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ORIENTATIONAL STATES OF A  $C_{60}$  MOLECULE  
IN CRYSTALS

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Ориентационные состояния молекулы  $C_{60}$  в кристаллах

Исследована локальная симметрия ориентационных состояний молекулы  $C_{60}$  в кристаллах. Показано, что различные ориентационные фазовые переходы связаны в разных кристаллах с разными ориентационными орбитами. Предложена модель ориентационных фазовых переходов, основанная на последовательности ориентационных состояний разной симметрии. Обнаружено повышение как локальной симметрии молекулы  $C_{60}$ , так и симметрии ее внутренних колебаний при понижении пространственной симметрии кристалла при фазовом переходе. Этот эффект имеет общий характер и может наблюдаться при ориентационных фазовых переходах типа порядок—беспорядок с волновым вектором на границе зоны Бриллюэна. Рассмотрены возможные проявления предсказанного эффекта в различных экспериментах.

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Orientational States of a  $C_{60}$  Molecule in Crystals

The local symmetry of the orientational states of a  $C_{60}$  molecule in crystals is investigated. It is shown that in different crystals different orientational phase transitions are connected with different orientational orbits. The model of orientational phase transitions based on a sequence of orientational states of different symmetry is proposed. It is discovered that the local symmetry and the symmetry of internal vibrations of a  $C_{60}$  molecule increase as the spatial symmetry of a crystal decreases at phase transition. This effect has the general character and may be observed following orientational phase transitions of the order-disorder type with wave vector at the boundary of the Brillouin zone. Possible manifestations of the predicted effect in different experiments are discussed.

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

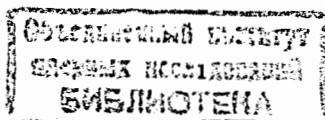
## 1. Introduction

It is known that phase transitions in fullerene crystals result in a change of the orientational state of a  $C_{60}$  molecule. Experimental investigations of a pure  $C_{60}$  crystal (fullerite) [1] show that  $C_{60}$  molecules in the high-symmetry phase  $Fm\bar{3}m$  experience anisotropic and retarded rotation and at the phase transition  $Fm\bar{3}m \rightarrow Pa\bar{3}$  the rotation disappears and orientational ordering of  $C_{60}$  molecules takes place. In  $AC_{60}$  crystals (fullerides), where  $A=K, Rb$ , a more complicated phase transition  $Fm\bar{3}m \rightarrow Pnmm$  occurs and in the low-symmetry phase  $Pnmm$  orientational ordering of molecules is accompanied with molecule strains. These two effects lead to formation of covalent bonds between neighboring  $C_{60}$  molecules [2]. In both of these cases the order parameter of the phase transition connects the averaged orientational states of  $C_{60}$  molecules in the high-symmetry and low-symmetry phases and describes orientational ordering of the molecules.

At present, there does not exist a unified theory of changes of the orientational states of a  $C_{60}$  molecule. As a result, two methods are used to describe phase transitions in fullerenes, the continuous and the discrete methods. Each describes adequately the orientational states of a  $C_{60}$  molecule in only one phase. The continuous method was used to describe rotating  $C_{60}$  molecules in the phase  $Fm\bar{3}m$ . The method uses an expansion of the averaged anisotropic distribution of  $C_{60}$  molecule orientations in symmetrized spherical functions transforming in accordance with irreducible representations of icosahedral ( $Y_h$ ) or cubic ( $O_h$ ) point groups [1]. In this approach it is difficult to describe the particular selected orientation of a  $C_{60}$  molecule in the low-symmetry phase of a crystal as well as the molecule strain at phase transition in  $AC_{60}$  fullerides. In the discrete approach to describe the orientational phase transition in fullerites, discrete orientational states of a rotating  $C_{60}$  molecule are used [3] (see also [1]). In this case, the orientational state of a  $C_{60}$  molecule in the low-symmetry phase is described exactly and the state of a rotating molecule in the high-symmetry phase is described approximately by a set of discrete orientational states. Since the discrete method describes exactly the orientational states of a  $C_{60}$  molecule in the low-symmetry phase of a crystal, it is obvious that other physical properties of the low-symmetry phase connected with the orientational phase transition are also described adequately by this method. For example, in [4], the strain of a  $C_{60}$  molecule at phase transition in a  $AC_{60}$  fulleride crystal is described with the help of the generalization of the discrete method.

In this paper, it is shown that some physical properties of the high-symmetry phase can be also described by the discrete method. This is possible due to the fact that different orientational states of a  $C_{60}$  molecule in a crystal have different local symmetry. Hence it follows that the physical phenomena observed in the high-symmetry phase and connected with definite discrete orientational states can be classified with respect to the orientational state symmetry.

