The Singlet-Triplet Pseudo-Jahn-Teller Centers in Copper Oxides.

A.S. Moskvin, Yu.D. Panov.

Department of Physics, Ural State University, Ekaterinburg, Russia

One of the most exciting features of the hole centers CuO_4^{5-} in doped cuprates is an unusually complicated ground state which is the result of the electronic quasi-degeneracy. An additional hole, doped to the basic CuO_4^{6-} cluster with the b_{1g} hole can occupy both the same hybrid $Cu3d - O2p$ orbital state resulting in a Zhang-Rice singlet $^1A_{1g}$ and the purely oxygen e_u molecular orbital resulting in a singlet or triplet $^{1,3}E_u$ term with the close energies. We present detailed analysis of the (pseudo)-Jahn-Teller effect driven by the near-degeneracy within the $^1A_{1g}, ^{1,3}E_u$-manifold.

I. INTRODUCTION.

Intuitive ideas concerning a specific role of Jahn-Teller ions (centers, polarons) have been used as a starting point of the pioneer investigations by K.A.Muller and J.G. Bednorz resulting in 1986 in the outstanding discovery of the high-T_c superconductivity [1]. Unfortunately, in the following years no breakthrough in understanding of this puzzling phenomenon occurred. In many respects such situation is accounted for the underestimation of Jahn-Teller-effect and related phenomena that is typical for the conventional "metallic" approaches to the description of the electronic structure of the cuprates: namely these approaches underly the majority of the popular scenario's for the high-T_c superconductivity. Additional argumentation of the opponents of the Jahn-Teller approach is based on the widespread opinion that the CuO_4 cluster with the doped hole forms a well-isolated spin and orbital singlet $^1A_{1g}$ (Zhang-Rice singlet).

Well-isolated Zhang-Rice singlet is a natural starting point for many model approaches including the well-known t-J-model. However, it does not provide an explanation of wide set of unconventional physical properties of the cuprates, in particular, those associated with anomalous lattice and electron-lattice effects, and should be reconsidered and generalized.

A considerable number of experimental data were accumulated which more or less directly give evidence in favor of existence of the copper-oxygen centers with near-degeneracy effects and anomalously strong electron-vibrational (or Jahn-Teller) correlations. More and more experimental data argue that a single band picture for the low energy excitations in the cuprates is inadequate.

An observation of the so-called mid-infrared (MIR) absorption bands in different CuO_4-cluster based oxides is one of the most impressive manifestations of near-degeneracy effects [2] and, moreover, this phenomenon provides an important information about the energy spectrum and electronic structure within the ground state manifold. An appearance of the MIR bands with specific transformation of the absorption spectra in cuprates upon doping leads to a conjecture that the latter is accompanied by the sharp correlational decrease in the energy of the charge transfer transition $b_{1g} \rightarrow e_u$ that determines the fundamental absorption band for the parent oxides [3]. Thus, "parent" absorption band shifts from rather usual position around $\sim 2 \div 3\,eV$ to the mid-infrared region forming the MIR band. An appearance of the MIR bands upon hole doping could be readily explained by assuming that additional hole doped to the basic CuO_4 cluster with the b_{1g} hole can occupy both the same hybrid $Cu3d - O2p$ orbital state resulting in the Zhang-Rice singlet $^1A_{1g}$ and the purely oxygen e_u molecular orbital resulting in the singlet or triplet $^{1,3}E_u$ term with the close energies. Then the MIR-absorption is determined by the allowed charge transfer transition $b_{1g}^2 : {}^1A_{1g} \rightarrow b_{1g}e_u : {}^1E_u$ and represents the correlation analogue of the corresponding single-particle $b_{1g} \rightarrow e_u$ transition (see Fig.1).

Perhaps, a detection of isolated PJT center would provide the direct manifestation of the validity of the Jahn-Teller conception. In this connection the paper [4] should be noted where the authors have performed NQR study of the isolated hole centers in $La_2Cu_{0.5}Li_{0.5}O_4$. The results can be interpreted as convincing evidence of the quasi-degenerated singlet-triplet structure of the hole center. This conclusion is based on the following:

1. The authors have detected spin singlet ground state ($S = 0$) and low lying spin triplet state ($S = 1$) with singlet-triplet separation $\Delta_{ST} = 0.13\,eV$.

2. They observed anomalously weak temperature dependence of the relaxation rate at low temperatures that gives evidence of occurrence of the spinless multiplet structure in the CuO_4 cluster ground state.

3. They've found considerable spin contribution to the low temperature relaxation indicating the simultaneous occurrence of the ground state multiplet structure, sufficiently low singlet-triplet separation and intrinsic singlet-triplet spin-orbital mixing.

4. They observed the relaxation inequivalence of the various Cu sites, which is quite natural for the PJT centers in the conditions of the static PJT effect.

The Jahn-Teller hole centers like CuO_4^{5-} with singlet-triplet quasi-degeneracy within ground state have been observed by ESR spectroscopy in $LaSrAl_{1-x}Cu_xO_4$ which is isostructural to $La_{2-x}Sr_xCuO_4$ [5]. Moreover, Yu. Yablokov et al. [6] conjectured that doped hole in the copper-oxygen clusters occupies a purely oxygen $a_{2g}(\pi)$, or $b_{2u}(\pi)$ like orbitals. An important indication to the $O2p(\pi)$ nature of doped holes and, hence, to the occurrence of near-degeneracy for configurations like b_{1g}^2 and $b_{1g}e_u(\pi)$ was obtained by Yoshinari [7] and Martindale et al. [8] after the analysis of the ^{17}O Knight shift data and temperature-dependent anisotropy of the planar oxygen nuclear spin-lattice relaxation rate in $YBa_2Cu_3O_{6+x}$, respectively. Analogous conclusion could be drawn out of the comparative analysis of the temperature behavior for the nuclear spin-lattice relaxation rate in $La_{2-x}Sr_xCuO_4$ [9]. All this implies a complicated nature of the ground state manifold for the CuO_4 center with a significant mixing of the Zhang-Rice singlet and some other molecular term, which symmetry should be distinct from $^1A_{1g}$. This conclusion conflicts with the widespread opinion regarding the well isolation of the Zhang-Rice singlet.

An important argument in favor of vibronic nature for ground state of CuO_4 clusters with the participation of e_u-orbitals in the 123 system was obtained after analysis of experimental data on EFG (electric field gradient) tensor for different nuclei in 123 system [10]: non-contradictory description of the data implies a considerable (10%!) difference in electron density for $O(2)$ and $O(3)$ oxygens. It is unlikely that this result could be obtained without PJT effect.

These and many other results of resonance (ESR, NQR/NMR) experiments being precise local probes cast doubt on the validity of popular conceptions which are widely used as a starting point for the analysis of resonance and in broader sense for many other physical effects in cuprates.

A considerable number of the experimental indications of Jahn-Teller (vibronic) effects is associated with observation of lattice instabilities, ferroelectric [11], pyro- and piezoelectric [12] anomalies, local static and dynamic distortions [13], various phonon anomalies and manifestation of substantial electron-phonon effects such as the line shift and Fano effect for the phonon modes associated with local PJT-active modes [14–16]. These observations and many other lattice effects are signatures of unconventional strong electron-lattice interaction at work in the cuprates [13] with highly nonlinear and nonadiabatic intrinsic dynamics. Up to now these phenomena are often considered as convincing evidence in favour of the "structural" scenario for the high-T_c superconductivity usually associated with polarons (pseudo-Jahn-Teller polarons) or bipolarons [13,17]. A number of the phonon anomalies could be associated with the vibronic pseudo-spin fluctuations or, in other words, with effects of the short-range cooperative Jahn-Teller ordering [18]. These anomalies are linked with the specific points both inside the BZ and on its boundary.

In our opinion the indirect evidence for Jahn-Teller nature of the CuO_4 centers with active role namely of the copper-oxygen hybrid Q_{e_u} mode was displayed by the maximum entropy method (MEM) in $YBa_2Cu_3O_{6+x}$ at $x \sim 1$ [19]. The authors observed characteristic squarish deformation of the nuclear density for Cu atoms in the CuO_2 plane due to the anomalously strong anharmonic low temperature ($T = 15K$) motion presumably of vibronic nature. Unconventional isotope effect and anomalous anisotropic pressure effect on T_c in doped cuprates could also be associated with vibronic effects.

Thus, numerous experimental data show that Zhang-Rice model should be generalized with inclusion of near-degeneracy effects accompanied by PJT effect.

Many authors have treated JT (or PJT) effect in doped cuprates in a rather general and various form both as a source of the local pairing [20] and as a source of the unconventional physical properties [21–24]. So, H. Kamimura [22] proposed a mechanism of the HTSC due to the coherent bipolaron conduction induced by JT distortions. A dynamic Van Hove Jahn-Teller effect has been introduced by R.S. Markiewicz [23]. The essence of the vibronic model by M. Georgiev et al., L. Mihailov et al. [24] is existence of off-centered apex oxygens as local polarizable states due to PJT effect. Their model is one of the numerous so-called anharmonic models of the HTSC based on the account of anharmonic motion of apical oxygen [16]. However, it should be noted that recent studies by pulsed neutron scattering suggest that it is the in-plane Cu site rather than the apical oxygen site that may be split into two positions [13]. The absence of strong apical anomalies was stated earlier in Ref. [14].

In the most cases JT (PJT) effect has been considered within standard $E-e$-problem [25] for Cu^{2+} ion in octahedral environment (214 systems) or in square pyramidal environment [26] (123 systems). Instead of standard $d_{x^2-y^2}$, d_{z^2} doublet some authors considered $d_{x^2-y^2}$, d_{xz}, d_{yz} manifold [27]. However, all approaches originated from the assumption of near-degeneracy for some predominantly $Cu3d$-states do not agree with experimentally observed large gap ($\sim 1.5\,eV$) separating ground $d_{x^2-y^2}$ and any other $Cu3d$-states. Besides, any JT model approach pretending to be universal should be originated from CuO_4 center as the only common element of the crystalline and electronic structure of all the cuprates.

A transformation of CuO_4 clusters into PJT centers upon hole or electron doping to CuO_2 planes is a principal element of the so called singlet-triplet PJT (ST-PJT) center model developed in [2,18,28–32]. In addition to cuprates like $YBa_2Cu_3O_{6+x}$, $La_{2-x}Sr_xCuO_4$, $La_2CuO_{4+\delta}$ this model could be readily extended to a series of strongly corre-lated oxides like $(K, Ba)BiO_3$, $La_{1-x}Sr_xMnO_3$, $La_2NiO_{4+\delta}$ including systems with the high-T_c superconductivity and colossal magnetoresistance. Their unconventional properties reflect a result of response of the system to non-

isovalent substitution that stabilizes phases providing the most effective screening of charge inhomogeneity. These phases in oxides can involve novel unconventional molecular cluster configurations like Jahn-Teller sp-center [28] with anomalous high local polarizability and multi-mode behavior.

The copper oxides based on CuO_4 clusters within this model are considered to be systems, which are unstable with regard to disproportionation reaction

$$2CuO_4^{6-} \rightarrow \left[CuO_4^{5-}\right]_{JT} + \left[CuO_4^{7-}\right]_{JT} \tag{1}$$

with formation of system of polar (hole - CuO_4^{5-} or electron - CuO_4^{7-}) pseudo-Jahn-Teller (PJT) centers. These centers are distinguished by the so-called local S-boson or two electrons paired in the completely filled molecular orbital of the CuO_4-cluster. In other words, the novel phase can be considered to be system of local spinless bosons moving in lattice of the hole PJT-centers $\left[CuO_4^{5-}\right]_{JT}$ or the generalized quantum lattice bose-gas (or liquid) with boson concentration near $N_B = 1/2$.

In a sense, this microscopic approach represents a particular generalization of Zhang-Rice model.

Though without detailed analysis of the $^1A_{1g}, ^{1,3}E_u - a_{1g} - b_{1g} - b_{2g} - e_u$ vibronic problem, this model approach has been successfully applied for qualitative and semi-quantitative description of many physical properties of cuprates: MIR absorption bands [2], isotope effect [32], static and dynamic magnetic properties [33], local structure distortions [34], hyperfine coupling [35], phonon anomalies [30], neutron scattering [36]. Further development of the model and, first of all, possibilities of quantitative predictions implies a detailed analysis of the $^1A_{1g}, ^{1,3}E_u - a_{1g} - b_{1g} - b_{2g} - e_u$ vibronic problem. Moreover, this problem is of great independent importance as a non-trivial example of multi-mode PJT effect.

Below, in our paper we consider in detail a vibronic structure of the isolated PJT center taking into account some effects associated with its singlet-triplet structure and spin-orbital coupling. First, in Section 2 a short consideration of the correlation driven near degeneracy effects for the CuO_4-clusters will be done. Section 3 contains a detailed analysis of the $^1A_{1g}, ^{1,3}E_u - a_{1g} - b_{1g} - b_{2g} - e_u$ vibronic problem within CuO_4 cluster including an adiabatic potential, vibronic states and tunnelling effects for three different regimes. Some effects of spin-orbital coupling within $(^1A_{1g}, ^{1,3}E_u)$ manifold are considered in Section 4.

