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Charge states of strongly correlated 3*d* oxides: from typical insulator to unconventional electron-hole Bose liquid

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We present a model approach to describe charge fluctuations and different charge phases in strongly correlated 3*d* oxides. As a generic model system one considers that of centers each with three possible valence states $M^{0,\pm}$ described in frames of $S=1$ pseudospin (isospin) formalism by an effective anisotropic non-Heisenberg Hamiltonian which includes both two types of single particle correlated hopping and the two-particle hopping. Simple uniform mean-field phases include an insulating monovalent M^0 phase, mixed-valence binary (disproportionated) $M^{\pm}$ phase, and mixed-valence ternary («under-disproportionated») $M^{0,\pm}$ phase. We consider two first phases in more details focusing on the problem of electron-hole states and different types of excitons in M^0 phase and formation of electron-hole Bose liquid in $M^{\pm}$ phase. Pseudospin formalism provides a useful framework for revealing and describing different topological charge fluctuations, in particular, like domain walls or bubble domains in antiferromagnets. Electron-lattice polarization effects are shown to be crucial for the stabilization of either phase. All the insulating systems such as M^0 phase are subdivided to two classes: stable and unstable ones with regard to the formation of self-trapped charge transfer (CT) excitons. The latter systems appear to be unstable with regard to the formation of CT exciton clusters, or droplets of the electron-hole Bose liquid. The model approach suggested is believed to be applied to describe a physics of strongly correlated oxides such as cuprates, manganites, bismuthates, and other systems with charge transfer excitonic instability and/or mixed valence. We shortly discuss an unconventional scenario of the essential physics of cuprates which implies their instability with regard to the self-trapping of charge transfer excitons and the formation of electron-hole Bose liquid.

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71.28.+d Narrow-band systems; intermediate-valence solids;
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1. Introduction

The discovery of the high-T_c superconductivity in doped cuprates [1], observation of many unconventional properties in doped manganites with their colossal magnetoresistance, bismuthates with high-T_c's nickellates and many other oxides [2] shows that we deal with a manifestation of novel strongly correlated states with a local charge instability, mixed valence, «metal–dielectric» duality, strong coupling of different (charge, spin, orbital, structural) degrees of freedom and non-Landau behavior of quasiparticles. All this has generated a flurry of ideas, models and scenarios of the puzzling transport phenomena and stimulated the intensive studies of various correlation effects and charge transfer (CT) phenomena in strongly correlated systems derived in either way from insulators unstable with regard to the CT fluctuations. Despite intense effort, the behavior of strongly correlated 3*d* oxides remains poorly understood and we are still far from a comprehensive understanding of the underlying physics. Moreover, it seems that there are missing qualitative aspects of the problem beyond the simple Hubbard scenario that so far escaped the identification and the recognition. Firstly it concerns strong electron-lattice

polarization effects which may be subdivided into electron-lattice interaction itself [3,4], and a contribution of an electronic background that is electronic subsystem which is not incorporated into effective Hubbard model Hamiltonian [5,6]. These effects are of great importance for the ground state electronic and crystalline structure, and can seriously modify the doping response of 3*d* oxide up to the crucial change of the seemingly natural ground state. This question has not received the attention it deserves. It should be emphasized that traditional Fröhlich approach to the electron-lattice coupling implies the description of linear effects whereas the charge fluctuations in the insulator do imply strongly nonlinear electron-lattice coupling with the predominance of polarization and relaxation effects, and another energy scale. Electron-lattice effects may be directly incorporated into effective Hubbard model. Assuming the coupling with the local displacement (configurational) coordinate Q in the effective potential energy we arrive at a generalized Peierls–Hubbard model [7]. From the other hand, the taking account of similar effects in the kinetic energy results in a generalized Su–Schrieffer–Heeger (SSH) model [8]. The correlation effect of an electronic background was shown [5,6] to be of primary importance for atomic systems with filled or almost filled electron shells. Namely such a situation is realized in oxides with $O^{2-}(2p^6)$ oxygen ions. In particular, the effect results in a correlated character of a charge transfer that seems to be one of the main features for 3*d* oxides.

Many strongly correlated 3*d* oxides reveal anomalous sensitivity to a small nonisovalent substitution. For example, only 2% Sr^{2+} substituted for La^{3+} in La_2CuO_4 result in a dramatical suppression of long-range copper antiferromagnetism, while it is suppressed with isovalent Cu^{2+} substitution by Zn^{2+} at a much higher concentration close to the site dilution percolating threshold. Simultaneously, the transport properties of $La_{2-x}Sr_xCuO_4$ system reveal unconventional insulator–metal duality starting from very low dopant level [9]. Most likely, all this points to a charge phase instability intrinsic for parent 214 system which somehow evolves with nonisovalent substitution due to a well developed charge potential inhomogeneity and/or hole doping effect. The problem seems to be closely related with the hidden *multistability* intrinsic to each solid [7,10]. If the ground state of a solid is pseudo-degenerate, being composed of true and false ground states with each structural and electronic orders different from others, one might call it *multi-stable*. In this connection it is worth noting the text-book example of $BaBiO_3$ system where we unexpectedly deal with the disproportionated Ba^{3+} + Ba^{5+} ground state instead of the conventional lattice of Ba^{4+} cations [11]. The bismuthate situation can be viewed also as a result of a condensation of CT excitons, in other words, the spontaneous generation of self-trapped CT excitons in the ground state with a proper transformation of lattice parameters. At present, a CT instability with regard to disproportionation is believed to be a rather typical property for a number of perovskite 3*d* transition-metal oxides such as $SrFeO_3$, $LaCuO_3$, $RNiO_3$ [12], moreover, in solid state chemistry one consider tens of disproportionated systems [13]. Novel principles must be developed to treat such CT unstable systems with their dramatical non-Fermi-liquid behavior. In particular, we have to change the current paradigm of the metal-to-insulator (MI) transition to that of an insulator-to-metal (IM) phase transition. These two approaches imply essentially different starting points: the former starts from a rather simple *metallic-like* scenario with inclusion of correlation effects, while the latter does from strongly correlated *atomic-like* scenario with the inclusion of a charge transfer. Electron-lattice polarization effects accompanying the charge transfer appear to be of primary importance to stabilize either phase state. One should emphasize that the theoretical description of such systems is one of the challenging problems in solid state physics. The electronic states in strongly correlated 3*d* oxides manifest both significant correlations and dispersional features. The dilemma posed by such a combination is the overwhelming number of configurations which must be considered in treating strong correlations in a truly bulk system. One strategy to deal with this dilemma is to restrict oneself to small 3*d*-metal-oxygen clusters, creating model Hamiltonians whose spectra may reasonably well represent the energy and dispersion of the important excitations of the full problem. Indeed, such clusters as CuO_4 in quasi-2D cuprates, MnO_6 in manganite perovskites are basic elements of crystalline and electronic structure. Despite a number of principal shortcomings, including the boundary conditions, the breaking of local symmetry of boundary atoms, sharing of common anions for *nn* clusters etc., the embedded molecular cluster method provides both, a clear physical picture of the complex electronic structure and the energy spectrum, as well as the possibility of quantitative modelling.

