

Photo-induced phase separation effect in cuprates

A S Moskvin

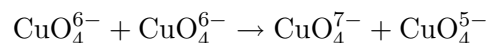
Ural State University, Ekaterinburg, 620083, Russia

E-mail: alexandr.moskvin@usu.ru

Abstract. Parent insulating cuprates appear to be unstable with regard to a self-trapping of the low-energy one- and two-center CT excitons with a nucleation of electron-hole (EH) droplets being actually the system of coupled electron CuO_4^{7-} and hole CuO_4^{5-} centers having been glued in lattice due to strong electron-lattice polarization effects. Such a system can be regarded as an EH Bose liquid described by the generalized Bose-Hubbard Hamiltonian. The scenario can readily explain photo-induced effects in underdoped cuprates. Indeed, illumination of a material with light leads to the generation of EH pairs that will proliferate and grow up to be a novel nonequilibrium EH droplet or simply to be trapped in either EH droplet with the rise in its volume fraction. During the illumination of underdoped cuprate near the insulator-metal transition, the material may even become superconducting.

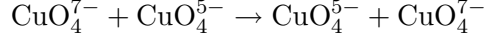
1. Introduction: Charge transfer excitons in insulating cuprates

Parent insulating cuprates such as CuO , La_2CuO_4 , $\text{YBa}_2\text{Cu}_3\text{O}_6$ are believed to be near excitonic instability when the self-trapped CT excitons form the candidate relaxed excited states to struggle with the conventional ground state [1]. Zhang and Ng [2] have proposed a model of charge transfer exciton to explain the EELS spectra in insulating 2D cuprate $\text{Sr}_2\text{CuO}_2\text{Cl}_2$. The Zhang-Ng (ZN)-exciton is associated with the charge transfer of the $b_{1g} \propto d_{x^2-y^2}$ hole from one CuO_4 plaquette to the neighboring one with the formation there of Zhang-Rice (ZR) singlet. Later on, [3] the ZN-model was modified in two directions. First, it was emphasized that the oxygen-copper CT process generates one- and two-center CT excitons depending on whether the electron-hole pair is localized on one or two neighboring CuO_4 plaquettes, respectively. Second, the extended model incorporated the complete set of Cu $3d$ and O $2p$ orbitals. As a result, Moskvin *et. al.* [3] could predict the energy positions of a large number of CT excitons and make the reasonable assignment of main features in the EELS spectra of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ for a rather wide (2 – 13 eV) spectral range. The respective one-center excitons may be represented rather simply as a hole rotating on the four nearest oxygens around an electron predominantly localized in the Cu $3d_{x^2-y^2}$ state with a minimal electron-hole separation $R_{eh} \approx R_{CuO} \approx 2 \text{ \AA}$. It is worth noting that namely these excitons are usually associated with p-d CT transitions. The two-center transitions between two CuO_4 plaquettes may be considered as quanta of the disproportionation reaction



with the creation of electron CuO_4^{7-} and hole CuO_4^{5-} centers. The former correspond to completely filled Cu $3d$ and O $2p$ shells, or the vacuum state for holes, while the latter may be found in different two-hole states. Naturally, for $A - B$ molecular cluster system like Cu_2O_7

with D_{2h} point symmetry one has two symmetry types of two-center excitations: $\Psi_{ES}^{eh} = \Phi_A^0 \Phi_B^2$, and $\Psi_{ES}^{he} = \Phi_A^2 \Phi_B^0$, respectively, differing only by the permutation of electron and hole. Most interestingly that these two will interact due to a something like resonance reaction $eh \rightarrow he$, or in other words



with an effective resonance two-particle transfer integral T_{AB} . This interaction leads to the splitting of two bare excitation states to two superposition states