In Sec. 2, all orientational states of a  $C_{60}$  molecule of different local symmetry in the phase  $Fm\bar{3}m$  are constructed. On the basis of the orientational states the phase transition is discussed (Sec. 3) and the atomic density distributions of a rotating  $C_{60}$  molecule are built (Sec. 4). The local symmetry and the symmetry of internal vibrations of a  $C_{60}$  molecule in a crystal are investigated in Sec. 5. In Sec. 6, we discuss possible experimental verifications of



the predicted orientational states by the neutron and X-ray diffraction methods. The effect of increasing the symmetry of internal vibrations of a  $C_{60}$  molecule at phase transition by investigating the scattering of light will be also discussed.

## 2. The symmetry of the orientational states of a $C_{60}$ molecule

To determine the type of the orientational states, let us investigate the orientations of  $C_{60}$  molecules of icosahedric symmetry occupying a position in the crystalline lattice of cubic symmetry. The molecules  $C_{60}$  have the point symmetry group  $Y_h$  which, as is shown in Table 1, has 6 five-fold symmetry axes ( $C_5$ ), 10 three-fold symmetry axes ( $C_3$ ), 15 two-fold ( $C_2$ ) symmetry axes, and the inversion ( $I$ ). In the crystalline lattice,  $C_{60}$  molecules occupy the positions with the local symmetry  $O_h$ . The point group  $O_h$  has 3 four-fold symmetry axes ( $C_4$ ), 4 three-fold axes, 6 two-fold, and inversion.

A comparison of the sets of symmetry axes for the groups  $O_h$  and  $Y_h$  shows that to obtain one of the four-fold symmetry axes of the cubic crystal, the  $C_{60}$  molecule must occupy two discrete orientational states, if a two-fold symmetry axis of the  $C_{60}$  molecule is directed along one of three  $\langle 100 \rangle$  directions, or four discrete states, if the  $C_{60}$  molecule has any other orientation. If in a crystal the two-fold symmetry axis of the  $C_{60}$  molecule is oriented along one of three  $\langle 100 \rangle$  directions, the  $C_{60}$  molecule can be rotated about this two-fold symmetry axis so that its three-fold symmetry axes would be oriented along the  $\langle 111 \rangle$  crystal directions. This provides most symmetric occupation by  $C_{60}$  molecules of positions in a cubic crystalline lattice (see Fig. 1a) and results in two so-called 'standard' orientations interrelated by  $90^\circ$  rotation about the axis coinciding with any direction of the  $\langle 100 \rangle$  type. The  $C_{60}$  molecule in the crystalline lattice of the phase  $Fm\bar{3}m$  which occupies a position with the symmetry  $O_h$  and has the standard orientation has the local symmetry  $T_h = O_h \cap Y_h$  [5]. This is realized in  $A_3C_{60}$  crystals, where the  $C_{60}$  molecules are statically disordered over two 'standard' orientations [6].

In what follows, we discuss the situation when only one of three-fold symmetry axes of a  $C_{60}$  molecule coincides with one of  $\langle 111 \rangle$  directions in a cubic crystal (see Fig. 1b). Accounting for the symmetry with respect to inversion we obtain that six elements of symmetry that form the point group  $S_6 = (E, C_3, C_3^2) \times (E, I)$ , where  $E$  is the identical symmetry element, are the common elements of the  $C_{60}$  molecule and the point group  $O_h$ . In this case, the local symmetry group of a molecule is the group  $S_6$ . Since the point group  $O_h$  has 48 different symmetry elements the number of different orientational states of  $C_{60}$  molecules for such occupation of a position in the cubic lattice is  $8 = 48/6$ . These eight orientational states were used to describe the phase transition in  $C_{60}$  fullerenes [3].

Table 1. The symmetry elements of a free  $C_{60}$  molecule and the position in the crystalline lattice of the cubic phase  $Fm\bar{3}m$  occupied by  $C_{60}$  molecule.

