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PSEUDO-JAHN–TELLER EFFECT AND OFF-CENTRE IONS IN CRYSTALS WITH SOFT LATTICE MODES

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Abstract. A mechanism of the formation of a new quantum paraelectric state (QPS) in incipient ferroelectrics of $SrTiO_3$ type and its role in spectroscopic effects are considered. The proposed model is based on the assumption that the tunnelling off-centre ions occur in the host lattice in the vicinity of strong elastic defects. The corresponding order–disorder-type clusters are responsible for QPS. The local transitions in such clusters lead to the formation of a ferroelectric microdomain. The corresponding new modes have an order–disorder (cooperative tunnelling modes) as well as a displacive (the new acoustic-like microdomain mode) nature. In both cases, however, the mixing of different types of modes plays an important role. This model gives a possibility to explain the main experimental results.

The creation of a multiwell potential in the region of the "iron-group impurity-oxygen vacancy" defect in incipient perovskite-type ferroelectrics is considered on the basis of the pseudo-Jahn–Teller effect (PJTE).

It is shown that a negative-*U* effect on the basis of the Jahn–Teller effect (JTE) and PJTE for an electron and a hole in an incipient perovskite-type ferroelectric leads to the creation of a bipolaron-type exciton in a perfect lattice as well as in the vicinity of an iron-group impurity.

Key words: Jahn–Teller effect, pseudo-Jahn–Teller effect, negative-*U* effect, incipient ferroelectric, perovskite, tunnelling, off-centre ion.

INTRODUCTION

The main topic of the present work is the consideration of JTE, PJTE, and an off-centre ion creation in the region of proper (vacancy) and impurity (iron-group impurity) defects in incipient perovskite-type ferroelectrics such as $SrTiO_3$ (STO) and $KTaO_3$ (KTO). These matrices are model objects for the analysis of the phenomena induced by soft lattice modes. The first part of this article considers the origin of low-temperature anomalies in STO and KTO on the basis of the model of host-lattice off-centre ion creation in the vicinity of a strong elastic defect such as vacancy. In the second part, we consider the vibronic mechanisms of the creation of single-particle and two-particle states in the same soft matrices. We predict the possibility of a multiwell potential with electric dipole states for vibronic centres of the type "iron-group impurity-oxygen vacancy" and a bipolaron-type exciton on the basis of JTE and PJTE for an electron and a hole. The related centres as well as the experimental situation are discussed.

1. POSSIBLE NATURE OF A NEW PARAELECTRIC REGIME IN INCIPIENT FERROELECTRICS: A ROLE OF ORDER–DISORDER CLUSTERS OF HOST-LATTICE OFF-CENTRE IONS

1) The discovery of a new QPS in the model system $SrTiO_3$ (STO) by Müller and co-workers [1–3] has brought forward an important question about its nature. The uncommon properties of this state were discovered on the basis of EPR, Mandelstam–Brillouin (MBS) and inelastic neutron (INS) scattering, internal friction and elastic compliance experiments [1–4]. By all these methods a new special temperature point in STO, $T_Q \approx 37$ K, was detected. The effect of the crystalline field in EPR is suppressed at this point [1]. In addition, at $T < T_Q$ the TA branches are strongly depressed in the case of small wave vectors and the INS selection rules are lifted for the $S(E_g)$ mode [4]. Besides, the Lyddane–Sachs–Teller relation is not fulfilled [4] for $T < T_Q$. Above all, a new acoustic branch (A mode) and a new peak of a finite frequency have been observed [4] in the broad MBS at $T < T_Q$. The goal of this work is to consider the possible origin of a set of anomalies at $T < T_Q$ in STO as well as of similar anomalies in related systems. An important role in our QPS model will belong to strong elastic defects such as oxygen vacancies.

An oxygen vacancy is a typical proper defect in oxygen-octahedral perovskite-type incipient ferroelectrics. In [5], it has been shown that oxygen-vacancy-induced luminescence centres in another model incipient perovskite ferroelectric, $KTaO_3$ (KTO), of the same type as STO, correlate with polar microregions. Besides, as it was shown recently in [6], the increasing of the oxygen vacancy concentration in KTO correlates with the increasing of the second harmonic generation (SHG) signal. The amplitude of the SHG signal is proportional to the average square of the polarization induced by polar microregions in the paraelectric phase. The appearance of polar microregions and the corresponding disorder effects in the paraelectric phase are well known in STO and KTO [5–9] but have no explanation up to this time. It is natural to consider a QPS model which may simultaneously illuminate the origin of polar microregions in the paraphase in the same systems. However, following the SHG and luminescence data, the existence of such microdomains is directly connected with the oxygen vacancy effect in the problem under consideration.

On the other hand, the actuality of the vacancy effect ensues from a strong elastic field and a strong distortion in the region of its core. The core includes the local tension field in the soft matrix of incipient perovskite-type ferroelectrics. These circumstances are important due to the existence of not-so-high frequencies of some host-lattice ions in such soft matrices. As a result a strong elastic field of the defect may drastically change the local dynamics of definite host-lattice ions. In particular, the local tension may induce a local instability effect for these ions, which in turn is connected with a local striction effect. The corresponding active ions may be called incipient off-centre ions of the host lattice. The existence of incipient off-centre host-lattice ions in oxygen-octahedral perovskite-type ferroelectrics is the main assumption of the proposed model.