$$\Psi_{ES}^{\pm} = \frac{1}{\sqrt{2}} [\Psi_{ES}^{eh} \pm \Psi_{ES}^{he}]$$

with energy $E_0 \pm |T_{AB}|$, respectively, which symmetry depends on that of the electron and hole states in exciton. For the σ -bond governed two-center CT transitions the Ψ_{ES}^+ , Ψ_{ES}^- states possess A_g , B_{1u} (S , $P_\sigma = \text{even}$, $\text{odd} = g, u$) symmetry for $b_{1g} \rightarrow b_{1g}, a_{1g}$ transfer, or B_{1u} , A_g (P_σ , $S = \text{odd}$, $\text{even} = u, g$) symmetry for $b_{1g} \rightarrow e_u(\sigma)$ transfer, respectively. It is worth noting that S, P excitons are centered at the geometrical center of the Cu_2O_7 molecular cluster, in other words, on the central oxygen ion, and its symmetry coincides with that of O 2s and O 2p σ orbitals. The magnitude of the effective resonance two-particle transfer integral T_{AB} which determines the even-odd splitting is of particular interest in exciton theory. In the real cuprate situation the bare two-center exciton represents a system of two neighboring electron CuO_4^{7-} and hole CuO_4^{5-} centers (given common oxygen). Thus, the resonance reaction corresponds to the inter-center transfer of *two holes*, or *two electrons*. The T_{AB} integral measures the internal kinetic energy of two-center exciton, and relates to the two-particle (local boson!) transfer integral which is likely to be one of the main parameters governing the unusual superconducting properties of cuprates. Contrary to P exciton the S exciton is dipole-forbidden and corresponds to a so-called two-photon state. However, these two excitons have a very strong dipole coupling with the large value of $S - P$ transition dipole matrix element:

$$d = |\langle S | \hat{\mathbf{d}} | P \rangle| \approx 2eR_{\text{CuCu}} \approx 2e \times 4\text{\AA}. \quad (1)$$

This points to a very important role played by this doublet in nonlinear optics, in particular in two-photon absorption and third-harmonic generation effects. The nonlinear optical measurements in Sr_2CuO_3 provide very significant information about the numerical value of SP separation, or transfer integral: $T_{AB} \approx 0.1$ eV. The lowest energy has the two-center CT exciton with the hole center forming famous ZR singlet. It should be noted that two-center CT excitons are often associated with inter-center d-d transitions. A unique opportunity to distinctly separate both types of CT excitons is realized in 1D insulating cuprate Sr_2CuO_3 with the chains of corner shared CuO_4 plaquettes where we can make use of different polarization properties of these excitons. High-resolution angle-resolved EELS measurements in Sr_2CuO_3 for transversal polarization with momentum oriented in the plane of CuO_4 plaquette but perpendicular to chain direction allowed to exclude the two-center CT excitons and observe only the localized dipole-allowed CT transitions to nonbonding O 2p π and O 2p σ orbitals with energy ≈ 2.0 eV and ≈ 5.5 eV, respectively. Comparative analysis of EELS spectra for longitudinal and transversal [4] polarizations with momentum oriented in the plane of CuO_4 plaquette allowed to elucidate the unconventional two-peak structure of the CT gap which is determined by a superposition of nearly degenerate one-center localized excitation and two-center CT excitons. The two-center nature of the most intensive low-lying CT exciton peaked at 2.6 eV is fairly well confirmed in the studies of nonlinear optical effects in Sr_2CuO_3 . Indeed, its effective size was estimated to be $\approx 4\text{\AA}$ in a remarkable accordance with Exp.(1). At first sight, these findings are restricted by the only 1D cuprate. However, a close examination shows the two-component structure of the CT gap appears to be a commonplace for all parent cuprates that means the insulating

cuprates are neither Mott insulators, nor CT insulators, if one applies the familiar classification by Zaanen, Sawatzky and Allen.

2. Electron-lattice polarization and self-trapping of CT excitons in cuprates

As it is mentioned above, the minimal energy cost of the optically excited disproportionation or electron-hole formation in insulating cuprates is 2.0 – 2.5 eV. However, the question arises, what is the energy cost for the thermal excitation of such a local disproportionation? What conditions are needed for two-center CT exciton to be self-trapped, and what is its energy? The answer implies first of all the knowledge of relaxation energy, or the energy gain due to the lattice polarization by the localized charges. The full polarization energy R includes the cumulative effect of *electronic* and *ionic* terms, associated with the displacement of electron shells and ionic cores, respectively. The former term R_{opt} is due to the non-retarded effect of the electronic polarization by the momentarily localized hole given the ionic cores fixed at their perfect crystal positions. Such a situation is typical for lattice response accompanying the Franck-Condon transitions (optical excitation, photoionization). On the other hand, all the long-lived excitations, i.e., all the intrinsic thermally activated states and the extrinsic particles produced as a result of doping, injection or optical pumping should be regarded as stationary states of a system with a deformed lattice structure. These relaxed states should be determined from the condition that the system energy has a local minimum when account is taken of the interaction of the electrons (holes) with the lattice deformations. At least, it means that we cannot, strictly speaking, make use of the same energy parameters to describe the optical (e.g. photoexcited) hole and thermal (e.g. doped) hole. For the illustration of polarization effects in cuprates we apply the shell model calculations to look specifically at energies associated with the localized holes of Cu^{3+} and O^- in "parent" La_2CuO_4 compound. It follows from these calculations that there is a large difference in the lattice relaxation energies for O^- and Cu^{3+} holes. The lattice relaxation energy, $-\Delta R_{th}^\alpha$, caused by the hole localization at the O-site (4.44 eV) appears to be significantly larger than that for the hole localized at the Cu-site (2.20 eV). This indicates the strong electron-lattice interaction in the case of the hole localized at the O-site and could suggest that the hole trapping is more preferential in the oxygen sublattice. In both cases we deal with the several eV-effect both for *electronic* and *ionic* contributions to relaxation energy.