Symmetry elements	$C_5$	$C_4$	$C_3$	$C_2$	$I$
$C_{60}$ molecule	6	-	10	15	1
Position in the lattice with symmetry $O_h$	-	3	4	6	1

If in a cubic crystal the two-fold symmetry axis of a  $C_{60}$  molecule is aligned with the  $[110]$  crystalline direction (see Fig. 1c), the common symmetry elements are  $(E, C_2) \times (E, I)$  and consequently, the number of different orientational states of  $C_{60}$  molecules is  $12 = 48/4$ . These 12 orientational states of  $C_{60}$  molecules are used to describe the phase transition in  $AC_{60}$  fullerenes [4]. The local symmetry group of a  $C_{60}$  molecule is the group  $C_{2h}$ . Note that if in a cubic crystal the two-fold symmetry axis of a  $C_{60}$  molecule is oriented along the  $[001]$  direction and the three-fold symmetry axes do not coincide with the  $\langle 111 \rangle$  directions, a different 12-fold orientational basis arises (see Fig. 1d). Below, we denote these two orientational bases by 12(a) and 12(b), respectively.

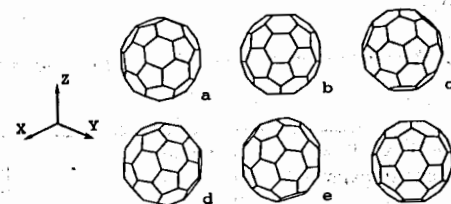


Fig. 1. The initial orientations of a  $C_{60}$  molecule for different orientational bases. a), b), c), d), e), and f) are one of the orientational states of a  $C_{60}$  molecule for the 2-, 8-, 12(a)-, 12(b)-, 24-, or the 6-fold bases.

If none of the symmetry axes of a  $C_{60}$  molecule coincides with the corresponding symmetric direction in the crystal, the only common elements of symmetry are  $(E, I)$  and consequently, the number of different orientational states of the  $C_{60}$  molecule is  $24 = 48/2$  and the local symmetry of the  $C_{60}$  molecule is determined by the group  $I$  (see Fig. 1e).

The orientational states belonging to one basis have the same continuous degrees of freedom. For example, an orientational state of the 8-fold basis may admit an arbitrary angle of rotation about the three-fold symmetry axis. It is analogous for the 12-fold basis but in this case, the arbitrary rotation can be accomplished about the two-fold symmetry axis. The 24-fold basis admits two independent rotations. Note that for some angle (angles) of rotation, additional degeneration of the orientational states of  $C_{60}$  molecules may take place. This happens due to the fact that for a particular orientation, additional coincidence of the symmetry axes of  $C_{60}$  molecules and symmetric directions of a crystal may take place. For the 8-fold basis, for example, the two-fold symmetry axes of the  $C_{60}$  molecule may coincide with the  $\langle 100 \rangle$  crystalline directions for a particular angle of rotation about the three-fold symmetry axis of the  $C_{60}$  molecule. This leads to degeneration of states of the orientational basis and as a result, of 8 states only two 'standard' orientations remain. For two 12-fold orientational bases, in the situation when the two-fold symmetry axis of a  $C_{60}$  molecule coincides with the  $\langle 100 \rangle$  direction for the basis 12(a) or the  $\langle 110 \rangle$  direction for the basis 12(b), the number of independent orientational states decreases to 6 (see Fig. 1f). In this case,

the local symmetry of the orientational state is described by the group  $D_{2h}$ . It is apparent that the enumerated bases can be obtained from the 24-fold basis as well. Also, note that the orientational states of 2- and 6-fold bases are the most symmetric states and, in contrast to the orientational states of other bases, do not have rotational degrees of freedom.

The orientational states belonging to one basis transform into one another under the action of the symmetry elements of the group  $Fm\bar{3}m$  and in this case, form (in the language of the group theory, see, e.g., [7]) an orbit.

In Table 2, different types of orientational orbits are summarized with an indication of compounds (fullerite  $C_{60}$  or fulleride  $AC_{60}$ ) for which these orbits are used to describe the phase transition. Let us note that in  $A_3C_{60}$  fullerides the orientational phase transition does not take place and in the phase  $Fm\bar{3}m$  static disordering of  $C_{60}$  molecules over two 'standard' orientations is observed [6].

Table 2. Different types of the orientational orbits of a  $C_{60}$  molecule in the phase  $Fm\bar{3}m$ .

