Low Temperature Physics/Fizyka Nyzkykh Temperatur, 2023, Vol. 49, No. 5, pp. 621–627

Phase structures and interaction of BEDT-TTF molecules

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Received December 19, 2022, published online March 23, 2023

Structural phases in crystal BEDT-TTF under the influence of doping molecules were studied. The system demonstrates the transition from a parallel aligned molecular phase (β-phase) to a new equilibrium state, where the molecules are rotated at a certain angle (α- or θ-phase). The precursor of this transition is the electrostatic and quadrupole interaction between BEDT-TTF and doping molecules. The modified potential of the Girifalco type is introduced, it depends on both intermolecular distance and the angle of the molecular rotation. It is found that the equilibrium distance between molecules in a stack increases and the deflection angle arises with an increase of the charge of doping molecules, which leads to new equilibrium states.

Keywords: two-dimensional model, organic molecule, Girifalco potential, electrostatic field, quadrupole interaction, phase transition.

1. Introduction

Organic crystals of BEDT-TTF (bis (ethylenedithio) tetrathiafulvalene) consist of a large number of atoms and have a complex structure. The unit cell of crystals of this type contains several molecules arranged in a certain way relative to other molecules. In a crystal, molecules collide with wide planes. The planes of the molecules are parallel to each other, and the molecules themselves form stacks with an axis perpendicular to these planes. From works devoted to organic TTF-conductors, it is worth noting the paper [1]. In this work, models of molecules consisting of one or more polygonal rings strongly connected to each other are considered. The composition of these rings includes atoms of sulfur, metals, or organic compounds. These molecules form stacks due to the interaction of individual sulfur atoms, as shown by the example of compounds BEDT-TTF (a) and BDT-TTP (2,5-bis(1,3-dithiol-2-ylidene)-1,3,4, 6-tetrathiapentalene) (b) (see Fig. 1). The interaction of molecules within one stack is much stronger than between stacks (the so-called lateral or lateral interaction) and it occurs due to van der Waals forces (Fig. 1).

The arrangement of molecules relative to each other is called the structural phase. A phase transition is a phenomenon in which the next parameters change: (1) the equilibrium distance between molecules, (2) the angle of deflection of molecules, (3) the associated contact area of wide planes of molecules, and (4) the interaction energy of such complex molecules. The phase transition at low temperatures was experimentally investigated in [2]. That paper shows that a phase transition during the cooling of a molecular crystal often occurs in a limited temperature range that is lower than the transition temperature. The liquid is one of the systems that illustrate the dependence of the phase transition kinetics on the cooling rate. With slow cooling, liquids crystallize at approximately the temperature of T_m and below. However, this first-order liquid-crystal transition is impossible during rapid cooling; thus, the glass can be in the form of a supercooled liquid even at a temperature lower than T_m. With further cooling, the thermal movements of atoms or molecules are suppressed and eventually freeze; the resulting disordered atomic/molecular configuration, called a glass or structural glass, is defined as the quenched state. Although the kinetic properties differ

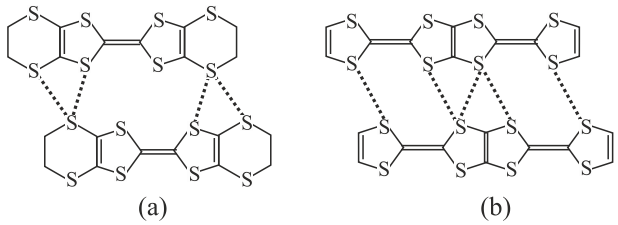

Fig. 1. (a) Schematic representation of the BEDT-TTF molecule and its connection to other molecules between two stacks; (b) the same model for BDT-TTP (according to [1]).

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significantly (and even nontrivially) between glass and supercooled liquid, there is no well-defined thermodynamic phase transition between them. Therefore, glass can be described as a nontrivial supercooled liquid state. Thus, depending on the cooling rate used, liquids can become either crystals (slow cooling mode) or metastable glass (quenching mode) [2].