The scenario of the QPS formation is as follows. (i) Elastic defects (oxygen vacancies) produce an elastic field and a local tension field in their vicinity. As a result some host-lattice ions (incipient off-centre ions) become off-centre due to local transitions. The local transitions and the defect-field-induced creation of off-centre ions in the host lattice are connected with the changing of force balance for the ions active in the formation of the soft mode (such as Ta^{5+} in KTO, Ti^{4+} in STO, and oxygen ions in both these matrices). (ii) The host-lattice off-centre ions have tunnel states. These tunnel states interact among themselves and with the soft lattice TO mode. (iii) As a result soft quasilocal tunnelling modes appear in the order–disorder-type clusters of tunnelling and interacting ions in the vicinity of elastic defects. Their condensation leads to a strong polarization and the increase of local susceptibility for such type of clusters. (iiii) Mesoscopic and macroscopic effects in this system are created due to percolation of polarization and tunnel excitations.

The creation of a defect-induced multiwell potential of a host-lattice ion takes place when (j) the decrease of the local frequency square, ω^2, due to the defect field deformed via local striction leads to $\omega^2 < 0$, and (jj) the interaction between different host-lattice ions produces a shift of the off-centre state energy which is less than the height of the potential barrier between different wells.

It should be underlined that a direct evaluation [10] of such type of effect for Ta^{5+} ions, which are active in the formation of a soft mode in KTO, has given an unstable behaviour and the creation of a deep multiwell potential for the values of local tension div u < 0.05 [10]. This inequality is not rigid in the vicinity of an oxygen vacancy. As a result the elastic defects such as vacancies can act as cores of the clusters of host-lattice off-centre ions in a soft matrix of an oxygen-octahedral incipient ferroelectric. The creation of an off-centre ion in the host-lattice takes place also in the vicinity of a pair centre such as "electron centre – vacancy". The "Fe^{3+} - oxygen vacancy" centre in STO (on which QPS was discovered for the first time [1]) and KTO as well as the "Ta^{3+} - oxygen vacancy" in KTO and "Ti^{2+} (or Ti^{3+}) - oxygen vacancy" in STO are examples of this effect.

In this way we can obtain a set of off-centre host-lattice ions near a strong elastic defect in a soft matrix. The overlapping of vibrational wave functions in different wells of a multiwell potential of such off-centre ions leads to the appearance of coherent tunnelling states. As a result a set of interacting tunnelling states appears.

Let us consider now the structure of a cluster of host-lattice off-centre ions in the vicinity of a strong elastic defect. The main peculiarity of such a cluster of off-centre ions is a self-consistent behaviour of its acting elastic field. The latter is related with the existence of induced elastic dipole moments and dilatation effects for the ions with the induced off-centre and tunnelling behaviour. The multiwell potential of these ions is induced by an elastic field produced not only by the oxygen vacancy but also by other ions whose multiwell potential is induced in the same manner. As a result off-centre ion displacement in the vicinity of such an elastic defect as an oxygen vacancy, as well as the corresponding elastic moments of these active ions, appear in the framework of the cooperative self-consistent behaviour. The latter can be described on the basis of a system of recursive relations with taking into account that the elastic moments and the elastic field induced by it are proportional to the square of the corresponding off-centre ion displacement. Its electric dipole field also takes part in this mechanism due to striction effects.

It should be underlined that active ions on the boundary of the order–disorder region under consideration are in a situation of local configurational instability ($\omega^2 \approx 0$).

An important parameter in this problem is the effective radius L of the order–disorder region where the host-lattice off-centre ions are created. The value of L can be estimated on the basis of the above-mentioned recursive procedure. The estimation of the value of L for strong elastic defects, such as oxygen vacancies and off-centre impurity ions in oxygen-octahedral perovskite-type incipient ferroelectrics, gives us a value which is larger than that of the usual correlation radius r_c of a displacive-type ferroelectric. Here, the condition $L \approx R_c$ is fulfilled, where R_c is the correlation radius in the considered order–disorder-type state with soft tunnelling modes.

Correlation effects vary strongly in a similar way not only in nominally pure systems but also in incipient perovskite ferroelectrics with off-centre impurities. The important parameter in this problem, $n_0 r_c{}^3$ (n_0 is the concentration of off-centre impurities), must be replaced by $n_0(L + r_c)^3$. It changes drastically the condition of ferroelectric ordering due to the condition $L > r_c$.

A characteristic peculiarity of the order–disorder-type cluster in the vicinity of an elastic defect in an incipient perovskite-type ferroelectric is the existence of new quasilocal tunnelling modes. A decrease of the off-centre ion displacement with a simultaneous increase of the tunnelling matrix element with the growth of the number of the coordination sphere around the elastic defect takes place there. Then we have a set of quasilocal tunnelling modes, each of which is related with a pseudospin in the same tension field and located in the same coordination sphere, whereby substantial effects of interaction of such modes take place.

