

# Phase transition in fulleride crystals $AC_{60}$ (A=K, Rb)

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A Landau phenomenological theory is constructed for a phase transition in  $AC_{60}$  (A=K, Rb). The changes occurring in the positions of the alkali-metal atoms as a result of the phase transition are investigated.

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Experimental investigations (see, for example, Ref. 1) have shown that a phase transition (PT) from a face-centered cubic phase with  $Fm\bar{3}m$  symmetry ( $O_h^5$ ) into a polymer-like phase with orthorhombic symmetry  $Pnmm(D_{2h}^{12})$  occurs in fulleride crystals  $AC_{60}$  (A=K, Rb). The orthorhombic phase is characterized by shorter distances between the nearest-neighbor  $C_{60}$  molecules in one of three crystalline directions along which the translation vectors of the lattice of the  $Fm\bar{3}m$  phase are directed. This difference is of the order of 8% and is due to the specific double bond between the two nearest  $C_{60}$  molecules.

At present, studies of the microscopic nature of phase transitions are of great interest. In this connection, it is important to make a comparative analysis of the physical properties of the phase transition in  $AC_{60}$  and  $C_{60}$  crystals. We note here that the orthorhombic phase is not observed in  $C_{60}$  at atmospheric pressure and the phase transition leads to a change in the symmetry  $Fm\bar{3}m$  ( $O_h^5$ )  $\rightarrow$   $Pa\bar{3}$  ( $T_h^6$ ). The phase-transition temperatures in  $AC_{60}$  crystals are higher than in  $C_{60}$ . For example, in  $RbC_{60}$   $T_c \sim 380$  K as compared to  $T_c \sim 260$  K in  $C_{60}$ .

In the present paper we construct a phenomenological theory, on the basis of a symmetry analysis, for the phase transition into the orthorhombic phase in  $AC_{60}$  crystals. The microscopic nature of the phase transition is discussed. The possible changes occurring in the meatl-atom subsystem as a result of the phase transition are investigated on the basis of an analysis of the interactions between the order parameters (OPs).

According to the experimental data,<sup>1</sup> the phase transition  $Fm\bar{3}m \rightarrow Pnmm$  leads to doubling of the volume of the primitive cell of the  $Fm\bar{3}m$  phase. Therefore, this phase transition is associated with one of the following wave vectors at the boundary of the Brillouin zone: (100), (010), or (001). These wave vectors form a single star of the wave vector  $\{\mathbf{k}_{10}\}$  in the  $Fm\bar{3}m$  phase.<sup>2</sup>

For definiteness, we shall consider a phase transition with the wave vector (001), i.e., a phase transition into one of the three ray domains (see Table I). For one-

TABLE I. Phase transitions out of the phase  $Fm\bar{3}m$  which occur with the wave vector (001).

IR:	$\tau_1$	$\tau_2$	$\tau_3$	$\tau_4$	$\tau_5$	$\tau_6$	$\tau_7$
SG:	$D_{4h}^1$	$D_{4h}^4$	$D_{4h}^6$	$D_{4h}^7$	$D_{4h}^{14}$	$D_{4h}^{15}$	$D_{4h}^9$
IR:	$\tau_8$	$\tau_9$	$\tau_9$	$\tau_9$	$\tau_{10}$	$\tau_{10}$	$\tau_{10}$
SG:	$D_{4h}^{12}$	$D_{2h}^{12}$	$D_{2h}^{18}$	$C_{2h}^5$	$D_{2h}^{13}$	$D_{2h}^{17}$	$C_{2h}^2$

dimensional irreducible representations (IRs)  $\tau_1, \dots, \tau_8$  the order parameter has only one component, whereas for the two-dimensional irreducible representations  $\tau_9$  and  $\tau_{10}$  the following combinations of the components of the order parameters are possible:  $C_1 \neq 0, C_2 = 0$  (or  $C_1 = 0, C_2 \neq 0$ ),  $C_1 = C_2 \neq 0$  and  $C_1 \neq C_2 \neq 0$ ; the space groups (SGs) of the low-symmetry phases for these combinations are given in Table I.

As one can see from the table, the experimentally observed low-symmetry phase with the space group  $Pnnm(D_{2h}^{12})$  can appear as a result of a condensation of the type  $C_1 \neq 0, C_2 = 0$  (or  $C_1 = 0, C_2 \neq 0$ ) for the order parameter with the symmetry  $\tau_9$ . We note that the order parameter with this symmetry  $(\tau_9)^3$  but with a different type of condensation  $C_1 = C_2 = C_3 = C_4 = C_5 = C_6 \neq 0$  leads to a change in symmetry  $Fm\bar{3}m \rightarrow Pa\bar{3}$  in the crystal  $C_{60}$ .

