THEORY OF PHOTOINDUCED PHASE TRANSITIONS IN CRYSTALS WITH CHARGE TRANSFER COMPLEXES

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A theoretical research of photoinduced phase transitions for crystals with charge transfer (CT) complexes is fulfilled in the mean field approximation. In the presented model, it is suggested that a unit cell can be in three states: neutral state, CT state, and highly excited electronic state. An external electromagnetic field transfers the system from some initial state to the excited state and afterwards the system may return into another low-energy state. In such a way the system may be tranformed from neutral state to CT state and conversely. The steady-state and the time-dependent solutions of the kinetic equations are analyzed, and the uniform and space-dependent processes are investigated. The phase transition occurs at a certain threshold pumping, whose value decreases if the temperature of a sample approaches the critical temperature. The dynamics of the phase transition has a retardation interval which decreases with increase in a pumping. Such peculiarities of photoinduced phase transitions are observed in experiments.

1. Introduction

Intense irradiaton can influence a phase transition in two ways: firstly, it can change parameters of the existed phases, and secondly, the stimulation can create a great concentration of quasiparticles, which form a new phase in the case of attractive interaction. Phenomena of the alteration of phase states under light irradiation are named photoinduced phase transitions (PIPT). They are examples of non-equilibrium phase transitions and are researched intensively by experimenters.

PIPT happen in various systems. The paper [1] is one of the first works in the PIPT investigation, in which a highly excited gas was considered. A substantial part of gas molecules was translated on the excited level. The authors showed that the dipole-dipole interaction of molecules, which were sited on different energetic levels, would be more essential than ordinary Van der Waals forces and cause a deviation of a gas from the ideal regime and its condensation.

Exciton condensation in crystals with great exciton concentration is another example of photoinduced tranformation. There are two types of condensation in this phenomena: into a metallic Fermi liquid and into molecular liquid likewise the hydrogen-based scenario. In the first case, excitons decay, and an electron-hole liquid is created [2]. Phases of interacting excitons (or biexcitons) are formed in the second one [3].

New peculiarities were obtained for crystals with CT complexes [4—7] and spin-crossover complexes [8, 9] under laser irradiation. The phase transition occurs between the state with neutral molecules and the CT state in organic crystals or between low- and high-spin configurations in metal organic polymers. The theory of structure transformations was investigated in [10, 11], in which the authors paid attention mainly to a change of the structure of the electron-nuclear system under photoexcitation. This work will be generally applied to the kinetics of phase transitions.

Tetrathiafulvalene-chloranil (TTF-CA) is a typical example of CT crystals. It is composed of one-dimensional chains of a donor (D: TTF) and an acceptor (A: CA), in which molecules are charged negatively and positively by turns. There is a weak interaction between chains. The system undergoes the first-order reversible phase transition between the neural and ionic phases at T_c = 81 K [4]. The transition is revealed by a finite jump of the ionicity (the ratio of the amount of ionic molecules to the total number of molecules), which is determined by intramolecular excitation. In [4—6], PIPT was observed at $T < T_c$ from the ionic phase to the neutral one, and the reverse transition occurs at $T > T_c$. Under photoexcitation, a specific direction of PIPT is controlled by tuning the photon frequency of the laser irradiation.

The following peculiarities of PIPT are observed in experiments [4—6] for TTF-CA: 1) Threshold-like behaviour in the excitation intensity dependence of the photoconverted fraction of molecules; 2) Enhancement of the photoresponse amplitude at temperatures of a specimen around the transition temperature; 3) An incubation period in the phase transition dynamics, which depends on the excitation intensity. A sharp growth of photoconverted molecules takes place after a certain time of irradiation. This time delay decreases with increase in a pumping.

Resembling physical regularities were revealed in polydiacetylene crystal (PDA) [7].

It is important that a one-molecule transition to another state induces transitions in many molecules of the crystal (hundreds, according to [4]). This is related with the phase tranformation cooperativity in the vicinity of a phase transition temperature.