2.1. Charge transfer instability and CT exciton self-trapping in cuprates

2.1.1. CT exciton self-trapping: a pseudo-Jahn-Teller model. To illustrate the principal features of CT exciton self-trapping effect we address a simplified two-level model of a single Cu_2O_7 cluster in which a ground state and a CT state are associated with a pseudospin 1/2 doublet, $|\uparrow\rangle$ and $|\downarrow\rangle$, respectively. In addition, we introduce some configurational coordinate Q associated with a deformation of Cu_2O_7 cluster, or respective anionic background. As a starting point of the model we introduce the effective electron-configurational Hamiltonian typical for (pseudo)Jahn-Teller systems and for systems with photo-induced phase transitions [5]

$$H_s = -\Delta\hat{s}_z - t\hat{s}_x - pQ + \frac{K}{2}Q^2 - aQ\hat{s}_z, \quad (2)$$

where s_z , s_x are Pauli matrices, and the first term describes the bare energy splitting of *up* and *down* states with energy gap Δ (CT energy), while the second term describes the coupling (mixing) between these pseudospin states. In terms of a pseudospin analogy the both parameters may be associated with effective fields. The third and fourth terms in (2) describe the linear and quadratic contributions to the configurational energy. Here, the linear term formally corresponds to the energy of an external configurational strain described by an effective strain parameter p , while quadratic term with effective elastic constant K is associated with a conventional harmonic

approximation for configurational energy. The last term describes the electron-configurational (vibronic) interaction with a being a electron-configurational coupling constant. Hereafter we make use of dimensionless configurational variable Q therefore all of the model parameters are assigned the energy units. The corresponding eigenvalues

$$E_{\pm}(Q) = \frac{K}{2}Q^2 - pQ \pm \frac{1}{2} [(\Delta + aQ)^2 + t^2]^{1/2} \quad (3)$$

define the upper and lower branches of the adiabatic potential (AP), respectively. These potential curves describe the energy of $|\pm\rangle$ states as functions of configurational coordinate Q . The impact of different model parameters on the shape of AP can be easily understood, if we

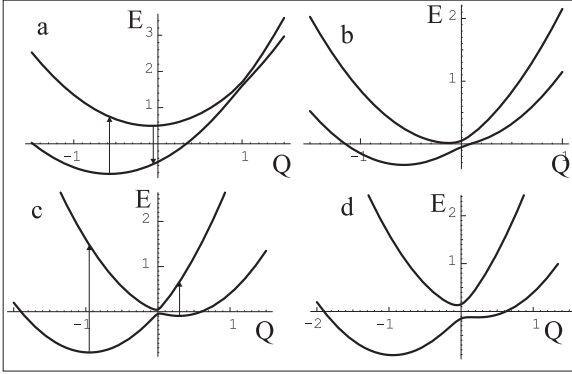


Figure 1. Typical adiabatic potentials of CT center: a) $\Delta = 1.0; t = 0.1; p = -0.65; a = 1.0; K = 2.0$; b) $\Delta = 0.0; t = 0.1; p = -0.65; a = 1.0; K = 2.0$; c) $\Delta = 0.0; t = 0.1; p = -0.65; a = 2.5; K = 2.0$; d) $\Delta = 0.0; t = 0.3; p = -0.65; a = 2.5; K = 2.0$. Arrows mark CT transitions (see text for details).