This interaction leads to repulsion and mixing of modes. The resulting quasilocal cooperative tunnel modes depend strongly on the symmetry of the defect and its microscopic structure. Besides, there is another important effect which determines the final expression for the frequencies of such quasilocal modes. This is the interaction with a displacive-type soft TO mode of the matrix. As a result, we have a set of soft quasilocal tunnel-polarization modes which repulse from one another. A corresponding set of condensation points of these soft quasilocal tunnel-polarization modes (and a related set of local transitions) appears in this order–disorder cluster in the vicinity of a strong elastic defect.

The first high-temperature local transition is induced by the condensation of the quasilocal mode which is connected with a pseudospin in the central part of the cluster of off-centre ions. The latter is caused by the minimum value of the quasilocal frequency of the mode localized in this region, which is realized due to the minimum values of tunnel splittings and an extended system of pseudospin–pseudospin interaction bonds in the central part of the pseudospin cluster. Both circumstances lead to the maximum softening of the corresponding quasilocal mode. The condensation temperature point may be connected with the special temperature of the appearance of the set of anomalies experimentally detected in STO: $T_Q \sim 37$ K. The creation of a local order parameter at this point leads to a strong polarization of the whole order–disorder-type tunnelling cluster.

Let us consider, for example, a situation for a not-so-strong elastic field of a vacancy, which produces multiwell potentials and tunnelling states only in the second and the third coordination sphere (for eight and six oxygen ions, respectively). Two Ti^{4+} ions in the first coordination sphere change drastically their positions due to displacements along the vacancy axis. They have strongly anharmonic but single-well potentials. We also assume that eight Ti^{4+} ions of the fourth coordination sphere are in a situation of local configuration instability ($\omega^2 \approx 0$) and their eigenstates are determined by local anharmonicity. This structure of the order–disorder region reflects the main peculiarities of the real case excluding the possibility of the increase of the size L of this region relative to the r_c value. The latter is essential only for cooperative phenomena which will be discussed separately.

In the framework of this model, we have three different tunnel splittings (Ω_1, Ω_2, Ω_3) which are connected with three different groups of oxygen pseudospins as a result of symmetry conditions. These three groups correspond to three different values of the off-centre host-lattice ion displacements.

There are two quarters of oxygen pseudospins in the second coordination sphere with the tunnel splitting Ω_1, and two (Ω_2) and four (Ω_3) ones of oxygen pseudospins in the third coordination sphere with the corresponding tunnel splittings $\Omega_2 \neq \Omega_3$. If we consider only the nearest neighbour interaction between pseudospins (with the parameter

J for interaction within the second coordination sphere and J^* for interaction between the second and the third coordination sphere), we shall obtain the basic quasilocal tunnel frequencies connected with two types of cooperative tunnel modes. The first one is a cooperative tunnel mode formed due to interaction between five nearest neighbouring oxygen pseudospins in each of the two groups of particles which belong to the second and partly to the third (with tunnel splitting Ω_2) coordination sphere. The intact four oxygen off-centre ions (with the tunnel splitting Ω_3) of the third sphere have no neighbours at this short distance as do the oxygen off-centre ions of the previous groups. That is why the basic mode here is a pure tunnelling single-particle mode.

The Hamiltonian of a cluster of the five above-mentioned interacting pseudospins has the form

$$H = J(S_1^z S_2^z + S_1^z S_3^z + S_2^z S_3^z + S_3^z S_4^z + S_4^z S_1^z) + \\ + J^*(S_5^z S_1^z + S_5^z S_2^z + S_5^z S_3^z + S_5^z S_4^z) - \\ - \Omega_1(S_1^x + S_2^x + S_3^x + S_4^x) - \Omega_2 S_5^x + \Delta_1(S_1^z + S_2^z + S_3^z + S_4^z) + \Delta_2 S_5^z \ , \quad (1)$$

where Δ_1 and Δ_2 are induced by the defect field. The last two terms in (1) can be neglected without any restrictions of generality. In addition, the random phase approximation (RPA) is valid outside the vicinity of the local transition point due to not-so-high value of fluctuations. In these cases the basic quasilocal tunnel modes are equal to

$$\omega_{1,2}{}^2 = A(T) \pm ([A(T)]^2 + B(T))^{1/2} , \quad (2)$$

$$A(T) = \frac{1}{2}[\Omega_1^2 \ - \ 2J\Omega_1 \langle S_1^x \rangle_T + J^2 \left(2\langle S_1^z \rangle_T + (J^*/J)\langle S_2^z \rangle_T\right)^2 + \\ + \ \Omega_2^2 + 16(J^*)^2 \langle S_1^z \rangle_T^2] , \quad (3)$$