2. Model of the System

Before the investigation of the irradiation influence on the phase transition, let us consider a simple model of phase tranformation in crystals with CT complexes (e.g., TTF-CA) in self-consistent field theory. Let us study an organic compound with donor (D) and acceptor (A) molecules and regard this system to be a lattice, at every site of which the complex of two molecules (D and A) is located. The lowest electron levels are of neutral state (0) and of donor-acceptor state (CT). We suppose that the CT state level is lower. The energy of the system consists of the energies of separate molecules and interactions with all other molecules, which can be in different states (CT or 0):

$$U = \sum_n \sum_{i=1}^{2} \varepsilon_i c_{in} + \frac{1}{2} {\sum_{n,n'}}' \sum_{i,i'=1}^{2} V_{in,i'n'} c_{in} c_{i'n'}. \tag{1}$$

Here, n — site number, $i = 1$ suits the CT state, $i = 2$ suits the neutral one, ε_i is the energy of a separated complex which is in the i state, $V_{in,i'n'}$ is the potential energy of interaction of the complex which is in the i state at the n site with the complex in the i' state at the n' site, and c_{in} defines the probability for the complex to be at the n site in the i state. Also the following conditions are fulfilled for every site:

$$c_{1n} + c_{2n} = 1. \tag{2}$$

At first, let us analyze this system in a thermodynamic equilibrium state. In the self-consistent field method, the distribution of molecules over states is determined by the minimum of the free energy $F = U - TS$ obeying the auxiliary conditions (2). The entropy of the system $S = -k_\mathrm{B} \sum\limits_n \sum\limits_{i=1}^{2} c_{in} \ln c_{in}$. The minimum of the free energy yields the following transcendental system of equations for the coefficients c_{in}:

$$c_{in} = \frac{1}{1 + \exp\left[\frac{(-1)^i \Delta E_n}{k_\mathrm{B} T}\right]}, \quad i = 1, 2, \tag{3}$$

where the energy difference at the n site is

$$\Delta E_n = (\varepsilon_2 - \varepsilon_1) + {\sum_{n'}}' \big(V_{2n,1n'} c_{1n'} +$$

$$+ V_{2n,2n'} c_{2n'} - V_{1n,1n'} c_{1n'} - V_{1n,2n'} c_{2n'}\big). \tag{4}$$

The system of equations (3) is transcendental, because ΔE_n depends on c_{in}.

It is important that the energy of the complex ε_i is determined by the transfer integral from a donor molecule to an acceptor one. Thus, this quantity can essentially depend on temperature, because the transfer integral is susceptible to the distance between D and A molecules which varies with temperature due to thermal expansion of the crystal. In the vicinity of the phase transition, we may approximate this dependence by a linear function:

$$\varepsilon_2 - \varepsilon_1 = \varepsilon - \gamma T, \quad \gamma > 0. \tag{5}$$

Taking into account conditions (2), the energy difference reduces to

$$\Delta E_n = E_n - \gamma T - {\sum_{n'}}' \nu_{n,n'} c_{2n'}, \tag{6}$$

where $E_n \equiv \varepsilon + {\sum_{n'}}' (V_{2n,1n'} - V_{1n,1n'})$, $\nu_{n,n'} \equiv V_{2n,1n'} - V_{2n,2n'} - V_{1n,1n'} + V_{1n,2n'}$.

Let us analyze a uniform case. Then $c_{in} = c_i$, $E_n = E$,

$$\Delta E_n = E - \gamma T - V c_2, \tag{7}$$

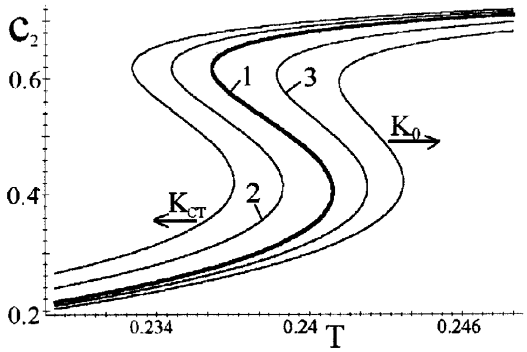

Fig. 1. The phase diagram $c_2\,(T)$: *1* — without pumping, *2* — at the pumping with $K_{\rm CT} = 0.02$, *3* — at the pumping with $K_0 = 0.02$. Parameters are $E = 0.835$, $\gamma = 1.4$, $E_v = 0$. Extreme curves concern the same irradiated system as *1* and *2*, but with the potential barrier $E_v = 0.15$