The phase transition in  $C_{60}$  is thus associated with three rays of the star  $\{\mathbf{k}_{10}\}$  and the phase transition in  $AC_{60}$  occurs along one of the three rays of the same star of the wave vector.

A phenomenological theory of the phase transition in a  $C_{60}$  crystal has been developed in a number of studies (see, for example, Refs. 4 and 5). The expansion of the free energy is written in the form

$$F_1 = F_c + F_{ce} + F_e. \quad (1)$$

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

$$F_c = a \sum_i C_i^2 + b(C_1 C_3 C_6 + C_1 C_4 C_5 + C_2 C_3 C_5 + C_2 C_4 C_6) + d_1 \left( \sum_i C_i^2 \right)^2 + d_2 \sum_i C_i^4 + \dots, \quad (2)$$

where  $a = \alpha(T - T_c)$ ,  $\alpha > 0$ ;  $b$  and  $d_i$  are the phenomenological constants of the theory; and,  $\{C_i\}$ ,  $i = 1, \dots, 6$ , is a six-component order parameter. The components  $C_1$  and  $C_2$  have the wave vector (001), the components  $C_3$  and  $C_4$  have the wave vector (100), and the components  $C_5$  and  $C_6$  have the wave vector (010). The elastic energy  $F_e$  for crystals with cubic symmetry has the standard form (see, for example, Ref. 6). The interaction between the components  $C_i$  of the order parameter and the components  $e_i$  of the deformation tensor can be expressed in the form<sup>5</sup>

$$F_{cc} = \gamma(C_1^2 + C_2^2 + C_3^2 + C_4^2 + C_5^2 + C_6^2)(e_1 + e_2 + e_3). \quad (3)$$

We note that the interaction (3) is sufficient to describe spontaneous deformations of the crystal lattice accompanying a phase transition in  $C_{60}$  with a condensation of the order parameter of the type  $C_1 = C_2 = C_3 = C_4 = C_5 = C_6 \neq 0$  but it is completely inadequate for describing the phase transition in  $AC_{60}$  crystals with condensation of the type  $C_1 \neq 0$ ,  $C_2 = 0$  (or  $C_2 \neq 0$ ,  $C_1 = 0$ ),  $C_3 = C_4 = C_5 = C_6 = 0$ . In the latter case additional interactions arise between the components of the order parameter and the components of the spontaneous-deformation tensor which transform according to the same irreducible representations. For example, the expressions  $(C_3^2 + C_4^2 - C_5^2 - C_6^2)$  and  $(2C_1^2 + 2C_2^2 - C_3^2 - C_4^2 - C_5^2 - C_6^2)$  transform according to a two-dimensional irreducible representation  $E_g$  with the wave vector  $\mathbf{k}=0$ , just as  $(e_1 - e_2, e_1 + e_2 - 2e_3)$ . The expressions  $(C_1^2 - C_2^2, C_3^2 - C_4^2, C_5^2 - C_6^2)$  and  $(e_6, e_4, e_5)$  transform according to the three-dimensional irreducible representation  $F_{2g}$ . In addition to the interaction (3), we thus have the interactions

$$F'_{ce} = \gamma'_1[3(C_3^2 + C_4^2 - C_5^2 - C_6^2)(e_1 - e_2) + (2C_1^2 + 2C_2^2 - C_3^2 - C_4^2 - C_5^2 - C_6^2)(e_1 + e_2 - 2e_3)] + \gamma'_2[(C_1^2 - C_2^2)e_6 + (C_3^2 - C_4^2)e_4 + (C_5^2 - C_6^2)e_5]. \quad (4)$$

The interactions (3) and (4) make it possible to describe completely the spontaneous deformations of a crystal lattice accompanying a phase transition of the type  $C_1 \neq 0$ ,  $C_2 = C_3 = C_4 = C_5 = C_6 = 0$ .

In addition to having a different type of condensation of the order parameter, a phase transition in the fulleride  $AC_{60}$  differs from a phase transition in  $C_{60}$  in that the  $AC_{60}$  crystal contains a subsystem of alkali-metal atoms. This subsystem of metal atoms has definite degrees of freedom which can possess the symmetry  $E_g, F_{2g}$  (the wave vector  $\mathbf{k}=0$ ), or  $\tau_9$  (the star of the wave vector  $\{\mathbf{k}_{10}\}$ ). We denote the secondary order parameters describing the degrees of freedom of the symmetries  $E_g, F_{2g}$ , and  $\tau_9$  as, respectively,  $\{\theta_i\}$ ,  $i=1,2$ ,  $\{\eta_i\}$ ,  $i=1,2,3$ , and  $\{\xi_i\}$ ,  $i=1,\dots,6$ . By analogy with the interactions (4), we write

$$F_{c\theta,c\eta} = \beta_1[\sqrt{3}(C_3^2 + C_4^2 - C_5^2 - C_6^2)\theta_1 + (2C_1^2 + 2C_2^2 - C_3^2 - C_4^2 - C_5^2 - C_6^2)\theta_2] + \beta_2[(C_1^2 - C_2^2)\eta_1 + (C_3^2 - C_4^2)\eta_2 + (C_5^2 - C_6^2)\eta_3]. \quad (5)$$