The set of carbon atoms also exhibits the various properties described above. Graphite is a thermodynamically stable material at room temperature and ambient pressure, but diamond also exists in ambient conditions as a metastable state of carbon. In nature, a diamond is formed in the Earth's mantle as a thermodynamically stable material under conditions of high temperature and high pressure; then it is transferred to the Earth's surface under high pressure and temperature. When this transfer is slow enough, the diamond becomes graphite. In contrast, when the transport is rapid, for example, due to an eruption, the structural transition is excluded and, therefore, the diamond remains in the hardened state. Thus, starting from the diamond at high temperatures and high pressure, the carbon takes the form of either graphite on slow cooling or diamond on hardening, depending on the cooling rate. The hardened state can be ordered, as in the case of a diamond. Despite the frequent use of rapid cooling in material synthesis to obtain metastable forms of solid states, rapid cooling has not often been used to obtain metastable electronic or magnetic states in the study of interacting electronic or spin systems, probably because it was not considered capable of drastically changing the low-temperature state. BEDT-TTF crystals can also exhibit structural and electronic disorders, which is close to the state of glass [2]. The toy model of the structure-disordered phase in BEDT-TTF was built in work [3].

2. Model of anisotropic molecular crystal

Molecules in molecular crystals and, accordingly, the crystals themselves have a complex structure. In the crystal, the molecules collide with wide planes parallel to each other, and the molecules themselves form stacks with an axis perpendicular to these planes. Such a crystal consists of molecules of a substance, the structure of which differs little from their structure in the gaseous state. An elementary cell contains several molecules, and its spatial lattice also has a complex structure. Since a large number of atoms can fit in one molecule, the size of a cell can reach tens of nanometers. It is not difficult to see that the analyzed system is similar to a highly anisotropic crystal, in which the interaction within the plane significantly exceeds the interaction between the planes (quasi-two-dimensional model). The reverse case is also possible when the interaction in the chain of atoms (molecules) significantly exceeds the interaction between the chains (quasi-one-dimensional model). The crystal has a layered structure, that is, let's assume that the interaction between the stacks is, as a rule, weaker than the interaction of the molecules inside the stack [4]. In this approximation, the weak interaction between adjacent atomic layers is taken into account. There is an important feature of the oscillations in an anisotropic crystal, the displacement vector which is perpendicular to the layers of strong interaction. In the case of very weak interaction between layers, bending waves may occur in non-interacting layers, so we will conventionally call them bending oscillations [4].

3. Structure phases of BEDT-TTF crystals

In this section, we review the conditions in which a phase transition occurs in the specimen during slow cooling. The molecular structure is characterized by the phase alignment of molecules which is determined by the potential interaction between BEDT-TTF disc-like molecules and also their interaction with doping molecules. We review α-, β-, and θ-phases and the mechanism of their appearance. β-phase occurs when the BEDT-TTF molecules are placed parallel to each other. There is a sector, where the molecules make a unit cell (see Fig. 2) [5].

We will show that if the specimen is doped with specific molecules which are placed in between two larger TTF molecules, a phase transition will occur. This transition leads to the molecules being inclined from their horizontal position. Adding a neutral dopant has almost no effect on the BEDT-TTF molecules alignment, the interaction inside the crystal is mostly limited to the van der Waals potential, which leads to the lattice period being doubled. In contrast, doping the specimen with charged molecules of semiconductors makes the TTF molecules incline at a certain angle. The inclination occurs due to electrostatic interaction, i.e., the BEDT-TTF molecule take electrons away from the dopant. This distribution is mostly connected to the energy band of semiconductors which has a forbidden energy gap between the valence and conductive bands. This condition does not allow the TTF molecules to align in pairs, as it happens in the case of doping with metallic molecules and κ-phase alignment [see Fig. 3(a)].

When the nonmetallic dopants (i.e., the molecules of nonmetals) are introduced, the crystal transforms either into the α-phase or the θ-phase [6]. They are characterized by a spruce-like alignment of molecules, differing by the equilibrium distance [see Figs. 3(b) and 3(c)].

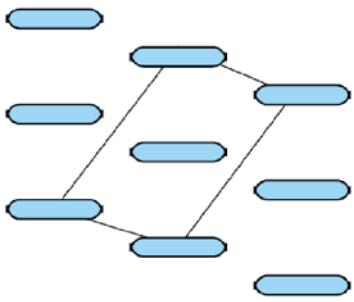

Fig. 2. The β-phase alignment of organic molecules in a unit cell of $(BEDT\text{-}TTF)_2I_3$ (displayed as a parallelogram) [5].