Hereafter, we develop a model approach to describe different charge fluctuations and charge phases in strongly correlated 3*d* oxides with main focus on the correlated CT effects. As an illustrative model system we address a simple mixed-valence system with three possible stable nondegenerate valent states of a cation-anionic cluster, hereafter M: $M^0, M^{\pm}$, forming the charge (isospin) triplet. The M^0 valent state is as-

sociated with the *conceptually simple* one like CuO_4^{6-} in insulating copper oxides (CuO, La_2CuO_4, $YBa_2Cu_3O_6$, $Sr_2CuO_2Cl_2$, ...) or MnO_6^{9-} in manganite $LaMnO_3$ or BiO_6^{9-} in bismuthates. It is worth noting that such a model is the most relevant one to describe different cuprates where novel concepts should compete with a traditional Hubbard model approach in a hole representation implying the vacuum state formed by M^- (CuO_4^{7-}) centers, and some concentration of holes. That is why overall the paper we refer the insulating cuprates to illustrate the main concepts of the approach developed. Our algebra is based on the $S=1$ pseudo-spin formalism to be the effective tool for the description of the essential physics both of insulators unstable with regard to the CT fluctuations and related mixed-valence systems. Such an approach provides the universal framework for a unified description of these systems as possible phase states of a certain *parent multi-stable system*. In addition, we may make use of powerful methods developed in the physics of spin systems. The model system of $M^{0,\pm}$ centers is described in frames of $S=1$ pseudo-spin formalism.

Our main goal is to describe different charge phases of the model system and a scenario of evolution of visibly typical insulator to unconventional electron-hole Bose liquid which reveals many unexpected properties, including superconductivity. The paper is organized as follows: In Sec. 2 we address the effects of electron-lattice polarization and relaxation. In Sec. 3 we introduce the $S=1$ pseudospin formalism to describe the model mixed-valence systems, present the effective pseudospin Hamiltonian and possible mean-field phase states. In Sec. 4 we analyse an eh-representation of different excitations in a monovalent M^0 phase, discuss a CT instability, and nucleation of electroh-hole (EH) droplets. Electron-hole Bose liquid is discussed in Sec. 5 with a main focus on topological phase separation effect that accompanies the deviation from half-filling. Implications for cuprates are discussed in Sec. 6.

2. Electron-lattice polarization effects

2.1. Correlation effects of electronic background

The correlation problem becomes of primary importance for atoms/ions near Coulomb instability when the one-electron gluing cannot get over the destructive effect of the electron-electron repulsion. Such a situation seems to realize in oxides where Hirsch et al. [5] have proposed an instability of $O^{2-}(2p^6)$ electronic background. The main suggestion in their theory of «anionic metal» concerns the occurrence of the nonrigid degenerate structure for a closed electron shell such as $O^{2-}(2p^6)$ with the internal purely correlation degrees of freedom. In other words, one should expect sizeable correlation effects not only from unfilled $3d$ or oxygen $2p$ shells, but from completely filled O $2p^6$ shell! In order to relevantly describe such a nonrigid atomic background and its coupling to the valent hole one might use a concept of the well-known «shell-droplet» model for nuclei after Bohr and Mottelson [14]. In accordance with the model a set of completely filled electron shells which form an atomic background or vacuum state for a hole representation is described by certain internal collective degrees of freedom and a number of physical quantities such as electric quadrupole and magnetic moments. Valent hole(s) moves around this nonrigid background with strong interaction inbetween. Such an approach strongly differs from the textbook one that implies a rigid atomic orbital basis irrespective of varying filling number and external potential.

None of the effective many-body Hamiltonians that are most widely used to study the effect of electron correlation in solids such as the Hubbard model, the Anderson impurity and lattice models, the Kondo model, contain this very basic and fundamental aspect of electron correlation that follows from the atomic analysis [15]. The Hubbard on-site repulsion U between opposite spin electrons on the same atomic orbital is widely regarded to be the only important source of electron correlation in solids. It is a clear oversimplification, and we need in a more realistic atomic models to describe these effects, especially for atoms in a specific external potential giving rise to a Coulomb instability. To this end we have proposed a generalized nonrigid shell model (see Ref. 6). The model represents a variational method for the many-electron atomic configurations with the trial parameters being the coordinates of the center of the one-particle atomic orbital. The resulting displacement of the atomic orbitals allows a simple interpretation of the electron density redistribution stemmed from taking into account the electron-electron repulsion, and the symmetry of a system can be readily used for the construction of the trial many-electron wave function. The model is a generalization of the well-known shell model by Dick and Overhauser [16] widely used in lattice dynamics. In frames of the model the ionic configuration with filled electron shells is considered to be composed of an outer spherical shell of $2(2l+1)$ electrons and a core consisting of the nucleus and the remaining electrons. In an electric field the rigid shell retains its spherical charge distribution but moves bodily with respect to the core. The polarizability is made finite by a harmonic restoring force of spring constant k which acts between the core and shell. The shells of two ions repel one another and tend to be-

come displaced with respect to the ion cores because of this repulsion. The respective displacement vector appears to be a simplest *collective* coordinate which specifies the change of the electron-nucleus attraction. It should be noted that such a displacement does not imply any variation in electron-electron repulsion and respective correlation energy.

However, a simple shell model can be easily generalized to take account of correlation effects. To this end we must consider the displacements of separate one-electron orbitals to form the set of the variational parameters in a correlation function. Then we can introduce both the displacement of the center of «gravity» for filled shell and a set of the relative displacements of separate one-electron orbitals with regard to each other. The former form an «acoustical» mode and are described in frames of conventional shell model, while the latter form different novel «optical» modes. Such a seemingly naive nonrigid shell picture can provide both the microscopic substantiation of the conventional shell model and its generalization. Moreover, this *nonrigid shell model* points to a physically clear procedure to account for the correlation effects. Indeed, the «optical» displacement mode is believed to minimize the electron-electron repulsion. It is worth noting that the optical displacement mode yields some sort of a *hidden* order parameter.

2.2. Electron-lattice relaxation effects

The minimal energy cost of the optically excited disproportionation or electron-hole formation in insulating cuprates is 2.0–2.5 eV [17]. However, the question arises, what is the energy cost for the thermal excitation of such a local disproportionation? 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 [3]. The former term R_{opt} is due to the *nonretarded* effect of the electronic polarization by the momentarily localized electron-hole pair 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 and 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, $-\Delta R^{\alpha}_{\text{th}}$, 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. Moreover, such an estimation seems to be typical for different insulators [3,4].

Transition metal oxides with strong electron and lattice polarization effects need in a revisit of many conventional theoretical concepts. In particular, we should modify the usual Hubbard model as it is done, for instance, in a «dynamic» Hubbard model by Hirsch [15] or a modified Peierls–Hubbard model [7] with a classical description of the anharmonic core/shell displacements. Depending on the parameters of the hole-configurational coupling and correlated hopping the modified Peierls–Hubbard model [7] 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.