The secondary order parameter  $\{\xi_i\}$  and the primary order parameter  $\{C_i\}$  possess the same symmetry and therefore they are linearly related with one another:

$$F_{c\xi} = \beta_3(C_1\xi_1 + \dots + C_6\xi_6). \quad (6)$$

Adding quadratic terms for all secondary order parameters which were introduced

$$F_{\theta,\eta,\xi} = \delta_1(\theta_1^2 + \theta_2^2) + \delta_2(\eta_1^2 + \eta_2^2 + \eta_3^2) + \delta_3(\xi_1^2 + \dots + \xi_6^2), \quad (7)$$

we obtain an expansion of the free energy which is a generalization of the expansion of the free energy for the fullerite  $C_{60}$  and which describes a phase transition in  $AC_{60}$  crystals:

$$F = F_1 + F'_{ce} + F_{c\xi} + F_{c\theta,c\eta} + F_{\theta,\eta,\xi}. \quad (8)$$

We now discuss the phase transition in  $AC_{60}$  crystals. By analogy with the phase transition in a  $C_{60}$  crystal, we assume that the primary order parameter  $\{C_i\}$  describes the

orientational ordering of the rotational axes of  $C_{60}$  molecules. The secondary order parameters  $\{\theta_i\}$ ,  $\{\eta_i\}$ , and  $\{\xi_i\}$  describe the changes occurring in the metal-atom subsystem.

In the case of the condensation of the type  $C_1 \neq 0$ ,  $C_2 = C_3 = C_4 = C_5 = C_6 = 0$  for the primary order parameter, condensation of the following secondary order parameters will occur as a result of the interactions (5) and (6):  $\xi_1 \neq 0$ ,  $\theta_2 \neq 0$ , and  $\eta_1 \neq 0$ , as well as different components of the spontaneous-deformation tensor. We now consider the deformations of the crystal lattice. Because of the interaction (3), just as in the case of a phase transition in  $C_{60}$ , there appear components  $e_1 = e_2 = e_3 \neq 0$  which do not change the cubic symmetry of the crystal lattice. Further, it is evident from the expression (4) that additional deformations of the form  $e_1 = e_2 = -2e_3 \neq 0$  and  $e_6 \neq 0$  arise. The deformations of the first type lower the symmetry of the crystal lattice to tetragonal, and the shear deformation  $e_6 \neq 0$  finally establishes the orthorhombic symmetry of the crystal lattice, as should happen in the case of the condensation of the primary order parameter which leads to the phase transition  $Fm\bar{3}m(O_h^5) \rightarrow Pnnm(D_{2h}^{12})$ . We note that the shear component  $e_6 \neq 0$  leads to strong compressive deformation of the unit cell in the directions  $[110]$  or  $[-110]$  [(for the wave vector  $(001)$ ] and therefore to shorter distances between the nearest molecules  $C_{60}$  in one of these crystallographic directions.

In summary, the representation obtained for the free energy (8) describes the experimental data of Ref. 1; specifically, the symmetry of the low-temperature phase and the deformation of the crystal lattice.

Next, we consider the changes occurring in the alkali-metal-atom subsystem as a result of a phase transition. At present, there are no experimental data on the behavior of the metal-atom subsystem in a phase transition. Consequently, all conclusions concerning structural changes accompanying a phase transition are predictions which are based on models and which can be checked with the aid of diffraction experiments.

The experimental data of Ref. 1 show that a metal atom has an octahedral environment of the  $C_{60}$  molecules (see Fig. 1a). According to Ref. 2, the following positions are possible in the phase  $Fm\bar{3}m$  for the octahedral environment: the central position **1b** with the coordinate  $(111)$  and local symmetry  $O_h$ , a sixfold position **6e** with the characteristic coordinate  $(00z)$  and  $C_{4v}$  symmetry, and the positions **8f**,  $(xxx)$ ,  $C_{3v}$ ; **12i**,  $(xx1)$ ,  $C_{2v}$ ; **24j**,  $(xy0)$ ,  $C_s$  and **24k**,  $(xxz)$ ,  $C_s$ .