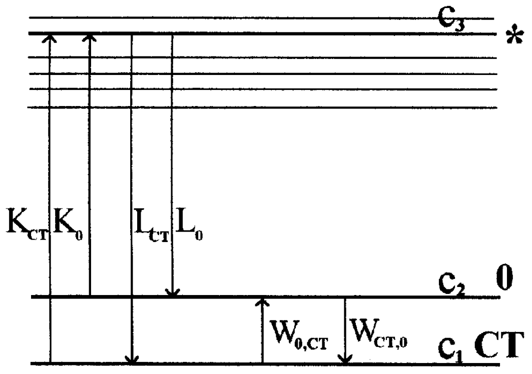

Fig. 2. Three-level system: 2 lowest levels of states CT and 0 and the excited one (*)

$V \equiv \sum\limits_{n'}{}' \nu_{n,n'}$. Choosing V as an energy unit and $\frac{V}{k_{\rm B}}$ as a temperature one, we can reduce Eq.(3) to

$$c_i = \frac{1}{1 + \exp\left[(-1)^i\left(\frac{E-c_i}{T} - \gamma\right)\right]}, \quad i = 1, 2\,. \tag{8}$$

The numerical solution of Eq.(8) yields the dependence of c_i on temperature, as curve *1* in Fig. 1 shows.

Such a phase diagram is typical of the first-order phase transition and contains a bistable region. A hysteresis on the phase diagram is present obeying the criteria:

$$\frac{1}{1+e^{-\gamma}} < E < \frac{1}{2} + \frac{\gamma}{4}, \quad E > 0 \tag{9}$$

The selection of V as energy unit needs fulfilling the condition $V > 0$, which means

$$2V_{1,2} - V_{2,2} - V_{1,1} > 0 \tag{10}$$

for a uniform system. The conducted analysis of (8) for other signs of the parameters V and E ascertained that conditions (10) and (9) were the only possible ones for the fitting of phenomena observed experimentally (the CT phase was at low temperatures, the ionic one was at high ones, and a narrow hysteresis was present).

The free energies in both phases are equal at the phase transition temperature

$$T_c = \left(E - \frac{1}{2}\right)/\gamma. \tag{11}$$

Let us suggest the following model of laser irradiation influence on the phase tranformation of the given system. Under the action of light, the complex is switched to an excited state, whose energy greatly exceeds the CT complex excitation energy. After the excitation, the complex state returns to low-excited states radiating a photon or through the relaxation processes with excitation of phonons. It is important that, after that the complex is excited from one ground state (CT or 0), it can return to another state. In such a way, the light "transfers" the complex from one state to another, from state 0 to state CT or vice versa. As shown in [4], the absortion coefficient of the complex in state 0 or CT depends on the light frequency, and this dependence is different for states CT and 0. This allows one to control the transfer processes between states by choosing the appropriate frequency.

Let us characterize the excited states by one level which is resonant to light frequencies. So, we deal with the model of a three-level system of D-A complexes (Fig. 2).

The probability for molecules to be on the excited level is designated as c_{3n}. This system can be described by the following kinetic equations:

$$\begin{cases} \frac{dc_{1n}}{dt} = -K_{\rm CT}c_{1n} + L_{\rm CT}c_{3n} - W^n_{2,1}c_{1n} + W^n_{1,2}c_{2n} \\ \frac{dc_{2n}}{dt} = -K_0c_{2n} + L_0c_{3n} - W^n_{1,2}c_{2n} + W^n_{2,1}c_{1n} \\ \frac{dc_{3n}}{dt} = K_{\rm CT}c_{1n} + K_0c_{2n} - (L_{\rm CT} + L_0)c_{3n}. \end{cases} \tag{12}$$

The designations are as follows: K_0 and $K_{\rm CT}$ are the pumping coefficients to the excited level from states 0 and CT, respectively, L_0 and $L_{\rm CT}$ are the relaxation coefficients from the excited level, $W^n_{2,1}$ and $W^n_{1,2}$ are the probabilities of the transitions CT → 0 and 0 → CT per time unit. One can define these probabilities as follows. If the potential barrier for the transition to a lower level

(CT) is E_v and the barrier $E_v+\Delta E_n$ must be overcome for the reverse transition, then

$$W^n_{2,1}=w\exp\left(-\frac{E_v+\Delta E_n}{k_{\mathrm{B}}T}\right),\ W_{1,2}=w\exp\left(-\frac{E_v}{k_{\mathrm{B}}T}\right), \tag{13}$$

where w is the coefficient which doesn't depend on temperature. At the same time, the probabilities of the direct and reverse transitions satisfy the detailed balancing principle for the ratio of the 0 → CT and CT → 0 transition probabilities. The full probability for the complex to be in a certain state at every site is equal to one (the normalization condition):

$$c_{1n}+c_{2n}+c_{3n}=1. \tag{14}$$

Due to a high speed of relaxation processes, the complexes don't stay too long on the excited level. Therefore, the number of excited complexes is rather small (by our estimations, $c_{3n}\sim 10^{-5}$). For this reason, the coefficients L_0 and L_{CT} were selected to be several orders higher than the pumping coefficients K_0 and K_{CT}.