3. Model mixed-valence system

3.1. Pseudospin operators

The problem of the multi-stability of solids looks rather trivial when one say about the orbital and/or spin degrees of freedom. Usually in such a case we start from the lattice of coupled orbital and/or spin momenta described by the relevant spin-Hamiltonian that implies the variety of possible collective orbital and/or spin orderings that compete with each other under different external conditions. In other words, the multi-stability accompanies the basic degeneracy inherent to a certain atom, ion, or center with a nonzero orbital and/or spin momentum. Such an outlook is believed to be easily extended to systems with charge degree of freedom which can be represented to be a system of either centers which possible charge states form a pseudo-multiplet. Below we address a simple

model of a mixed-valence system with three possible stable valent states of a cation-anionic cluster, hereafter M: $M^0, M^{\pm}$, forming the charge (isospin) triplet. Similarly to the neutral-to-ionic electronic-structural transformation in organic charge-transfer crystals (see paper by T. Luty in Ref. 10) the system of charge triplets can be described in frames of the $S=1$ pseudospin formalism. To this end we associate three charge states of the M center with different valence: $M^0, M^{\pm}$ with three components of $S=1$ pseudospin (isospin) triplet with $M_S = 0,+1,-1$, respectively. The $S=1$ spin algebra includes three independent irreducible tensors $\hat{V}_q^k$ of rank $k=0,1,2$ with one, three, and five components, respectively, obeying the Wigner–Eckart theorem [18]

$$\langle SM_S|\hat{V}_q^k|SM_S^{'}\rangle = \\ = (-1)^{S-M_S}\begin{pmatrix} S & k & S \\ -M_S & q & M_S^{'}\end{pmatrix}\langle S||\hat{V}^k||S\rangle. \quad (1)$$

Here we make use of standard symbols for the Wigner coefficients and reduced matrix elements. In a more conventional Cartesian scheme a complete set of the nontrivial pseudospin operators would include both $\mathbf{S}$ and a number of symmetrized bilinear forms $\{S_iS_j\} = (S_iS_j + S_jS_i)$, or spin-quadrupole operators, which are linearly coupled to V_q^1 and V_q^2, respectively:

$$V_q^1 = S_q; \quad S_0 = S_z, \quad S_{\pm} = \mp\frac{1}{\sqrt{2}}(S_x \pm iS_y);$$

$$V_0^2 \propto (3S_z^2 - \mathbf{S}^2), \quad V_{\pm1}^2 \propto (S_zS_{\pm} + S_{\pm}S_z),$$

$$V_{\pm2}^2 \propto S_{\pm}^2.$$

To describe different types of pseudospin ordering in a mixed-valence system we have to introduce eight order parameters: two *diagonal* order parameters $\langle S_z\rangle$ and $\langle S_z^2\rangle$, and six *off-diagonal* order parameters $\langle V_q^k\rangle$ $(q \neq 0)$. Two former order parameters can be termed as *valence* and *ionicity*, respectively. The *off-diagonal* order parameters describe different types of the valence mixing. Indeed, operators V_q^k $(q \neq 0)$ change the z-projection of pseudospin and transform the $|SM_S\rangle$ state into $|SM_S + q\rangle$ one. In other words, these can change *valence* and *ionicity*. It should be noted that for the $S=1$ pseudospin algebra there are two operators: $V_{\pm1}^1$ and $V_{\pm1}^2$, that change the pseudospin projection by ±1, with slightly different properties: $\langle 0|\hat{S}_{\pm}|\mp1\rangle = \langle\pm1|\hat{S}_{\pm}|0\rangle = \mp1$, but

$$\langle 0|(S_zS_{\pm} + S_{\pm}S_z)|\mp1\rangle = -\langle\pm1|(S_zS_{\pm} + S_{\pm}S_z)|0\rangle = +1.$$

Three spin-linear (dipole) operators $\hat{S}_{1,2,3}$ and five independent spin-quadrupole operators $\{\hat{S}_i, \hat{S}_j\} - \frac{2}{3}\hat{\mathbf{S}}^2\delta_{ij}$ given $S=1$ form eight Gell-Mann operators being the generators of the SU(3) group [19]. The generalized spin-1 model can be described by the Hamiltonian bilinear on the SU(3)-generators $\Lambda^{(k)}$

$$\hat{H} = -\sum_{i,\eta}\sum_{k,m=1}^{8} J_{km}\hat{\Lambda}_i^{(k)}\hat{\Lambda}_{i+\eta}^{(m)}. \quad (2)$$

Here i, η denote lattice sites and nearest neighbors, respectively. This is a $S=1$ counterpart of the $S=1/2$ model Heisenberg Hamiltonian with three generators of the SU(2) group or Pauli matrices included instead of eight Gell-Mann matrices. In frames of a classical, or mean-field description of the $S=1$ quantum pseudospin system we start with trial on-site functions [19]: $\mathbf{\Psi}_j = (\mathbf{c}(j)\cdot\mathbf{\Psi}(j))$, where j labels a lattice site and the spin functions ψ in a Cartesian basis are used: $\psi_z = |10\rangle$ and $\psi_{x,y} \sim (|11\rangle \pm|1\,-1\rangle)/\sqrt{2}$; $\mathbf{c} = \mathbf{a} + i\mathbf{b}$ is a vector order parameter. The linear (dipole) pseudospin operator within $|x,y,z\rangle$ basis is represented by a simple matrix: $\langle\psi_i|S_j|\psi_k\rangle = -i\varepsilon_{ijk}$, and for the order parameters one easily obtains: $\langle\hat{\mathbf{S}}\rangle = -2[\mathbf{a}\times\mathbf{b}]$; $\langle\{\hat{S}_i\hat{S}_j\}\rangle = 2(\delta_{ij} - a_ia_j - b_ib_j)$ given the normalization constraint $\mathbf{a}^2 + \mathbf{b}^2 = 1$. Thus, for the case of spin-1 system the order parameters are determined by two classical vectors (two real components of one complex vector $\mathbf{c} = \mathbf{a} + i\mathbf{b}$). The two vectors are coupled, so the minimal number of dynamic variables describing the $S=1$ spin system appears to be equal to four.

