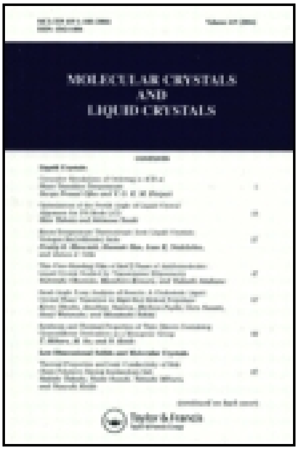

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Model of Photoinduced Phase Transitions in Crystals with Charge Transfer Complexes

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A theory of photoinduced phase transitions for crystals with charge transfer complexes is proposed employing the mean field approximation. In the presented model, a unit cell is suggested to be in three states: neutral state, charge transfer state, and highly excited electronic state. The system can be transformed from neutral state to ionic one or vice versa through the excited level by an external electromagnetic field. The system of kinetic equations has been solved in uniform and spatially restricted cases. The phase transition occurs at a certain threshold pump, the value of which decreases if temperature of a sample approaches to the critical temperature. The dynamics of the transition has a retardation interval, which decreases with a pump rising.

Keywords: charge transfer complexes; photoinduced transition

INTRODUCTION

A number of organic crystals with charge transfer complexes were observed to have the phase transition between neutral and ionic ground states under the action of ambient pressure or due to thermal contraction [1,2]. Having anomalous behaviour, the phenomenon attracted theoretical papers, which proposed models to interpret data obtained. Taking into account various arrangement modes of chains, the Hubbard model [3] explained a broad temperature range between different phases. Nagaosa [4] studied the extended-modified Hubbard model including the electron-lattice and interchain interactions; a new kind of elementary excitations – neutral-ionic domain wall – was proposed.

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Recently, the photoinduced phase transition (PIPT) has called attention as a method of photoswitching states of a crystal. The transition has been observed in crystals with charge transfer (CT) complexes [5–8] and spin crossover complexes [9,10] 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 [11,12], where the authors paid attention mainly to changes of the structure of an electron-nuclear system under photoexcitation. This work will be generally applied to the kinetics of phase transitions.

TTF-CA (tetrathiafulvalene-chloranil) 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 alternatively charged negatively or positively. The system undergoes the first-order reversible phase transition between the neutral and ionic phases at $T_c = 81K$ [5]. The transition is revealed by a finite jump of the ionicity (the ratio of the number of ionic molecules to the total number of molecules) which is determined by intramolecular excitation. In [5–7], PIPT at $T < T_c$ from the ionic phase to the neutral one and the reverse transition at $T > T_c$ were observed. Under photoexcitation, a specific direction of PIPT is controlled by tuning the photon frequency of laser irradiation.

The following peculiarities of PIPT were observed for TTF-CA [5–7] and PDA [8]: 1) Threshold-like behaviour in the dependence of a photoconverted fraction of molecules on the excitation intensity; 2) Enhancement of the photoresponse amplitude at the specimen temperatures around the transition temperature; 3) An incubation period in the phase transition dynamics depending on the excitation intensity. A sharp growth of the share of photoconverted molecules takes place after a certain time of irradiation. This time delay decreases with pump rising.

It is to be noted that a transition of one molecule into another state induces transitions in many molecules of the crystal (hundreds, according to [5]). This is related with the cooperativity of phase transformation in the vicinity of the phase transition temperature.

MODEL OF THE SYSTEM

Let us investigate 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 electronic levels are those of the neutral state (0) and donor-acceptor state (CT). The CT state level is supposed to be lower.

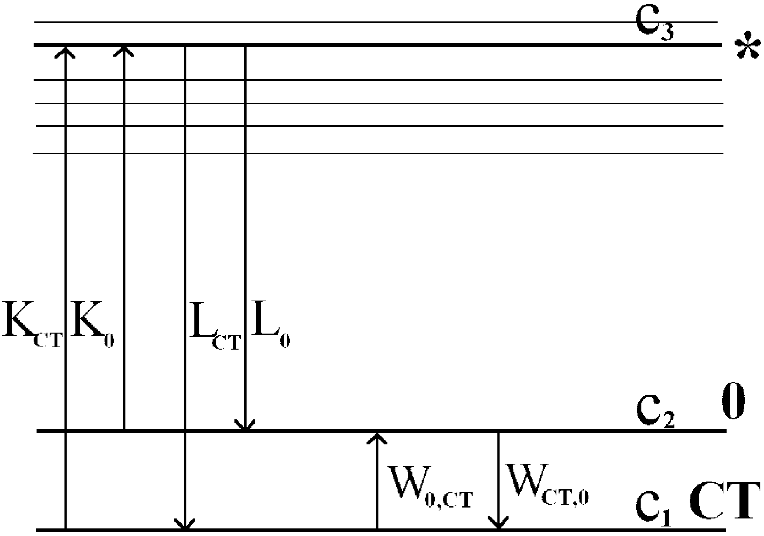

FIGURE 1 Three-level system: 2 lowest levels of CT and 0 states and the excited one (*).