The stationary solutions of the system of kinetic equations (12) are

$$c_{1n}=\frac{1}{1+I_{\mathrm{CT}}+(1+I_0)\,(\frac{I_{\mathrm{CT}}}{\tau_0}+W^n_{2,1})/(\frac{I_0}{\tau_{\mathrm{CT}}}+W_{1,2})}, \tag{15}$$

$$c_{2n}=\frac{1}{1+I_0+(1+I_{\mathrm{CT}})\,(\frac{I_0}{\tau_{\mathrm{CT}}}+W_{1,2})/(\frac{I_{\mathrm{CT}}}{\tau_0}+W^n_{2,1})}, \tag{16}$$

$$c_{3n}=I_{\mathrm{CT}}c_{1n}+I_0c_{2n}, \tag{17}$$

where the following designations are introduced: $\tau_{\mathrm{CT}}=\frac{1}{L_{\mathrm{CT}}}$, $\tau_0=\frac{1}{L_0}$, $\tau=\left(\frac{1}{\tau_{\mathrm{CT}}}+\frac{1}{\tau_0}\right)^{-1}$ which are the average time intervals of the transitions to CT and 0 levels from the excited one and the total average transition time, respectively; $I_{\mathrm{CT}}=K_{\mathrm{CT}}\tau$, $I_0=K_0\tau$ which mean the relative efficiencies of the pumping. Without irradiation, solutions (15), (16) turn into Eq.(3) which is obtained from the equilibrium distribution.

Let us find an approximation for the system of equations (3), (12) in the case of the distribution of spatially heterogeneous phases. It can be shown for a system with translational symmetry that

$$\sum_{n'}v_{n,n'}c_{2,n'}=V\left(-i\vec{\nabla}\right)c_2\left(\vec{r}\right)\Big|_{\vec{r}=n}, \tag{18}$$

where $V(k)\equiv\sum\limits_{n'}v_{n,n'}\exp\left(ik\left(n'-n\right)\right)$. If $c_2\left(\vec{r}\right)$ changes slowly in space, $V(k)$ can be expanded in a power series in $\left(-i\vec{\nabla}\right)$ and we obtain from (6) (energy difference) that

$$\Delta E_n=E_n-V\,c_{2n}+\sum_{i,j=1}^{3}a_{i,j}\frac{\partial^2 c_{2n}}{\partial x_{in}x_{jn}}-\gamma T, \tag{19}$$

where x_{in} is the coordinate of the n site and $a_{i,j}\equiv\frac{1}{2}\frac{\partial^2 V(k)}{\partial k_i k_j}$.

Phase nucleations and their growth are the important moments of first-order phase transitions. As known, the analysis of phase nucleation with regard for fluctuations is an accurate method, but it isn't considered here in details, because we use a self-consistent approach. However, the phase growth can be described by the kinetic equations (12) we investigate.

In the case of the essentially anisotropic system we research, a plane boundary is the most probable boundary of a phase interface. Therefore, the equations we solve must correspond to a realistic dynamics of the phase growth. So, we study the dynamics with the following boundary conditions: the system has equal or different phases on different sides of the plate.

For calculations, let us choose $\frac{1}{w}$ for a time unit, so that the kinetic coefficients (K_0, K_{CT}, L_0, L_{CT}) will be measured in units of w.

3. Numerical Computations and Discussion of Results

3.1. Stationary Irradiation of the Uniform System

Let us consider uniform solutions of the system with pumping which induces the transition between states CT and 0. Experimentally, such transformations are attained by tuning the irradiation frequencies .

At temperatures lower than T_c, the ionic phase dominates. Thus, the K_{CT}-pumping contributes to the CT → 0 conversion. The stationary solutions of the kinetic equations (15) for different pumpings are represented in Fig. 1. In the absence of irradiation, the solution coincides with the obtained earlier results for the equilibrium state. As one can see, for the considered pumping type, the phase diagram shifts to lower temperatures, and the temperature range of the ionic phase shortens.