3.2. Effective pseudospin Hamiltonian

Effective pseudospin Hamiltonian for our model mixed-valence system should incorporate a large number of contributions that describe different long- and short-range coupling between $M^{0,\pm}$ centers, single-ion and two-ion terms. Single-site terms can be subdivided into *single-ion* anisotropy and *pseudo-Zeeman* interaction. Bilinear and biquadratic two-site terms can be subdivided into *diagonal* interactions like «density-density», and *off-diagonal* terms that describe charge fluctuations conserving the total charge of the system, such as one-electron (hole) and two-electron (hole) transport. An effective pseudospin Hamiltonian of the model mixed-valence system which takes into account the main part of aforementioned contributions can be represented as follows

$$\hat{H} = \sum_i(\Delta_iS_{iz}^2 - h_iS_{iz}) + \sum_{\langle i,j\rangle}v_{ij}S_{iz}^2S_{jz}^2 + \\ + \sum_{\langle i,j\rangle}V_{ij}S_{iz}S_{jz} + \sum_{\langle i,j\rangle}[D_{ij}^{(1)}(S_{i+}S_{j-} + S_{i-}S_{j+}) +$$

$$+ D_{ij}^{(2)}(T_{i+}T_{j-} + T_{i-}T_{j+})] + \sum_{\langle i,j\rangle} t_{ij}(S_{i+}^2 S_{j-}^2 + S_{i-}^2 S_{j+}^2), \quad (3)$$

where $T_{\pm} = (S_z S_{\pm} + S_{\pm} S_z)$. Two first single-ion terms describe the effects of bare pseudospin splitting, or the local energy of $M^{0,\pm}$ centers. Interestingly, the parameter Δ can be related with correlation Hubbard parameter U: $U = 2\Delta$. The second term may be associated with a pseudomagnetic field h_i, in particular, a real electric field. It is easy to see that it describes an electron/hole assymetry. The third and fourth terms describe the effects of long- and short-range inter-ionic interaction including screened Coulomb and covalent coupling. If to apply the familiar spin terminology, the first term in (3) represents a single-ion anisotropy, the second does the Zeeman term, the fourth and fifth do the anisotropic Heisenberg exchange, and the third and sixth do the biquadratic spin-quadrupolar coupling.

One should note that despite many simplifications, the effective Hamiltonian (3) is rather complex, and represents one of the most general forms of the anisotropic $S = 1$ non-Heisenberg Hamiltonians. For the system there are two classical (*diagonal*) order parameters: $\langle S_z \rangle = n$ being a valence, or charge density with electro-neutrality constraint $\sum n_i = \sum S_{iz} = 0$, and $\langle S_z^2 \rangle = n_p$ being the density of polar centers $M^{\pm}$, or «ionicity». In addition, there are two unconventional *off-diagonal* order parameters: «fermionic» $\langle S_+ \rangle$ and «bosonic» $\langle S_+^2 \rangle$; the former describes a phase ordering for the disproportionation reaction, or the single-particle transfer, while the latter does for exchange reaction, or for the two-particle transfer. Indeed, the $\hat{S}_+$ operator creates a hole and is fermionic in nature, whereas the $\hat{S}_+^2$ does a hole pair, and is bosonic in nature.

3.3. Single and two-particle transport

The last three terms in (3) representing the one- and two-particle hopping, respectively, are of primary importance for the transport properties, and deserve special interest. Two types of one-particle hopping are governed by two transfer integrals $D^{(1,2)}$, respectively. The transfer integral $t'_{ij} = (D_{ij}^{(1)} + D_{ij}^{(2)})$ specifies the probability amplitude for a *local disproportionation, or the eh-pair creation*: $M^0 + M^0 \to M^{\pm} + M^{\mp}$; and the inverse process of the *eh-pair recombination*: $M^{\pm} + M^{\mp} \to M^0 + M^0$, while the transfer integral $t''_{ij} = (D_{ij}^{(1)} - D_{ij}^{(2)})$ specifies the probability amplitude for a polar center transfer: $M^{\pm} + M^0 \to M^0 + M^{\pm}$, or the *motion of the electron (hole) center in the matrix of* M^0 *centers* or motion of the M^0 center in the matrix of $M^{\pm}$ centers. It should be noted that, if $t''_{ij} = 0$ but $t'_{ij} \neq 0$, the eh-pair is locked in two-site configuration. The two-electron (hole) hopping is governed by transfer integral t_{ij}, or a probability amplitude for the exchange reaction: $M^{\pm} + M^{\mp} \to M^{\mp} + M^{\pm}$, or the *motion of the electron (hole) center in the matrix of hole (electron) centers*. It is worth noting that in Hubbard-like models all the types of one-electron (hole) transport are governed by the same transfer integral: $t'_{ij} = t''_{ij} = t_{ij}$, while our model implies independent parameters for a disproportionation/recombination process and simple quasiparticle motion in the matrix of M^0 centers. In other words, we deal with a «correlated» single particle transport [5].

3.4. Generic MFA phases

First of all we would like to emphasize the difference between classical and quantum mixed-valence systems. Classical (or chemical) description implies the neglect of the *off-diagonal* purely quantum CT effects: $D^{(1,2)} = t = 0$, hence the valence of any site remains to be definite: 0,±1, and we deal with a system of localized polar centers. In quantum systems with a nonzero charge transfer we arrive at *quantum superpositions of different valence states* resulting in an *indefinite* on-site valence and ionicity which effective, or mean values $\langle S_z \rangle$ and $\langle S_z^2 \rangle$ can vary from −1 to +1 and 0 to +1, respectively.

Making projection of the effective pseudospin Hamiltonian for the system onto a space of on-site states like $\Psi(j)$, we obtain an energy functional which equivalent to a classical energy of the two coupled vector $(\mathbf{a}, \mathbf{b})$ fields defined on the common lattice. Thus, in the framework of the pseudospin $S = 1$ centers model when the collective wave function is represented to be a product of the site functions, the quantum problem is reduced to a classical variation problem for a minimum of the energy for two coupled vector fields. All the MFA phases one may subdivide into those with a definite and indefinite ionicity, respectively. There are two MFA phases with definite ionicity

3.4.1. Insulating monovalent M^0 phase with $\langle S_z^2 \rangle = 0$

The M^0 phase is specified by a simple uniform arrangement of **a** and **b** vectors parallel to z axis: $\mathbf{a} \| \mathbf{b} \| O_z$. In such a case the on-site wave function is specified by unit vector (**a**, or **b**) parallel to z axis. It is a rather conventional ground-state phase for various charge transfer insulators such as oxides with a positive magnitude of Δ parameter ($U > 0$). All the centers have the same bare M^0 valence state. In other words, the M^0 phase is characterized both by definite site ionicity and valence. So, all the order parameters turn into zero: $\langle S_z \rangle = \langle S_z^2 \rangle = \langle S_+ \rangle = \langle S_+^2 \rangle = 0$. This is an

«easy-plane» phase for the pseudospins, but an «easy-axis» one for the **a** and/or **b** vectors. This phase is a typical one for the ground state of insulating transition metal oxides, or Mott–Hubbard insulators. It is worth noting that in frame of conventional band model approach the M^0 phase, e.g., in parent cuprates, is associated with a metallic half-filled hole band system.

