Charge transfer vibronic excitons: charge transfer-lattice instability effects

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Two aspects for the development of bi-polaronic exciton (charge transfer vibronic exciton–CTVE) investigations in ionic-covalent solids are considered. These are predictions of charge transfer-lattice instability corresponding to charge transfer and lattice anharmonicity as well as to repulsion between different type CTVEs in the order parameter field. Oxide crystals ($SrTiO_3$, $BaTiO_3$, $K_3Na(CrO_4)_2$) are considered as an example.

1. Introduction

Bi-polaronic excitons (CTVE, see, for example, [1–5] and references therein) are one of recent topics for ferroelectric oxides. CTVEs are correlated polaronic electron-hole pairs or triads. Our first phenomenological models for CTVEs [1] were based on the validity of the strong vibronic coupling limit (including charge transfer-lattice coupling). It was confirmed by us [2,3] in the framework of the semi-empirical Hartree–Fock calculations of CTVE in the INDO approach. These first CTVE-calculations confirmed a realization of CTVE selflocalization with formation of good defined CTVE dipole moment as well as its triad structure in model ferroelectric oxides. Another new step [5] was done where CTVE dipole reorientations due to CTVE-CTVE cross-relaxation were considered and manifested in the experiments. As a result, CTVEs have an electric dipole moment (evaluated, for instance, in [6,7]) which can reorient due to CTVE-CTVE cross-relaxation. Hence, CTVEs manifest themselves as dipole reorienting centres which can directly interact with the soft polarisation mode. Namely due to this reason the CTVEs in ferroelectric oxides can shift (or induce) ferroelectric phase transitions [6,7]. The main topics of this paper will be the following.

(i) Local (Fig. 1, a) and cluster-type (Fig. 1, b) transitions connected with first order charge transfer-lattice instability [4] in the low lying excited state of the ionic-covalent crystal due to charge transfer and lattice anharmonicity will be considered. Such a phenomenon could be a candidate for the explanation of detected recently [8] strong order-disorder type fluctuations in the soft dynamic temperature regions in $SrTiO_3$ and in $BaTiO_3$ nominally pure crystals. (ii) Another mechanism of charge transfer-lattice instability could be related with order parameter induced mixing between different type of CTVEs. Namely, it will be a ferroelastic order parameter which mixes CTVE-I which exists even in the linear approximation on the one hand, and pure anharmonic CTVE-III on the other (in accord with a classification in [4]). We shall connect such a behavior with anomalous EPR-spectrum transformation in oxide ferroelastic $K_3Na(CrO_4)_2$ at low temperature detected recently [9].

2. Local and macroscopic charge transfer-lattice instability corresponding to anharmonic charge transfer excitations

The considerations in this section will be based on dynamical model with on-center single-well potential for an active vibration in each cell of the crystal. Nevertheless, the multi-well potential with off-center behavior takes place here
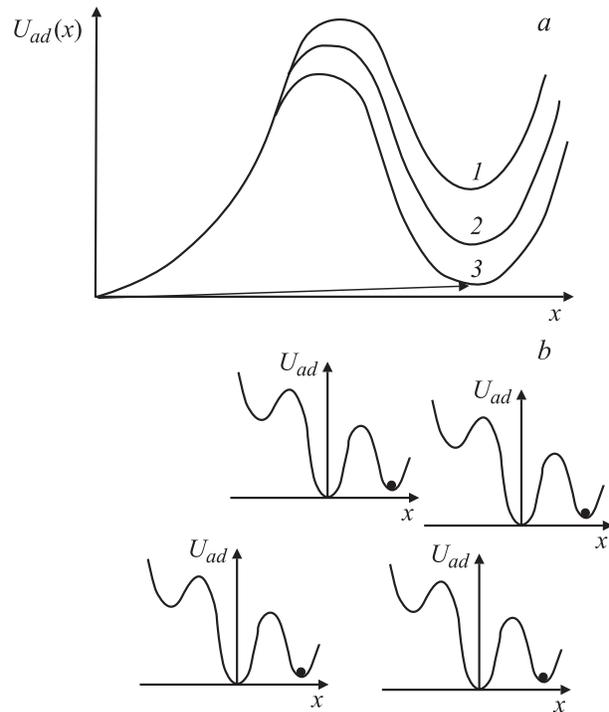
Figure 1. a — local charge transfer-lattice transition with occupation of anharmonic charge transfer related minimum of adiabatic potential. The potential curves *1–3* correspond to the following inequalities realization: $T_1 > T_2 > T_3 \geq T_{loc...}$, T_{loc} is a local transition temperature. b — precursor polar cluster formation due to preferable occupation of low lying excited anharmonic charge transfer states in the neighbouring cells in the vicinity of local charge transfer-lattice transitions.

for low lying excited anharmonic state. Such a potential could be induced by charge transfer-lattice interaction relating to specific anharmonic CTVE due to ground state potential anharmonicity (so-called CTVE-III, see [4]).