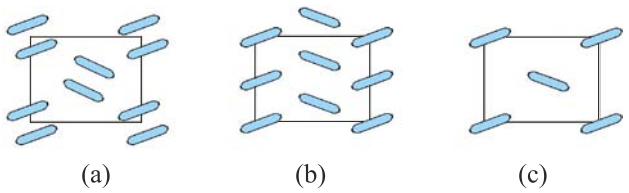

Fig. 3. (a) The κ-phase, (b) the α-phase, (c) the θ-phase [5, 6].

It was mentioned in [3] that molecules interact via the Lennard-Jones potential of Girifalco type [7]:

$$U(r) = \varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right]. \quad (1)$$

We introduce an analog of the Girifalco potential which describes an average intermolecular or interatomic interaction:

$$U(r) = \langle n_{\text{int}} \rangle \varepsilon_0 \left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right], \quad (2)$$

where

$$\langle n_{\text{int}} \rangle = \frac{S_{\text{mol}}}{S_{\text{at}}}, \quad (3)$$

which is ideally an integer, S_{mol} and S_{at} correspond to the areas of the molecule and atomic surfaces. For the contact of the narrow sides of the molecules, the ratio $\langle n_{\text{int}} \rangle = \frac{L_{\text{mol}}}{L_{\text{at}}}$ is used, i.e., the ratio of the molecular contact line to the atomic length. The coefficient ε_0 corresponds to the depth of the potential well, r_0 is an equilibrium distance and r is a variable distance between molecules. For such complex systems, we use average values of these parameters: $\langle \varepsilon \rangle = \varepsilon$, $\langle r \rangle = r$ and $\langle r_0 \rangle = r_0$.

The disc model approach is used to describe the interaction of flat cylindrical molecules of benzene type. Analogically to this model, we consider flat molecules, which have a more complex form than that of benzene. We replace in the plane the complex shape of flat molecules with a continuous rectangle, which covers the edge atoms of the BEDT-TTF molecule (Fig. 4). In a perpendicular projection of these molecules, we also use a continuous rectangle with one-atom thickness. As a result, instead of complicated molecules, we get a rectangular parallelepiped. When it is necessary, this parallelepiped is supplemented with a rounded shell on the distance R_0, which marks the limits of the average atomic radius. Let's name it: the model of molecules-rectangular parallelepipeds (rectangular plates). This is the model of rectangular plates.

Interaction for different directions and rectangular plate model of molecules are already enough to describe the crystal structure very much close to the β-phase of the (BEDT-TTF), which is shown in Fig. 5.

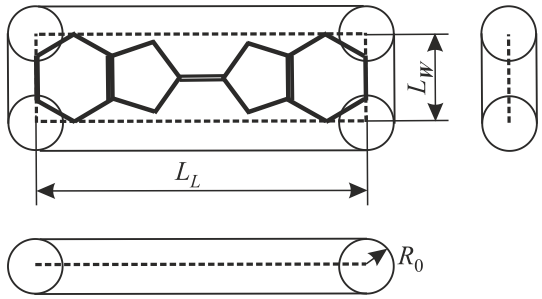

Fig. 4. A rectangular plate model of a molecule in the form of a rectangle parallelepiped superimposed on the real structure BEDT-TTF molecules. Top left view is the plane of the BEDT-TTF molecule and its models. The top right is the projection view along the longest axis of the molecule. The bottom is the projection view of the model parallelepiped along the middle axis. L_L and L_W are the largest (Long) and average (Width) dimensions of the molecule. R_0 is the average atomic radius during the interaction of molecules.

In the β-phase alignment, the contact of two molecules in one stack goes along the line of their electrostatic fields which repeat the shapes of the molecules (Fig. 6). The energy of interaction between molecules is greater in places where the van der Waals fields touch each other than in places where these fields intersect.