3.4.2. Mixed-valence binary (disproportionated) $M^{\pm}$ phase with $\langle S_z^2 \rangle = 1$

This phase usually implies an overall disproportionation $M^0 + M^0 \to M^{\pm} + M^{\mp}$ that seems to be realizable if Δ parameter becomes negative one (negative $U < 0$ effect). It is a rather unconventional phase for insulators. All the centers have the «ionized» valence state, one half the M^+ state, and another half the M^- one, though one may in common conceive of deviation from fifty-fifty distribution. A simplified «chemical» approach to $M^{\pm}$ phase as to a classical disproportionated phase is widely spread in solid state chemistry [13]. In contrast with the M^0 phase the $M^{\pm}$ phase is specified by a planar orientation of **a** and **b** vectors ($\mathbf{a}, \mathbf{b} \perp O_z$) with a varied angle in between. There is no fermionic transport: $\langle S_+ \rangle = 0$, while the bosonic one may exist, and, in common, $\langle S_+^2 \rangle = -\cos(\varphi_a - \varphi_b) e^{i(\varphi_a + \varphi_b)} \neq 0$. This is an «easy-axis» phase for the pseudospins, but an «easy-plane» one for the **a** and **b** vectors. The mixed valence $M^{\pm}$ phase as a system of strongly correlated electron and hole centers is equivalent to the lattice hard-core Bose system with an inter-site repulsion, or *electron-hole Bose liquid* (EHBL) in contrast with EH liquid in conventional semiconductors like Ge, Si where we deal with a two-component *Fermi liquid*. Indeed, one may address the electron M^- center to be a system of a local boson (e^2) localized on the hole M^+ center: $M^- = M^+ + e^2$. In accordance with this analogy we assign three well known molecular-field uniform phase states of the $M^{\pm}$ binary mixture:

i) *charge ordered (CO) insulating state* with $\langle S_z \rangle = \pm 1$, $\mathbf{a} \perp \mathbf{b}$, and zero modulus of bosonic off-diagonal order parameter: $|\langle S_+^2 \rangle| = 0$;

ii) *Bose-superfluid (BS) superconducting state* with $\langle S_z \rangle = 0$, **a** and **b** being collinear, $\langle S_+^2 \rangle = e^{2i\varphi}$;

iii) *mixed Bose-superfluid-charge ordering (BS + + CO) superconducting state (supersolid)* with $0 < |\langle S_z \rangle| < 1$, **a** and **b** being oriented in xy plane, but not collinear, $\langle S_+^2 \rangle = -\cos(\varphi_a - \varphi_b) e^{i(\varphi_a + \varphi_b)} \neq 0$. In addition, we should mention the high-temperature nonordered (NO) Bose-metallic phase with $\langle\langle S_z \rangle\rangle = 0$. Rich phase diagram of $M^{\pm}$ binary mixture with unconventional superfluid and supersolid regions looks tempting, however, actually, their stabilization requires strong suppression of Coulomb repulsion between electron (hole) centers. Despite significant screening effect, the stabilization of uniform BS or BS + CO superconducting state as a result of a disproportionation reaction in a bare insulator [13] seems to be unrealistic.

3.4.3. Mixed-valence ternary («under-disproportionated») $M^{0,\pm}$ phase

For two preceding cases the order parameter $\langle S_z^2 \rangle$, or ionicity relates to its limiting values (0 or 1, respectively). For the MFA phase with indefinite ionicity, or mixed-valence ternary («under-disproportionated») $M^{0,\pm}$ phase, $0 < \langle S_z^2 \rangle < 1$, that is we have a mixture of the $M^0, M^{\pm}$ centers. From the viewpoint of the classical **a**, **b** vectors formalism the phase corresponds to the arbitrarily space-oriented $\mathbf{l} = [\mathbf{a} \times \mathbf{b}]$ vector. Both off-diagonal order parameters, fermionic $\langle S_+ \rangle$ and bosonic $\langle S_+^2 \rangle$ are, in common, non-zero, albeit with some correlation in between. So, for the ternary system one expects a coexistence of fermionic and bosonic transport. It should be noted that a complete pseudospin description of the two last model mixed-valence systems implies a two-sublattice approximation to be a minimal model compatible with a sign of Coulomb interaction and a respective tendency towards the checkerboard-like charge ordering.

4. Insulating monovalent M^0 phase

4.1. Electron, hole, and electron-hole excitations

Starting from monovalent M^0 phase as a vacuum state $|0\rangle$ we introduce an electron-hole representation where M_i^- center is derived as a result of an electron creation $\hat{a}_i^\dagger |0\rangle$, and M_i^+ center is derived as a result of a hole creation $\hat{b}_i^\dagger |0\rangle$. Then we transform pseudospin Hamiltonian (3) into that of a system of effective electrons and holes

$$\hat{H} = \Delta \sum_i (n_i^h + n_i^e) + \sum_{\langle ij \rangle} t_{ij} (\hat{a}_i^\dagger \hat{a}_j + \hat{b}_i^\dagger \hat{b}_j) + \sum_{i,j} [V^{hh}(ij)(n_i^h n_j^h + V^{ee}(ij) n_i^e n_j^e + V^{eh}(ij)(n_i^h n_j^e + n_j^h n_i^e)] + \sum_{\langle ij \rangle} t''_{ij} (\hat{a}_i^\dagger \hat{b}_j^\dagger + \hat{a}_i \hat{b}_j). \quad (4)$$

where $V_{ii} \to \infty$ to prohibit two-particle occupation of a single site. Here we suppose $h = 0$ that provides an electron-hole symmetry and neglect the two-particle transport. The first two sums in (4) represents the single particle (electrons/holes) terms, the third one does the interparticle coupling, while the fourth one describes the creation and annihilation (recombination) of eh-pairs. It is worth noting that the latter terms

describe some sort of eh-coupling. In terms of a pseudospin analogy the electrons and holes are associated with pseudospin $\Delta S_z = \pm 1$ deviations for an easy-plane magnet, localized or delocalized (pseudospin wave).

The behavior of electron/hole system crucially depends on the relation between two transfer integrals t'_{ij}, t''_{ij}. Below we address two distinct limiting situations:

I. $t''_{ij} = 0$: *Forbidden recombination/creation regime*. In this case we deal with the bands of well defined electrons and holes with a charge gap $E_g^{e,h} = \Delta - z|t'_{nn}|$ for both types of carriers. Optical gap for unbound eh-pairs is $E_g^{eh} = 2E_g^{e,h}$. However, in such a case we may expect for the formation of Wannier excitons, or eh-pairs bound due to a screened Coulomb eh-coupling. In terms of pseudospin formalism the Wannier excitons may be regarded as two pseudospin waves having formed a quasilocalized state due to a long-range antiferromagnetic Ising exchange: $V_{ij} S_{iz} S_{jz}$.

II. $t'_{ij} = 0$: *Regime of localized electrons and holes with a dimerization effect and well defined nn eh-pairs, or CT excitons*. In such a case the charge gap is $E_g^{e,h} = \Delta$ for both types of localized quasiparticles. The $t''_{ij} \neq 0$ hopping results in a dimerization effect with a quantum renormalization of the vacuum state and indefinite ionicity, the formation of two types of localized eh-pairs, or CT excitons of even S and odd P type. In frames of our *nn* approximation the CT excitons are localized. Optical gap is determined by the energy of P type CT exciton: $E_g^{eh} = 2\Delta + \delta$, with δ being a covalent correction to the ground state energy.