II. CORRELATIONS AND THE NEAR DEGENERACY EFFECTS FOR THE CUO_4 CLUSTERS.

At a glance the analysis of electronic structure and energy spectrum of the parent compounds such as $La_{2-x}M_xCuO_4$, $YBa_2Cu_3O_{6+x}$ at $x = 0$ does not display any exotic peculiarities except quasi-two-dimensional antiferromagnetism determined by the strong exchange interaction for the $b_{1g}(d_{x^2-y^2})$ holes in the "basic" CuO_4^{6-} clusters. At the same time it is worth to pay attention to one important feature, namely to the exciton-band form of the fundamental absorption in the $1.5 \div 3.0\ eV$ region strictly pronounced in the systems like R_2CuO_4, $YBa_2Cu_3O_{6+x}$, CuO [29].

A peculiar character of this absorption connected with the allowed charge-transfer transition $b_{1g} \rightarrow e_u$ between the copper-oxygen b_{1g}-hybrid and the purely oxygen e_u-orbital provides evidence of the strongly correlated nature of the e_u-electrons with formal occurrence of two types of the e_u-states with and without strong correlation. This peculiarity is associated with the maximal hole density occurred for oxygen ions just in the e_u-states of the CuO_4-cluster and can be easily explained in the framework of the *non-rigid anionic background model* [37]. This model introduces new correlation degree of freedom with two possible states of anionic background for the valent $O2p$-holes corresponding to two possible projections of the correlation pseudospin $s = 1/2$ and is described by simplified Hamiltonian

$$H_{corr} = V_1 \hat{\sigma}_x + V_3 \hat{\sigma}_z, \tag{2}$$

where $V_{1,3}$ are two electronic operators for the valent states. Simple approximation used in [37] conjectures the linear n_{2p}-dependence for $V_{1,3}$, where n_{2p} is the $O2p$-hole number. According to optical data [29], the correlation pseudospin splitting can achieve the value $\sim 0.5\ eV$.

An increase in the $O2p$-hole concentration with hole doping $CuO_4^{6-} \rightarrow CuO_4^{5-}$ results in a sharp increase of the e_u correlation splitting in the hole CuO_4^{5-}-centers with transformation of the $b_{1g} \rightarrow e_u$ fundamental band to the high-energy $(b_{1g}^2) \rightarrow (b_{1g}e_u)$ subband and the low-energy $b_{1g}^2 \rightarrow b_{1g}^* e_u^*$ subband to be well known as MIR (mid-infrared) absorption band [2].

Fig.1 shows qualitatively the main results of the taking account of the considered "e_u correlations" for energy spectrum of basic CuO_4^{6-} cluster and hole CuO_4^{5-} cluster. It is important to mention an appearance in our model of two types of the orthogonal (!) molecular orbitals; for instance b_{1g} (upper correlation sublevel) and b_{1g}^* (lower correlation sublevel) states, e_u and e_u^*.

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Thus, we come to a conclusion about a near-degeneracy for two configurations $b_{1g}^{*\,2}$ and $b_{1g}^{*}e_{u}^{*}$ with b_{1g}^{*} and e_{u}^{*} being the lowest correlation sublevels. This result does not drastically changes with taking account of an electrostatic interaction V_{ee} between two holes. Moreover, just the V_{ee} contribution was considered earlier [2] as a main reason for a near-degeneracy for the $^{1}A_{1g}$ and $^{1,3}E_{u}$ terms formed by $b_{1g}^{*\,2}$ and $b_{1g}^{*}e_{u}^{*}$ configurations. So, the both correlation effects lead to a near-degeneracy in ground state of the hole center CuO_{4}^{5-}.

Unusual properties of the $(^{1}A_{1g},\,^{1,3}E_{u})$ manifold involving terms distinguished by the spin multiplicity, parity and orbital degeneracy provides unconventional behavior for the hole center CuO_{4}^{5-} with active interplay of various modes. As an extremely important result one should note that E_{u}-doublet has a nonquenched Izing like orbital moment that can be directed only along the C_{4}-axis.

A near degeneracy within $(^{1}A_{1g},\,^{1,3}E_{u})$ manifold can lead to conditions for the pseudo-Jahn-Teller effect [25] with anomalously strong electron-lattice correlations with active local displacements modes of the $Q_{e_{u}}$, $Q_{b_{1g}}$ and $Q_{b_{2g}}$ types. It should be noted here that the $Q_{e_{u}}$ modes are the only hybrid copper-oxygen modes, while the $Q_{b_{1g}}$ and $Q_{b_{2g}}$ modes are the pure oxygen ones.

III. VIBRONIC COUPLING FOR THE CUO_{4}^{5-} CENTERS.

A. Adiabatic potential.

Below we'll make use of the notation $|SM_{S}\Gamma\gamma\rangle$ for basis wave functions from the $(^{1}A_{1g},\,^{1,3}E_{u})$ manifold (see Fig.1). Here, S $(=0,1)$, M_{S} are the total spin and its projection, $\Gamma\gamma$ $(=A_{1g},\,E_{u}^{x},\,E_{u}^{y})$ labels the irreducible representation of symmetry group D_{4h} for the CuO_{4} center and its row, respectively, indicating the transformation properties of the orbital functions. Subsequently, we restrict ourselves with the linear vibronic coupling within the $(^{1}A_{1g},\,^{1,3}E_{u})$ manifold with the JT-active vibrational coordinates of the a_{1g}, b_{1g}, b_{2g}, e_{u} symmetry.

Vibronic coupling for the isolated singlet or triplet $^{1,3}E_{u}$ term has a well known for the $E-b_{1}-b_{2}$-problem [25] form diagonal in S and M_{S}

$$\begin{pmatrix} V_{b_{1g}}^{\tau}Q_{b_{1g}} & V_{b_{2g}}^{\tau}Q_{b_{2g}} \\ V_{b_{2g}}^{\tau}Q_{b_{2g}} & -V_{b_{1g}}^{\tau}Q_{b_{1g}} \end{pmatrix}, \quad \tau = {}^{1}E_{u},\ {}^{3}E_{u}. \tag{3}$$

Singlet terms $^{1}E_{u}$ and $^{1}A_{1g}$ interact due to linear vibronic coupling

$$\left\langle 00A_{1g}|\hat{V}_{vib}|00E_{u}^{i}\right\rangle = \sum_{e_{u}} V_{e}Q_{e_{u}^{i}} \tag{4}$$

determined by active vibrational coordinates $Q_{e_{u}^{x}}, Q_{e_{u}^{y}}$. For the CuO_{4} cluster there are three normal coordinates with e_{u} symmetry, however, below we restrict ourselves with the choice of one active e_{u} vibration with an appropriate linear vibronic coupling constant V_{e}.

The sum of elastic energy $\hat{V}_{Q}$, electronic Hamiltonian $\hat{V}_{el}$, and vibronic Hamiltonian $\hat{V}_{vib}$ for the singlet $S=0$ spin manifold $(^{1}A_{1g},^{1}E_{u})$ with bare separation Δ_{AE} (see Fig.1) could be written as:

$$\hat{U}(Q) = \sum_{i} \frac{\omega_{i}^{2}Q_{i}^{2}}{2}\cdot\hat{I} + \begin{pmatrix} -\Delta + V_{z}Q_{z} & V_{e}Q_{x} & V_{e}Q_{y} \\ V_{e}Q_{x} & V_{\alpha}Q_{\alpha} & V_{\beta}Q_{\beta} \\ V_{e}Q_{y} & V_{\beta}Q_{\beta} & -V_{\alpha}Q_{\alpha} \end{pmatrix}, \tag{5}$$

where the indices both for the coupling coefficient and normal coodinates are defined as follows: $a_{1g} \to z$, $e_{u}^{x} \to x$, $e_{u}^{y} \to y$, $b_{1g} \to \alpha$, $b_{2g} \to \beta$, and $\Delta = \Delta_{AE} - V_{z}q_{z}^{(0)}$, $V_{z} = V_{z}^{A_{1g}} - V_{z}^{E_{u}}$, $q_{i}^{(0)} = V_{i}/\omega_{i}^{2}$.

An important information for the PJT center could be obtained with examination of the adiabatic potential (AP) surfaces $\varepsilon(Q)$, which are the roots of characteristic equation for $\hat{U}(Q)$. In our case this is reduced to a cubic equation with an extremely complicated expression for the roots. The coordinates of the minima Q^{0}, energy and structure of electronic wave function at Q^{0} and curvature of energy surface near Q^{0} can be obtained by the Opik-Pryce method [38], where an eigenvalue problem is treated only for extremal points of the AP. It should be noted that the Opik-Pryce method does not permit to find specific points of the AP without definite values of the derivative, however namely such a situation occurs for the upper sheets of the AP. The type of minima can be derived from curvature analysis for $\varepsilon(Q)$ near Q^{0}.

The relations between the extremum coordinates and the wave function coefficients are

$$Q_z^0 = -q_e^{(0)} z^2, \quad Q_x^0 = -2q_e^{(0)} zx, \quad Q_y^0 = -2q_e^{(0)} zy, \tag{6}$$
$$Q_\alpha^0 = -q_\alpha^{(0)} \left(x^2 - y^2\right), \quad Q_\beta^0 = -2q_\beta^{(0)} xy,$$

where we have denoted the coefficients of decomposition of the electronic wave function as z, x and y for $|00A_{1g}\rangle$, $|00E_u^x\rangle$ and $|00E_u^y\rangle$, respectively. The eigenvalue problem for V_{vib} in the AP extremum points is given by:

$$\begin{pmatrix} -\Delta - 2E_{JT}^z \; z^2 & -4E_{JT}^e \; zx & -4E_{JT}^e \; zy \\ -4E_{JT}^e \; zx & -2E_{JT}^\alpha \left(x^2 - y^2\right) & -4E_{JT}^\beta \; xy \\ -4E_{JT}^e \; zy & -4E_{JT}^\beta \; xy & 2E_{JT}^\alpha \left(x^2 - y^2\right) \end{pmatrix} \begin{pmatrix} z \\ x \\ y \end{pmatrix} = \lambda \begin{pmatrix} z \\ x \\ y \end{pmatrix}, \tag{7}$$

where $E_{JT}^i = \frac{1}{2} V_i q_i^{(0)} = V_i^2 / 2\omega_i^2$ is the specific JT energy.

The system (7) complemented with a normalization condition $x^2 + y^2 + z^2 = 1$ has 13 solutions, which are listed in the Table I. Also the expressions for the quadratic form of the AP surface near the extremal points are given. These solutions could be divided into three groups.

1. The first group NJT (non-JT) contains the only solution. Electronic part of wave function in the extremal point is pure $|00A_{1g}\rangle$. The NJT-extremum is the minimum on lower sheet of AP, if $b < 0$ ($b = -\Delta + 4E_{JT}^e - 2E_{JT}^z$) or on the upper sheet, if $(\Delta + 2E_{JT}^z) < 0$. In both cases the weak pseudo-Jahn-Teller effect takes place, when due to weakness of the vibronic coupling in comparison with the bare separation of electronic levels Δ, there are no low-symmetry distortions of the CuO_4 cluster, and only the renormalization of the local e_u vibration frequency occurs:

$$\left(\tilde{\omega}_e^{(NJT)}\right)^2 = \omega_e^2 \left(1 - \eta_z\right), \quad \eta_z = \frac{4E_{JT}^e}{\Delta + 2E_{JT}^z} \; . \tag{8}$$

2. The second group JT$_i$ ($i = \alpha, \beta$) contains four solutions, which are similar to results of the well-known $E - b_1 - b_2$-problem. The wave function at the extremum points is a pure E_u superposition. In further analysis the rhombic mode with larger JT energy will be called the "strong" (σ) mode, and that with smaller JT energy will be called the "weak" (σ') one: $E_{JT}^\sigma > E_{JT}^{\sigma'}$, ($\sigma, \sigma' = \alpha, \beta$); for the $E - b_1 - b_2$-problem the E_{JT}^σ is the JT stabilization energy. Among four extremum points only the JT$_\sigma$ pair will correspond to minima. The minima are located on the lower sheet of the AP, if $a_\sigma < 0$ ($a_\sigma = \Delta + 4E_{JT}^e - 2E_{JT}^\sigma$), and on the middle one, if $(\Delta - 2E_{JT}^\sigma) > 0$. The JT$_{\sigma'}$ pair represents saddle points. The wave functions at the minima are orthogonal each other. If $E_{JT}^\sigma = E_{JT}^{\sigma'}$, the equipotential continuum of minima, or trough, exists. The σ mode frequency does not vary, and that of σ' mode is renormalized due to vibronic coupling:

$$\tilde{\omega}_\sigma^2 = \omega_\sigma^2 \;, \quad \tilde{\omega}_{\sigma'}^2 = \omega_{\sigma'}^2 \left(1 - \lambda_\sigma\right), \quad \lambda_\sigma = \frac{E_{JT}^{\sigma'}}{E_{JT}^\sigma} \; . \tag{9}$$

It should be noted here that a type (B_{1g} or B_{2g}) of the ground JT mode is of principal importance for the physics of the copper oxides. This is determined by the competition of vibronic parameters for the $Cu3d - O2p$ and $O2p - O2p$ bonds minimizing the B_{1g} and B_{2g} modes, respectively.