The molecule of BEDT-TTF being reviewed has eleven pairs of sulfur and nine pairs of carbon, which makes twenty pairs, i.e., forty atoms. It was shown in (3) that the average amount of atoms is numerically equal to the ratio $\frac{S_{\text{mol}}}{S_{\text{at}}}$. By approximation of atoms to balls, we got areas $S_{\text{C}} = 4\pi R^2 = 6.157 \cdot 10^{-20}$ m^2 for carbon and $S_{\text{S}} = 4\pi R^2 = 1.25 \cdot 10^{-19}$ m^2 for sulfur. The total area of the

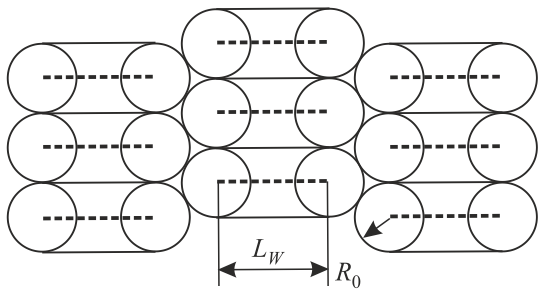

Fig. 5. Model packing of (BEDT-TTF) molecules-plates in the β-phase crystal structure with no quadrupole interaction included. Three stacks of molecules are shown. The distance between planes of molecules and with their long ends $2R_0 = r_0$ is the average distance and equilibrium distance between adjacent atoms of different molecules. The view is directed along the long axis of molecules. We will see a similar picture in the direction of vision along the middle axis by replacing L_W with L_L.

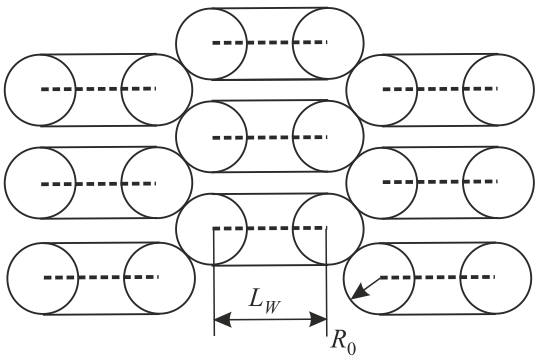

Fig. 6. Interaction of molecules in the β-phase. We see here that the molecules interact via van der Waals and quadrupole interaction which keeps them at a certain distance.

molecule is $S_{\text{mol}} = 3.73 \cdot 10^{-19}$ m^2. The intermolecular force is proportional to the contact area of two interacting molecules.

The interaction between organic molecules is complex and includes van der Waals force, quadrupole interaction, and electrostatic repel. The van der Waals force keeps the molecules attracted to each other over long distances. This is caused by the opposite sign charges of adjacent molecules placed at a sufficiently large distance, and the molecule itself has an electric field that rapidly decreases proportionally to the square of the distance. The BEDT-TTF molecule consists of two connected pentagonal rings with hexagonal rings on two sides (so-called "benzene" rings). In the next chapters, we will consider the quadrupole and electrostatic interaction of BEDT-TTF molecules. When adding dopant molecules (ions) of non-metals, for example, iodine, the structural phase of the crystal changes. As a result, we get the $(\text{BEDT-TTF})_2\text{I}_3$ organic salt, where the molecules incline at a certain angle θ. This angle depends on the following dopant parameters: (1) the size of the "large" molecule, (2) the dopant charge, and (3) the equilibrium distance between molecules.

4. Quadrupole interaction

The quadrupole interaction is characterized by the quadrupole term added to the general expression of the Girifalco potential:

$$U(r) = \langle n_{\text{int}} \rangle \varepsilon_0 \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^{6} \right] + U_{\text{quad}}, \qquad (4)$$

where [8, 9]

$$U_{\text{quad}} = \frac{9Q^2}{4r^5} \left(1 - 10 \cos^2 \theta + \frac{35}{3} \cos^4 \theta \right). \qquad (5)$$

Q is denoted as the quadrupole momentum, θ is the angle of deflection. All molecules are deflected at the same angle. The potential is inversely proportional to the 5th power of the distance between two quadrupole centers. The value $U_{\text{quad}} \geq 0$, i.e., the interaction of quadrupoles consists of the molecules' repulsion. When the value of cosθ gradually decreases from 1 to 0, the bracket part of (5) decreases from 8 to 3, i.e., almost by the factor of 3. The increase of the angle leads to increasing depth of the potential well. As it was mentioned above, the α- and θ-phases are characterized by the fact that the molecules in the crystal BEDT-TTF deflect by the angle θ relative to the stack axis. The angle change between two large molecules is proportional to the concentration of dopant molecules in θ-BEDT-TTF [6] or, in other words, the amount of the transferred charge.