Number of orientational states in orbit	Local symmetry of orientational state	Crystal	Comments
2	$T_h$	$A_3C_{60}$	static disordering
6	$D_{2h}$		
8	$S_6$	$C_{60}$	dynamic disordering
12 (a)	$C_{2h}$	$AC_{60}$	dynamic disordering
12 (b)	$C_{2h}$		
24	I		

### 3. The orientational phase transition

Diffraction investigations of  $C_{60}$  fullerites in the phase  $Fm\bar{3}m$  [1] show that rotating  $C_{60}$  molecules have an anisotropic orientational distribution in the crystal. Hence it follows that the orientational states of  $C_{60}$  are not equally probable. In the previous Section it is shown that it is possible to combine orientational states into orientational orbits which differ in local symmetry (see Table 2). The orientational states of one orientational orbit are physically equivalent. Therefore,  $C_{60}$  molecules occupy them with equal probabilities. So, to explain the anisotropic distribution of molecular orientations it is necessary to assume that the states of different orbits are occupied by a rotating  $C_{60}$  molecule with different probabilities determined by

$$P_n = \exp(-V_n/kT) / \sum_m \exp(-V_m/kT), \quad (1)$$

where  $k$  - is the Boltzmann constant,  $V_n$  - is the potential energy of the state  $n$  of the orientational orbit, and the summation runs over all orientational states of all orientational orbits.

Thus, the following model of the orientational phase transition in fullerene crystals can be suggested. At high temperatures ( $T \gg T_c$ ), a rotating  $C_{60}$  molecule occupies all orientational states from all orientational orbits. At temperatures close to the phase transition temperature ( $T > T_c$ ), a rotating  $C_{60}$  molecule occupies, most of the time, the states of one orientational orbit, i.e., of the orbit that corresponds to a particular orientational potential of the  $C_{60}$  molecule in a particular crystal. At phase transition 'freezing' of an orbit takes place and the molecule occupies one of the orientational states of this orbit.

Comparing orientational phase transitions and structural phase transitions of the displacement type we can make the following conclusions. The set of states in all orientational orbits is an analogue of the possible displacements of all atoms in a crystalline cell. The particular orientational orbit can be understood as an analogue of the displacements of only atoms connected with the soft mode of the structural transition. Thus, different orientational orbits are the microscopic realizations of the order parameter of different orientational phase transitions.

Table 3 gives the orientational orbits and states necessary for the description of orientational phase transitions in  $C_{60}$  fullerites and  $AC_{60}$  fullerides.

Table 3. The orientational states of a  $C_{60}$  molecule in different phases of  $C_{60}$  and  $AC_{60}$  crystals.

Crystal	High-symmetry phase		Low-symmetry phase
	$T \gg T_c$	$T > T_c$	$T < T_c$
fullerite $C_{60}$	{2,6,8,...}	{8}	8
fulleride $AC_{60}$	{2,6,8,...}	{12}	12

Table 3 illustrates the orientational transition. In the  $C_{60}$  ( $AC_{60}$ ) crystal at high temperatures rotating  $C_{60}$  molecules occupy all orientational states from all orientational orbits (2-fold, 6-fold orbits, etc.). In the vicinity of the phase transition ( $T > T_c$ ) the molecules occupy, most of the time, the states from 8- (12-) fold orbits. In the low-symmetry phase, orientational ordering of  $C_{60}$  molecules in one of the states of 8- (12-) fold orbits takes place.

### 4. The atomic density distributions of rotating $C_{60}$ molecules

In the previous Section, it is shown that in the vicinity of the phase transition temperature rotating  $C_{60}$  molecules in the phase  $Fm\bar{3}m$  occupy, most of the time, the orientational states of one orbit and therefore the anisotropic distribution of orientations of a  $C_{60}$  molecule in a crystal is determined by the states of one orbit. Let us investigate a certain orientational state. Then, for this (first) orientation  $\psi_1$  the atomic density on the surface of a  $C_{60}$  molecule at the point determined by the angles  $\Omega = (\theta, \varphi)$  ( $\theta$  and  $\varphi$  are the polar angles in the coordinate system shown in Fig. 1) is

$$\rho_1(\Omega) = \sum_n \delta_1(\Omega - \Omega_n), \quad (2)$$

where  $\delta$  - is the Dirac  $\delta$ -function and the summation runs over 60 carbon atoms in the molecule. Accounting for the remaining orientational states in the selected orbit and modeling

the thermal motion of a  $C_{60}$  molecule according to the normal distribution law with the rotational angle dispersion  $\sigma$  it is possible to calculate the mean anisotropy of the atomic density  $\langle \rho(\Omega) \rangle$

$$\begin{aligned} \langle \rho(\Omega) \rangle &= C \int dS' \exp[-(\Omega - \Omega')^2 / 2\sigma^2] \sum_k \rho_k(\Omega') = \\ &= \int dS' \exp[-(\Omega - \Omega')^2 / 2\sigma^2] \sum_{k,n} \delta_k(\Omega' - \Omega_n), \end{aligned} \quad (3)$$

where  $C$  is the numerical constant, the integration is over the surface of a  $C_{60}$  molecule,  $|\Omega - \Omega'|$  is the distance between the  $\Omega$  and  $\Omega'$  points on the surface of a  $C_{60}$  molecule measured in degrees, and the summation is over the orientational states in the orbit (index  $k$ ) and 60 carbon atoms in  $C_{60}$  molecules (index  $n$ ).