Thus we arrive at two limiting types of monovalent M^0 insulators with a dramatic difference in behavior of electrons and holes, as well as electron-hole pairs. In type I insulators ($t'_{ij} >> t''_{ij}$) we deal with well defined bands of electrons and holes forming Wannier excitons, while in type II insulators ($t''_{ij} >> t'_{ij}$) we deal with localized electrons and holes which can form *nn* eh-pairs, or CT excitons. The most part of 3*d* oxides are characterized by an antiferromagnetic spin background that implies strong spin reduction of one-particle transfer integrals t'_{ij}. In other words, these, seemingly, belong to type II insulators, where spin-singlet CT excitons can move through the lattice freely without disturbing the antiferromagnetic spin background, in contrast to the single hole motion. So, it seems that the situation in antiferromagnetic 3*d* insulators differs substantially from that in usual semiconductors or in other bandlike insulators where, as a rule, the effective mass of the electron-hole pair is larger than that of an unbound electron and hole. The Wannier excitons are formed due to an eh-coupling, while the CT excitons are formed due to a *kinetic cutoff*, or a specific feature of correlated hopping, in other words, the former have a *potential*, while the latter a *kinetic* nature. It is worth noting that both M centers within P type CT excitons have a certain ionicity in contrast to S type CT excitons which can mix with bare M^0M^0 ground state. CT excitons form peculiar quanta of a disproportionation reaction and may be viewed to be a minimal droplet of electron-hole Bose liquid. In general, eh-excitations in M^0 phase consist of superpositions of pairs of free electrons and holes, and CT excitons. One expects two types of superpositions: CT exciton-like and band-like. The former have a nearly localized character, while the latter have a nearly itinerant one.

The nature of the optical excitations accompanied by creation of electron-hole pairs in 3*d* oxides is not fully understood. One of the central issues in the analysis of electron-hole excitations is whether low-lying states are comprised of free charge carriers or excitons. A conventional approach implies that if the Coulomb interaction is effectively screened and weak, then the electrons and holes are only weakly bound and move essentially independently as free charge-carriers. However, if the Coulomb interaction between electron and hole is strong, excitons are believed to form, i.e., bound particle-hole pairs with strong correlation of their mutual motion. To distinguish bound and unbound electron-hole states one might use the density-density correlation function [20] $C(i,j) = \langle(\hat{n}_i - \langle\hat{n}_i\rangle)(\hat{n}_j - \langle\hat{n}_j\rangle)\rangle$, which measures a correlation of charge fluctuations on site i to a charge fluctuations on site j. A negative value correlates an excess (deficit) of charge with deficit (excess), or electron-hole distribution. In frame of pseudospin approach this correlation function measures the longitudinal ($||z$) short-range antiferromagnetic fluctuations $C(i,j) = \langle\hat{S}_{iz}\hat{S}_{jz}\rangle - \langle\hat{S}_{iz}\rangle\langle\hat{S}_{jz}\rangle$.

4.2. Charge transfer instability and CT exciton self-trapping

Electron and hole in a CT exciton in type II M^0 insulator are strongly coupled both in between and with the lattice. In contrast with conventional wide-band semiconductors where the excitons dissociate easily producing two-component electron-hole gas or plasma [22], small CT excitons both free and self-trapped are likely to be stable with regard the eh-dissociation. To illustrate the principal features of CT exciton self-trapping effect we addressed recently [21] a simplified two-level model of a two-center MM 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 introduced some configurational coordinate Q associated with a deformation of

the cluster, or respective anionic background [6]. For lower branch of adiabatic potential (AP) in the system 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 with and without CT, respectively, 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. Thus one concludes that all the systems such as copper oxides may be divided to two classes: *CT stable systems* with the only lower AP branch minimum for a certain charge configuration, and bistable, or *CT unstable systems* with two lower AP branch minima for two local charge configurations one of which is associated with self-trapped CT excitons resulting from self-consistent charge transfer and electron-lattice relaxation [4].

4.3. Nucleation of EH droplets and phase separation effects in CT unstable M^0 phase

The AP bistability in CT unstable insulators points to tempting perspectives of their evolution under either external impact. Metastable CT excitons in the CT unstable M^0 phase being the disproportionation quanta present candidate «relaxed excited states» to struggle for stability with ground state and the natural nucleation centers for electron-hole liquid phase. What way the CT unstable M^0 phase can be transformed into novel phase? It seems likely that such a phase transition could be realized due to a mechanism familiar to semiconductors with filled bands such as Ge and Si where given certain conditions one observes a formation of metallic EH liquid as a result of the exciton decay [22]. However, the system of strongly correlated electron M^- and hole M^+ centers appears to be equivalent to an electron-hole Bose liquid in contrast with the electron-hole Fermi liquid in conventional semiconductors. The Wannier excitons in the latter wide-band systems dissociate easily producing two-component electron-hole gas or plasma [22], while small CT excitons both free and self-trapped are likely to be stable with regard to the eh-dissociation. At the same time, the two-center CT excitons have a very large fluctuating electrical dipole moment $|d| \sim 2eR_{MM}$ and can be involved into attractive electrostatic dipole-dipole interaction. Namely this is believed to be important incentive to the proliferation of excitons and its clusterization. The CT excitons are proved to attract and form molecules called biexcitons, and more complex clusters where the individuality of the separate exciton is likely to be lost. Moreover, one may assume that like the semiconductors with indirect band gap structure, it is energetically favorable for the system to separate into a low-density exciton phase coexisting with the microregions of a high-density two-component phase composed of electron M^- and hole M^+ centers, or EH droplets. Indeed, the excitons may be considered to be well defined entities only at small content, whereas at large densities their coupling is screened and their overlap becomes so considerable that they loose individuality and we come to the system of electron M^- and hole M^+ centers, which form a electron-hole Bose liquid. An increase of injected excitons in this case merely increases the size of the EH droplets, without changing the free exciton density.

Homogeneous nucleation implies the spontaneous formation of EH droplets due to the thermodynamic fluctuations in exciton gas. Generally speaking, such a state with a nonzero volume fraction of EH droplets and the spontaneous breaking of translational symmetry can be stable in nominally pure insulating crystal. However, the level of intrinsic nonstoihiometry in 3*d* oxides is significant (one charged defect every 100–1000 molecular units is common). The charged defect produces random electric field, which can be very large (up to 10^8 V/cm) thus promoting the condensation of CT excitons and the *inhomogeneous nucleation* of EH droplets. Deviation from the neutrality implies the existence of additional electron, or hole centers that can be the natural centers for the inhomogeneous nucleation of the EH droplets. Such droplets are believed to provide the more effective screening of the electrostatic repulsion for additional electron/hole centers, than the parent insulating phase. As a result, the electron/hole injection to the insulating M^0 phase due to a nonisovalent substitution as in $La_{2-x}Sr_xCuO_4$, $Nd_{2-x}Ce_xCuO_4$, or change in oxygen stoihiometry as in $YBa_2Cu_3O_{6+x}$, $La_2CuO_{4-\delta}$, $La_2Cu_{1-x}Li_xO_4$, or field-effect is believed to shift the phase equilibrium from the insulating state to the unconventional electron-hole Bose liquid, or in other words induce the insulator-to-EHBL phase transition. This process results in an increase of the energy of the parent phase and creates proper conditions for its competing with others phases capable to provide an effective screening of the charge inhomogeneity potential. The strongly degenerate system of electron and hole centers in EH droplet is one of the most preferable ones for this purpose. At the beginning (nucleation regime) an EH droplet nucleates as a nanoscopic cluster composed of several number of neighboring electron and hole centers pinned by disorder potential. Charged defects supporting the EH droplet nucleation promote the formation of metastable («superheated») clusters of parent phase. It is clear that such a situation does not exclude the self-doping with the formation of a self-organized collective charge-inhomogeneous state in systems which are near the charge instability. EH droplets can manifest it-