For the e_u vibrations the JT$_i$ solutions correspond to the weak PJT effect: only renormalization of local e_u vibration occurs. If α mode is strong, the coordinates of minimum determine the rhombic distortion of the CuO_4 cluster along x- or y -direction (Fig.2). Accordingly, the softening of the e_u^x or e_u^y vibration occurs; but as the both minima are equivalent, the frequencies of local e_u modes remain twice degenerate. In a case of "strong" β mode with rectangular distortion of the CuO_4 cluster, the softening of that of e_u modes occurs, which co-directs to the cluster distortion. In all cases the expression for the renormalized local e_u mode frequency is written as:

$$\left(\tilde{\omega}_e^{(JT)}\right)^2 = \omega_e^2 \left(1 - \kappa_\sigma\right) \;, \quad \kappa_\sigma = \frac{4E_{JT}^e}{-\Delta + 2E_{JT}^\sigma} \; . \tag{10}$$

3. The third group PJT$_i$ ($i = \alpha, \beta$) includes eight solutions and corresponds to the most complicated case of the strong pseudo-Jahn-Teller effect. In this case the wave functions at the extremum points are the $A_{1g} - E_u$ hybrid states, and coefficients of superposition depend on the bare splitting Δ and the JT energies. The four from the eight PJT$_\sigma$ extrema (σ is the "strong" rhombic mode) are minima, if $a_\sigma > 0$ and $b > 0$. All the PJT$_\sigma$ minima are equivalent and allocated on the lower sheet of the AP. An arrangement of minima in space of the normal coordinates of the CuO_4 cluster is schematically shown in Fig.3. The wave functions at the minima are not orthogonal each other, that is a characteristic feature of strong pseudo-Jahn-Teller effect. The four PJT$_{\sigma'}$ extrema (σ' is the "weak" rhombic mode) are saddle points. A specific case of degeneracy for the JT energies of rhombic modes should be examined separately.

The rhombic distortion of the CuO_4 cluster at the minimum points with the nonzero plane quadrupole moment is accompanied by the co-directed e_u distortion with the electric dipole moment. The possible PJT_σ distortions are shown in Fig.2.

Close to minimum M the equipotential surface of the quadratic form $\varepsilon(Q - Q^{(0,M)})$ is a five-dimensional ellipsoid with center located at $Q^{(0,M)}$ and principal axes to be turned with regard to basic ones. The σ mode at minimum is mixed with co-directed e_u mode and a_{1g} mode giving rise to three local hybrid modes. The σ' mode is mixed with the second e_u mode giving rise to two local hybrid modes. The mixing coefficients are proportional to the appropriate vibronic coupling constants.

In a case, when $V_z = 0$, the frequencies of normal local hybrid modes are written as:

$$\left(Q_{\sigma'}, \tilde{Q}_1\right): \qquad \omega_\pm^2 = \frac{A + B}{2} \pm \sqrt{\left(\frac{A - B}{2}\right)^2 + C^2}, \tag{11}$$

where

$$A = \omega_e^2 \left(1 - v_\sigma^2\right), \ B = \omega_{\sigma'}^2 \left(1 - \rho_\sigma^2\right), \ C = \omega_e \omega_{\sigma'} v_\sigma \rho_\sigma,$$

$$v_\sigma = \sqrt{\frac{E_{JT}^e \, a_\sigma}{E_{JT}^e \, a_\sigma + E_{JT}^\sigma \, b}}, \quad \rho_\sigma = \sqrt{\frac{E_{JT}^{\sigma'} \, b}{E_{JT}^e \, a_\sigma + E_{JT}^\sigma \, b}},$$

and

$$\left(Q_\sigma, \tilde{Q}_2\right): \qquad \omega_\pm'^2 = \frac{D + E}{2} \pm \sqrt{\left(\frac{D - E}{2}\right)^2 + F^2}, \tag{12}$$

where

$$D = \omega_e^2 \left(1 - \nu_\sigma^2\right), \ B = \omega_\sigma^2 \left(1 - \mu_\sigma^2\right), \ F = \omega_e \omega_\sigma \nu_\sigma \mu_\sigma,$$

$$\mu_\sigma = \sqrt{\frac{E_{JT}^\sigma \, a_\sigma b}{E_{JT}^e \, (a_\sigma + b)^2}}, \quad \nu_\sigma = \frac{a_\sigma - b}{a_\sigma + b}.$$

For the minima 1 and 3 $\tilde{Q}_1 = Q_x$, if $\sigma = \alpha$ (Q_1, if $\sigma = \beta$), $\tilde{Q}_2 = Q_y$, if $\sigma = \alpha$ (Q_2, if $\sigma = \beta$); for minima 2 and 4 $\tilde{Q}_1 = Q_y$, if $\sigma = \alpha$ (Q_2, if $\sigma = \beta$), $\tilde{Q}_2 = Q_x$, if $\sigma = \alpha$ (Q_1, if $\sigma = \beta$). Due to an equivalence of minima all local frequencies coincide.

The type of minima on the lower AP sheet will be determined mainly by following quantities:

$$a_\sigma = \Delta + 4E_{JT}^e - 2E_{JT}^\sigma, \quad b = -\Delta + 4E_{JT}^e - 2E_{JT}^z \tag{13}$$

in the following way:
   a) NJT, if $a_\sigma > 0$ and $b < 0$;
   b) JT_σ, if $a_\sigma < 0$ and $b > 0$;
   c) PJT_σ, if $a_\sigma > 0$ and $b > 0$;
   d) NJT and JT_σ, if $a_\sigma < 0$ and $b < 0$.

The diagram of states of the lower AP sheet in space of parameters Δ, E_{JT}^σ and E_{JT}^e at constant value of $E_{JT}^{z,0}$ is shown in Fig.4. A cross-section of the parameter space for constant value of E_{JT}^e is shown in Fig.5a. If $\Delta \to +\infty$, the lowest $^1A_{1g}$ level is well isolated and the lower AP sheet has a trivial NJT minimum. In contrast, at $\Delta \to -\infty$ the ^1E_u term becomes the lower one and usual $E - b_1 - b_2$-problem with two JT_σ minima on the lower AP sheet occurs. When coming together, the $^1A_{1g}$ and ^1E_u terms are mixed by the e_u mode, and the e_u frequency is renormalized. This is accompanied by a formation of four PJT_σ minima or three (NJT+JT_σ) minima depending on magnitude of E_{JT}^σ. These two possibilities correspond to lines $E_{JT}^\sigma = E_{JT}^{\sigma,1}$ and $E_{JT}^\sigma = E_{JT}^{\sigma,2}$ in Fig.5a.

With a motion along the line $E_{JT}^\sigma = E_{JT}^{\sigma,1}$ from $-\infty$ up to $+\infty$ the curvature of the JT_σ minima along e_u directions decreases up to zero on the line $a_\sigma = 0$. At this point the JT_σ minima transform into saddle points with simultaneous appearence of the PJT_σ minima (one of the JT_σ minima splits along Q_1, another one splits along Q_2 direction). Moving from the line $a_\sigma = 0$ up to $b = 0$ the magnitude of rhombic distortion decreases up to zero on the line $b = 0$. The magnitude of e_u coordinates of minima firstly increases, then decreases up to zero, reaching a maximum on the line $\Delta = -E_{JT}^\sigma + E_{JT}^z$. The Q_z coordinate increases linearly ($\sim a_\sigma$) from zero up to $-q_z^{(0)}$ on the line $b = 0$. Thus,

the four PJT_σ minima transform into one NJT minimum. Further, with $\Delta \to +\infty$ the A_{1g} and E_u terms interact weaker and $\tilde{\omega}_e \to \omega_e$.

The PJT_σ minima occur, if the e_u mode driven interaction of the A_{1g} and E_u terms is rather effective. When $E_{JT}^\sigma > 4E_{JT}^e - E_{JT}^z$ (for example $E_{JT}^\sigma = E_{JT}^{\sigma,2}$), the σ mode driven interaction becomes more effective. In this case at $b = 0$ the NJT minimum appears on the lower AP sheet together with JT_σ minima. All three minima have the same energy on the line $\Delta = -E_{JT}^\sigma + E_{JT}^z$. Further, at $\Delta \to +\infty$ the JT_σ minima become more flat, without varying their coordinates, and at $a_\sigma = 0$ only the NJT minimum remains.

In Fig.5b the diagram of the upper AP sheets is shown.

B. Tunnel splitting.

The most complicated case of strong pseudo-Jahn-Teller effect can be treated in a framework of the tunnel Hamiltonian [39],when the localized vibrations at the AP minima are considered with taking account of the inter-well tunneling. It is supposed, that the minimum depth is larger than the typical phonon energy, hence the tunnel frequency is rather small.

We consider the minimization problem for the total energy functional $E\left[\Psi\right] = \left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle$ with Hamiltonian

$$\hat{H} = \hat{T}_Q + \hat{V}_{el} + \hat{V}_Q + \hat{V}_{vib} , \tag{14}$$

where $\hat{T}_Q$ is kinetic energy of nuclei, $\hat{V}_{el}$ is electronic energy operator, $\hat{V}_Q$ is elastic energy, $\hat{V}_{vib}$ is vibronic Hamiltonian. The Ψ is written as

$$\Psi = \sum_{M=1}^{4} c_M \, \varphi_M^{(\sigma)} \, \chi_M^{(\sigma)} , \tag{15}$$

where $\varphi_M^{(\sigma)}$ and $\chi_M^{(\sigma)}$ are electronic (see Table I) and vibrational wave functions, respectively, centered at the minimum $PJT_\sigma^{(M)}$. The ground state vibrational wave function $\chi_M^{(\sigma)}$ has a form

$$\chi_M^{(\sigma)} = \prod_{k=1}^{5} \left(\frac{\omega_k^M}{\pi}\right)^{\frac{1}{4}} \exp\left\{ -\frac{1}{2}\omega_k^M \left(\sum_{j=1}^{5} U_{jk}^M \left(Q_j - Q_j^{(0,M)}\right)\right)^2 \right\} , \tag{16}$$

where $\left(\omega_k^M\right)^2$ are the eigenvalues of a matrix of the quadratic form $\varepsilon\left(Q - Q^{(0,M)}\right)$, U^M is matrix for the unitary transformation to principal axes for $\varepsilon\left(Q - Q^{(0,M)}\right)$. If $V_z = 0$, the frequencies ω_k^M are equal to $\omega_\pm$ Eq. (11), $\omega_\pm'$ Eq. (12) and ω_z, respectively.

The variation of the energy functional $E\left[\Psi\right]$ gives

$$H \, \vec{c} = E \, S \, \vec{c}, \tag{17}$$

where H and S are the Hamiltonian Eq. (14) and overlap matrix, respectively. The solutions of the system Eq. (17) give the tunnel states and the tunnel energy levels, respectively.