In Fig. 2, the atomic density distributions of rotating  $C_{60}$  molecules in  $AC_{60}$  crystals in the phase  $Fm\bar{3}m$  are illustrated. The calculation is performed by Eq.(3) with the orientational states of the 12-fold orbit. We take the orientational state shown in Fig. 1c as the initial state ( $\psi_1$ ). Other orientational states of  $C_{60}$  are obtained from the initial orientation by means of the following rotations:  $\psi_2 = C_4\psi_1$ ,  $\psi_3 = C_4^2\psi_1$ ,  $\psi_4 = C_4^3\psi_1$ . The remaining orientational states are obtained with the help of the rotations  $C_3$  and  $C_3^2$  by the following symbolic scheme ( $\psi_5, \psi_6, \psi_7, \psi_8 = C_3(\psi_1, \psi_2, \psi_3, \psi_4)$ , and ( $\psi_9, \psi_{10}, \psi_{11}, \psi_{12} = C_3^2(\psi_1, \psi_2, \psi_3, \psi_4)$ ), where  $C_4$  is the rotation by  $90^\circ$  about the axis  $z$  and  $C_3$  is the rotation by  $120^\circ$  about  $[111]$ .

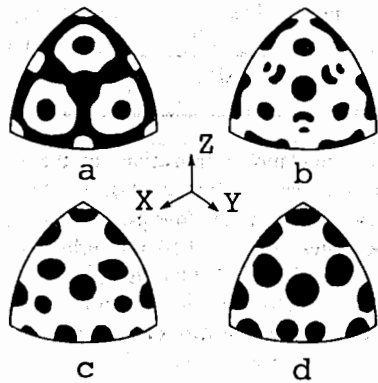


Fig. 2. a). The fragment (1/8th of the surface of a molecule) of the atomic density distribution of a  $C_{60}$  molecule in the phase  $Fm\bar{3}m$ . The dark regions correspond to the maximum density (100 % to 66 %), lighter regions correspond to the atomic density of 66 % to 33 %, and the light regions - 33 % to 0 %. The orientational states are distributed according to the normal law with  $5^\circ$  dispersion. b), c), and d). The same as for a) but with the dispersion  $3^\circ$ . In addition, for c) and d) we considered the strain of the type  $e_{xx} = e_{yy} = -2e_{zz} \neq 0$ . In d), the same strain as for c) plus the additional shear strain  $e_{xy} \neq 0$ .

The symmetry analysis of the phase transition in  $AC_{60}$  [8] shows that the low-symmetry phase arises as a result of condensation of one of six order parameter components and consequently, the appearance of six domains can be expected in the low-symmetry phase. The atomic density distribution (see Figs. 2a and 2b) constructed on the basis of all 12 orientational states is connected with all six domains. However, in a deformed crystal, the 12 orientational states are not physically equivalent. This causes a change of the occupation probability for different states. The symmetry analysis of the phase transition [4,8] makes it possible to understand which of 12 orientational states and how they are connected with different types of deformation. For external stresses  $\sigma_{xx} = \sigma_{yy} = -2\sigma_{zz} \neq 0$ , the atomic density distribution is illustrated in Fig. 2c. It is constructed using of the orientational states  $\psi_1, \psi_2, \psi_3$ , and  $\psi_4$ . Applying the additional shear stress  $\sigma_{xy} \neq 0$  to the deformed crystal it is possible to restrict further the orientational degrees of freedom of a  $C_{60}$  molecule. For this case, the atomic density distribution constructed on the basis of two orientational states  $\psi_1$  and  $\psi_3$  is illustrated in Fig. 2d.

### 5. The local symmetry and the symmetry of internal vibrations of $C_{60}$ molecules in crystals

In previous Sections it is shown that the rotating  $C_{60}$  molecules occupy all orientational states from all orbits. In the vicinity of the phase transition (in the phase  $Fm\bar{3}m$ ), however, they occupy, most of the time, the states from only one orbit. Because of this, the atomic density distribution is anisotropic. In crystals, the local symmetry of a rotating  $C_{60}$  molecule is determined by the symmetry of the lowest symmetry state that the molecule occupies. Consequently, in the high-symmetry phase  $Fm\bar{3}m$  the local symmetry of rotating  $C_{60}$  molecules is described by the inversion group  $I$ . On the other hand, in the low-symmetry phase, the  $C_{60}$  molecules are orientationally ordered and occupy one state from a particular orientational orbit. For example, in  $C_{60}$  fullerites in the low-symmetry phase  $Pa\bar{3}$ ,  $C_{60}$  molecules occupy the orientational state with the local symmetry  $S_6$  and in  $AC_{60}$  fullerides in the low-symmetry phase  $Pnmm$ , the state with the local symmetry  $C_{2h}$ . Hence it follows that at phase transition, on the background of generally decreasing spatial symmetry of a crystal the local symmetry of a  $C_{60}$  molecule increases (see Table 4).