The quadrupole interaction has the greatest value if the molecules are located parallel to each other, and gradually decreases as the molecules incline relative to the axis of the stack. The inclination of molecules occurs due to the electrostatic action of dopant molecules. The energy of quadrupole interaction decreases due to the fact that when the molecules are tilted, which leads to the contact area decrease. It is worth noting that the direct quadrupole interaction cannot lead to the deflection of molecules, but its magnitude depends on the angle the molecules are placed relative to each other and affects the shape of the Girifalco potential.

5. Electrostatic interaction

Further analysis of the molecular interaction consists in adding the term of electrostatic interaction (repulsion) during crystal doping and charge transfer of molecules. This gives the following expression:

$$U_{Qq}(r) = \langle n_{\text{int}} \rangle \varepsilon \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^{6} \right]$$

$$+ \frac{9Q^2}{4r^5} \left(\frac{r_0}{r} \right)^{5} f(\theta) + \frac{q^2}{r_0} \left(\frac{r_0}{r} \right), \qquad (6)$$

where

$$f(\theta) = \left[1 - 10 \cos^2 \theta + \frac{35}{3} \cos^4 \theta \right],$$

q is the charge transferred from the dopant to the molecule in the given model, which is the same for all molecules. For the convenience of comparing potentials, all distances are reduced to a dimensionless form $\frac{r_0}{r} = \frac{1}{\rho}$. We also introduce the dimensionless potential:

$$u(r) = \left[\left(\frac{1}{\rho} \right)^{12} - 2 \left(\frac{1}{\rho} \right)^{6} \right] + A_Q \left(\frac{1}{\rho} \right)^{5} f(\theta) + A_q \left(\frac{1}{\rho} \right), \qquad (7)$$

where

$$u(r) = \frac{U_{Qq}(r)}{\langle n_{\text{int}} \rangle \varepsilon}; \; A_Q = \frac{1}{\langle n_{\text{int}} \rangle \varepsilon} \frac{9Q^2}{4r_0^5}; \; A_q = \frac{1}{\langle n_{\text{int}} \rangle \varepsilon} \frac{q^2}{r_0}.$$

The dependence of the electrostatic interaction on the distance r is the model. Considering the wave function of the ground state of the charge carrier on the molecule as a sine function from each coordinate in a rectangular parallelepiped, the highest density of charges is in the parallelepiped center. As a model, we choose a point charge in the parallelepiped center. Finding the real charge distribution and real electrostatic interaction is likely to be a separate and quite complex problem, but the specified approximation gives qualitatively correct dependence. In this approximate, the dependence of electrostatic interaction on the angle of deflection of the molecule around the long axis of the molecule is absent. Figure 8 shows the influence of these interactions (repulsion) on the location of BEDT-TTF molecules in the β-phase without turning the molecules.

6. Interatomic interaction in the stack with the deflection of molecules

The distance between the planes of repulsive molecules in the experiment decreases due to the tilt of molecules. We will describe how the interactions change as molecules deflect (see Fig. 7).

First of all, the contact area of the molecular flat sides is $\langle n_{\text{int}} \rangle = \dfrac{S_{\text{mol}}}{S_{\text{at}}}$ [see (2) and (3)]. The contact area in the plane of two adjacent molecules before deflection is $S_{\text{mol}} = L_L L_W$. After deflection, the contact area is

$$S_{\text{mols}} = S_{\text{mol}} \left(1 - \frac{r_{Qq}}{L_W} \sin\theta \right). \tag{8}$$