Due to equivalence of the PJT_σ minima the H and S matrices include only three types of the non-zero matrix elements:

a) the diagonal matrix elements:
$\left\langle \varphi_M^{(\sigma)} \, \chi_M^{(\sigma)} \left| \hat{H} \right| \varphi_M^{(\sigma)} \, \chi_M^{(\sigma)} \right\rangle = H, \quad \left\langle \varphi_M^{(\sigma)} \, \chi_M^{(\sigma)} | \varphi_M^{(\sigma)} \, \chi_M^{(\sigma)} \right\rangle = 1;$

b) the non-diagonal matrix elements for the states with different both dipole and quadrupole moments:
$\left\langle \varphi_M^{(\sigma)} \, \chi_M^{(\sigma)} \left| \hat{H} \right| \varphi_{M+1}^{(\sigma)} \, \chi_{M+1}^{(\sigma)} \right\rangle = H_q, \quad \left\langle \varphi_M^{(\sigma)} \, \chi_M^{(\sigma)} | \varphi_{M+1}^{(\sigma)} \, \chi_{M+1}^{(\sigma)} \right\rangle = S_q;$

c) the non-diagonal matrix elements for the states with different dipole moment but the same quadrupole one:
$\left\langle \varphi_M^{(\sigma)} \, \chi_M^{(\sigma)} \left| \hat{H} \right| \varphi_{M+2}^{(\sigma)} \, \chi_{M+2}^{(\sigma)} \right\rangle = H_d, \quad \left\langle \varphi_M^{(\sigma)} \, \chi_M^{(\sigma)} | \varphi_{M+2}^{(\sigma)} \, \chi_{M+2}^{(\sigma)} \right\rangle = S_d.$

The explicit expressions for these quantities at $V_z = 0$ are listed in Table II. Thus, the system Eq. (17) is written as:

$$
\begin{pmatrix} H & H_q & H_d & H_q \\ H_q & H & H_q & H_d \\ H_d & H_q & H & H_q \\ H_q & H_d & H_q & H \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = E \begin{pmatrix} 1 & S_q & S_d & S_q \\ S_q & 1 & S_q & S_d \\ S_d & S_q & 1 & S_q \\ S_q & S_d & S_q & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}
\tag{18}
$$

with eigenvectors

$$
\begin{aligned}
\vec{c}_1 &= \frac{1}{2} \left(1, 1, 1, 1 \right), \quad \vec{c}_1 = \frac{1}{2} \left(1, -1, 1, -1 \right), \\
\vec{c}_3 &= \frac{1}{\sqrt{2}} \left(-\sin\theta, \cos\theta, \sin\theta, -\cos\theta \right), \\
\vec{c}_4 &= \frac{1}{\sqrt{2}} \left(\cos\theta, \sin\theta, -\cos\theta, -\sin\theta \right)
\end{aligned}
\tag{19}
$$

Vectors $\vec{c}_3$ and $\vec{c}_4$ are degenerated, hence there is a freedom in choice of θ. We assume $\theta = 0$, then

$$
\begin{aligned}
\left| \Psi_{A_{1g}} \right\rangle &= c_\sigma \left| A_{1g} \right\rangle \chi_{a_{1g}} + \frac{d_\sigma}{\sqrt{2}} \left\{ \left| E_u^{(1)} \right\rangle \chi_{e_u^{(1)}} + \left| E_u^{(2)} \right\rangle \chi_{e_u^{(2)}} \right\}, \\
\left| \Psi_\Sigma \right\rangle &= -c_\sigma \left| A_{1g} \right\rangle \chi_\Sigma - \frac{d_\sigma}{\sqrt{2}} \left\{ \left| E_u^{(1)} \right\rangle \chi_{e_u^{(1)}} - \left| E_u^{(2)} \right\rangle \chi_{e_u^{(2)}} \right\}, \\
\left| \Psi_{E_u^{(1)}} \right\rangle &= c_\sigma \left| A_{1g} \right\rangle \chi_{e_u^{(1)}} + \frac{d_\sigma}{\sqrt{2}} \left| E_u^{(1)} \right\rangle \left\{ \chi_{a_{1g}} + \chi_\Sigma \right\}, \\
\left| \Psi_{E_u^{(2)}} \right\rangle &= c_\sigma \left| A_{1g} \right\rangle \chi_{e_u^{(2)}} + \frac{d_\sigma}{\sqrt{2}} \left| E_u^{(2)} \right\rangle \left\{ \chi_{a_{1g}} - \chi_\Sigma \right\},
\end{aligned}
\tag{20}
$$

where functions $\left\{ \left| E_u^{(1)} \right\rangle, \left| E_u^{(2)} \right\rangle \right\}$ coincide, respectively, with $\{ |00E_u^x\rangle, |00E_u^y\rangle \}$, if $\sigma = \alpha$ or with $\{ (|00E_u^x\rangle + |00E_u^y\rangle)/\sqrt{2}, (-|00E_u^x\rangle + |00E_u^y\rangle)/\sqrt{2} \}$, if $\sigma = \beta$. Symmetric combinations of vibrational functions are:

$$
\begin{aligned}
\chi_{a_{1g}} &= \frac{1}{2} \left(\chi_1^{(\sigma)} + \chi_2^{(\sigma)} + \chi_3^{(\sigma)} + \chi_4^{(\sigma)} \right), \quad \chi_{e_u^{(1)}} = \frac{1}{\sqrt{2}} \left(\chi_2^{(\sigma)} - \chi_4^{(\sigma)} \right), \\
\chi_\Sigma &= \frac{1}{2} \left(-\chi_1^{(\sigma)} + \chi_2^{(\sigma)} - \chi_3^{(\sigma)} + \chi_4^{(\sigma)} \right), \quad \chi_{e_u^{(2)}} = \frac{1}{\sqrt{2}} \left(\chi_1^{(\sigma)} - \chi_3^{(\sigma)} \right).
\end{aligned}
\tag{21}
$$

The symmetry Σ of the vibronic and vibrational functions coincide with that of σ mode. With taking account of the normalization for tunnel states

$$
\begin{aligned}
N_{A_{1g}}^2 &= \left\langle \Psi_{A_{1g}} | \Psi_{A_{1g}} \right\rangle = 1 + 2S_q + S_d, \\
N_{E_u}^2 &= \left\langle \Psi_{E_u^{(1)}} | \Psi_{E_u^{(1)}} \right\rangle = 1 - S_d, \\
N_\Sigma^2 &= \left\langle \Psi_\Sigma | \Psi_\Sigma \right\rangle = 1 - 2S_q + S_d,
\end{aligned}
\tag{22}
$$

we come to following expressions for the tunnel energy levels:

$$
E_{A_{1g}} = \frac{H + 2H_q + H_d}{1 + 2S_q + S_d}, \quad E_{E_u} = \frac{H - H_d}{1 - S_d}, \quad E_\Sigma = \frac{H - 2H_q + H_d}{1 - 2S_q + S_d}.
\tag{23}
$$

These are shown in Fig.6 as a function of Δ with dimensionless coupling constant $k_e = 3$. The frequencies of tunneling between the equivalent distorted configurations of the CuO_4 cluster are determined by the splittings of the tunnel energy levels, which are much less than typical phonon energies. It should be noted, that for the pseudo-Jahn-Teller effect the symmetry of the ground vibronic and bare electronic states could be different unlike the conventional Jahn-Teller effect ("Ham's law") [40]. Fig.6 illustrates the situation, when $\Delta < 0$ (electronic $^1A_{1g}$ level is higher than ^1E_u), but $E_{A_{1g}} < E_{E_u}$. The reason is that in the pseudo-effect the vibronic interaction mixes different electronic levels, contrary to a case of the degenerated electronic states. It is worthy to note that in our case the vibronic Σ level is always higher in energy than the A_{1g} and E_u ones.

C. Degeneracy of JT energies for rhombic modes.

When $E_{JT}^\alpha = E_{JT}^\beta$ (and with $a_\sigma > 0$, $b > 0$) the trough of minima appears on the lower AP sheet. It is a curve in four-dimensional space, which has following parametric form:

$$Q_z = -q_z^{(0)} c_\sigma, \quad Q_x = -2q_e^{(0)} c_\sigma d_\sigma \cos\frac{\varphi}{2}, \quad Q_y = -2q_e^{(0)} c_\sigma d_\sigma \sin\frac{\varphi}{2}, \tag{24}$$

$$Q_\alpha = -2q_\sigma^{(0)} d_\sigma^2 \cos\varphi, \quad Q_\beta = -2q_\sigma^{(0)} d_\sigma^2 \sin\varphi,$$

where $c_\sigma = \sqrt{\frac{a_\sigma}{a_\sigma + b}}$, $d_\sigma = \sqrt{\frac{b}{a_\sigma + b}}$. The energy and wave function are

$$\varepsilon_0 = -E_{JT}^\sigma - \frac{1}{2} c_\sigma^2 a_\sigma \tag{25}$$

$$|\Phi\rangle = c_\sigma |A_{1g}\rangle + d_\sigma \left(\cos\frac{\varphi}{2} |E_u^x\rangle + \sin\frac{\varphi}{2} |E_u^y\rangle \right),$$

respectively. The CuO_4 cluster distortions as a function of φ are shown in Fig.7.

For JT_σ case, when $c_\sigma = 0$, the situation is similar to the $E - e$-problem with the doublet ground vibronic state. Its type are not changed in PJT_σ case, if $c_\sigma \ll 1$. However, with the increasing of c_σ from the one hand the continuum of $E - e$ type splits into two parts in e_u direction and from the other hand the $A_{1g} - E_u$ mixing reduces the symmetry of electronic wave function resulting in a singlet ground state. The potential energy in a small vicinity of the continuum minima is

$$\varepsilon = \varepsilon_0 + \frac{\omega_z^2 q_z^2}{2} + \frac{Dr^2}{2} + \frac{E\rho^2}{2} - Fr\rho, \tag{26}$$

where q_z, r and ρ are count out from

$$Q_z^{(0)} = -q_z^{(0)} c_\sigma^2, \quad r_0 = -2q_e^{(0)} c_\sigma d_\sigma, \quad \rho_0 = -q_\sigma^{(0)} d_\sigma^2.$$

The radial vibration frequencies along the principal directions of the quadratic form Eq. (26) are ω_+' and ω_-' Eq. (12), respectively. If $r_0^2 + \rho_0^2 \gg \hbar/\omega_-'$, $\varepsilon_0 \gg \hbar\omega_+'$, then the energy and wave function of the ground vibronic singlet are

$$E_0 = \varepsilon_0 + \frac{\hbar}{2} \left(\omega_+' + \omega_-' \right), \quad |\Psi_0\rangle = |\Phi\rangle \frac{\chi_0(r_+) \, \chi_0(\rho_-)}{\sqrt{2\pi (r_0 + r)(\rho_0 + \rho)}}, \tag{27}$$

where χ_0 is the ground state vibrational function.

If the parameters approach to those typical for the NJT situation, the radius of trough is small, so the rotational term is not a small perturbation. The energy barrier in the higher symmetry point lowers, and the system turns into vibrational regime near the NJT minima with a singlet ground state, which is not described by the Eq. (27).

IV. VIBRONIC STATES IN PRESENCE OF THE SPIN-ORBIT COUPLING.

Without taking account of the spin-orbit coupling the ^3E_u term is isolated, and it has the six-fold degenerated ground vibronic state. The spin-orbit coupling mixes the $M_S = 0$ states of the ^3E_u and ^1E_u terms. As well, this coupling splits lower vibronic states of the ^3E_u term, which have $M_S = \pm 1$.

A. The $M_S = 0$ states.

1. Well-isolated $^{1,3}E_u$ terms.

If the $^1A_{1g}$ and $^{1,3}E_u$ terms are well separated in energy ($\Delta_{AE} \gg \Delta_E, \lambda$), it is possible to consider the AP within a basis of the $|00E_u^x\rangle$, $|00E_u^y\rangle$, $|10E_u^x\rangle$, $|10E_u^y\rangle$ states, and then take into account the vibronic coupling with the of $^1A_{1g}$ term as perturbation. The potential energy matrix $\hat{U}(Q)$ acquires a form:

$$\sum_i \frac{\omega_i^2 Q_i^2}{2} \cdot \hat{I} + \begin{pmatrix} -\Delta_E + V_\alpha Q_\alpha & V_\beta Q_\beta & 0 & -i\lambda \\ V_\beta Q_\beta & -\Delta_E - V_\alpha Q_\alpha & i\lambda & 0 \\ 0 & -i\lambda & \Delta_E + V_\alpha Q_\alpha & V_\beta Q_\beta \\ i\lambda & 0 & V_\beta Q_\beta & \Delta_E - V_\alpha Q_\alpha \end{pmatrix}, \tag{28}$$

where λ is submatrix element of the spin-orbit coupling. The eigenvalues and eigenvectors of $\hat{U}(Q)$ are written as follows

$$
\begin{aligned}
\varepsilon_1 &= \Sigma - \sqrt{(\Delta_E + \rho)^2 + \lambda^2}, & |1\rangle &= -i\sin\eta_1 \, |-\rho, 0\rangle + \cos\eta_1 \, |\rho, 1\rangle \ , \\
\varepsilon_2 &= \Sigma - \sqrt{(\Delta_E - \rho)^2 + \lambda^2}, & |2\rangle &= i\sin\eta_2 \, |\rho, 0\rangle + \cos\eta_2 \, |-\rho, 1\rangle \ , \\
\varepsilon_3 &= \Sigma + \sqrt{(\Delta_E - \rho)^2 + \lambda^2}, & |3\rangle &= \cos\eta_2 \, |\rho, 0\rangle + i\sin\eta_2 \, |-\rho, 1\rangle \ , \\
\varepsilon_4 &= \Sigma + \sqrt{(\Delta_E + \rho)^2 + \lambda^2}, & |4\rangle &= \cos\eta_1 \, |-\rho, 0\rangle - i\sin\eta_1 \, |\rho, 1\rangle \ ,
\end{aligned}
\tag{29}
$$

where

$$\Sigma = \sum_i \frac{\omega_i^2 Q_i^2}{2}, \quad \rho = \sqrt{(V_\alpha Q_\alpha)^2 + (V_\beta Q_\beta)^2}, \tag{30}$$

$$
\begin{aligned}
|\rho, S\rangle &= \cos\theta \, |S0E_u^x\rangle + \sin\theta \, |S0E_u^y\rangle, \\
|-\rho, S\rangle &= -\sin\theta \, |S0E_u^x\rangle + \cos\theta \, |S0E_u^y\rangle, \\
\tan 2\theta &= \frac{V_\beta Q_\beta}{V_\alpha Q_\alpha} \quad \tan 2\eta_1 = \frac{\lambda}{-\Delta_E - \rho} \ , \quad \tan 2\eta_2 = \frac{\lambda}{-\Delta_E + \rho} \ .
\end{aligned}
$$