Table 4. The local symmetry of  $C_{60}$  molecules in different phases of  $C_{60}$  fullerite and  $AC_{60}$  fulleride.

Crystal	Phase $Fm\bar{3}m$	Phase $Pa\bar{3}$	Phase $Pnmm$
fullerite $C_{60}$	$I$	$S_6$	-
fulleride $AC_{60}$	$I$	-	$C_{2h}$

Below, we discuss the symmetry of phonons in the phase  $Fm\bar{3}m$ . For phonons with different energies, two possibilities exist. If the frequency of a phonon is higher than the characteristic frequency of rotation of a  $C_{60}$  molecule, the phonon moves in a crystal with differently oriented  $C_{60}$  molecules and due to slow rotation of  $C_{60}$  molecules, the symmetry of

the crystal for such a phonon is lower than it could be expected for the spatial group  $Fm\bar{3}m$ . On the other hand, if the frequency of a phonon is considerably lower than the characteristic rotation frequency of a  $C_{60}$  molecule, the symmetry of the crystal completely corresponds to the spatial group  $Fm\bar{3}m$ .

As an example, we discuss the internal vibrations of a  $C_{60}$  molecule in  $C_{60}$  and  $AC_{60}$  crystals that can be studied in light scattering experiments. It is common knowledge that in infrared and Raman scattering of light phonons with a wave vector close to zero are observed and their symmetry is determined by the group of the wave vector  $k=0$ , i.e.,  $G_{k=0}$ , or the point symmetry group (see, e.g., [9] about local, point and other symmetry groups in crystals). In a primitive cell of  $C_{60}$  and  $AC_{60}$  crystals in the phase  $Fm\bar{3}m$  only one rotating  $C_{60}$  molecule occupies the position with the local symmetry  $O_h$ . Hence it is assumed that the internal vibrations of  $C_{60}$  in the phase  $Fm\bar{3}m$  can be analyzed with a reasonable precision on the basis of the icosahedral group  $Y_h$  [10] or the point group  $O_h$  if we need to take into account splitting of internal vibrations of the molecule in the crystalline field. However,  $C_{60}$  molecules do not have four-fold symmetry axes (see above) and therefore, only group  $T_h = O_h \cap Y_h$  can be the maximum group of the local symmetry of  $C_{60}$  molecules. This is one of the reasons why in [11], the symmetry analysis of internal vibrations of  $C_{60}$  molecules in the phase  $Fm\bar{3}m$  was carried out according to irreducible representations of the group  $T_h$ . The analysis of the orientational states of  $C_{60}$  molecules performed above shows that it is possible to classify the internal vibrations of the molecules according to irreducible representations of the group  $T_h$  only if the  $C_{60}$  molecules occupy the states from a 2-fold orbit. In  $C_{60}$  and  $AC_{60}$  crystals the orientational crystalline potential requires that the 8- and 12-fold orbits with lower local symmetry  $S_6$  and  $C_{2h}$ , respectively, must be considered. Since the frequency of internal vibrations is considerably (10 to 100 times) higher than the characteristic rotation frequency of a  $C_{60}$  molecule, such phonons propagate through the crystals where  $C_{60}$  molecules look statically disordered. For these phonons the point symmetry group is even lower. Thus, the symmetry of the internal vibrations of a  $C_{60}$  molecule in the phase  $Fm\bar{3}m$  is not higher than  $S_6$  and  $C_{2h}$  for  $C_{60}$  and  $AC_{60}$ , respectively. Since the point groups of low-symmetry phases for these crystals are  $T_h$  and  $D_{2h}$ , respectively, the conclusion can be made that the symmetry of the internal vibrations of a  $C_{60}$  molecule increases despite of the fact that the spatial symmetry decreases at orientational phase transition.