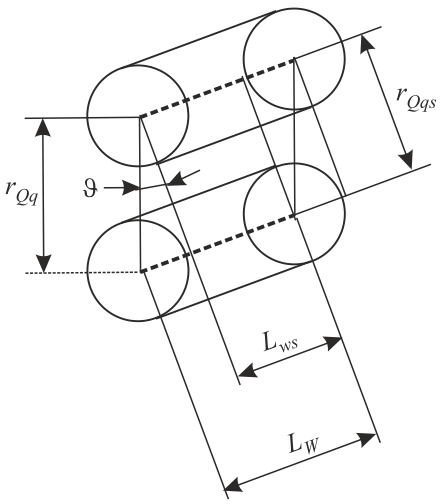

Fig. 7. Model packing of (BEDT-TTF) molecules: rectangular plates in the crystal structure, taking into account the deflection angle θ. r_{Qs} is the distance between two planes of molecules, r_{Qq} is the distance between their long axes (along the stack of molecules). The vision is directed along the long axis of molecules. L_W is the average intermediate size of the molecule (see Fig. 4), L_{ws} is a shortened length of a contact line.

At the same time, the distance between two adjacent molecules reduces to

$$r_{Qqs} = r_{Qq} \cos\theta; \; r_0 = r_{Qq} \cos\theta_{\max}. \tag{9}$$

We introduce $r = r_{Qq}$, i.e., the distance between the long molecular axes in the stacks and the dimensionless unit $\lambda = \dfrac{L_W}{r_0}$. As a result, relation (2) takes the form

$$u(\rho,\theta) = \frac{U(\rho)}{< n_{\text{int}} > \varepsilon}$$

$$= \left[1 - \frac{\rho}{\lambda} \sin\theta \right] \left[\left(\frac{1}{\rho\cos\theta} \right)^{12} - 2 \left(\frac{1}{\rho\cos\theta} \right)^{6} \right]. \tag{10}$$

All three interactions depend on the dimensionless distance between the planes molecules and the angle of a synchronous deflection of molecules in the stack:

$$u_{Qq}(\rho,\theta) = \left(1 - \frac{\rho}{\lambda} \sin\theta \right) \left[\left(\frac{1}{\rho\cos\theta} \right)^{12} - 2 \left(\frac{1}{\rho\cos\theta} \right)^{6} \right]$$

$$+ A_Q \left(\frac{1}{\rho} \right)^5 f(\theta) + A_q \left(\frac{1}{\rho} \right), \tag{11}$$

where $f(\theta)$ is defined in (6).

We construct the general form of the van der Waals potential with the angular dependence, i.e., the first term in (8), see Fig. 8. In this figure, we see the general dependence of the potential terrain on the distance between molecules and the angle of their tilt. The value θ = 0 has the form of an ordinary van der Waals dependence.

As our analysis has shown, taking into account a quadrupole and Coulomb interactions of molecules leads in particular to the occurrence of new local minima. The occurrence of new local minima is most likely due to the presence of a singularity $1/r$ at small r during the electrostatic interaction of molecules. When $1/r$ is superimposed on the original almost linear growth of the van der Waals potential, the formation of new local minimums is unavoidable. The singularity action $1/r$ manifests itself at much larger distances than $1/r^5$ for the quadrupole interaction. However, at weak doping or weak charge transfer, the impact of electrostatic interaction may also be insufficient for the transition. That is, the structural transition we obtained has a threshold character in terms of the parameter of the charge transfer to the BEDT-TTF molecules and of the temperature (the first-order phase transition).

The depth of the initial equilibrium state decreases significantly, i.e., the level rises. The main potential changes that affect the emergence of new equilibrium states occur in a narrow valley. As the quadrupole and then the electrostatic interactions are included in the consideration, the