neglect transfer integral ($t = 0$) and deal with two ideal parabolas describing the configurational energy for *up* and *down* states $|\uparrow, \downarrow\rangle$, respectively. These identical parabolas with minima at $Q_{\pm}^{(0)} = (p \mp a/2)/K$ are shifted relative to each other. The shift in configurational coordinate is $\Delta Q = Q_{+}^{(0)} - Q_{-}^{(0)} = a/2K$, while the shift in energy is $\Delta E^{(0)} = E_{+}^{(0)} - E_{-}^{(0)} = pa/K + \Delta$, where $E_{\pm}^{(0)} = E_{\pm}(Q_{\pm}^{(0)})$ or the energy of the bottoms of respective parabolas. Interestingly, the energy shift is determined both by *mechanic* and *electronic* forces. It is worth noting that the Q -shift of the center of gravity of AP is determined by the effective strain p . The electron-configurational coupling leads to a pulling apart the parabolas for *up* and *down* electronic states. The condition $|\Delta E^{(0)}| = |pa/K + \Delta| = a^2/2K$ defines two specific points, where the minimum of one of the branches crosses another branch, thus specifying the parameters range admissible of a *bistability* effect. If $E_{+}^{(0)} > E_{-}(Q_{+}^{(0)})$ we arrive at rather conventional situation which is typical for long-lived CT states capable of decaying due to spontaneous Franck-Condon radiative transitions. In opposite case $E_{+}^{(0)} < E_{-}(Q_{+}^{(0)})$ we deal with only radiativeless relaxation channels, and the situation strongly depends on the magnitude of transfer integral $t \neq 0$ which leads to a crucial rearrangement of AP near the crossection point of two branches with a number of novel effects of principal importance. First, we obtain two isolated branches of AP, the upper and lower ones, respectively, with quantum superpositions Ψ_{\pm} which describe unconventional states with a mixed valence of CuO_4 plaquettes. An illustrative example of typical adiabatic potentials is shown in figure 1. Upper branch of AP has a single minimum point with approximately *fifty – fifty* composition $|\uparrow, \downarrow\rangle$ of the respective superposition state Ψ_{+} . For lower branch of AP we have either a single minimum point or the two-well structure with two local minimum points, leading to a bistability effect which is of primary importance for our analysis. Indeed, these two points may be associated with two (meta)stable charge states which form two candidates to struggle for a ground state. It is easy to see, that for large values of the transfer integral the system does not manifest bistability, i.e. the lower branch of conformational potential has only a single minimum.

Thus we conclude that all the systems such as copper oxides may be divided to two classes: *CT stable systems* with the only AP minimum for a certain charge configuration, and bistable, or *CT unstable systems* with two local AP minima for two local charge configurations. Our simple model analysis allows to uncover the relative role of different parameters governing the charge stability in the system. At the same time one should note that actually we deal with more complex multimode problem with a large body of intermediate metastable states which can be seen in luminescence spectra.

2.1.2. Generalized Peierls-Hubbard model and “negative- U ” effect Transition metal oxides with strong electron and lattice polarization effects need in a revisit of many conventional theoretical concepts and approaches. In particular, we should modify conventional Hubbard model as it is done, for instance, in a *dynamic* Hubbard model by Hirsch [6] and a modified Peierls-Hubbard model [7] with a classical description of the anharmonic core/shell displacements. Let address a square lattice Hubbard model with a half-filling and a strong on-site coupling of valent hole with core/shell displacements, which is described by the following Hamiltonian

$$\hat{H} = - \sum_{\langle i,j \rangle, \sigma} t(ij) \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + U \sum_{i, \sigma\sigma'} n_{i\sigma} n_{i\sigma'} + \sum_i v_{an}(q_i, n_i) + \sum_{\langle i,j \rangle} v_{int}(q_i, q_j), \quad (4)$$

where $\hat{c}_{i\sigma}^\dagger$ ($\hat{c}_{j\sigma}$) are creation (annihilation) operators for valent hole; $t(ij) = t(q_i, q_j)$ is the electron transfer integral between two neighboring lattice sites which depends on the dimensionless core/shell displacement coordinate; U is the on-site electron-electron repulsion energy; $v_{an}(q_i, n_i)$ is the configurational energy that incorporates the coupling between valent electrons and the site-localized anharmonic core/shell mode with dimensionless displacement coordinate q_i : $v_{an}(q_i, n_i) = a(n_i)q_i^2 - b(n_i)q_i^4 + c(n_i)q_i^6$, where a, b, c are the functions of the hole occupation number such as $a(n_i) = a_0 + a_1 n_i + a_2 n_i^2$. It is clear that $v_{an}(q_i, n_i)$ includes the renormalization both of the one-particle energy and the on-site hole-hole repulsion. The last term in (4) represents the intersite configurational coupling. The q -dependence of transfer integral implies the correlated character of the hole hopping. The conventional Hubbard Hamiltonian, or t - U -model, stabilizes the spin density wave (SDW) electron order with $n_i = 1$. In a strongly correlated limit $U \geq t$ the Hubbard model reduces to a Heisenberg antiferromagnetic model. Depending on the parameters of the hole-configurational coupling and correlated hopping the modified Hubbard Hamiltonian (4) can stabilize the “disproportionated” or charge ordered (CO) electron phase with the on-site filling numbers $n = 0$, and $n = 2$ thus leading to the “negative- U ” effect. Even simple modified model turns out to be very complicated and leads to a very rich physics[6]. Depending on the values of parameters the system yields the SDW phase with no core/shell displacements as a *true* ground state with a global minimum of free energy, and CO phase with shell displacements as a *false* ground state with a local minimum, or vice versa[7]. Strong anharmonicity $v_{an}(q_i, n_i)$ makes possible phase transitions between the phases the first order ones.