$$B(T) = 4(J^*)^2 \Omega_1 \Omega_2 \langle S_1^x \rangle_T \langle S_2^x \rangle_T - \\ - \left[\Omega_2^2 + 16(J^*)^2 \langle S_1^z \rangle_T^2\right] \times \left[\Omega_1^2 - 2J\Omega_1 \langle S_1^x \rangle_T + (2J\langle S_1^z \rangle_T + J^* \langle S_2^z \rangle_T)^2\right] \quad (4)$$

for the first type of the basic quasilocal tunnel mode and $\omega_3 = \Omega_3$, for the second one. Here $\langle S_1^z \rangle_T$ is a local ferroelectric-type order parameter for the four pseudospins which belong to the second sphere in this group with five pseudospins under consideration, $\langle S_2^z \rangle_T$ is a local order parameter for the fifth oxygen pseudospin which belongs to the third sphere in the same group, $\langle S_1^x \rangle_T$ and $\langle S_2^x \rangle_T$ are the average values of the corresponding tunnel operators, respectively.

As a final step we must take into account the interaction between the soft TO mode of a displacive type and the basic quasilocal tunnel modes in the vicinity of the defect. The corresponding interaction appears in general in the whole region of such an order–disorder cluster with the radius L which may satisfy the inequality $L > r_c$. In the framework of our simple approach we consider in detail only the case $L < r_c$. That is why we take into account the interaction of the soft TO mode with only two types of the basic tunnel modes with the frequencies $\omega_{1,2}$ and Ω_3. This description has been made in a way similar to that of the well-known Kobayashi model, however, with an important difference. Namely, the interaction with TO states with all the values of the wave number k from zero up to (π/L) has been taken into account. The latter is connected with the effective interaction of only long-wave $k < \pi/L$ TO modes with defect modes. The interaction is essentially decreased for $k > \pi/L$ due to the interference effects in the core (with the size L) of the defect under consideration. As a result the expression for the ith quasilocal pseudospin-polarization mode with the frequency $\omega_{-(i)}$ in the actual case of not-so-strong interaction between the basic quasilocal tunnel mode and the lattice TO mode $[(\omega_{\mathbf{k}}{}^2 - \omega_i(T)^2)^2 >> 4A_i(T)^2]$ has the following form:

$$\omega^2_{-(i)} \simeq \omega_i(T)^2 - \frac{L^3 A_i(T)^2 \left[\frac{1}{L} - \frac{1}{2}\left\{\left[\omega_0(T)^2 - \omega_i(T)^2\right]/v\right\}^{1/2}\right]}{2\pi v}. \quad (5)$$

Here A_i is the mode interaction parameter, $A_i(T) \sim \sum_j N_i{}^{(j)}(x^{(j)})^2\Omega_j\langle S_j^x\rangle_T^{(i)}$, where j denotes the number of a coordination sphere with $N_i{}^{(j)}$ pseudospins which take part in the formation of the ith basic quasilocal tunnel mode, $x^{(j)}$, Ω_j, and $\langle S_j^x\rangle_T^{(i)}$ are the corresponding equilibrium off-centre displacement, tunnel splitting and the average value of the tunnel operator for the i-type mode in the j sphere, respectively. Besides, $\omega_i(T)$ is the ith basic quasilocal tunnel mode frequency (in our simple approach $i = 1, 2, 3$), $\omega_{\mathbf{k}}$ is the soft TO mode frequency, $\omega_{\mathbf{k}}{}^2 = \omega_0(T)^2 + vk^2$; in the expression for $\omega_0(T)$ we take into account the stability effect on the soft mode, which is due to quantum fluctuations in the low-temperature region. From (5) we can obtain the condition of a local transition corresponding to the ith quasilocal mode condensation, which is the solution of the equation $[\omega_{-(i)}(T_l{}^{(i)})]^2 = 0$. As a result a set of local transitions appears in the order–disorder-type clusters near the elastic defect at the temperatures $T_l{}^{(i)}$. There are three such local transitions in the limiting case under consideration.

It is important to underline that the fluctuations of the local order parameter increase rapidly when we approach the region of local transition. That is why RPA becomes invalid near $T_L{}^{(i)}$. We must take into account a fluctuating local peudospin field $H(t)$ in the local transition region and add a fluctuation term to the Hamiltonian of RPA, $H_{\mathbf{RPA}}$, which is constructed on the basis of (1) in the limiting case under consideration. As a result in this approach $H = H_{\mathbf{RPA}} + S_z H(t)$, where $H(t)$ satisfies the expression $\langle H(t)H(0)\rangle_i = \Delta^2 \exp(-t/\tau_i)$. Here the amplitude of fluctuations, Δ, has a value which is close to the maximum value of the local pseudospin field in the local transition region, τ_i is the relaxation time of fluctuations. As follows from [11], for the tunnel dynamic case $\Omega_i > \Delta$ the actual for us damping of the basic quasilocal tunnel mode γ_i corresponds to $\gamma \approx$

$(\pi/8)^{1/2}\Delta$. These arguments lead to the inequality $\omega_i << \gamma_i$ taking place near the local transition point. This corresponds to a relaxation-type dynamics where the relaxation time τ_i near local transition increases up to its saturation. For the actual case, $\Omega_i > J, J^*, \Delta$, there exist tunnel excitations of the oscillator type in that local transition region, but they are localized on separate pseudospins. In this case the relaxation dynamics and the value of τ_i are connected with the cross-relaxation of tunnel excitation between different tunnelling pseudospins. Only in the low-temperature phase in the region of the validity of $\omega_i >> \gamma_i$ there exist again cooperative tunnel modes which can be considered in the framework of RPA like the local para-state in the region not near to $T_L{}^{(i)}$. However, the local transition points $\{T_L{}^{(i)}\}$ as centres of transition regions (with extended fluctuations) between different RPA phases are correctly defined by RPA expressions (Expr. (2)).