In the case of the position **1b** (Fig. 1) a metal atom can oscillate only relative to its only equilibrium position. Such displacements with the wave vector  $\mathbf{k}=0$  transform according to the three-dimensional irreducible representation  $F_{1u}$  and therefore they are not described by secondary order parameters with the symmetry  $E_g$  or  $F_{2g}$ . Displacements with the wave vector  $(001)$  transform according to the irreducible representations  $\tau_4$  and  $\tau_{10}$  and likewise are not associated with the order parameter  $\xi_1 \neq 0$ , which possesses  $\tau_9$  symmetry. Accordingly, in a phase transition no changes occur with the metal atom that occupies the single position at the center of an octahedron.

If the metal atom occupies a noncentral position, then in a phase transition partial ordering occurs at the positions indicated in Figs. 1b–1d. For the position **6e** the only secondary order parameter  $\theta_2 \neq 0$  with the symmetry  $E_g$  describes a partial ordering of the metal atoms either in the horizontal plane (filled circles) or over two positions above

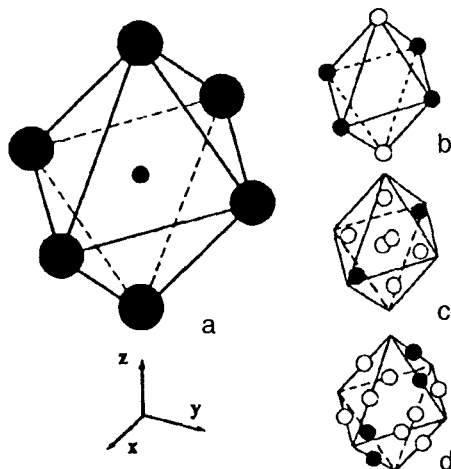


FIG. 1. Possible types of positions for the metal atom (small circles) in the octahedral environment of  $C_{60}$  molecules (large circles): a — Central position **1b**; b, c and d — positions **6e**, **8f**, and **12i**, respectively.

and below the plane (open circles). For the positions **8f** and **12i** we have, respectively,  $\eta_1 \neq 0$ ,  $\xi_1 \neq 0$ , and  $\theta_2 \neq 0$ ,  $\eta_1 \neq 0$ ,  $\xi_1 \neq 0$ . The filled circles represent occupied positions. The positions **24j** and **24k** of lower symmetry originate from the positions **12i** and **8f**. The ordering of the metal atoms for these positions is described by the three secondary order parameters and is not presented in this study.

It can be assumed that further lowering of the temperature will result in complete ordering of the metal atoms and that such a phase transition will lead to a further lowering of the symmetry of the crystal. Here the space group is determined completely by the type of positions. As an example, a variant of complete ordering of the metal atoms for the position **8f** with the wave vector  $\mathbf{k}=0$  leads to the space group  $C_{2v}^7$ .

We note that a phase transition into a glassy phase is observed in a  $C_{60}$  crystal as the temperature is lowered. Therefore, the above-considered situation of complete ordering of the metal atoms is possible in the case in which the temperature of the phase transition into the glassy phase is lower than the temperature of a phase transition of the ordering type.

In conclusion, we note that the expansion (8) obtained for the free energy on the basis of a symmetry analysis describes a phase transition into the orthorhombic phase in the fullerides  $AC_{60}$ . In this expansion the main order parameter, which is associated with the orientational degrees of freedom of the  $C_{60}$  molecules, and the secondary order parameters, which is associated with different degrees of freedom of the metal atoms A, interact with deformations of the lattice. The representation obtained for the free energy describes the existing experimental observations of the spontaneous deformations of the lattice in a phase transition and makes it possible to predict the possible changes in the positions of the metal atoms. We note that a linear interaction between the primary order parameters  $C_i$  and the secondary order parameters  $\xi_i$  occurs for the positions **8f**, **12i**, **24j**, and **24k**. Such an interaction always increases the phase-transition temperature.<sup>7</sup>

$$T_c(\text{AC}_{60}) = T_c(\text{C}_{60}) + \beta_3^2/4\alpha\delta_3. \quad (9)$$

Here  $\alpha > 0$  [see Eq. (2)] and all  $\delta_i > 0$ , which follows from the requirement that the crystal must remain stable with respect to small changes in the secondary order parameters [see Eq. (7)]. Therefore, the theory presented above makes it possible to explain the fact that the phase-transition temperature is higher in fullerides than in  $\text{C}_{60}$  crystals.

To determine experimentally the positions of the metal atoms in  $\text{AC}_{60}$ , we are planning to perform diffraction measurements with x-rays or neutrons, such as the measurements reported in Ref. 1, with allowance for the symmetry analysis performed in the present paper.

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