## 6. The results and discussion

Let us briefly summarize the obtained results. In the framework of the discrete method a model of the orientational phase transitions in fulleride crystals is suggested. The symmetry classification of all orientational states of a rotating  $C_{60}$  molecule is done. It is shown that the orientational states of the molecule can be distributed between different orientational orbits with different local symmetries. It is found that particular orientational orbits are connected with the corresponding orientational phase transitions and the orientational states from one orbit are the analogs of atomic displacements connected with the soft mode of the structural phase transition. Namely, the orientational states from one orbit determine the anisotropy of the atomic density distribution of a  $C_{60}$  molecule in the phase  $Fm\bar{3}m$ . The atomic density distributions reflect the physical nature of the orientational phase transition the scheme of which is proposed in Sec. 3. On the basis of an analysis of the symmetry of the orientational states of  $C_{60}$  molecules the effect of increasing both the local symmetry and the symmetry of

internal vibrations of  $C_{60}$  molecules in a crystal despite of decreasing spatial symmetry of crystals at phase transition, is predicted.

Below, let us discuss the possibility of the experimental verification of the obtained results. The calculated atomic density distributions of rotating  $C_{60}$  molecules (see Fig. 2) are connected with the diffraction spectra obtained in the experiments. It is known (see, e.g., [13]) that the Bragg peak intensities depend on a particular arrangement of atoms in a primitive cell of a crystal. In our case, the primitive cell contains a rotating  $C_{60}$  molecule. The Bragg peak intensities (from  $C_{60}$  molecules) are defined by the square of the structural factor

$$F(Q) = b_c \{ c_{con} 60 \exp[-W_1(Q)] j^*(QR) + c_{disc} \exp[-W_2(Q)] \int dr' \langle \sum_{k,n} \delta_k(r'-r_n) \rangle \exp(-iQ \cdot r') \}, \quad (4)$$

where  $b_c$  is the coherent neutron scattering length on a carbon nucleus (or the atomic form factor for X-ray scattering), the continuous  $c_{con}$  and discrete  $c_{disc}$  weight factors are the fitting parameters that satisfy the condition  $c_{con} + c_{disc} = 1$ , for  $C_{60}$  fullerite  $c_{con} = 0.31$ ,  $c_{disc} = 0.69$  [1],  $j(QR) = \sin(QR)/(QR)$  is the Bessel function,  $W_1(Q)$  and  $W_2(Q)$  are the Debye-Waller factors of carbon atom of  $C_{60}$  molecule. Due to different types of averaging the values of  $W_1(Q)$  and  $W_2(Q)$  can be different from one another. From Eq. (4) it is seen that the averaged atomic density,  $\langle \sum_{k,n} \delta_k(r'-r_n) \rangle$  used in Sec. 4 to describe the anisotropy of the atomic density, enters into the structural factor.

Note that rotating  $C_{60}$  molecules occupy the orientational states from all orientational orbits but only one orientational orbit is connected with the orientational phase transition. The summation in the term  $\langle \sum_{k,n} \delta_k(r'-r_n) \rangle$  runs over the states of this orbit (index  $k$ ) and the contribution of other orientational states from the remaining orbits is modelled by the Bessel function  $j(QR)$ .

Thus, the distributions shown in Fig. 2 determine the Bragg peak intensities in the phase  $Fm\bar{3}m$  and, therefore, one can verify experimentally by neutron or X-ray diffraction the atomic density distributions of rotating  $C_{60}$  molecules.

It is known that the symmetry of crystalline lattice vibrations can be determined in light scattering experiments. In paper [14], Raman light scattering spectra of fullerite  $C_{60}$  were reported. From these spectra it is seen that the lines in the spectrum obtained at  $T = 259$  K in the low-symmetry phase  $Pa\bar{3}$  have a finer structure than the lines obtained at the temperature two degrees higher in the high-symmetry phase  $Fm\bar{3}m$ . The physical origin of a large width of the lines corresponding to the internal vibrations of  $C_{60}$  molecules in the phase  $Fm\bar{3}m$  is not completely clear yet and in principle, can be due to many physical reasons. In a pure  $C_{60}$  crystal, however, the  $C_{60}$  molecules are neutral and this reduces the number of possible reasons. For example, owing to the Jan-Teller effect the charged  $C_{60}^{-1}$  (or  $C_{60}^{-3}$ ) molecule can go to the strain state and this leads to splitting of the internal vibrations of molecule. In addition, the charged molecules lead to the appearance of a macroscopic electric field in dielectric crystals and this leads to the splitting of the longitudinal and transverse optic vibrations. So, the large width of the lines for  $C_{60}$  fullerite can be explained by the anharmonic interaction of the internal vibrations of  $C_{60}$  molecules with other phonons or the low local symmetry of  $C_{60}$  molecules in crystals (splitting in the crystalline field) and/or the interaction between randomly disoriented molecules (analogous to Davydov splitting [15]).