2) Local transitions in order–disorder clusters near elastic defects in soft matrices change substantially both the static and the dynamic property of the system.

Firstly, there appear polar microregions of the size $(L + r_c)$. This is connected with the correlation of the dipoles of the host-lattice off-centre ions near the elastic defect as a core in this situation. Such polar microdomains exist at temperatures $T < T_L{}^{(1)}$ where $T_L{}^{(1)}$ is the highest local transition temperature. As a result we can explain the existence of a correlated microdomain in the paraelectric phase and the disorder effects observed in nominally pure STO and KTO in many experiments.

Secondly, two types of percolation may take place in the system of the order–disorder-type microdomains under consideration. For $T > T_L{}^{(1)}$, we have the percolation of tunnelling excitation in the system of tunnel states of order–disorder-type microdomains. At $T < T_L{}^{(1)}$ there may exist a percolation cluster of correlated polar microdomains. The percolation threshold [12] for our case in $(4\pi/3)n(L_p + r_c)^3 \simeq 2.77$, where n is the concentration of elastic defects (vacancies). For the low-temperature region, where $r_c \simeq 23\mathring{A}$ in STO, we can get for $n \sim 10^{18}$ cm^{-3} the threshold value approximately equal to $L_p \approx 65\mathring{A}$. The average size of the critical percolation cluster is $L_c \approx n^{-1/3}|(L - L_p)/(L_p + r_c)|^{-\nu}$, where $\nu \sim 0.83 - 0.94$ in accordance with [12]. Such-type percolation effects will appear in the framework of SHG, MBS, and INS experiments. A new quasilocal tunnel mode and the existence of a percolation of tunnelling excitation can explain the appearance of a new peak at a finite frequency which has been observed in broad MBS [4].

Alongside with vacancies, off-centre impurities such as Ca^{2+} in STO are favourable to the inducing of order–disorder-type clusters of off-centre ions in a host lattice and as a result to the formation of this-type cooperative QPS phenomena. A similar role of the off-centre impurity ions Li^+, Na^+, and Nb^{5+} in an another incipient ferroelectric KTO may be of no less importance. It should also be noted that the uncommon temperature dependence and the absolute value of the correlation radius for STO:Ca^{2+} [13] can be explained on the basis of the $(L+r_c)$ behaviour in the framework of our model.

Thirdly, new quasi-phonon modes appear in the microdomains under consideration. These new modes are the distorted acoustical and optical phonon modes whose properties depend on the new conditions in such microdomains. In particular, the size of the microdomain determines the minimum value of the wave number of these new quasi-phonon modes. In the framework of this consideration the new A mode discovered in [4] can be explained as a microdomain quasi-phonon mode created as a "distorted" acoustical TA mode. This mode appears as a result of the repulsion of the short-wave part ($k > \pi/L$) of the TA mode (with Q_{TA} variable) and a pseudospin-polarization mode (with $Q_{pp}{}^{(i)}$ variable) in the microdomain due to the following interaction: $H^{(1)}{}_{\mathrm{int}} = \sum_{\mathbf{k}(k>\pi/L)}[F_{(i)}(\mathbf{k})Q_{\mathrm{TA}}(\mathbf{k})Q_{pp}{}^{(i)}]$. In this expression $F_{(i)}(\mathbf{k})$ is a mode interaction function.

The "usual" TA phonons which exist outside the microdomains under consideration have also new properties. The main one is the appearance of strong scattering of the TA phonon with $(k) < \pi/L$ due to interaction with microdomains. That is why long-wave TA phonons are strongly depressed in accordance with the experiment [4].

Fourthly, a polar microdomain appearing at $T < T_L^{(1)} = T_Q$ leads to the mixing of soft $S(E)_g$ and soft TO modes (with Q_S and Q_{TO} variables, respectively), as well as to the mixing of TO and TA modes. This is caused by a piezoelectric effect induced by polar microdomains. These interactions can be expressed respectively as $H^{(2)}{}_{\mathrm{int}} = \sum_{\mathbf{k},\mathbf{k}'}[A(\mathbf{k},\mathbf{k}')Q_S(\mathbf{k})Q_{\mathrm{TO}}(\mathbf{k}')]$ and $H^{(3)}{}_{\mathrm{int}} = \sum_{\mathbf{k},\mathbf{k}'}[B(\mathbf{k},\mathbf{k}')Q_{\mathrm{TA}}(\mathbf{k})Q_{\mathrm{TO}}(\mathbf{k}')]$, where $A(\mathbf{k},\mathbf{k}')$ and $B(\mathbf{k},\mathbf{k}')$ are the corresponding mode interaction functions. Such type of mode mixing can explain the anomalous behaviour [2, 4] of $S(E)_g$, TA, and TO modes at $T < T_Q$. It is important to underline that the conversion rule in phonon–phonon interaction, usual for a perfect lattice pulse, is broken in the last expressions due to the mixing of phonon pulses in the polar microdomain.