Let us consider the free energy of such a CTVE-III system interacting with a soft TO polarization for the topical case of a soft direction for such a polarisation, namely, along the [001]-type direction. Here only two from six possible CTVE — orientations (which are parallel and anti-parallel to **P** orientation) interact with **P**. As a result, the CTVE-related free energy has the following form:

$$
\begin{aligned}
\delta F_{\text{CTVE}} = &-N_{\text{CTVE}}kT \ln\Big[1 + \exp\big\{\big[(4\pi/3)d_i^{\text{CTVE}}P_i \\
&- \Delta_0 + \Delta_1(T)\big]/kT\big\} + 4\exp\big\{[-\Delta_0 + \Delta_1(T)]/kT\big\} \\
&+ \exp\big\{\big[-(4\pi/3)d_i^{\text{CTVE}}P_i - \Delta_0 + \Delta_1(T)\big]/kT\big\}\Big] \\
&+ \frac{\alpha_0(T-T_C)}{2}P_i^2 + \frac{\beta}{4}P_i^4 + \dots
\end{aligned} \tag{1}
$$

T_C is the initial ferroelectric phase transition temperature, and N_{CTVE} is the CTVE concentration. Here CTVE activation energies which are related with CTVE-induced lattice polarization for non-critical, Δ_0, and for soft lattice, $\Delta_1(T)$, degrees of freedom of ferroelectric as well as „CTVE effective dipole moment-soft polarization" $d_i^{\text{CTVE}} - P_i$ interaction all of them form resulting CTVE-III excitation energy. Corresponding splitting appears between the lowest CTVE-III type excitation in the off-center potential well located along total internal field on the one hand, and the on-center ground state on the other, $[\Delta_0 - (4\pi/3)d_i^{\text{CTVE}}P_{i0} - \Delta_1(T)]$. Note also that temperature dependence for $\Delta_1(T)$ could be evaluated here in the framework of minimization of the soft mode polarization field induced by CTVE-III total electric dipole moment bi-linearly interacting with soft polarization, $\sim d_i^{\text{CTVE}}P_i$. Taking into account a contribution of a soft polarization mode, $\omega_0^2(T) = \lambda(T - T_C)$, we get rather smooth $\Delta_1(T)$ dependence for a parabolic dispersion law for soft mode and for fulfilling of an inequality $a \ll R_C(T)$, $R_C(T)$ is soft polarization correlation redius, a is a lattice constant: $\Delta_1(T) \propto [1 - (a/2R_C)]$.

In general, we could get here the phase transition of the second order due to fast enough CTVE-III reorientations and possibility of their alignment with mean field effect formation. Such a phenomenon is similar to a phase transition induced by reorientable CTVE-I which are pumped by irradiation [4]. Here we have a situation of thermal population of off-center potential minima. As a result, the approximate equation for the free energy at high CTVE-III activation energies, at not so small temperatures, and at small enough magnitudes of soft polarization, when the inequalities $(\Delta_0 - \Delta_1(T)) \gg kT \gg (4\pi/3)d_i^{\text{CTVE}}P_i$, are fulfilled, becomes

$$
\begin{aligned}
\delta F_{\text{CTVE}} = &\left(\frac{\alpha_0(T-T_C)}{2}\right. \\
&- \left.\frac{N_0 \exp\{(-\Delta_0 + \Delta_1(T))/kT\}\{(4\pi/3)d_i^{\text{CTVE}}\}^2}{6kT}\right)P_i^2 \\
&+ \frac{\beta}{4}P_i^4 + \dots
\end{aligned} \tag{2}
$$

and leads to the following transcendental equation for CTVE-III induced second order ferroelectric phase transition:

$$
(T - T_C)T = \frac{N_0 \exp\{(-\Delta_0 + \Delta_1(T))/kT\}\{(4\pi/3)d_i^{\text{CTVE}}\}^2}{3k\alpha_0}. \tag{3}
$$

Such an equation could be solved numerically.

