] it is known that a metal atom is in the octahedral environment of C_{60} molecules (see Fig.2a). The small value of the alkali atom radius with respect to the size of the octahedron composed of large C_{60} molecules, as well as strong anisotropic Debye-Waller factors for metal atoms [1], allow an assumption that the true position of the alkali atom is different from the central position shown in Fig. 2a. In the general case, according to [3], in the $Fm\bar{3}m$ phase the following positions for the octahedral environment are possible: the central position **1b** with the (111) coordinate and local symmetry O_h; the six-fold position **6e** with the characteristic coordinate (00z) and C_{4v} symmetry, as well as the **8f** position, (xxx), C_{3v}; **12i**, (xx1), C_{2v}; **24j**, (xy0), C_s and **24k**, (xxz), C_s.

In the **1b** position (Fig.2a) the metal atom can only oscillate relative to its equilibrium position. Such displacements with the wave vector **k**=0 transform in accordance with the three dimensional F_{1u} IR and, therefore, can not be related to secondary OR of the E_g or F_{2g} symmetries. The same displacements with the wave vector (001) transform in accordance with the τ_4 and τ_{10} IR and also can not be described by the $\xi_1 \neq 0$ OP which has the τ_9 symmetry. As a consequence, a metal atom in the octahedral center position experiences no structural changes following PT.

If a metal atom occupies a noncentral position, then partial ordering over the positions indicated in Figs. 2b, c), and d) takes place following PT. For the **6e** position the single secondary OP $\theta_2 \neq 0$ of the E_g symmetry describes partial ordering of the metal atoms either on the horizontal plane (dark circles) or over two positions situated above or below the plane (shaded circles). For the **8f** and **12i** positions (Fig. 2c and d)) one has $\eta_1 \neq 0$, $\xi_1 \neq 0$ and $\theta_2 \neq 0$, $\eta_1 \neq 0$, $\xi_1 \neq 0$, respectively. The occupied positions are shown by dark circles. The lower symmetry positions, **24j** and **24k**, arise from the **12i** and **8f** positions, respectively. Ordering of metal atoms over these positions is described by three secondary OP and are not considered in the present paper.

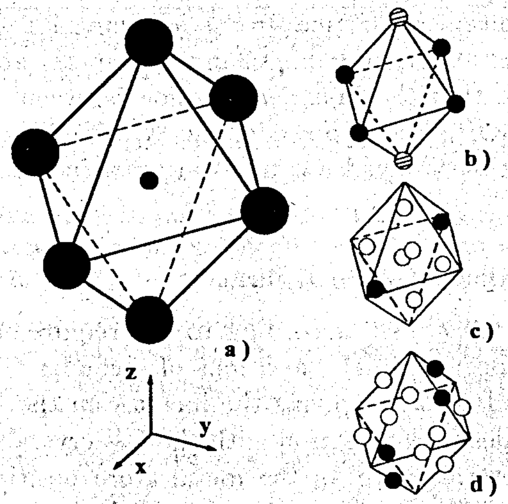

Fig.2.
Possible types of positions for metal atoms (smaller circles) in the octahedral environment of C_{60} molecules (large circles): a) The central position **1b**; b), c) and d) are the **6e**, **8f** and **12i** positions, respectively.

One can assume that at a further decrease in the temperature, complete ordering of metal atoms will take place and such PT will lead to a lower crystal symmetry which will be fully determined by the type of positions. For instance, one of the three possible variants of complete ordering of the metal atoms for the position **8f** with the wave vector **k**=0 leads to C^7_{2v} SG.

Note here that PT to the glass-like phase is observed in the C_{60} crystal at decreasing temperature. Hence, the above situation of complete ordering of the metal atoms will probably take place in the case when the PT temperature to the glass-like phase is below the ordering type PT temperature.

4. Results

In conclusion, one can note that the free energy expansion (11) obtained on the basis of symmetry analysis describes the PT to the orthorhombic phase in AC_{60} fullerides. In this expansion the primary OP connected with the orientational degrees of freedom of C_{60} molecules and the secondary OP connected with different degrees of freedom of the metal atoms interact with each other and the lattice strains. The obtained free energy representation describes the experimental observations of spontaneous lattice strains following PT and also permits the predictions about probable changes in metal atom positions to be made. Note that the linear interaction between primary OP C_i and secondary OP ξ_i takes place for the **8f**, **12i**, **24j** and **24k** positions. This interaction always leads to an increase in the PT temperature [8]:

$$T_c(AC_{60}) = T_c(C_{60}) + \beta_3^2/4\alpha\delta_3, \tag{12}$$

where $\alpha > 0$ (see (2)) and all $\delta_i > 0$ according to the requirement of crystal stability with respect to small variations of secondary OP (see (10)). So, the presented theory explains the increase in the PT temperature in AC_{60} fullerides in comparison with the C_{60} crystal.

For the experimental determination of the metal atom positions in AC_{60} we plan to perform diffraction measurements with X–rays or neutrons of the type reported in paper [1] but using the symmetry analysis made in this paper.

References

1. P.W. Stephens, G. Bortel, G. Faigel et al., *Nature*, **370**, 636 (1994).
2. O. Chauvet, G. Oszlanyi, L. Forro et al., *Phys. Rev. Lett.*, **72**, 2721 (1994).
3. O.V. Kovalev *Irreducible and induced representations and co–representations of Fedorov groups*, Moscow, 1986.
4. K.H. Michel, *Z. Phys.*, **B**, **88**, 71 (1992).
5. K. Rapcewicz, J. Przystawa, *Phys. Rev.*, **B**, **49**, 13193 (1994).
6. D. Lamoen, K.H. Michel, *Phys. Rev.*, **B**, **48**, 807 (1993).
7. J. Nye *Physical properties of crystals*, Moscow, 1967.
8. Yu.A. Izyumov, V.N. Syromiatnikov *Phase transitions and symmetry of crystals*, Moscow, 1984.

Received by Publishing Department
on October 12, 1995