self remarkably in various properties of the 3*d* oxides even at small volume fraction, or in a «pseudoimpurity regime». Insulators in this regime should be considered as phase inhomogeneous systems with, in general, thermo-activated mobility of the inter-phase boundaries. On the one hand, main features of this «pseudoimpurity regime» would be determined by the partial intrinsic contributions of the appropriate phase components with possible limitations imposed by the finite size effects. On the other hand, the real properties will be determined by the peculiar geometrical factors such as a volume fraction, average size of droplets and its dispersion, the shape and possible texture of the droplets, the geometrical relaxation rates. These factors are tightly coupled, especially near phase transitions for either phase (long range antiferromagnetic ordering for the parent phase, the charge ordering and other phase transformations for the EH droplets) accompanied by the variation in a relative volume fraction.

Numerous examples of the unconventional behavior of the 3*d* oxides in the pseudo-impurity regime could be easily explained with taking into account the inter-phase boundary effects (coercitivity, the mobility threshold, non-ohmic conductivity, oscillations, relaxation etc.) and corresponding characteristic quantities. Under increasing doping the «pseudo-impurity regime» with a relatively small volume fraction of EH droplets (nanoscopic phase separation) can gradually transform into a macro- (chemical) «phase-separation regime» with a sizeable volume fraction of EH droplets, and finally to a new EH liquid phase. Our scenario can readily explain photo-induced effects in pseudo-impurity phase [21]. Indeed, the 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 YBCO system [23], where the oxygen reodering 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 YBCO near the insulator–metal transition, the material may even become superconducting.

5. Electron-hole Bose liquid

The pseudospin Hamiltonian (3) for the mixed-valence binary (disproportionated) $M^{\pm}$ phase, or electron-hole Bose liquid can be mapped onto the Hamiltonian of hard-core Bose gas on a lattice (Bose – Hubbard model) [24]:

$$H_{BG} = -\sum_{i>j} t_{ij}(B_i^{\dagger}B_j + B_j^{\dagger}B_i) + \\ + \sum_{i>j} V_{ij}N_iN_j - \mu\sum_{\iota} N_i, \qquad (5)$$

where $N_i = B_i^{\dagger}B_i$, μ is a chemical potential derived from the condition of fixed full number of bosons $N_l = \sum_{i=1}^{N} \langle N_i \rangle$, or concentration $n = N_l/N \in [0,1]$. The t_{ij} denotes an effective transfer integral, V_{ij} is an intersite interaction between the bosons. Here $B^{\dagger}(B)$ are the Pauli creation (annihilation) operators; N is a full number of sites. From the other hand this Hamiltonian is equivalent to a system of spins $S = 1/2$ exposed to an external magnetic field in the z direction. Indeed, the charge (e,h), or $M^{\mp}$ doublet one might associate with two possible states of the *charge pseudospin* (isospin) $s = 1/2$: $|+1/2\rangle$ and $|-1/2\rangle$ for electron M^- and hole M^+ centers, respectively. Then the effective Hamiltonian can be written as follows [24–26]:

$$H_{BG} = \sum_{i>j} J_{ij}^{xy}(s_i^+ s_j^- + s_j^+ s_i^-) + \\ + \sum_{i>j} J_{ij}^z s_i^z s_j^z - h\sum_i s_i^z, \qquad (6)$$

where

$$J_{ij}^{xy} = 2t_{ij}, \quad J_{ij}^z = V_{ij}, \quad h = \mu - \sum_{j(j\neq i)} V_{ij}, \quad s^- = \frac{1}{\sqrt{2}}B,$$

$$s^+ = -\frac{1}{\sqrt{2}}B^{\dagger}, \quad s^z = -\frac{1}{2} + B_i^{\dagger}B_i, \quad s^{\pm} = \mp\frac{1}{\sqrt{2}}(s^x \pm is^y).$$

The model exhibits many fascinating quantum phases and phase transitions. Early investigations predict at $T = 0$ charge order (CO), Bose superfluid (BS) and mixed (BS + CO) supersolid uniform phases with an Ising-type melting transition (CO–NO) and Kosterlitz–Thouless-type (BS–NO) phase transitions to a nonordered normal fluid (NO) in 2D systems [24].

5.1. Topological phase separation in 2D EH Bose liquid away from half-filling

Above we focused on the homogeneous phase states of the mixed-valence system. Main short-length scale charge fluctuations in M^0 and $M^{\pm}$ systems are associated with a thermal exciton creation, or annihilation due to a reaction: $(M^0 - M^0) \leftrightarrow (M^+ - M^-)$. Amongst the long-length scale charge fluctuations in a model system we would like to address the topological defects in quasi-2D systems such as cuprates, in particular, different bubble-like entities like skyrmions, or another out-of-plane vortices. Namely these one can play the main role in a nucleation of unconventional charge phases.

One of the fundamental hot debated problems in bosonic physics concerns the evolution of the charge ordered ground state of 2D hard-core BH model (hc-BH) with a doping away from half-filling which in our case relates closely with the doping response of nominal insulating phase. The most recent quantum Monte Carlo (QMC) simulations [27] found two significant features of the 2D Bose–Hubbard model with a screened Coulomb repulsion: the absence of supersolid phase at half-filling, and a growing tendency to phase separation (CO + BS) upon doping away from half-filling. The physics of the CO + BS phase separation in Bose–Hubbard model is associated with a rapid increase of the energy of a homogeneous CO state with doping away from half-filling due to a large «pseudospin-flip» energy cost. Hence, it appears to be energetically more favorable to «extract» extra bosons (holes) from the CO state and arrange them into finite clusters with a relatively small number of particles. Such a droplet scenario is believed to minimize the long-range Coulomb repulsion.