The minima of the lower AP sheet are located on Q_σ axis (with $E_{JT}^\sigma > E_{JT}^{\sigma'}$, $\sigma, \sigma' = \alpha, \beta$) at points, which represent solutions of the equation:

$$\frac{|Q_\sigma|}{q_\sigma^{(0)}} = \left(1 + \frac{\lambda^2}{(V_\sigma |Q_\sigma| + \Delta_E)^2}\right)^{-\frac{1}{2}}. \tag{31}$$

The $Q_{\Gamma\gamma} = 0$ is a point of discontinuity of the derivative. The non-trivial minima, which correspond to the low-symmetry cluster distortions, exist for the arbitrary large λ, if $\Delta_E \neq 0$, but with $\lambda \to \infty$ the minima depth and the distortions magnitude become negligibly small. The ground vibronic state is twice degenerated. In strong coupling scheme this is realized due to orthogonality of electronic states belonging to different minima of AP. In a case $\lambda \ll E_{JT}^\sigma$ the expressions for the minimum points and their energy are written as follows:

$$Q_\sigma = \pm\tilde{q}_\sigma^{(0)}, \quad \tilde{q}_\sigma^{(0)} = q_\sigma^{(0)}\left(1 - \frac{\lambda^2}{2\left(\Delta_E + 2E_{JT}^\sigma\right)^2}\right), \tag{32}$$

$$\varepsilon_0 = -\Delta_E - E_{JT}^\sigma - \frac{\lambda^2}{2\left(\Delta_E + 2E_{JT}^\sigma\right)} \ .$$

The mixing coefficient for the triplet spin states with the singlet $^1A_{1g}$ term wave function is proportional to

$$\frac{\lambda}{\Delta_E + \Delta_{AE} + E_{JT}^e} \ . \tag{33}$$

2. Strong PJT-effect for the singlet spin states.

In this case it is neccessary to consider the spin-orbit mixing of the tunnel states with lower vibronic states of ^3E_u term. The only non-zero matrix elements are those between the tunnel E_u-states and the lower vibronic states of ^3E_u term with $M_S = 0$. The effective Hamiltonian matrix is

$$\begin{pmatrix} -\Delta_E' & 0 & 0 & -i\lambda' \\ 0 & -\Delta_E' & i\lambda' & 0 \\ 0 & -i\lambda' & \Delta_E' & 0 \\ i\lambda' & 0 & 0 & \Delta_E' \end{pmatrix}, \tag{34}$$

where $2\Delta'_E$ is an appropriate energy splitting, λ' is a modified matrix element of the spin-orbit coupling:

$$\lambda' = \lambda\, N_{E_u}^{-1}\sqrt{2}d_\sigma\left\langle\chi_M^{(\sigma)}|\tilde{\chi}_0^{(\sigma)}\right\rangle\ , \tag{35}$$

where $\chi_M^{(\sigma)}$ and $\tilde{\chi}_0^{(\sigma)}$ are the ground state vibrational functions, which are centered at the minimum M of PJT_σ type and at the minimum of AP of the $E-b_1-b_2$-problem with opposite to M sign of σ mode, respectively.

3. The singlet-triplet asymmetry of the vibronic coupling.

Let the difference in the linear vibronic coupling constants for the singlet ^1E_u and triplet ^3E_u states corresponds to the following inequalities for the JT energies: $E_{JT}^\alpha(^1E_u) > E_{JT}^\beta(^3E_u)$ and $E_{JT}^\alpha(^1E_u) < E_{JT}^\beta(^3E_u)$. Then the minima of AP for the ^1E_u term are located on the Q_α axis, and those of the ^3E_u therm are located on the Q_β axis. If the surfaces of AP for different terms intersect, than the taking account of the spin-orbit coupling could result in a complicated form of the AP with four minima. The states in minima located on the same axis are orthogonal to each other, and those located on different axis are not. Hence, even if $\Delta_E = 0$ the lower vibronic states are two doublets, which are separated by the tunnel splitting $\tilde{\Delta}$. The frequency related to $\tilde{\Delta}$ corresponds to the combined pulsing motion of the electronic and nuclear density between b_{1g} and b_{2g} distortions of the CuO_4 cluster.

B. The $M_S = \pm1$ states.

A joint operation of the vibronic and spin-orbital coupling for the $M_S = \pm1$ states within the ^3E_u term is described by the matrix

$$V_\alpha Q_\alpha\hat{\sigma}_z + V_\beta Q_\beta\hat{\sigma}_x + iM_S\lambda_1\hat{\sigma}_y\ , \tag{36}$$

where λ_1 is a submatrix element for the spin-orbital coupling within the orbital part of the ^3E_u manifold, $\hat{\sigma}_i$ are the Pauli matrices, and the energy is counted off the ^3E_u manifold.

The lower AP sheet has four extrema at points

$$q_i^{(0,\pm)} = \pm l_i\sqrt{2\tilde{E}_{JT}^i\left(1-p_i^2\right)}\ , \quad i = \alpha, \beta, \tag{37}$$

where $l_i = \sqrt{\hbar/\omega_i}$, $\tilde{E}_{JT}^i = E_{JT}^i/\hbar\omega_i$, $p_i = \lambda_1/2E_{JT}^i$, and $q_i^{(0,\pm)} = 0$ at $|p_i|\geq 1$. The parameter p_i equals to the ratio of the E_u level splitting due to the spin-orbital coupling $(2\lambda_1)$ to that of due to the vibronic coupling $(4E_{JT}^i)$. At $|p_i|\geq 1$ $(i=\alpha,\beta)$ we come to the weak pseudo-Jahn-Teller effect with the only minimum at $q_i^{(0,\pm)} = 0$ $(i=\alpha,\beta)$ and effective local vibration frequencies

$$\tilde{\omega}_i^2 = \omega_i^2\left(1-|p_i|^{-1}\right). \tag{38}$$

At $|p_i|\leq 1$ ($E_{JT}^\sigma > E_{JT}^{\sigma'}$) the strong pseudo-Jahn-Teller effect occurs with the AP minima at $q_\sigma^{(0,\pm)}$, and with the AP saddle points at $q_{\sigma'}^{(0,\pm)}$. The effective frequencies for the local vibrations at the AP minima and corresponding energies are derived as follows:

$$\tilde{\omega}_\sigma^2 = \omega_\sigma^2\left(1-p_\sigma^2\right),\ \tilde{\omega}_{\sigma'}^2 = \omega_{\sigma'}^2\left(1-\lambda_\sigma\right),\ \lambda_\sigma = \frac{E_{JT}^{\sigma'}}{E_{JT}^\sigma}\ , \tag{39}$$

$$\varepsilon_-\left(q_\sigma^{(0,\pm)}\right) = -E_{JT}^\sigma - \hbar\omega_\sigma p_\sigma\ .$$

As is seen, unlike the usual $E-b_1-b_2$-problem, the σ mode frequency is renormalized due to the spin-orbital coupling.

The electronic wave functions $\varphi_\pm^{(M_S)}$ at the minima $q_\sigma^{(0,\pm)}$ are reduced to the following form:

$$\varphi_+^{(M_S)} = \frac{1}{\sqrt{2}}\left(i\,M_S\sqrt{1-\sqrt{1-p_\sigma^2}}\left|E_u^{(1)}\right\rangle + \sqrt{1+\sqrt{1-p_\sigma^2}}\left|E_u^{(2)}\right\rangle\right), \tag{40}$$

$$\varphi_-^{(M_S)} = \frac{1}{\sqrt{2}}\left(\sqrt{1+\sqrt{1-p_\sigma^2}}\left|E_u^{(1)}\right\rangle - i\,M_S\sqrt{1-\sqrt{1-p_\sigma^2}}\left|E_u^{(2)}\right\rangle\right).$$

In contrast to the above considered $E - b_1 - b_2$-problem, the spin-orbital coupling now results in the non-orthogonality of the wave functions located in the minima:

$$\left\langle \varphi_+^{(M_S)} | \varphi_-^{(M_S)} \right\rangle = -i \; M_S \; p_\sigma \tag{41}$$

that leads to the tunnel splitting.

Varying the energy functional with the basis functions

$$\Psi = a \; \varphi_+^{(M_S)} \chi_+ + b \; \varphi_-^{(M_S)} \chi_-, \tag{42}$$

where $\chi_\pm$ are the vibrational functions centered at $q_\sigma^{(0,\pm)}$, results in a matrix equation:

$$\begin{pmatrix} H_{++} & H_{+-} \\ H_{+-}^* & H_{++} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} 1 & S_{+-} \\ S_{+-}^* & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}, \tag{43}$$

where

$$S = \left\langle \varphi_+^{(M_S)} \chi_+ | \varphi_-^{(M_S)} \chi_- \right\rangle = -i \; M_S \; p_\sigma \; \exp\left[-2\tilde{E}_{JT}^\sigma \left(1 - p_\sigma^2 \right)^{\frac{3}{2}} \right], \tag{44}$$

$$H_{++} = \hbar\omega_\sigma \left[\frac{2 - p_\sigma^2}{4\sqrt{1 - p_\sigma^2}} - \tilde{E}_{JT}^\sigma \left(1 + p_\sigma^2 \right) \right] + \hbar\omega_{\sigma'} \frac{2 - \lambda_\sigma}{4\sqrt{1 - \lambda_\sigma}} \; ,$$

$$H_{+-} = (H_{++} - \hbar\omega_\sigma B) \, S \; , \quad B = \tilde{E}_{JT}^\sigma \left(1 - p_\sigma^2 \right) \left(2 - p_\sigma^2 \right) .$$

The tunnel level energies and tunnel splitting are determined as follows:

$$E_g = H_{++} - \frac{\hbar\omega_\sigma B \, |S|}{1 + |S|} \; , \quad E_u = H_{++} + \frac{\hbar\omega_\sigma B \, |S|}{1 - |S|} \; , \tag{45}$$

$$\Delta_1 = E_g - E_u = 2\hbar\omega_\sigma \frac{B \, |S|}{1 - |S|^2} \; .$$

Appropriate vibronic wave functions can be represented as:

$$\Psi_g^{(1)} = N_g \left(\varphi_+^{(1)} \chi_+ + i\varphi_-^{(1)} \chi_- \right), \quad \Psi_u^{(1)} = N_u \left(i\varphi_+^{(1)} \chi_+ + \varphi_-^{(1)} \chi_- \right), \tag{46}$$

$$\Psi_g^{(-1)} = N_g \left(i\varphi_+^{(-1)} \chi_+ + \varphi_-^{(-1)} \chi_- \right), \; \Psi_u^{(-1)} = N_u \left(\varphi_+^{(-1)} \chi_+ + i\varphi_-^{(-1)} \chi_- \right),$$

where

$$N_g = \frac{1}{\sqrt{2 \left(1 + |S| \right)}}, \quad N_u = \frac{1}{\sqrt{2 \left(1 - |S| \right)}}.$$

In the limit $|p_\sigma| \ll 1$ for the magnitude of tunnel splitting one obtains:

$$\Delta_1 = 2\lambda_1 \exp\left(-2\tilde{E}_{JT}^\sigma \right), \tag{47}$$

that might be interpreted as a result of vibronic reduction for the purely spin-orbital splitting.

V. REDUCTION FACTORS.

A concept of vibronic reduction is widely used in a theory of the Jahn-Teller effect. The reduction factor is equal to a ratio of the reduced matrix element of the electronic operator, which is calculated for vibronic ground states, to this one for the bare electronic states. In a case of the pseudo-Jahn-Teller effect the vibronic reduced matrix element is commonly a linear combination of the electronic ones.

Within the strong coupling scheme the vibronic state is written as

$$\Psi_{\Gamma\gamma} = \frac{1}{N_\Gamma} \sum_{\Gamma_1} c\left(\Gamma\Gamma_1\right) \sum_{\gamma_1\Gamma_2\gamma_2} \varphi_{\Gamma_1\gamma_1} \chi_{\Gamma_2\gamma_2} \left\langle \Gamma_1\gamma_1\Gamma_2\gamma_2 | \Gamma\gamma \right\rangle \; , \tag{48}$$

where $\Gamma_2 \in \Gamma \times \Gamma_1$, N_Γ is the normalization factor; $c(\Gamma\Gamma_1)$ is the amplitude of contribution to the vibronic function Γ, which is generated by the electronic Γ_1 state; $\chi_{\Gamma_2\gamma_2}$ is a symmetric linear combination of the vibrational states of equivalent minima; $\langle\Gamma_1\gamma_1\Gamma_2\gamma_2|\Gamma\gamma\rangle$ is the Clebsh-Gordan coefficient.