The new quasi-phonon microdomain modes and quasilocal tunnel modes will directly take part in spin–lattice relaxation and acoustic absorption. Besides, the piezoelectric mixing of acoustical and optical phonon modes in ferroelectric microdomains plays also an important role in these processes. As the corresponding strengthening of ultrasound absorption is already indicated [3], the increasing of the spin–lattice relaxation rate as well as its peak's appearance at temperatures near T_Q in a new QPS may be predicted on the basis of this model.

Last but not least, the critical peculiarities in the temperature dependences of axial and cubic crystalline field constants of the spin-Hamiltonian of the Fe^{3+}-V_0 centre in STO at $T \sim T_Q$= 37 K [1] are explained as a result of a screening of the critical crystalline field in this temperature region. The latter is directly connected with local transition in an order–disorder-type cluster in the vicinity of the Fe^{3+}-V_0 centre. This transition leads to the increase of local polarizability and to the screening of the crystalline field.

We conclude that the order–disorder cluster model, with taking into account cooperative tunnel modes, respective local transitions, and new types of mode mixing induced by such clusters, can serve as a basis for the explanation of the main features of the anomalous behaviour of incipient perovskite-type ferroelectrics in the low-temperature region.

2. SINGLE-PARTICLE AND TWO-PARTICLE VIBRONIC STATES IN INCIPIENT PEROVSKITE FERROELECTRICS: OFF-CENTRE IONS IN IMPURITY-VACANCY CENTRES AND A NEW-TYPE EXCITON WITH A VIBRONIC NATURE

1) Let us consider a "Cu^{2+}-oxygen vacancy" centre in KTO as an example of an "iron-group impurity-vacancy" centre with a possible important role of vibronic interactions. In this case the E state of the Cu^{2+} ion is split due to the vacancy field. As a result, the E_θ state becomes a ground nondegenerate state and the E_ϵ state becomes an excited state. The PJTE under the action of tetragonal distortions can be suppressed due to a relatively high value of the corresponding splitting of the E states, Δ. On the other hand, the polar vacancy field induces a linear vibronic interaction of the ground E_θ state with polar distortion along the vacancy axis. This circumstance is connected with a simultaneous action of the quadratic vibronic interaction with polar distortions and the additional static polar field. The linear PJTE with the polar distortion appears here without any threshold condition. This is connected with the adiabatic nature of such-type PJTE. Indeed, the vibronic Hamiltonian in this case has the following form:

$$H_{\mathrm{PJTE}} = \Delta\sigma_z + VQ_z\sigma_z + K_zQ_z^2, \qquad (6)$$

where Q_z is a polar distortion along the vacancy axis, σ_z is the Pauli matrix on the basis of the E_θ and the E_ϵ states and 2Δ is a splitting between these two E states in the field of vacancy, V is a vibronic constant and K_z is an elasticity constant for polar vibrations along the vacancy axis. In the framework of strong linear PJTE on polar distortion the two minima of the adiabatic potential appear with equilibrium displacements and corresponding potential depths:

$$Q_{z(+)} = -V/2K_z, \qquad U_{(+)} = [\Delta - (V^2/2K_z)]/2, \qquad (7)$$

$$Q_{z(-)} = V/2K_z, \qquad U_{(-)} = -[\Delta - (V^2/2K_z)]/2. \qquad (8)$$

As a result, a two-well potential appears for the Cu^{2+}-V_0 centre in KTO. The hopping motion between these two wells creates the dipole relaxator.

It should be underlined that two types of axial Cu^{2+} centres in KTO [14] can be explained in the framework of this consideration as vibronic Cu^{2+}-V_0 centres localized in two different wells of the PJTE-induced potential.

2) Another important example of a centre of the vibronic nature in STO and KTO is the vibronic exciton. It should be noted that in such soft matrices with the dielectric constant $\epsilon >> 1$ the usual Wannier–Mott exciton has a sufficiently small bond energy and the usual internal fields of the defect can destroy this type of exciton. The exciton bond energy, sufficient for the state stability in real internal defect fields, appears under the action of vibronic interactions. In the present work, we consider such type of an exciton on the basis of a bipolaron effect for an electron and a hole, which corresponds to a negative-U effect in this pair. The latter can be considered as a pair JTE (PJTE). The strengthening of this pair JTE (PJTE) is connected with the action of soft lattice modes in vibronic interaction.