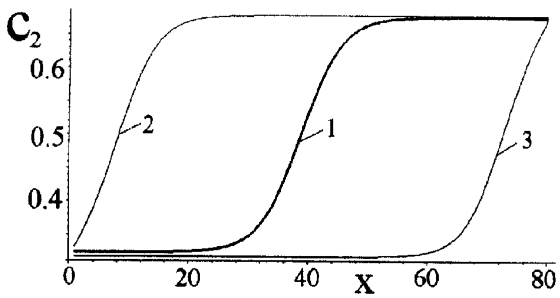

Fig. 3. Spatial phase distribution. $T = T_c = 0.2393$. At the boundaries different phases are supported. *1* — without pumping, *2* — at a pumping with $K_{\mathrm{CT}} = 0.01$, *3* — at a pumping with $K_0 = 0.01$

The 0 → CT conversion ought to be examined for temperatures $T > T_c$. The K_0-pumping leads to the neutral phase establishment at higher temperatures (curve *3* in Fig. 1).

The E_v barrier causes a further displacement of the phase diagrams (extreme thin curves in Fig. 1). This circumstance allows us to choose smaller values of a pumping for the same threshold effects by introducing bigger E_v.

Bistability of the system in the vicinity of T_c defines a jumping behaviour of the phase transformation in a steady case, because a stable phase can appear to be unstable due to the irradiation. The steady-task computations indicate that the phase transition occurs if the pumping magnitude is larger than some threshold value. The threshold depends on temperature and is linear under remoting the sample temperature from the phase transition temperature.

We analyze the phase transitions at switching the only one pumping type (K_{CT} or K_0). But PIPT will take place in case of $K_{\mathrm{CT}} \neq 0$, $K_0 \neq 0$, if a new phase is suitable for the steady stable state on the phase diagram. It is ascertained that, in the case of $K_0 = K_{\mathrm{CT}}$, a hysteresis on the phase diagram becomes shorter and, respectively, threshold effects will occur at a temperature which is less remoted from T_c, than in the tasks analyzed above.

3.2. Distribution of the Spatial Phase and Threshold Behaviour of the Population of Levels under Pumping

Let us consider spatially heterogeneous solutions of the system with parameters that correspond to the hysteresis region. We numerically solve the stationary equations (12) taking into account non-uniformity by Eq.(19). Assume that, on the boundaries of the crystal (e.g., on the parallel plates), different stable steady states are supported. The spatial distribution of molecules along the line which joins these plates is shown in Fig. 3 at $T = T_c$. The spatial separation of phases (curve *1*) is caused by the equality of the free energies in states 0 and CT. It changes to the domination of CT or 0 phases that is related to a deformation of the phase diagram of the irradiated system and, thus, the critical point modification.

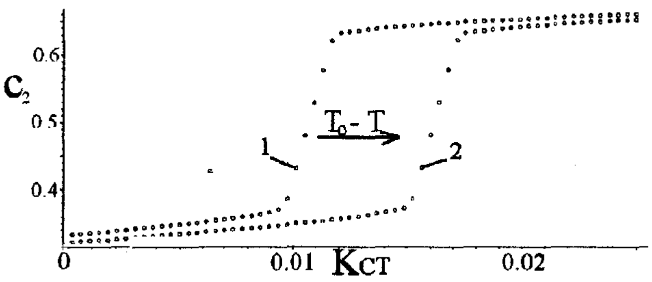

Fig. 4. Phase transition threshold. *1* — at $T = 0.2383$, *2* — at $T = 0.2378$

If the same phases are supported on the boundaries of the crystal (e.g., CT), then the K_{CT}-pumping can lead to the disappearance of the bistable region and compel the system to pass to another phase (0). The numerical simulation reveals a phase transition, if the irradiation intensity exceeds the threshold (Fig. 4). Otherwise (at weak pumpings), the irradiation don't cause a phase transition. For the same boundary conditions, we emphasize that a finite size of the crystal leads to the increase in the threshold comparing to an infinite system.

Now we determine the dependence of the threshold on the pumping for spatially restricted systems. Let us deal with the CT → 0 transition in a crystal with different boundary conditions at $T < T_c$. If irradiation is absent, the CT phase is established on the whole length. But, with increase in the K_{CT}-pumping, the 0-phase will be stable and the phase transition will occur. An example of such dependences is given in Fig. 5 for the system with different phases supported on the boundaries.