Consider the vibronic matrix element of electronic operator $\hat{V}_{\tilde{\Gamma}\tilde{\gamma}}$

$$
\left\langle \Psi_{\Gamma\gamma} \left| \hat{V}_{\tilde{\Gamma}\tilde{\gamma}} \right| \Psi_{\Gamma'\gamma'} \right\rangle = \frac{1}{N_\Gamma N_{\Gamma'}} \sum_{\Gamma_1\Gamma'_1} c(\Gamma\Gamma_1)\, c(\Gamma'\Gamma'_1) \frac{\left\langle \varphi_{\Gamma_1} \left\| \hat{V}_{\tilde{\Gamma}} \right\| \varphi_{\Gamma_1} \right\rangle}{\sqrt{g_{\Gamma_1}}} \times
$$
$$
\sum_{\Gamma_2} \left\langle \chi^2_{\Gamma_2} \right\rangle \sum_{\gamma_1\gamma'_1\gamma_2} \left\langle \Gamma_1\gamma_1|\tilde{\Gamma}\tilde{\gamma}\Gamma'_1\gamma'_1 \right\rangle \langle\Gamma_1\gamma_1\Gamma_2\gamma_2|\Gamma\gamma\rangle \langle\Gamma'_1\gamma'_1\Gamma_2\gamma_2|\Gamma'\gamma'\rangle .
$$

(49)

Here we used the Wigner-Eckart-Koster [41] theorem for the electronic matrix element in a case of the simply reducible group:

$$
\left\langle \Gamma\gamma \left| \tilde{\Gamma}\tilde{\gamma} \right| \Gamma'\gamma' \right\rangle = \frac{\left\langle \Gamma \left\| \tilde{\Gamma} \right\| \Gamma' \right\rangle}{\sqrt{g_\Gamma}} \left\langle \Gamma\gamma|\tilde{\Gamma}\tilde{\gamma}\Gamma'\gamma' \right\rangle ,
$$

(50)

and the orthogonality relation for the vibrational functions:

$$
\left\langle \chi_{\Gamma_2\gamma_2}|\chi_{\Gamma'_2\gamma'_2} \right\rangle = \left\langle \chi^2_{\Gamma_2} \right\rangle \delta_{\Gamma_2\Gamma'_2}\delta_{\gamma_2\gamma'_2} ,
$$

(51)

where $\left\langle \chi^2_{\Gamma_2} \right\rangle$ is the normalization factor. Applying the Wigner-Eckart-Koster theorem for the vibronic matrix element we find for real representations:

$$
\left\langle \Psi_\Gamma \left\| \hat{V}_{\tilde{\Gamma}} \right\| \Psi_{\Gamma'} \right\rangle = \sum_{\Gamma_1\Gamma'_1} K_{\tilde{\Gamma}} \begin{pmatrix} \Gamma & \Gamma' \\ \Gamma_1 & \Gamma'_1 \end{pmatrix} \left\langle \varphi_{\Gamma_1} \left\| \hat{V}_{\tilde{\Gamma}} \right\| \varphi_{\Gamma'_1} \right\rangle ,
$$

(52)

where

$$
K_{\tilde{\Gamma}} \begin{pmatrix} \Gamma & \Gamma' \\ \Gamma_1 & \Gamma'_1 \end{pmatrix} = \frac{\sqrt{g_\Gamma g_{\Gamma'}}}{N_\Gamma N_{\Gamma'}} (-1)^{\Gamma+\tilde{\Gamma}+\Gamma_1} c(\Gamma\Gamma_1)\, c(\Gamma'\Gamma'_1) \times
$$
$$
\sum_{\Gamma_2} (-1)^{\Gamma_2} \left\langle \chi^2_{\Gamma_2} \right\rangle \begin{bmatrix} \Gamma & \tilde{\Gamma} & \Gamma' \\ \Gamma'_1 & \Gamma_2 & \Gamma_1 \end{bmatrix} .
$$

(53)

Here $[]$ is the 6Γ-symbol for point group G [42]. The factor $(-1)^\Gamma$ is 1 for all irreducible represenation of D_{4h} except $(-1)^{A_{2g}} = -1$ [43]. In the usual Jahn-Teller situation Eq. (53) gives the well-known result for the vibronic reduction factors [44]. Note that

$$
K_{\tilde{\Gamma}} \begin{pmatrix} \Gamma & \Gamma' \\ \Gamma_1 & \Gamma'_1 \end{pmatrix} = (-1)^{\Gamma+\Gamma'+\Gamma_1+\Gamma'_1} K_{\tilde{\Gamma}} \begin{pmatrix} \Gamma' & \Gamma \\ \Gamma'_1 & \Gamma_1 \end{pmatrix} .
$$

(54)

In our problem $\Gamma_1, \Gamma'_1 = A_{1g}, E_u$; $\Gamma, \Gamma', \Gamma_2, \Gamma'_2 = A_{1g}, \Sigma, E_u$; only the operators of symmetry $\tilde{\Gamma} = A_{1g}, A_{2g}, B_{1g}, B_{2g}, E_u$ have the non-zero matrix elements. The non-trivial reduction factors are given in Table III; the remaining ones could be derived with help of Eq. (54). The reduction factors as functions of Δ are shown in Fig.8a. One can see that Σ' operators are reduced very strongly. With an increase in the vibronic coupling the reduction factors tend to their limit values (Fig.8b), which can be obtained from Eq. (53) with $N_\Gamma \to 1$, $\left\langle \chi^2_{\Gamma_2} \right\rangle \to 1$.

The components of external electric field parallel to the CuO_4 cluster plane ($\vec{E} \perp C_4$) induce an electro-dipole transitions between tunnel A_{1g} and E_u states. The reduced vibronic matrix element of the E_u operator is written as:

$$
\left\langle \Psi_{A_{1g}} \left\| \hat{V}_{E_u} \right\| \Psi_{E_u} \right\rangle = \frac{c_\sigma d_\sigma}{N_{A_{1g}} N_{E_u}} \left(\left\langle \chi^2_{A_{1g}} \right\rangle + \left\langle \chi^2_{E_u} \right\rangle \right) \left\langle A_{1g} \left\| \hat{V}_{E_u} \right\| E_u \right\rangle .
$$

(55)

Thus, at strong vibronic coupling ($N_\Gamma \to 1$, $\left\langle \chi^2_{\Gamma_2} \right\rangle \to 1$) and at $c_\sigma = d_\sigma = 1/\sqrt{2}$ the matrix element of electro-dipole transition is not renormalized.

For the singlet E_u states an orbital contribution to the Zeeman energy is not zero only for the non-zero values of the z-component of external magnetic field. This situation could be examined with a help of an effective spin Hamiltonian

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for the non-Kramers doublet [45]. The vibronic coupling results in an essential renormalization of reduced matrix element of the z-component of angular momentum:

$$\left\langle \Psi_{E_u} \left\| \hat{V}_{A_{2g}} \right\| \Psi_{E_u} \right\rangle = \frac{\sqrt{2} d_\sigma^2 S_q^n}{N_{E_u}^2} \left\langle E_u \left\| \hat{V}_{A_{2g}} \right\| E_u \right\rangle . \tag{56}$$

In this case the vibronic reduction factor is proportional to overlap integral S_q^n of the vibrational states centered at neighboring minima on the lower AP sheet. With the increasing in the vibronic coupling $S_q^n \to 0$, that leads to a complete quenching of the angular momentum.

VI. SPIN HAMILTONIAN OF THE PJT CENTER.

A detailed pattern of the energy spectrum in external magnetic field and magneto-resonance properties of the PJT centers are substantially depend on the bare $A - E$ splitting Δ, vibronic parameters and relative magnitude of the vibronic and spin-orbital coupling.

However, some common features are determined only by the symmetry considerations, in particular, by the C_4 axial symmetry and specific properties of the bare electronic basis functions. So, the orbital doublet $^{1,3}E_u$ terms are characterized by the nonquenched highly anisotropic (Izing like) effective orbital moment $\tilde{l} = 1/2$ oriented only along the C_4 axis.

Without taking account of vibronic coupling the effective spin Hamiltonian for the $^{1,3}E_u$ terms could be represented as follows:

$$H = \lambda_1 \tilde{l}_z \hat{S}_z + \beta H_z g_l \tilde{l}_z \hat{I} + 2\beta \sum_{i=x,y,z} H_i \hat{S}_i, \tag{57}$$

where β is the Bohr magneton, $\hat{S}_i$ are spin matrices ($S = 0$ for the spin singlet ^1E_u term), g_l is an effective orbital g-factor for the $^{1,3}E_u$ term, which magnitude is determined by the structure of electronic e_u function. Here, the first term describes the spin-orbital coupling, the second and the third ones correspond to the orbital and spin Zeeman coupling, respectively, with the purely isotropic spin g-tensor: $g_x = g_y = g_z = 2$. Taking account of the spin-orbital ^1E_u-^3E_u mixing leads to emergence of the spin anisotropy with additive contribution to the effective spin Hamiltonian:

$$V_{an} = D\hat{S}_z^2 , \quad D = \Delta_{st} - \sqrt{\Delta_{st}^2 + \lambda^2} \approx -\frac{\lambda^2}{2\Delta_{st}} , \tag{58}$$

and to the effective axial anisotropy of the spin g-tensor: $g_z = 2$, $g_x = g_y = 2\cos\theta$, where

$$\cos\theta = \frac{1}{\sqrt{2}} \sqrt{1 + \frac{\Delta_{st}}{\sqrt{\Delta_{st}^2 + \lambda^2}}} \approx 1 - \frac{\lambda^2}{8\Delta_{st}^2} . \tag{59}$$

Taking account of the vibronic coupling upon the conditions of weak pseudo-Jahn-Teller effect ($p_\sigma = \lambda_1/2E_{JT}^\sigma > 1$) does not vary a form of the effective spin Hamiltonian since the vibronic distortions are suppressed by the spin-orbital coupling. With the strong pseudo-Jahn-Teller effect ($p_\sigma = \lambda_1/2E_{JT}^\sigma < 1$) one should make use of the vibronic states (46), that results in a very complicated spin-vibronic effective Hamiltonian. A relatively simple situation occurs at $p_\sigma^2 \ll 1$, and small magnitude of the overlap for the vibrational functions, when, neglecting the spin-orbital ^1E_u-^3E_u mixing, we come to an effective Hamiltonian:

$$H = -\beta H_z g_1 \left\langle \chi_+ | \chi_- \right\rangle \tilde{l}_z \hat{I} + \beta \sum_{i=x,y,z} H_i g_{ij} \hat{S}_j , \tag{60}$$

where the overlap integral $\left\langle \chi_+ | \chi_- \right\rangle$ is determined according to Eq. (44) and for the axial g-tensor: $g_z = 2 - p_\sigma g_1$, $g_x = g_y = 2$. It should be noted the principal difference in the g-factor anisotropy with and without vibronic effects.

The doublet of the states with different ($\pm$) projections of the effective orbital moment corresponds to the functions $\{\Psi_g^{(1)}, \Psi_g^{(0)}, \Psi_u^{(-1)}\}$ and $\{\Psi_u^{(1)}, \Psi_u^{(0)}, \Psi_g^{(-1)}\}$, respectively, where, along with the above defined functions Eq. (46), we have introduced

$$\Psi_g^{(0)} = \frac{1}{\sqrt{2}} \left(\left| E_u^{(2)} \right\rangle \chi_+^{(0)} + i \left| E_u^{(1)} \right\rangle \chi_-^{(0)} \right), \tag{61}$$

$$\Psi_u^{(0)} = \frac{1}{\sqrt{2}} \left(i \left| E_u^{(2)} \right\rangle \chi_+^{(0)} + \left| E_u^{(1)} \right\rangle \chi_-^{(0)} \right).$$

An upper label for the vibrational function underlines the difference in the location of the minima for the $M_S = 0$ and $M_S \neq 0$ spin ^3E_u states on the lower AP sheet. It should be noted also, that, in general, the overlap integral $\langle \chi_+ | \chi_- \rangle$ depends on the z-component of magnetic field due to the orbital Zeeman coupling, which contributes to the energy of the lower sheet of the adiabatic potential. At $\beta H_z \gg \lambda_1$ an expression for the corresponding energy acquires a form:

$$\varepsilon_- = \frac{1}{2} \left(\omega_\alpha^2 Q_\alpha^2 + \omega_\beta^2 Q_\beta^2 \right) - \sqrt{ (V_\alpha Q_\alpha)^2 + (V_\beta Q_\beta)^2 + (\beta H_z g_1)^2 }. \tag{62}$$

VII. CONCLUSIONS

We have presented a detailed analysis of the pseudo-Jahn-Teller effect within a bare electronic $(^1A_{1g}, ^{1,3}E_u)$ manifold for the hole or electron CuO_4 centers in doped cuprates. Above we did not consider a number of problems generated by the occurrence of the PJT centers. Firstly, one should note strong inter-center coupling effects caused by the common oxygen ion and the related effects of the coupling with either tilting or buckling modes. The PJT centers are responsible for the numerous effects of the short-range or long-range cooperative PJT ordering observed for the cuprates: some of them have been considered earlier [27,30]. Note Ref. [27], where some effects of the cooperative PJT ordering are considered within a model that could be readily modified for our scenario. Authors have performed a model calculation of the specific heat, the elastic moduli and the thermal expansion coefficient for the cuprates with cooperative PJT effect accompanied by the strong fluctuations of crystalline fields.