The effective exciton radius is decreased up to the value of the lattice constant due to strong bipolaron effect of JTE nature. This is why we can consider the TiO_6^{8-} cluster in STO and the TaO_6^{7-} cluster in KTO as the regions of localization of a such-type exciton. As the electron density is mainly localized in the region of the central metallic ion, the hole density is mainly localized on oxygen ions in these clusters. The electron and the hole have degenerate (or pseudodegenerate) states which take part in the pair JTE (PJTE). We can consider these exciton states as the states of the corresponding molecules (TiO_6^{8-} or TaO_6^{7-}) which are under the action of strong vibronic distortion. In this problem the isolation of molecule-type states is a vibronic effect. In constant to a usual Frenkel exciton the electronic state and its radius are completely determined by a bipolaron-type pair JTE and have a vibronic nature. For such type of states we use the name "vibronic exciton".

Let us consider a vibronic exciton in a perfect STO lattice and a localized one in the vicinity of the defect (impurity of iron group or vacancy) as an example of this type of excitations.

The former case is that of a "free" exciton. In a real crystal, however, this exciton is localized due to strong lattice distortion. Such an exciton takes part in the hopping motion in the lattice. We shall use here the MO LCAO orbitals t_{2g}, t_{1u}, and t_{2g}^* (antibonding) of the TiO_6^{8-} cluster in STO as the basic electron states taking part in vibronic interaction and producing the vibronic exciton state. There are two excitons: (i) an electron in the t_{2g}^* state and a hole in the t_{1u} state; (ii) an electron in the t_{2g}^* state but a hole in the t_{2g} state. In both cases the pair JTE with negative-U effect takes place. The corresponding vibronic interaction for the first case is $[t_{2g}^*(e) + t_{1u}(h)] \times e_{g\epsilon}$ and for the second case, $[t_{2g}^*(e) + t_{2g}(h)] \times e_{g\epsilon}$, where (e) and (h) denote an electron and a hole, respectively. Here we consider the vibronic interaction only with the $e_{g\epsilon}$ lattice mode. This approach is based on the existence of a soft mode (E_g) with the same symmetry in STO. This soft mode takes directly part in the pair JTE and produces the main total energy lowering due to its low frequency.

The vibronic Hamiltonian of our exciton in (i) and (ii) cases has the following form:

$$H_{\mathrm{JTE}} = [A\sigma_z(e) + B_{1u,2g}\sigma_z(h)]\sum_{\mathbf{k}}\eta_\epsilon(\mathbf{k}) +$$

$$+ 1/2\sum_{\mathbf{k}}\{[\omega_0(T)]^2 + v_0 k^2\}\eta_\epsilon(\mathbf{k})\eta_\epsilon(-\mathbf{k}), \qquad (9)$$

where $\eta_\epsilon(\mathbf{k})$ is a soft mode variable, $\sigma_z(e)$ and $\sigma_z(h)$ are the Pauli matrices for the electron in t^*_{2g} states (on the basis of $t^*_{2g}(xz)$ and $t^*_{2g}(yz)$ functions) and for the hole in t_{1u} or t_{2g} states (on the basis of $t_{1u}(x)$ and $t_{1u}(y)$ or $t_{2g}(xz)$ and $t_{2g}(yz)$ functions), respectively; A and B_{1u} or B_{2g} are the corresponding vibronic constants; ω_0 is a limiting soft mode frequency and v_0 is a dispersion coefficient of the soft mode. The same expression is also valid for vibronic interaction with two other possible e_g distortions after two cycle changes of x, y, z in the previous wave functions and distortions. That is why we have the threefold degeneration of three Jahn–Teller configurations. The equilibrium Jahn–Teller distortion and the lowering of the vibronic energy for the adiabatic pair JTE under consideration are equal to

$$(\eta_\epsilon)_0 = [|A| + |B_{1u,2g}|]v_0 k_{\max}{}^3\{3[k_{\max} - (r'_c)^{-1}\,\mathrm{arctg}(k_{\max} r'_c)]\}^{-1}, \qquad (10)$$

$$U_- = -(1/2)[|A| + |B_{1u,2g}|](\eta_\epsilon)_0\,, \qquad (11)$$

respectively. Here r'_c is the correlation radius of the order parameter of the structural phase transition in STO. As a result the strengthening of the vibronic effect takes place in the vicinity of phase transition where r'_c has increased. Besides, there is an evident negative-U effect: $U_- \sim [|A|^2 + 2|A||B| + |B|^2]$, where the second term in the last expression has the same order as does the sum of the first and the third term. In the case under consideration an estimation gives $U_- \sim 1$–2 eV. It should be underlined that two possible exciton states ($t^*_{2g}(e) - t_{1u}(h)$ and $t^*_{2g}(e) - t_{2g}(h)$) are realized here, both of which have three different Jahn–Teller configurations.

The vibronic exciton localized in the vicinity of an iron-group impurity or of an oxygen vacancy can be considered in the same way when the lowering of the vibronic energy (U_-) is much larger than the energy change due to the defect (U_{def}). In the latter case this defect field lifts the threefold degeneracy of both vibronic exciton ground states. As a result the both three-well potentials involve one nondegenerate and one double-degenerate vibronic state in the multiplet of ground states.