Now we shall discuss the CTVE clustering effects (see also Fig. 1, *b*). First, we have to deal here with additional CTVE energy lowering due to co-operative „Negative-U effect". As a result, clustering becomes advantageous. Second, let us take now into account that CTVEs are mobile excitations due to cross-relaxation processes [5]. These two circumstances together leads to possibility of clustering for CTVE-III under consideration. Necessary condition for its effective realization is a fulfilling of the requirement that average CTVE-CTVE distance, $\langle R_{\text{CTVE-CTVE}}\rangle$, is less or at least has the same order than distance which can pass CTVE in the framework of random cross-relaxation hopping before its recombination. Such a condition can be expressed in the following form:

$$
\langle R_{\text{CTVE/CTVE}}\rangle \le a\sqrt{\frac{1/\tau_{\text{cross}}}{1/\tau_{\text{recomb}}}} \tag{4}
$$

a is a lattice constant, $(1/\tau_{\text{cross}})$, $(1/\tau_{\text{recomb}})$ are the rates of CTVE-CTVE cross relaxation and of CTVE recombination, respectively. It should be noted that the latter rate has a tunnelling-related nature for the case of CTVE-III, and is rather slow. This aspect is favourable for inequality (4) fulfilling. So, let us consider now the CTVE-III clustering. For instance, free energy of the system with density of the CTVE-III clusters (N_{cluster}), and with number of the CTVE-III within each cluster (n_{CTVE}) has the following form

$$
\begin{aligned}
\delta F_{\text{CTVE}} = &-N_{\text{cluster}}kT \ln\Big[1 + \exp\big\{\big[(4\pi/3)n_{\text{CTVE}}d_i^{\text{CTVE}}P_i \\
&- \Delta_0 n_{\text{CTVE}} + \Delta_1(T)n_{\text{CTVE}} + \Delta_2 n_{\text{CTVE}}^2\big]/kT\big\} \\
&+ 4\exp\big\{\big[-\Delta_0 n_{\text{CTVE}} + \Delta_1(T)n_{\text{CTVE}} + \Delta_2 n_{\text{CTVE}}^2\big]/kT\big\} \\
&+ \exp\big\{\big[-(4\pi/3)n_{\text{CTVE}}d_i^{\text{CTVE}}P_i - \Delta_0 n_{\text{CTVE}} + \Delta_1(T)n_{\text{CTVE}} \\
&+ \Delta_2 n_{\text{CTVE}}^2\big]/kT\big\}\Big] + \frac{\alpha_0(T-T_C)}{2}P_i^2 + \frac{\beta}{4}P_i^4 + \dots
\end{aligned} \tag{5}
$$

Here $\Delta_2 n_{\text{CTVE}}^2$-term is related with co-operative „Negative-U" effect, and leads to essential decreasing of off-center CTVE-III minima energies. Under similar approximations as it was done above, $(\Delta_0 n_{\text{CTVE}} - \Delta_1(T)n_{\text{CTVE}} - \Delta_2 n_{\text{CTVE}}^2) \gg kT \gg (4\pi/3)n_{\text{CTVE}}d_i^{\text{CTVE}}P_i$, we obtain the following approximate free energy equation for its har-

monic part:

$$\delta F_{\text{CTVE}} = \left(\frac{\alpha_0(T - T_C)}{2} - \frac{N_{\text{cluster}}}{6kT} \right.$$

$$\times \exp\{(-\Delta_0 n_{\text{CTVE}} + \Delta_1(T)n_{\text{CTVE}} + \Delta_2 n_{\text{CTVE}}^2)/kT\}$$

$$\left. \times \{(4\pi/3)n_{\text{CTVE}}d_i^{\text{CTVE}}\}^2 \right) P_i^2 + \dots. \quad (6)$$

The latter leads to an equation for the second order ferroelectric phase transition temperature induced by CTVE-III related reorienting polar clusters:

$$(T - T_c)T = \frac{N_{\text{cluster}}}{3k\alpha_0}$$

$$\times \exp\{(-\Delta_0 n_{\text{CTVE}} + \Delta_1(T)n_{\text{CTVE}} + \Delta_2 n_{\text{CTVE}}^2)/kT\}$$

$$\times \{(4\pi/3)n_{\text{CTVE}}d_i^{\text{CTVE}}\}^2. \quad (7)$$

The solution of equation (7) is corresponding to soft mode condensation point. It is seen from this equation that new critical temperture induced by thermally occupied CTVE-III states is increasing with concentration dependent factors $\exp\{(-\Delta_0 n_{\text{CTVE}} + \Delta_1(T)n_{\text{CTVE}} + \Delta_2 n_{\text{CTVE}}^2)/kT\}$ and $N_{\text{cluster}}n_{\text{CTVE}}^2$. On the other hand, namely these factors are increasing with clustering together with free energy decreasing.

Note also that the total number of the CTVEs could be also increased if the CTVE-III excitation energy becomes not so high. Such a situation takes place, for instance, in the vicinity of the second type phase transition in the framework of our model. This is the first order ferroelectric phase transition. Corresponding critical temperature for such a phase transition will be the solution of the following equation:

$$\left[(4\pi/3)d_i^{\text{CTVE}}P_i(T) - \Delta_0 + \Delta_1(T) + \Delta_2 n_{\text{CTVE}} \right] = 0. \quad (8)$$

Here equilibrium soft polarization $P_i(T)$ could be evaluated by the minimization of free energy equation (5).