An important problem is associated with an influence of the PJT centers to the local boson kinetics and superconductivity. As a whole, this is an item for separate discussion though some effects of the vibronic reduction and isotope shift were briefly considered earlier [32].

In conclusion, we would like to pick up and shortly list again a number of experimental data which confirm namely an above developed specific scenario of the PJT centers in cuprates:

1. Appearance of the MIR absorption bands for all considered cuprates.
2. The numerous NQR-NMR reveal of the singlet-triplet near-degeneracy within ground state manifold for the hole centers.
3. Observation of the anomalously strong anharmonic low temperature thermal motion of the copper atoms within the copper-oxygen hybrid Q_{e_u} mode displayed by the maximum entropy method.
4. Observation of the ferroelectric anomalies.
5. Unusual copper isotope-shift effect in superconducting cuprates.
6. Observation of the specific phonon anomalies.

Among diverse peculiarities of the singlet-triplet PJT centers it should be especially emphasized a possible appearance of the so-called "tunnel paramagnetic centers" [18] which spin states $S = 1, M_S = \pm 1$ and $S = 1, M_S = 0$, respectively, are localized within different wells of the adiabatic potential. In other words, different spin states correspond to different local distortions of the CuO_4 cluster. Spin dynamics and relaxation for the tunnel paramagnetic centers are cruiciably dependent on the magnitude and orientation of external magnetic field. These centers could be relatively readily transferred to the metastable state. An occurrence of the tunnel paramagnetic centers inside the small droplets of the PJT center phase was considered [18] as an origin of the magnetization and magnetostriction anomalies in cuprate CuO. Perhaps, these are responsible for the unusual magnetic resonance signals observed in cuprate Eu_2CuO_4 [46].

It should be noted that we did not undertake the task of reviewing all the available experimental data confirming the PJT nature of the CuO_4 clusters in doped cuprates and comparing them with our model approach: it is a separate problem. At the same time, it should be noted that the PJT center model is entirely based on the vast amount of the experimental material.

We consider the above results as an essential first step to the elaboration of the comprehensive theory of the PJT lattice in the doped cuprates.

VIII. ACKNOWLEDGMENTS

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TABLE I.
Expressions of the decomposition coefficients for electronic wave function, extremum coordinates of AP surface and quadratic form of AP surface near the extremal points. The following notations are used: $q_i^{(0)} = V_i/\omega_i^2$, $c_\sigma = \sqrt{\frac{a_\sigma}{a_\sigma+b}}$, $d_\sigma = \sqrt{\frac{b}{a_\sigma+b}}$, $q_1 = (q_x+q_y)/\sqrt{2}$, $q_2 = (-q_x+q_y)/\sqrt{2}$. For the NJT extremum $\varepsilon_0^\sigma = -\Delta - E_{JT}^z$; for the JT_σ extrema: $\varepsilon_0^\sigma = -E_{JT}^\sigma$; for the PJT_σ extrema: $\varepsilon_0^\sigma = -E_{JT}^\sigma - \frac{1}{2}c_\sigma^2 a_\sigma$.

Type	N	z	x	y	Q_z^0	Q_α^0	Q_β^0	Q_x^0	Q_y^0	$2\varepsilon(q) - 2\varepsilon_0^\sigma - \sum_i \omega_i^2 q_i^2$
NJT	1	1	0	0	$-q_z^{(0)}$	0	0	0	0	$-\omega_e^2 \eta_z \left(q_x^2 + q_y^2\right)$
JT_α	1	0	0	1	0	$q_\alpha^{(0)}$	0	0	0	$-\omega_e^2 \kappa_\alpha q_y^2 - \omega_\beta^2 \lambda_\alpha q_\beta^2$
	2	0	1	0	0	$-q_\alpha^{(0)}$	0	0	0	$-\omega_e^2 \kappa_\alpha q_x^2 - \omega_\beta^2 \lambda_\alpha q_\beta^2$
JT_β	1	0	$\frac{-1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0	0	$q_\beta^{(0)}$	0	0	$-\omega_e^2 \kappa_\beta q_2^2 - \omega_\alpha^2 \lambda_\beta q_\alpha^2$
	2	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0	0	$-q_\beta^{(0)}$	0	0	$-\omega_e^2 \kappa_\beta q_1^2 - \omega_\alpha^2 \lambda_\beta q_\alpha^2$
PJT_α	1	c_α	0	d_α	$-q_z^{(0)}c_\alpha^2$	$q_\alpha^{(0)}d_\alpha^2$	0	0	$-q_e^{(0)}2c_\alpha d_\alpha$	$-\left(\omega_e \upsilon_\alpha q_x + \omega_\beta \rho_\alpha q_\beta\right)^2 -$ $-\left(\omega_z \tau_\alpha q_z + \omega_\alpha \mu_\alpha q_\alpha - \omega_e \nu_\alpha q_y\right)^2$
	2	c_α	d_α	0	$-q_z^{(0)}c_\alpha^2$	$-q_\alpha^{(0)}d_\alpha^2$	0	$-q_e^{(0)}2c_\alpha d_\alpha$	0	$-\left(\omega_e \upsilon_\alpha q_y + \omega_\beta \rho_\alpha q_\beta\right)^2 -$ $-\left(\omega_z \tau_\alpha q_z - \omega_\alpha \mu_\alpha q_\alpha - \omega_e \nu_\alpha q_x\right)^2$
	3	c_α	0	$-d_\alpha$	$-q_z^{(0)}c_\alpha^2$	$q_\alpha^{(0)}d_\alpha^2$	0	0	$q_e^{(0)}2c_\alpha d_\alpha$	$-\left(\omega_e \upsilon_\alpha q_x - \omega_\beta \rho_\alpha q_\beta\right)^2 -$ $-\left(\omega_z \tau_\alpha q_z + \omega_\alpha \mu_\alpha q_\alpha + \omega_e \nu_\alpha q_y\right)^2$
	4	c_α	$-d_\alpha$	0	$-q_z^{(0)}c_\alpha^2$	$-q_\alpha^{(0)}d_\alpha^2$	0	$q_e^{(0)}2c_\alpha d_\alpha$	0	$-\left(\omega_e \upsilon_\alpha q_y - \omega_\beta \rho_\alpha q_\beta\right)^2 -$ $-\left(\omega_z \tau_\alpha q_z - \omega_\alpha \mu_\alpha q_\alpha + \omega_e \nu_\alpha q_x\right)^2$
PJT_β	1	c_β	$\frac{-d_\beta}{\sqrt{2}}$	$\frac{d_\beta}{\sqrt{2}}$	$-q_z^{(0)}c_\beta^2$	0	$q_\alpha^{(0)}d_\beta^2$	$q_e^{(0)}\sqrt{2}c_\beta d_\beta$	$-q_e^{(0)}\sqrt{2}c_\beta d_\beta$	$-\left(\omega_e \upsilon_\beta q_1 - \omega_\alpha \rho_\beta q_\alpha\right)^2 -$ $-\left(\omega_z \tau_\beta q_z + \omega_\beta \mu_\beta q_\beta - \omega_e \nu_\beta q_2\right)^2$
	2	c_β	$\frac{d_\beta}{\sqrt{2}}$	$\frac{d_\beta}{\sqrt{2}}$	$-q_z^{(0)}c_\beta^2$	0	$-q_\alpha^{(0)}d_\beta^2$	$-q_e^{(0)}\sqrt{2}c_\beta d_\beta$	$-q_e^{(0)}\sqrt{2}c_\beta d_\beta$	$-\left(\omega_e \upsilon_\beta q_2 - \omega_\alpha \rho_\beta q_\alpha\right)^2 -$ $-\left(\omega_z \tau_\beta q_z - \omega_\beta \mu_\beta q_\beta - \omega_e \nu_\beta q_1\right)^2$
	3	c_β	$\frac{d_\beta}{\sqrt{2}}$	$\frac{-d_\beta}{\sqrt{2}}$	$-q_z^{(0)}c_\beta^2$	0	$q_\alpha^{(0)}d_\beta^2$	$-q_e^{(0)}\sqrt{2}c_\beta d_\beta$	$q_e^{(0)}\sqrt{2}c_\beta d_\beta$	$-\left(\omega_e \upsilon_\beta q_1 + \omega_\alpha \rho_\beta q_\alpha\right)^2 -$ $-\left(\omega_z \tau_\beta q_z + \omega_\beta \mu_\beta q_\beta + \omega_e \nu_\beta q_2\right)^2$
	4	c_β	$\frac{-d_\beta}{\sqrt{2}}$	$\frac{-d_\beta}{\sqrt{2}}$	$-q_z^{(0)}c_\beta^2$	0	$-q_\alpha^{(0)}d_\beta^2$	$q_e^{(0)}\sqrt{2}c_\beta d_\beta$	$q_e^{(0)}\sqrt{2}c_\beta d_\beta$	$-\left(\omega_e \upsilon_\beta q_2 + \omega_\alpha \rho_\beta q_\alpha\right)^2 -$ $-\left(\omega_z \tau_\beta q_z - \omega_\beta \mu_\beta q_\beta + \omega_e \nu_\beta q_1\right)^2$

TABLE II.
The overlap and tunnel Hamiltonian matrix elements. The following notations are used: $\sigma_0 = q_\sigma^{(0)} d_\sigma^2$, $\sigma_0' = q_{\sigma'}^{(0)} d_\sigma^2$,

$\gamma_0 = q_e^{(0)} 2 c_\sigma d_\sigma$,

$q_1 = \gamma_0 \cos\psi - \sigma_0 \sin\psi$, $q_2 = \gamma_0 \sin\psi + \sigma_0 \cos\psi$,

$\Omega_1 = \omega_+ \cos^2\varphi + \omega_- \sin^2\varphi$, $\Omega_1' = \omega_+' \cos^2\psi + \omega_-' \sin^2\psi$,

$\Omega_2 = \omega_+ \sin^2\varphi + \omega_- \cos^2\varphi$, $\Omega_2' = \omega_+' \sin^2\psi + \omega_-' \cos^2\psi$,

$\Omega_3 = (-\omega_+ + \omega_-) \sin\varphi\cos\varphi$, $\Omega_3' = (-\omega_+' + \omega_-') \sin\psi\cos\psi$,

$\cos\varphi = \frac{1}{\sqrt{2}}\sqrt{1 + \frac{A-B}{\sqrt{(A-B)^2 + 4C^2}}}$, $\sin\varphi = \frac{1}{\sqrt{2}}\sqrt{1 - \frac{A-B}{\sqrt{(A-B)^2 + 4C^2}}}$,

$\cos\psi = \frac{1}{\sqrt{2}}\sqrt{1 + \frac{D-E}{\sqrt{(D-E)^2 + 4F^2}}}$, $\sin\psi = \frac{1}{\sqrt{2}}\sqrt{1 - \frac{D-E}{\sqrt{(D-E)^2 + 4F^2}}}$.