It was checked that the phase transition thresholds for both last heterogeneous tasks grew proportionally with a sample temperature deviation from the critical point for both pumping types.

3.3. Phase Transition Dynamics

Let us investigate the transition dynamics by solving the kinetic equations (12). We describe the peculiarity of the

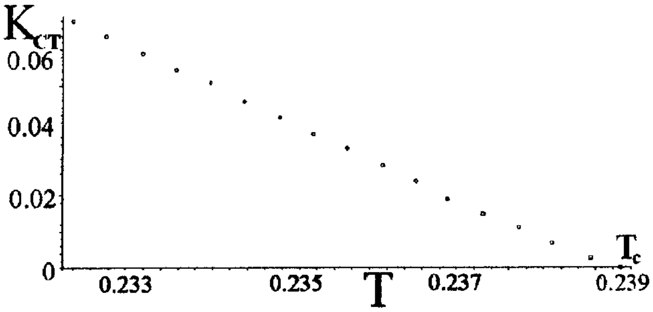

Fig. 5. Temperature dependence of the threshold pumping K_{CT}

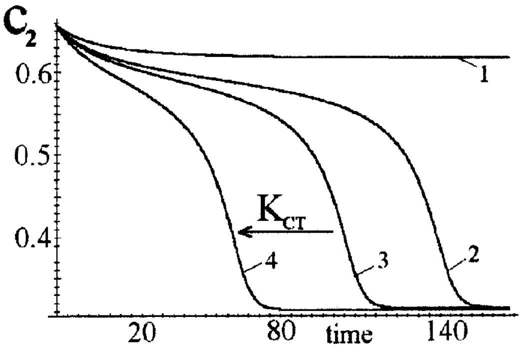

Fig. 6. Phase transformation dynamics. $T = 0.24$. *1* — $K_{\mathrm{CT}} = 0.006$, *2* — 0.008, *3* — 0.011, *4* — 0.014

increase in the fraction of neutral molecules by the example of a pumping on the higher level (0 state). The results of numerical computations for a uniform system are shown in Fig. 6. From the beginning, the ionic phase decreases slowly and, only after some satiation, abruptly transforms into another phase. That is, some time delay (the so-called incubation period) is present in the transition dynamics. The incubation period depends on the pumping: the transition takes place later at a weaker pumping.

Such a phase transformation behaviour dependent on the irradiation intensity is observed in the experiments and is related to the cooperativity of processes in the vicinity of the phase transition temperature.

The reverse transition 0 → CT induced by the K_0-pumping and the transition in a spatially restricted system reveal a similar behaviour.

4. Conclusions

Here, a theory of PIPT for crystals with CT complexes has been developed. The numerical computations of the system of kinetic equations have revealed the following results:

1. A phase transition occurs at some threshold pumping. The value of the threshold is proportional to the difference between the temperature of a sample and the phase transition temperature of the crystal.

2. The PIPT dynamics has an incubation period: a sharp growth of the photoconverted fraction of molecules takes place after a certain time of irradiation. This time delay decreases with rise in a pumping.

3. A finite size of the crystal leads to increasing the threshold.

As we see, the theoretical findings are in compliance with the experimental data for organic CT crystals like TTF-CA and PDA [4—7] emphasized in Introduction.

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ТЕОРІЯ ФОТОІНДУКОВАНИХ ФАЗОВИХ ПЕРЕТВОРЕНЬ В КРИСТАЛАХ З КОМПЛЕКСАМИ З ПЕРЕНОСОМ ЗАРЯДУ

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Резюме

У наближенні середнього поля побудовано теорію фотоіндукованих фазових перетворень для кристалів з комплексами з переносом заряду. У даній моделі вважається, що елементарна комірка може перебувати у нейтральному стані, стані з переносом заряду і у високозбудженому електронному стані. Зовнішнє електромагнітне поле переводить систему з деякого початкового стану в збуджений стан, а потім система повертається у інший низькоенергетичний стан. В такий спосіб система може бути переведена з нейтрального стану в стан з переносом заряду чи навпаки. Проаналізовано стаціонарний і нестаціонарний розв'язки кінетичних рівнянь, досліджено процеси в однорідній та неоднорідній системах. Фазовий перехід відбувається при пороговій накачці, величина якої зменшується з наближенням температури зразка до критичного значення. Динаміці фазового переходу властивий певний час запізнення, який зменшується зі збільшенням накачки. Такі властивості фотоіндукованих фазових перетворень спостерігаються і на експерименті.