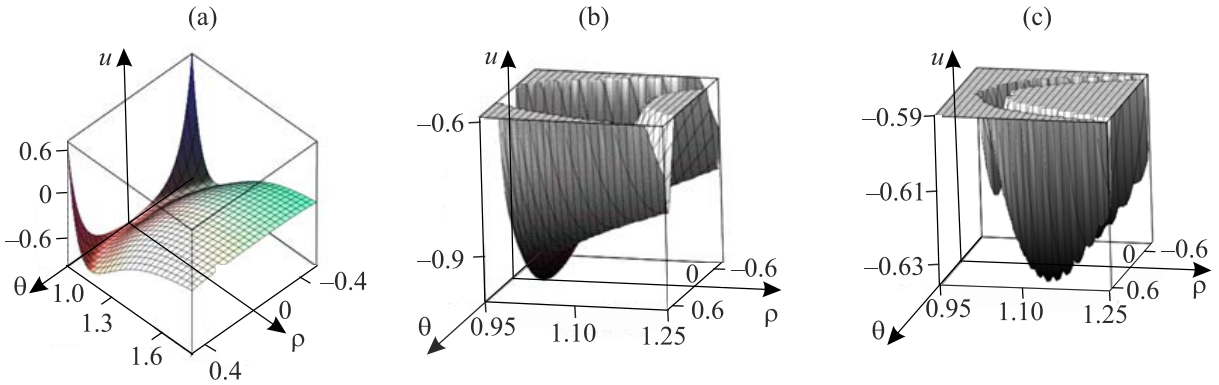

Fig. 8. (Color online) (a) General view of Lennard-Jones potential in form (11) with angular dependence on θ in the first term. (b) The similar enlarged image, with the minimum visible at ρ = 1, θ = 0. (c) The same fragment for the full potential (11), two new minima (new phase) are visible at $\rho \approx 1.13$, $\theta = \pm 0.48$ rad. The initial minima at ρ = 1, θ = 0 is considerably higher and divided by barriers.

valley width gets narrowed strongly, and its bottom rise is nonuniform. This nonuniform rise leads to the appearance of new minima in the potential, i.e., new equilibrium states of the system, and then to the phase transitions.

7. Conclusion and discussion

In this paper, the mechanism of the phase transition in the doped molecular crystals BEDT-TTF has been proposed using a too-simple model of the rectangular plates with interaction with the base of modified Lennard-Jones type potential.

A change in the state of the system (phase transition) occurs when moving to the ρ–θ plane at the bottom of a very narrow valley of the potential. At the same time, the path of this movement cannot be described by the change of only one of the variables, but only by their joint change. Physically, this means that during rearrangement in a molecular system (crystal) and mutual slip of molecules, their rotation relative to the long axis and an increase in the stacking distance between the long axes of molecules occur simultaneously. Let us recall that in general, the stability of each stack of BEDT-TTF molecules is provided by the interaction with neighboring stacks of molecules. The lattice structure of the arrangement of BEDT-TTF molecules in the α-phase and the θ-phase of the crystal (Fig. 3) provides a minimum of macroscopic stress during the phase transition. The free energy of the crystal includes kinetic and potential energies of interacting molecules and an entropy term [10]. Kinetic energy is a smooth and monotonic function of temperature. The same behavior must have the potential energy of the contact of narrow sides of the molecules. The entropy term is reconstructed in a new phase; it follows the structure change. Therefore, in the crystal's free energy, the main changing part is the potential energy of interaction of the planar sides, see (11) and Fig. 8. The controlling parameter of order is the value of the transferred charge (from doping small molecules to BEDT-TTF ones). The system needs a threshold value of the transferred charge to cause the phase transition. The transferred charge depends on the doping molecules' nature and contains metal atoms [1, 2, 5]. We can expect the first-order phase transition because Fig. 8(c) demonstrates the distinct maximum between minimums of old and new phases' potential energies (free energy).

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Фазові структури та взаємодія молекул BEDT-TTF

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Досліджено структурні фази в кристалі BEDT-TTF під впливом легуючих молекул. Система демонструє перехід від паралельно розташованої молекулярної фази (β-фази) до нового рівноважного стану, де молекули повернуті на певний кут (α- або θ-фаза). Показано, що причиною цього переходу є електростатична та квадрупольна взаємодія між молекулами BEDT-TTF та молекулами. Введено модифікований потенціал типа Жиріфалько, який залежить як від міжмолекулярної відстані, так і від кута повороту молекул. Виявлено, що рівноважна відстань між молекулами в стопці збільшується, а кут відхилення виникає при збільшенні заряду молекул домішок, що призводить до нових рівноважних станів.

Ключові слова: двовимірна модель, органічна молекула, потенціал Жиріфалько, електростатичне поле, квадрупольна взаємодія, фазовий перехід.