In contrast to anharmonic interaction, the last two effects determine the point group that can be verified in light scattering experiments with a polarization analysis.

The symmetry analysis (see, e.g., [10]) shows that the internal vibrations of the  $C_{60}$  molecules active in Raman light scattering have the symmetry  $2A_g \oplus 8H_g$ . As a result, in Raman scattering spectrum ten different lines, two with the symmetry  $A_g$  (nondegenerate vibrations) and eight with the symmetry  $H_g$  (five-fold degeneration), must be observed. In the crystalline field with cubic symmetry (point group  $T_h$ ) degeneration of vibrations with the symmetry  $H_g = E_g \oplus F_g$  is removed. In this, the vibration with the symmetry  $F_g$  has three-fold degeneracy and  $E_g$  - two-fold degeneracy. As is seen from [14], such splitting is experimentally observed for the vibrations  $H_g(1)$  and  $H_g(2)$  ( $T=261$  K). Analogous splitting may probably take place for the vibrations  $H_g(6)$  and  $H_g(7)$  as well (see [14]). According to the polarization analysis [14] the vibrations  $H_g(1)$  with a lower frequency ( $266.2 \text{ cm}^{-1}$ ) have the symmetry  $E_g(1)$  and vibrations with the frequency  $272.4 \text{ cm}^{-1}$  have the symmetry  $F_g$ . For the vibrations  $H_g(2)$  we have the opposite situation: the vibrations with the frequency  $430.3 \text{ cm}^{-1}$  have the symmetry  $F_g$  and the vibrations with the frequency  $434.3 \text{ cm}^{-1}$  - the symmetry  $E_g$ .

Since the vibrations with the symmetry  $A_g$  are nondegenerate, the large width of the corresponding lines can be due to the interaction of neighboring molecules with different orientations. In this case, modeling of the strongest interaction between the closest  $C_{60}$  neighbors with different orientations in the phase  $Fm\bar{3}m$  (the first coordination sphere contains 12 molecules) is possible using large crystalline cells (containing more than one  $C_{60}$  molecule). Such crystals with a larger size of cells can be obtained from the phase  $Fm\bar{3}m$  by symmetry analysis of all possible phase transitions leading to an increase of the volume of a primitive cell. (In the cluster approach, accounting for the interaction of the closest  $C_{60}$  neighbors it can be assumed that the large width of the  $A_g$  symmetry vibrations is formed by a set of separate lines (1 to 13) with different intensities which, in general, are proportional to the time a  $C_{60}$  molecule is in a particular orientational state).

Hence it follows that the large width of the lines with the symmetry  $A_g$  is explained by the interaction between the closest  $C_{60}$  molecules, i.e., Davydov splitting [15]. In this case, the point group of a crystal with an increased size of primitive cells must decrease due to uncorrelated orientations of the closest neighbors.

In what follows, we discuss the width of the lines with the symmetry  $F_g$  and  $E_g$ . The above symmetry analysis of the orientational states of  $C_{60}$  molecules in  $C_{60}$  and  $AC_{60}$  crystals shows that the  $C_{60}$  molecules mainly occupy the states with the symmetry  $S_6$  and  $C_{2h}$ , respectively. In this case, further removing of degeneration of the  $F_g$  symmetry vibrations with three-fold degeneracy and two-fold vibrations of the  $E_g$  symmetry takes place due to low symmetry of the crystalline field. In addition, in full analogy with the  $A_g$  symmetry lines, Davydov splitting due to the interaction of the closest  $C_{60}$  neighbors with different orientations also takes place.

Thus, the symmetry of the internal vibrations of  $C_{60}$  molecules in  $C_{60}$  and  $AC_{60}$  crystals cannot be higher than  $S_6$  and  $C_{2h}$ , respectively, due to low local symmetry of the orientational states and the interaction between misoriented closest neighbors. This means that the vibrations with the symmetry  $F_g$  which in the phase  $Fm\bar{3}m$  are observed only for the perpendicular orientation of the polarization vectors of incident and scattered light must be observed for the parallel orientation as well and vice versa the vibrations with the symmetry  $E_g$  must be observed for the perpendicular orientation. Therefore it is interesting to conduct an accurate polarization analysis of vibrations with the symmetry  $F_g$  and  $E_g$  in  $C_{60}$  fullerite (phase  $Fm\bar{3}m$ ) by carrying out Raman light scattering experiments.

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