We suggest the following model for the influence of laser irradiation on the phase transformation 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 by radiating a photon or, as a result of relaxation processes, with excitations of phonons. It is important that, after the excitation of the complex from a 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 0 state to CT state or vice versa. As shown in [5], the absorption coefficient of the complex in 0 or CT state depends on the light frequency and this dependence is different for CT and 0 states. This allows one to control the transfer processes between states by choosing the appropriate frequency. Let us characterize excited states by one level resonant for light frequencies. So, we'll deal with the model of a three-level system of D-A complexes (Fig.1). This system can be described by the following kinetic equations

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

where c_{in} defines the probability for the complex to be at site n in state i ($i = 1$ and $i = 2$ stand for the CT state and neutral one, respectively, and $i = 3$ corresponds to the excited level). Other designations are: K_0, K_{CT} – pump coefficients to the excited level from 0 and CT states respectively (they are proportional to the light intensity); L_0, L_{CT} – relaxation coefficients from the excited level; $W^n_{2,1}$, $W^n_{1,2}$ – $CT \to 0$ and $0 \to CT$ are the transition probabilities per unit time. Let us denote the energy difference at site n by ΔE_n.

One can define now the aforementioned probabilities. If the potential barrier for the transition to the lower level is E_v and, for the reverse transition, the potential barrier $E_v + \Delta E_n$ must be overcome, then

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

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 balance principle for the ratio $W^n_{2,1}/W_{1,2}$. The full probability for a complex to be in a certain state at every site is equal to one (normalization condition):

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

Without irradiation, the stationary solutions of system (1) must coincide which those got from the equilibrium distribution:

$$c_{in} = \frac{1}{1 + \exp\left[\frac{(-1)^i \Delta E_n}{k_B T}\right]}, \quad i = 1, 2. \tag{4}$$

The last formula can be obtained by minimizing the free energy of the crystal of D-A chains.

Assuming the complex energy to be

$$E_i = \varepsilon_i + \sum_{n'}{}' V_{in,i'n'} c_{i'n'}, \quad i = 1, 2, \tag{5}$$

one can expand ΔE_n as

$$\Delta E_n = U_n - \sum_{n'}{}' v_{n,n'} c_{2n'}, \tag{6}$$

$U_n \equiv \varepsilon_2 - \varepsilon_1 + \sum_{n'}{}' \big(V_{2n,1n'} - V_{1n,1n'}\big)$, $v_{n,n'} \equiv V_{2n,1n'} - V_{2n,2n'} - V_{1n,1n'} + V_{1n,2n'}$. Here, ε_i is the energy of a separated complex which is in state i and $V_{in,i'n'}$ is the potential energy of the interaction of a complex located at site n in state i with a complex located at site n' in state i'.

It is worth noting that the complex energy ε_i is determined by the transfer integral from a donor molecule to an acceptor one. Thus, this quantity can strongly depend on temperature because the transfer integral is susceptible to the distance between D and A molecules which varies with temperature due to crystal thermal expansion. We approximated this dependence by a linear function:

$$\varepsilon_2 - \varepsilon_1 = \varepsilon - \gamma T, \quad \gamma > 0. \tag{7}$$

In the uniform case, $c_{in} = c_i$, $\Delta E_n = E - \gamma T - Vc_2$, where $V \equiv \sum_{n'}{}' v_{n,n'}$. Choosing V as an energy unit V/k_B as a temperature one, we can reduce Eq. (4) to the form:

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

The numerical solution of Eq. (8) yields the dependence of the fraction of neutral molecules on temperature as depicts (solid curve). Such a phase diagram $c_2(T)$ is typical of first-order phase transitions and contains a bistable region. The hysteresis on the phase diagram is present and obey the criteria

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

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

$$T_c = \frac{E - \frac{1}{2}}{\gamma}. \tag{10}$$

Due to a high speed of relaxation processes, complexes don't stay too long on excited levels. Consequently, the number of excited complexes is rather small (in this work, the evaluation gives $c_{3n} < 10^{-5}$). For this reason, the coefficients L_0, L_{CT} were selected to be by several orders higher than the pump coefficients K_0, K_{CT}. Pumping was taken to be continuous and constant for all the tasks calculated.