Besides, there exist the orientation degeneracy (above the structural phase transition point T_C) and quasidegeneracy (for $T < T_C$) of the positions of $\mathrm{TiO_6}$ clusters in which the vibronic exciton is localized. There are six quasidegenerate orientation states around the iron-group impurity as a trapping centre for the vibronic exciton at $T < T_C$, and two degenerate orientation states along the crystallographic axis corresponding to the opposite directions in the vicinity of the oxygen vacancy for a trapped vibronic exciton. The cross-relaxation processes lead to a hopping motion between these states corresponding to different configurations in such multiwell potentials. It should be underlined that the polar defect field induces the electric dipole moment of a localized exciton in the corresponding single wells of a multiwell potential. These dipole moments appear mainly due to the mixing of the t_{2g} and t_{1u} states of the TiO_6 cluster by a defect electric field. As a result the cross-relaxation-induced hopping motion between potential wells with different electric dipole moments leads to electric dipole relaxation. The interaction of such type of relaxator with the soft TO mode in STO creates the central peak phenomenon induced by the vibronic exciton.

The possible examples of a vibronic exciton trapped on an iron-group impurity in STO are "$Cr^{3+} - h - e$" and "$Fe^{3+} - h - e$" vibronic excitons. These localized excitations take part in optical transitions via "$Cr^{3+} - h$" and "$Fe^{3+} - h$" localized hole centres of a polaronic nature.

In the case when the inequality $U_- \leq U_{\text{def}}$ holds, the problem of a vibronic exciton can be solved on the basis of not only pair JTE but pair PJTE and JTE–PJTE situations. The qualitative conclusions, however, are the same as in the previous case when the vibronic effect predominates.

In conclusion it should be underlined that the small-radius hole pair localized in the vicinity of an iron-group impurity in STO and KTO can be considered in a similar way as pair PJTE. This pair PJTE (and the corresponding negative-U effect) competes with the Coulomb repulsive interaction. In this case the $2p_\pi$ functions of oxygen play the main role in pseudo-Jahn–Teller interaction. In such type of a centre the hopping motion of a hole pair as well as coherent tunnelling in the vicinity of a centre core (iron-group impurity) take place. The consideration of a pair oxygen hole centre in the vicinity of the Fe^{3+} ion in the Ta^{5+} site in KTO in the framework of this vibronic model leads to the coexistence of tetragonal, rhombic, and cubic states in accordance with the EPR experiment. Here the off-centre ion phenomenon appears in the rhombic state.

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JAHNI–TELLERI PSEUDOEFEKT JA MITTETSENTRAALSED IOONID PEHMETE MOODIDEGA KRISTALLIDES

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On vaadeldud uue paraelektrilise kvantoleku tekkemehhanismi $SrTiO_3$-tüüpi senjettelektrikutes ja selle rolli spektroskoopilistes nähtustes. Esitatud mudel eeldab, et põhikristalli tugevate elastsusdefektide naabruses esinevad tunneleeruvad mittetsentraalsed ioonid. Paraelektrilise kvantoleku teke on seotud vastavate kord–korrastamatus-tüüpi klastritega. Lokaalsiirded sellistes klastrites tekitavad senjettelektrilise mikrodomeeni, mille uued moodid on kord–korrastamatus-tüüpi (kooperatiivsed tunnelmoodid), samuti nihke tüüpi (mikrodomeeni uus akustiline mood). Mudel võimaldab selgitada põhilised katsetulemused.

Jahni–Telleri pseudoefekti baasil on vaadeldud rauarühma lisandi ja hapniku vakantsi liitdefekti potentsiaalpinda virtuaalsetes perovskiidi tüüpi senjettelektrikutes, milles on käsitletud ka bipolaroni tüüpi eksitoni nii korrapärases võres kui ka rauarühma lisandi läheduses.

ПСЕВДОЭФФЕКТ ЯНА–ТЕЛЛЕРА И НЕЦЕНТРАЛЬНЫЕ ИОНЫ В КРИСТАЛЛАХ С МЯГКИМИ МОДАМИ

Валентин ВИХНИН

Рассмотрены механизм формирования параэлектрического квантового состояния (ПКС) нового типа в виртуальных сегнетоэлектриках ($SrTiO_3$) и его роль в спектроскопических явлениях. Предложенная модель предполагает, что в соседстве сильных упругих дефектов появляются туннелирующие нецентральные ионы. Соответствующие кластеры типа порядок–беспорядок ответственны за ПКС. Локальные переходы в этих кластерах приводят к формированию сегнетоэлектрического микродомена, новые моды которого будут типа порядок–беспорядок (кооперативные туннелирующие моды), а также типа смещения (новая акустическая мода микродомена). Модель позволяет объяснить основные экспериментальные результаты.

Основываясь на псевдоэффекте Яна–Теллера рассмотрена потенциальная поверхность составного дефекта примеси группы железа и кислородной вакансии в виртуальных сегнетоэлектриках типа перовскита, в которых изучен также экситон типа биполярона как в совершенной решетке, так и вблизи примеси группы железа.