Note in the conclusion that specific feature of the model is natural co-existence of order-disorder and displacive type degrees of freedom. Such a co-existence strengthening is appeared namely in the vicinity of the first order phase transition mentioned above. It does not disregarded that order-disorder dynamics and related CTVE-fluctuations within such a model could be possible explanation for order-disorder behavior discovered recently by R. Blinc, B. Zalar, and V. Lagura [8] in BaTiO$_3$ and SrTiO$_3$ ferroelectric oxides.

3. Charge transfer-lattice instability induced by interaction between charge transfer vibronic excitons of different nature due to order parameter field

Let us consider now another mechanism of charge transfer-lattice instability of the first order but again related with discussed in the previous section CTVE-III state. Such
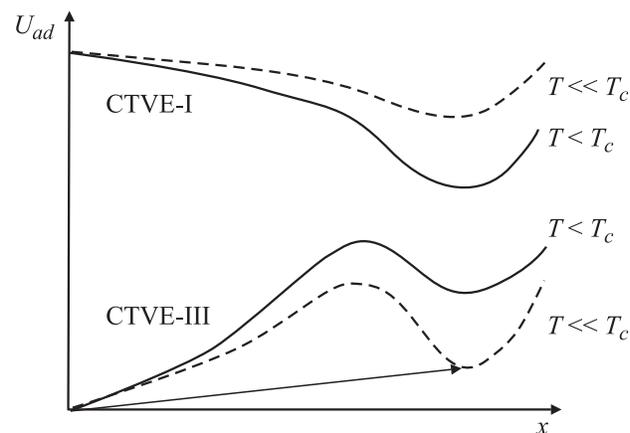
Figure 2. Order parameter induced repulsion of CTVE-I and CTVE-III states as a mechanism of local charge transfer-lattice transition. The arrow corresponds to local transition realization with anharmonic state energy lowering.

a state is characterised by additional, anharmonic potential well for potential branch of the ground state (in accord with classification in [4]). We shall consider a co-existing of CTVE-III with the CTVE-I type state [4] (Fig. 2) for the proper ferroelastic case. For simplicity, we shall discuss here the case of one component order parameter η_1 realization. Nevertheless, proper ferroelastic K$_3$Na(CrO$_4$)$_2$ [9] which very probably manifests local instability of the same type as it is discussed here belongs to two component order parameter case. Needed generalization of the model will be published later. We shall also consider the situation where CTVE-III and CTVE-I states have the minima for adiabatic potential which are rather near to each other. As a result, the overlap of related vibrational wave functions for CTVE-III and CTVE-I will be high enough. The latter corresponds to these states effective mixing under the action of internal or external fields. For instance, the ferroelastic order parameter η_1 can mix CTVE-III and CTVE-I states mentioned above due to linear vibronic interaction. Such a field can also form diagonal matrix elements of the vibronic interaction on the basis of both two CTVE states discussed. These vibronic interactions can be presented in the following form:

$$H_{\text{III–I}} = W\eta_1\sigma_x, \quad (9)$$

$$H_- = V_1\eta_1\sigma_z, \quad (10)$$

$$H_+ = V_2\eta_1 I, \quad (11)$$

where W, V_1, V_2 are vibronic constants, and the operators σ_x, σ_z, and I have the form $\sigma_x = |a\rangle\langle b| + |b\rangle\langle a|$, $\sigma_z = |a\rangle\langle a| - |b\rangle\langle b|$, $I = |a\rangle\langle a| + |b\rangle\langle b|$, a, b states are corresponding to CTVE-I and CTVE-II vibrational states respectively. Taking into account the equations (9), (10), (11), and an initial energy splitting between CTVE-I and CTVE-III vibrational states Δ, the final equation for CTVE-III energy in the order parameter field will be

presented as

$$E_{\text{CTVE-III}} = V_2\eta_1 + \sqrt{\frac{(\Delta + V_1\eta_1)^2}{4} + (W\eta_1)^2}. \qquad (12)$$

It is important to underline that $E_{\text{CTVE-III}}$ energy can be equal to zero (at the first order local transition point). Such an important point could be reached taking into account temperature dependence of the order parameter in the equation (12), $\eta_1(T)$. Corresponding equation for the temperature of the first order local transition point could be derived from (12):

$$\left(V_2\eta_1(T)\right)^2 = \frac{\left(\Delta + V_1\eta_1(T)\right)^2}{4} + \left(W\eta_1(T)\right)^2. \qquad (13)$$

Such type local transition related with charge transfer-lattice instability of the first order probably was detected by EPR at low temperatures for proper ferroelastic $K_3Na(CrO_4)_2$ [9].

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