3. Photo-induced dynamics in the CT centers lattice

The effective model Hamiltonian of the lattice formed by the CT centers can be written as a superposition of single center Hamiltonians (2) and an inter-center electronic $H_{ss} = \frac{1}{2} \sum_{m,n} I_{mn} \hat{s}_{zm} \hat{s}_{zn}$ and configurational $H_{QQ} = \frac{1}{2} \sum_{m,n} K_{mn} Q_m Q_n$ coupling, respectively, where m, n labels different CT centers, and I_{mn}, K_{mn} are coupling constants. To simulate the response of the CT centers lattice on the photo-excitation we addressed 11×11 square lattice after the momentary excitation of a single, centrally located CT center ($m = 0$). The in-branch dynamics is assumed to be governed by Langevin equation with no temperature fluctuations. We studied such a simplified Newtonian dynamics of the lattice as a function of two parameters: effective

strain p and configurational coupling constant k , specifying nearest neighbour configurational coupling. In figure 2 we present a specific phase pk -diagram with three types of the lattice response: fast recombination mode (inactivation mode I), single CT exciton self-trapping mode II, and electron-hole (EH) droplet nucleation mode III. Mode I is typical for CT *stable* systems, while modes II-III relate to the CT instability with formation of single self-trapped CT excitons or EH droplets, respectively. Parent insulating cuprates are believed to be unconventional

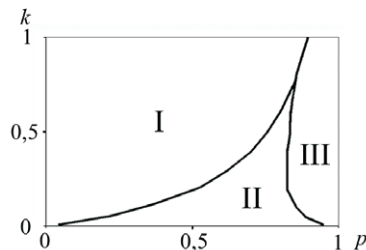


Figure 2. The (p,k) -phase diagram, showing three modes of 11×11 square lattice of CT centers: inactivation mode I, single CT exciton self-trapping mode II, EH droplet nucleation mode III. The remaining parameters were as follows: $t = 0.1$, $\Delta = 0$, $a = 2.5$, $K = 2$, $\Gamma = 5$.

systems which are unstable with regard to a self-trapping of the low-energy charge transfer excitons with a nucleation of EH droplets being actually the system of coupled electron CuO_4^{7-} and hole CuO_4^{5-} centers having been glued in a lattice due to a strong electron-lattice polarization effects. Such a system can be regarded as EH Bose liquid, or a system of effective local bosons moving in a lattice formed by hole centers. Thus we may anticipate the effects of charge ordering and superconductivity. Charged defects support the EH droplet nucleation and/or formation of metastable ("superheated") clusters of parent phase. Our scenario can readily explain photo-induced effects in underdoped cuprates. Indeed, illumination of a material with light leads to the generation of EH pairs that will proliferate and grow up to be a novel nonequilibrium EH droplet or simply to be trapped in either EH droplet with the rise in its volume fraction. The excitation energy appears to be lower when exciton is closer to the EH droplet. Therefore once the excitation transfer is finite, the optical excitation is attracted to the nearest neighbour of the EH clusters so that this cluster expands effectively under the light irradiation. In other words, the photoexcitation would result in an increase of the EH droplet volume fraction, that is why its effect in optical response resembles that of chemical doping. After switching off the light the droplet phase would relax to the thermodynamically stable state. Furthermore, such a simple model can immediately explain the persistent photoconductivity (PPC) phenomena, found in insulating YBaCuO system, where the oxygen reordering provides the mechanism of a long-time stability for the EH droplets. In PPC phenomena, an illumination of a material with light leads to a long-lived photoconductive state. During the illumination of underdoped YBaCuO near the insulator-metal transition, the material may even become superconducting.

Acknowledgments

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