The systems of Eqs. (1) or (4) are transcendental because the transition probabilities include ΔE_n containing the interaction, and therefore they depend on c_{in} nonlinearly.

Let us find an approximation in case of the distribution of spatially heterogeneous phases. For the system with translational symmetry, it

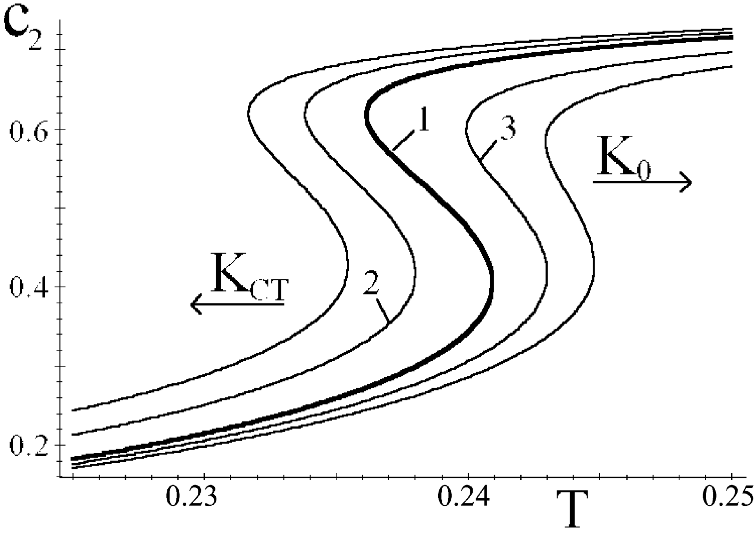

FIGURE 2 The phase diagram $c_2(T)$: 1 – without pump, 2 – at pump $K_{CT} = 0.03$, 3 – at pump $K_0 = 0.03$. The parameters are $E = 0.835$, $\gamma = 1.4$, $E_v = 0$. Extremes curves concern the same irradiated system as 1 and 2, but with the potential barrier $E_v = 0.15$.

can be shown that

$$\sum_{n'} v_{n,n'} c_{2n'} = V(-i\vec{\nabla}) c_2(\vec{r})|_{\vec{r}=n}, \tag{11}$$

where $V(k) = \sum_{n'} v_{n,n'} \exp(ik(n'-n))$. If $c_2(\vec{r})$ changes slowly in space, $V(k)$ can be expanded in a power series of $(-i\vec{\nabla})$ and Eq. (6) (the energy difference) is modified as

$$\Delta E_n = E_n - V_n c_{2n} + \sum_{i,j=1}^{3} a_{i,j}^n \frac{\partial^2 c_{2n}}{\partial x_{in} x_{jn}} - \gamma T. \tag{12}$$

where x_{in} – the coordinate of site n, $a_{i,j}^n \equiv \partial^2 V_n / \partial x_{in} x_{jn}$, $E_n - \gamma T = U_n$.

The phase nucleation and its growth are the important aspects of first-order phase transitions. The statistical approach considering fluctuations is an accurate method for phase nucleation analysis. We focused on the self-consistent approach, because a phase growth can be readily described by the kinetic Eq. (1).

A plane boundary is the most probable boundary of an phase interface. So, we will investigate the dynamics with the following boundary conditions: the system had the same or different phases on different sides of the plate.

For calculations, w^{-1} is chosen for a time unit. The kinetic coefficients K_0, K_{CT}, L_0, L_{CT} are measured in units of w.

NUMERICAL COMPUTATIONS AND DISCUSSION OF THE RESULTS

1. Phase Diagram of a Steadily Irradiated Uniform System

Let us consider uniform solutions of the system at pumping, which induces the transition between CT and 0 states. As was mentioned, the pump types differ by photon energy. At temperatures lower than T_c the ionic phase dominates, thus the pump with K_{CT} contributes to the $CT \rightarrow 0$ conversion. The stationary solutions of kinetic Eq. (1) for different pump types are represented in Figure 2. In the case of absence of irradiation, the solution coincides with the results obtained earlier for the equilibrium state. As one can see, for the pump with K_{CT}, the phase diagram shifts to lower temperatures, and the temperature range of the ionic phase shortens (curve 2 in Fig. 2). The $0 \rightarrow CT$ conversion should be examined for temperatures $T > T_c$: the