a) $H = V_{el} + T_Q + U_Q + V_{vib}$	
V_{el}	$c_\sigma^2 \Delta$
T_Q	$\frac{1}{4}(\omega_+ + \omega_- + \omega_+' + \omega_-')$
U_Q	$\frac{1}{4}\left(\frac{\Omega_2}{\omega_+\omega_-} + \frac{\Omega_2'}{\omega_+'\omega_-'}\right) + \frac{\omega_\sigma^2 \Omega_1'}{4\omega_+'\omega_-'} + \frac{\omega_{\sigma'}^2 \Omega_1}{4\omega_+\omega_-} + \frac{\omega_e^2}{2}\gamma_0^2 + \frac{\omega_\sigma^2}{2}\sigma_0^2$
V_{vib}	$-\omega_e^2\gamma_0^2 - \omega_\sigma^2\sigma_0^2$
b) $S_q = S_q^{el} S_q^n$ and $H_q = V_{el}^q + T_Q^q + U_Q^q + V_{vib}^q$	
S_q^{el}	c_σ^2
S_q^n	$2\left[\frac{\omega_+\omega_-\omega_+'\omega_-'}{(\omega_+\omega_- + \Omega_2\Omega_1')(\omega_+'\omega_-' + \Omega_1\Omega_2')}\right]^{1/2} \exp\left\{-\frac{\omega_+\omega_-(\omega_+'q_1^2 + \omega_-'q_2^2) + \omega_+'\omega_-'\Omega_2\sigma_0^2}{\omega_+\omega_- + \Omega_2\Omega_1'}\right\}$
V_{el}^q	$c_\sigma^2 \Delta S_q^n$
T_Q^q	$S_q\left[\frac{1}{2}(\omega_+ + \omega_- + \omega_+' + \omega_-') - \frac{\Omega_2^2(A+D) + \Omega_3^2 B + 2\Omega_2\Omega_3 C}{2(\omega_+\omega_- + \Omega_2\Omega_1')^2}(\gamma_0\Omega_2' + \sigma_0\Omega_3')^2 - \right.$ $\left. -\frac{1}{4}\left(\frac{(\Omega_1 + \Omega_1')B + \Omega_2(A+B) + 2\Omega_3 C}{\omega_+\omega_- + \Omega_2\Omega_1'} + \frac{(\Omega_1 + \Omega_1')E + \Omega_2'(A+B) + 2\Omega_3'F}{\omega_+'\omega_-' + \Omega_1\Omega_2'}\right) - \frac{\Omega_2(\gamma_0\Omega_2' + \sigma_0\Omega_3')(\sigma_0 F - \gamma_0 D)}{\omega_+\omega_- + \Omega_2\Omega_1'} - \frac{D}{2}\gamma_0^2 - \frac{E}{2}\sigma_0^2 + F\sigma_0\gamma_0\right]$
U_Q^q	$S_q\left[\frac{1}{4}\left(\frac{2\omega_e^2\Omega_2 + \omega_\beta^2(\Omega_1 + \Omega_1')}{\omega_+\omega_- + \Omega_2\Omega_1'} + \frac{2\omega_e^2\Omega_2' + \omega_\sigma^2(\Omega_1 + \Omega_1')}{\omega_+'\omega_-' + \Omega_1\Omega_2'}\right) + \frac{2\omega_e^2\Omega_2^2 + \omega_{\sigma'}^2\Omega_3^2}{2(\omega_+\omega_- + \Omega_2\Omega_1')^2}(\gamma_0\Omega_2' + \sigma_0\Omega_3')^2\right]$
V_{vib}^q	$S_q^n\left[-\omega_e^2\Omega_2\gamma_0 + \omega_{\sigma'}^2\Omega_3\sigma_0'\right]\frac{\gamma_0\Omega_2' + \sigma_0\Omega_3'}{\omega_+\omega_- + \Omega_2\Omega_1'}$
c) $S_d = S_d^{el} S_d^n$ and $H_d = V_{el}^d + T_Q^d + U_Q^d + V_{vib}^d$	
S_d^{el}	$c_\sigma^2 - d_\sigma^2$
S_d^n	$\left[\frac{\omega_+\omega_-\omega_+'\omega_-'}{\Omega_1\Omega_2\Omega_1'\Omega_2'}\right]^{1/2}\exp\left\{-\frac{\omega_+'\omega_-'}{\Omega_2'}\gamma_0^2\right\}$
V_{el}^d	$c_\sigma^2 \Delta S_d^n$
T_Q^d	$S_d^n\left[\frac{1}{2}(\omega_+ + \omega_- + \omega_+' + \omega_-') - \frac{1}{4}\left(\frac{A}{\Omega_1} + \frac{B}{\Omega_2} + \frac{D}{\Omega_1'} + \frac{E}{\Omega_2'}\right) - \frac{\omega_+'^2\omega_-'^2}{2\Omega_2'^2}\gamma_0^2\right]$
U_Q^d	$S_d\left[\frac{1}{4}\left(\frac{\omega_e^2}{\Omega_1} + \frac{\omega_e^2}{\Omega_1'} + \frac{\omega_\sigma^2}{\Omega_2'} + \frac{\omega_{\sigma'}^2}{\Omega_2}\right) + \frac{\omega_\sigma^2}{2}\sigma_0^2\right]$
V_{vib}^d	$S_d^n\omega_\sigma^2\sigma_0\left(\sigma_0 + \frac{\Omega_3'}{\Omega_2'}\gamma_0\right)$

TABLE III. The reduction factors: the $\tilde{\Gamma}$; Γ, Γ'; Γ_1, Γ'_1 label the transformation properties of the electronic operator (with $\Sigma = \alpha$ at $\Sigma' = \beta$, and $\Sigma = \beta$ at $\Sigma' = \alpha$), the vibronic wave function and the electronic wave function, respectively. Additional notations: $\langle\chi_{a_{1g}}^2\rangle = 1 + 2S_q^n + S_d^n$, $\langle\chi_\sigma^2\rangle = 1 - 2S_q^n + S_d^n$, $\langle\chi_{e_u}^2\rangle = 1 - S_d^n$.

$\tilde{\Gamma}$	Γ	Γ'	Γ_1	Γ'_1	$K_{\tilde{\Gamma}}\begin{pmatrix}\Gamma & \Gamma' \\ \Gamma_1 & \Gamma'_1\end{pmatrix}$
A_{1g}	A_{1g}	A_{1g}	A_{1g}	A_{1g}	$N_{A_{1g}}^{-2}\, c_\sigma^2\, \langle\chi_{a_{1g}}^2\rangle$
	A_{1g}	A_{1g}	E_u	E_u	$2^{-1/2}\, N_{A_{1g}}^{-2}\, d_\sigma^2\, \langle\chi_{e_u}^2\rangle$
	E_u	E_u	A_{1g}	A_{1g}	$2^{1/2}\, N_{E_u}^{-2}\, c_\sigma^2\, \langle\chi_{e_u}^2\rangle$
	E_u	E_u	E_u	E_u	$2^{-1}\, N_{E_u}^{-2}\, d_\sigma^2\, \{\langle\chi_{a_{1g}}^2\rangle + \langle\chi_{e_u}^2\rangle\}$
	Σ	Σ	A_{1g}	A_{1g}	$N_{\Sigma}^{-2}\, c_\sigma^2\, \langle\chi_\sigma^2\rangle$
	Σ	Σ	E_u	E_u	$2^{-1/2}\, N_{\Sigma}^{-2}\, d_\sigma^2\, \langle\chi_{e_u}^2\rangle$
Σ	E_u	E_u	E_u	E_u	$2^{-1}\, N_{E_u}^{-2}\, d_\sigma^2\, \{\langle\chi_{a_{1g}}^2\rangle + \langle\chi_{e_u}^2\rangle\}$
	A_{1g}	Σ	E_u	E_u	$-2^{-1/2}\, N_{A_{1g}}^{-1}\, N_{\Sigma}^{-1}\, d_\sigma^2\, \langle\chi_{e_u}^2\rangle$
Σ'	E_u	E_u	E_u	E_u	$2^{-1}\, N_{E_u}^{-2}\, d_\sigma^2\, \{\langle\chi_{a_{1g}}^2\rangle - \langle\chi_{e_u}^2\rangle\}$
A_{2g}	E_u	E_u	E_u	E_u	$2^{-1}\, N_{E_u}^{-2}\, d_\sigma^2\, \{\langle\chi_{a_{1g}}^2\rangle - \langle\chi_{e_u}^2\rangle\}$
E_u	A_{1g}	E_u	A_{1g}	E_u	$2^{-1/2}\, N_{A_{1g}}^{-1}\, N_{B_{1g}}^{-1}\, c_\sigma\, d_\sigma\, \langle\chi_{a_{1g}}^2\rangle$
	A_{1g}	E_u	E_u	A_{1g}	$2^{-1/2}\, N_{A_{1g}}^{-1}\, N_{B_{1g}}^{-1}\, c_\sigma\, d_\sigma\, \langle\chi_{e_u}^2\rangle$
	Σ	E_u	A_{1g}	E_u	$-2^{-1/2}\, N_{\Sigma}^{-1}\, N_{E_u}^{-1}\, c_\sigma\, d_\sigma\, \langle\chi_\sigma^2\rangle$
	Σ	E_u	E_u	E_u	$-2^{-1/2}\, N_{\Sigma}^{-1}\, N_{E_u}^{-1}\, c_\sigma\, d_\sigma\, \langle\chi_{e_u}^2\rangle$

Figure captions

FIG. 1. Correlation effects in the energy spectrum of the basic CuO_4^{6-} cluster and the hole CuO_4^{5-} center with numerical values (in eV) typical for oxides like CuO. On the right hand side we show a formation of the fundamental absorption spectra for the parent and hole doped oxides with peculiar MIR band in the latter case.The lower panel is an illustration of the bare (a) CuO_4^{5-} center energy spectrum modification with taking into account the strong pseudo-Jahn-Teller-effect (b) and the tunnel splitting of the ground vibronic states (c). Distortions of the CuO_4 cluster assotiated with the different AP minima are shown schematically in the insert.

FIG. 2. Possible distortions of the CuO_4 cluster in the a) JT_α minimum; b) JT_β minimum; c) PJT_α minimum (the dipole moment is oriented along the CuO_4 cluster diagonal); b) PJT_β minimum (the rotation angle value for the dipole moment with respect to that in PJT_α minima is $\phi = \pi/4$).

FIG. 3. The allocation of the PJT_σ minima in a space of symmetric coordinates Q_σ, Q_1, Q_2 (σ is the "strong" rhombic mode). If $\sigma = \alpha$, then $Q_1 = Q_x$, $Q_2 = Q_y$; if $\sigma = \beta$, then $Q_1 = \frac{Q_x + Q_y}{2}$, $Q_2 = \frac{-Q_x + Q_y}{2}$.

FIG. 4. The diagram of the lower AP sheet states in the $(\Delta, E_{JT}^\sigma, E_{JT}^e)$ space at certain fixed $E_{JT}^z = E_{JT}^{z,0}$ value. The planes $a_\sigma = 0$ and $b = 0$ divide the $(\Delta, E_{JT}^\sigma, E_{JT}^e)$ space into four parts corresponding to NJT-, JT_σ-, PJT_σ- or NJT+JT_σ-type of the lower AP sheet minima. In the NJT+JT_σ region the plane is shown, where the NJT- and JT_σ minimum energies are equal.

FIG. 5. a) The diagram of states of the lower AP sheet on the (Δ, E_{JT}^σ) plane at certain fixed E_{JT}^z and E_{JT}^e value. The boundaries $a_\sigma = 0$ and $b = 0$ of the regions with different type of the lower AP sheet minima are shown. The lines $E_{JT}^\sigma = E_{JT}^{\sigma,1}$ and $E_{JT}^\sigma = E_{JT}^{\sigma,2}$ correspond to the two different relative intensities of the vibronic coupling via σ mode and e_u mode. b) The diagram of states of the upper AP sheets on the (Δ, E_{JT}^σ) plane at certain fixed E_{JT}^z and E_{JT}^e value. In the region to the left of the $\Delta = -2E_{JT}^z$ line there is NJT minimum on the upper AP sheet and only the trivial non-analytical minimum on the middle AP sheet. In the region to the right of the $\Delta = 2E_{JT}^\sigma$ line there is JT_σ minima on the middle AP sheet and the trivial non-analytical minimum on the upper AP sheet. At $E_{JT}^z < 2E_{JT}^e$ the regions of parameters exist, where the PJT_σ minima on the lower AP sheet coexist with the NJT minimum on the upper sheet or with the JT_σ minima on the middle sheet. Between the $\Delta = -2E_{JT}^z$ and $\Delta = 2E_{JT}^\sigma$ lines only the trivial non-analytical minima on the upper sheets exist.

FIG. 6. The Δ dependencies of a) the lower tunnel energy levels and b) the corresponding tunnel splittings at $k_e = 3$, $k_\sigma/k_e = 0.5$, $k_{\sigma'}/k_\sigma = 0.5$, $k_z = 0$ where $k_i^2 = 2E_{JT}^i/\hbar\omega_i$. A significant increasing of the Σ level energy at the Δ interval border is connected with non-applicability of the chosen basis for a description of the exited vibronic states in the situation of shallow minima.

FIG. 7. The possible CuO_4 cluster distortions in the equipotential continuum of minima as function of φ angle (see text). The n points correspond to the ion allocations at $\varphi = n\pi/2$. The a) and b) panels differ by the initial mutual orientation of the b_{1g} and b_{2g} distortions. The top and bottom fragments on each panel correspond to different initial mutual orientation of the (b_{1g}, b_{2g}) and e_u distortions. The possible trajectories of the oxygen ions for the different values of $\left| 2\frac{q_e^{(0)}}{q_\sigma^{(0)}} \left(\frac{a_\sigma}{b}\right)^{(1/2)} \right|$ are shown. The radius of the copper ion trajectory is proportional to $q_e^{(0)}$. The equivalent CuO_4 cluster distortions with opposite phase of the copper ion ($n_{Cu} \to n_{Cu} + 4$) are also possible.

FIG. 8. The reduction factor dependencies a) as a function of Δ at $k_e = 3$, $k_\sigma/k_e = 0.5$, $k_{\sigma'}/k_\sigma = 0.5$, $k_z = 0$ ($k_i^2 = 2E_{JT}^i/\hbar\omega_i$); b) as a function of dimensionless coupling constant k at $k_e = k$, $k_\sigma/k_e = 0.5$, $k_{\sigma'}/k_\sigma = 0.5$, $k_z = 0$.