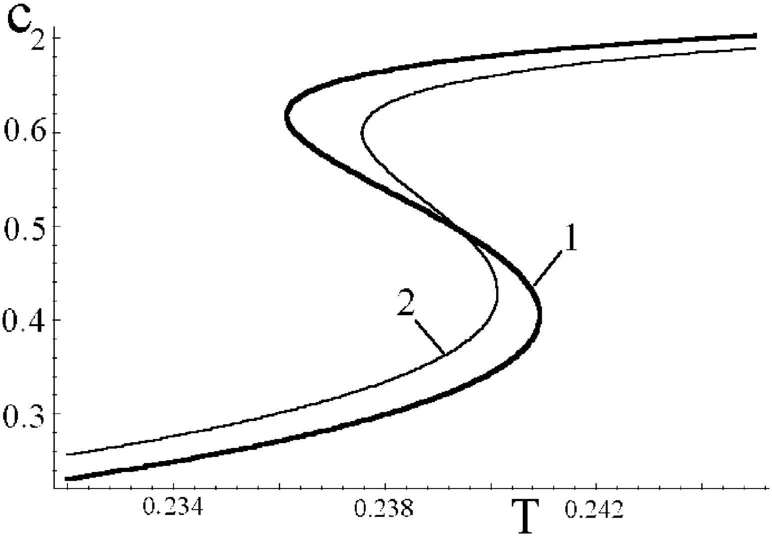

FIGURE 3 Phase diagram: 1 – without irradiation, 2 – in case of double pumping $K_{CT} = K_0 = 0.03$.

pump with K_0 leads to the neutral phase establishment at higher temperatures (curve 3 in Fig. 2).

The potential barrier E_v gives rise to a further displacement of the phase diagram (extreme thin curves in Fig. 2). This circumstance allows us to choose smaller values of pumps for the same threshold effects by introducing bigger E_v.

Bistability of the system in the vicinity of T_c causes a jumping behaviour of the phase transformation in a steady regime, because a stable phase can become unstable due to irradiation. The steady task computations point that a phase transition occurs if the pump magnitude is larger than some threshold value. The threshold depends on temperature and is linear in the difference of a temperature of the sample and the phase transition temperature.

We analyzed phase transitions at switching on only one pump type (K_{CT} or K_0). But PIPT takes place in case of $K_{CT} \neq 0$ and $K_{CT} \neq 0$, if a new phase is suitable for the stationary stable state on the phase diagram. It is ascertained that, in the case of $K_{CT} = K_0$, the hysteresis on the phase diagram becomes shorter (Fig. 3) and, consequently, threshold effects occur at temperatures which are closer to T_c, than in the tasks analyzed above.

2. Phase Stratification and Threshold Behaviour in the Population of Levels Under Pumping a Heterogeneous System

Let us consider spatially heterogeneous solutions of the system of equations at parameters corresponding to the hysteresis region. We numerically solved the stationary Eq. (4) taking into account nonuniformity by Eq. (12). On the boundaries of the crystal (e.g., on the parallel plates) different stable stationary states were assumed to be supported. The spatial distribution of molecules lengthwise the line joining these plates is shown in Figure 4 at $T = T_c$. The spatial separation of phases (curve 1 in Fig. 4) is explained by the equality of the free energies in 0 and CT states. It changes to the domination of the CT or 0 phase, that is related to a deformation of the phase diagram of the irradiated system and thus to a shift of the critical point.

If the same phases are supported on the boundaries of the crystal (e.g., CT), then the pump with K_{CT} can lead to the disappearance of the bistable region and compel the system to pass to another phase (0). Numerical stimulation reveals a phase transition if the irradiation intensity exceeds the threshold value. Otherwise (at weak pumps), the irradiation doesn't give rise to a phase transition. For the same boundary conditions, it is essential that a final size of the crystal leads to

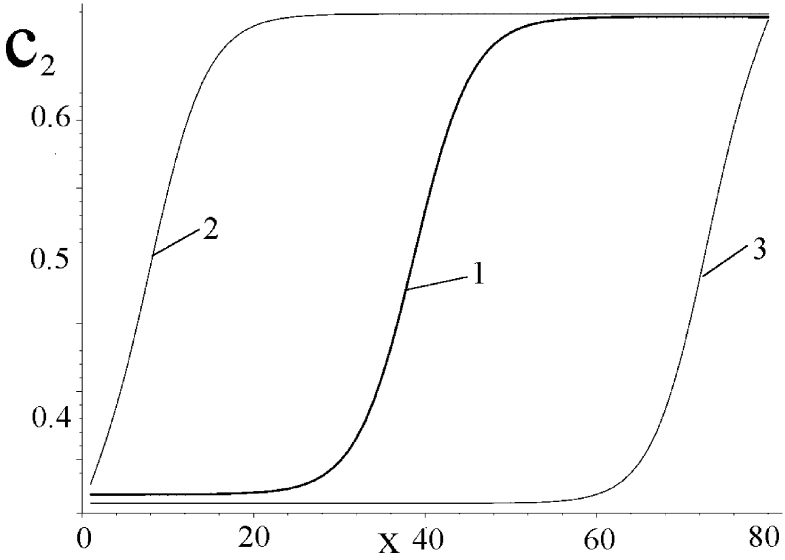

FIGURE 4 The spatial phase distribution. $T = T_c = 0.2393$. At the boundaries different phases are supported. 1 – without pump, 2 – at pump $K_{CT} = 0.01$, 3 – at pump $K_0 = 0.01$.

an increase in the threshold comparing with that of the infinite system.

Now we determine the threshold dependence on the pumping of spatially restricted systems. Let us deal with the $CT \rightarrow 0$ transition in a crystal with different boundary conditions at $T < T_c$. If the irradiation is absent, the CT phase is established on the whole length. But for the pump with K_{CT}, the increasing 0 phase becomes stable and the phase transition happens.

It was checked that the phase transition thresholds for the both heterogeneous tasks grow proportionally to the sample temperature deviation from the critical temperature for both pump types.

3. Transition Dynamics

Now we'll investigate the transition dynamics by solving the kinetic Eq. (1). Let us follow the increasing fraction of neutral molecules by an example of the pumping on the higher level (0 state). The results of numerical computations for the uniform system are shown in Figure 5. At first, the ionic phase decreases slowly and, only after some saturation, abruptly transforms into another phase, i.e. some time

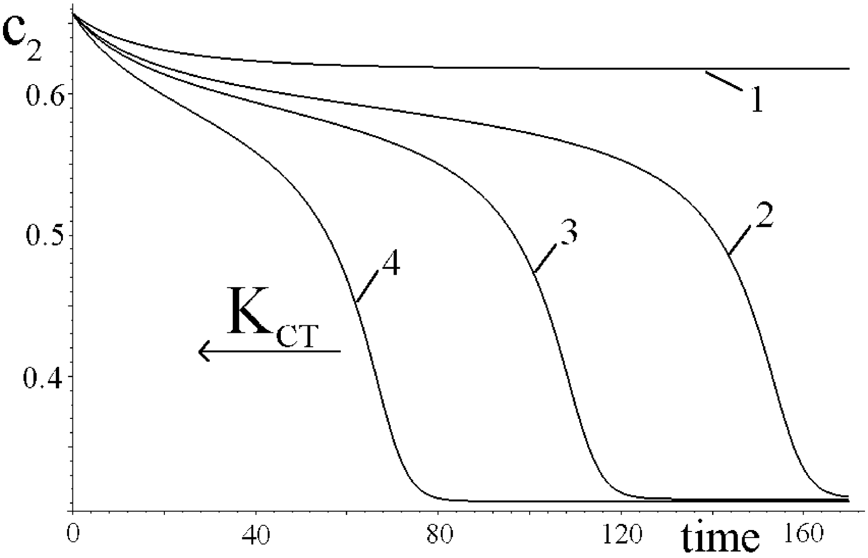

FIGURE 5 Dynamics of phase transformation. $T = 0.24$. 1 – $K_{CT} = 0.008$, 2 – $K_{CT} = 0.0112$, 3 – $K_{CT} = 0.0125$, 4 – $K_{CT} = 0.016$.

delay (the so-called incubation period) is present in the transition dynamics. The incubation period depends on the pump: the transition takes place later at a weaker pump. The reverse transition $0 \rightarrow CT$ induced by the pump with K_0 and also the transition in a spatially restricted system reveal a similar time delay. Such a behaviour of the phase transformation dependent on the irradiation intensity was observed in experiments [5] and is related to the cooperativity of processes in the vicinity of the phase transition temperature.

CONCLUSIONS

In the present paper, a theory of phase transitions for the crystals with CT complexes under steady light irradiation has been built. Numerical computations of the system of kinetic equations have revealed the following results: 1) The phase transition occurs at some threshold pump. 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: the sharp growth of the photoconverted fraction of molecules takes place after a certain period of irradiation. This time delay decreases with pump rising. 3) A finite size of the crystal leads to the need of a greater pump for the threshold phenomena to arise.

The theoretical findings are in compliance with experimental data for organic CT crystals like TTF-CA [5–7] discussed in Introduction.

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