Magnetic analogy allows us to make unambiguous predictions as regards the doping of BH system away from half-filling. Indeed, the boson/hole doping of checkerboard CO phase corresponds to the magnetization of an antiferromagnet in z direction. In the uniform easy-axis l_z phase of anisotropic antiferromagnet the local spin-flip energy cost is rather big. In other words, the energy cost for boson/hole doping into checkerboard CO phase appears to be big one due to a large contribution of boson-boson repulsion. However, the magnetization of the anisotropic antiferromagnet in an easy axis direction may proceed as a first order phase transition with a «topological phase separation» due to the existence of antiphase domains. The antiphase domain walls provide the natural nucleation centers for a spin-flop phase having enhanced magnetic susceptibility as compared with small if any longitudinal susceptibility thus providing the advantage of the field energy. Namely domain walls would specify the inhomogeneous magnetization pattern for such an anisotropic easy-axis antiferromagnet in relatively weak external magnetic field. As concerns the domain type in quasi-two-dimensional antiferromagnet one should emphasize the specific role played by the cylindrical, or bubble domains which have finite energy and size. These topological solitons have the vortex-like in-plane spin structure and resemble classical, or Belavin–Polyakov skyrmions [28]. Although some questions were not completely clarified and remain open until now, the classical and quantum skyrmion-like topological defects are believed to be a genuine element of essential physics both of ferro- and antiferromagnetic 2D easy-axis systems. The magnetic analogy seems to be a little bit naive, however, it catches the essential physics of doping the hc-BH system. Recently [26] we have shown that the doping, or deviation from half-filling in 2D EH Bose liquid is accompanied by the formation of multi-center topological defect such as charge order bubble domain(s) with Bose superfluid and extra bosons both localized in domain wall(s), or a topological CO + BS phase separation, rather than an uniform mixed CO + BS supersolid phase. The number of such entities in a multigranular texture nucleated with doping has to nearly linearly depend on the doping. Generally speaking, each individual bubble may be characterized by its position, nanoscale size, and the orientation of U(1) degree of freedom. In contrast with the uniform states the phase of the superfluid order parameter for a bubble is assumed to be unordered. In the long-wavelength limit the off-diagonal ordering can be described by an effective Hamiltonian in terms of U(1) (phase) degree of freedom associated with each bubble. Such a Hamiltonian contains a repulsive, long-range Coulomb part and a short-range contribution related to the phase degree of freedom. The latter term can be written out in the standard for the XY model form of a so-called Josephson coupling [25,29]

$$H_J = -\sum_{\langle i,j \rangle} J_{ij} \cos(\varphi_i - \varphi_j), \qquad (7)$$

where φ_i, φ_j are global phases for micrograins centered at points i, j, respectively, J_{ij} is Josephson coupling parameter. Namely the Josephson coupling gives rise to the long-range ordering of the phase of the superfluid order parameter in such a multi-center texture. Such a Hamiltonian represents a starting point for the analysis of disordered superconductors, granular superconductivity, insulator–superconductor transition with $\langle i,j \rangle$ array of superconducting islands with phases φ_i, φ_j. To account for Coulomb interaction and allow for quantum corrections we should introduce into effective Hamiltonian the charging energy [29]

$$H_{\rm ch} = -\frac{1}{2} q^2 \sum_{i,j} n_i (C^{-1})_{ij} n_j \ ,$$

where n_i is a number operator for particles bound in i-th micrograin; it is quantum-mechanically conjugated to φ: $n_i = -i\partial/\partial\varphi_i$, $(C^{-1})_{ij}$ stands for the capacitance matrix, q for a particle charge. Such a system appears to reveal a tremendously rich quantum-critical structure [30,31]. In the absence of disorder, the $T = 0$ phase diagram of the multi-bubble system implies either triangular, or square crystalline arrangements with possible melting transition to a liquid. The critical properties of a two-dimensional lattice without any internal degree of freedom are successfully described applying the BKT (Berezinsky–Kosterlitz–Thowless) theory to dislocations and disclinations of the lattice, and proceeds in two steps. The first implies the transition to a liquid-crystal phase with a short-range translational order, the second does the transition to isotropic liquid. For such a system provided the bubble positions fixed at all temperatures, the long-wave-length physics would be described by an (anti)ferromagnetic XY model with expectable BKT transition and gapless XY spin-wave mode. The low-temperature physics in a multi-bubble system is governed by an interplay of two BKT transitions, for the U(1) phase and positional degrees of freedom, respectively [31]. Dislocations lead to a mismatch in the U(1) degree of freedom, which makes the dislocations bind fractional vortices and lead to a coupling of translational and phase excitations. Both BKT temperatures either coincide (square lattice) or the melting one is higher (triangular lattice) [31].

Quantum fluctuations can substantially affect these results. Quantum melting can destroy U(1) order at sufficiently low densities where the Josephson coupling becomes exponentially small. In terms of our model, the positional order corresponds to an incommensurate charge density wave, while the U(1) order does to a superconductivity. In other words, we arrive at a subtle interplay between two orders. The superconducting state evolves from a charge order with $T_C \le T_m$, where T_m is the temperature of a melting transition which could be termed as a temperature of the opening of the insulating gap (pseudogap!?). The normal modes of a dilute multi-bubble system include the pseudospin waves propagating inbetween the bubbles, the positional fluctuations, or quasiphonon modes, which are gapless in a pure system, but gapped when the lattice is pinned, and, finally, fluctuations in the U(1) order parameter.

The orientational fluctuations of the multi-bubble system are governed by the gapless XY model [30]. The relevant model description is most familiar as an effective theory of the Josephson junction array. An important feature of the model is that it displays a quantum-critical point. The low-energy collective excitations of a multi-bubble liquid includes an usual longitudinal acoustic phonon-like branch. The liquid crystal phases differ from the isotropic liquid in that they have massive topological excitations, i.e., the disclinations. One should note that the liquids do not support transverse modes, these could survive in a liquid state only as overdamped modes. So that it is reasonable to assume that solidification of the bubble lattice would be accompanied by a stabilization of transverse phonon-like modes with its sharpening below melting transition. In other words, an instability of transverse phonon-like modes signals the onset of melting. The phonon-like modes in the bubble crystal have much in common with usual phonon modes, however, due to electronic nature these can hardly be detected if any by inelastic neutron scattering. A generic property of the positionally ordered bubble configuration is the sliding mode which is usually pinned by the disorder. The depinning of sliding mode(s) can be detected in a low-frequency and low-temperature optical response.

6. Implications for cuprates

The unconventional behavior of cuprates strongly differs from that of ordinary metals and merely resembles that of doped semiconductor. The copper oxides start out life as insulators in contrast with BCS superconductors being conventional metals. In our view, the essential physics of the doped cuprates, as well as other strongly correlated oxides, is driven by a self-trapping of the CT excitons, both one-center, and two-center [17]. Such excitons are the result of self-consistent charge transfer and lattice distortion with the appearance of the «negative-U» effect [3,4]. Thus, three types of CuO_4 centers $CuO_4^{5,6,7-}$ should be considered in cuprates on equal footing. As regards the self-trapped CT excitons (STE) in cuprates, we have some straightforward experimental indications. A key characteristic of the STE is its luminescence: STE are short-lived luminescent states of excited crystals. The observation of photoluminescence (PL) near 2.0–2.4 eV in La_2CuO_4, near 1.3 and 2.4 eV in $YBa_2Cu_3O_6$, near 1.78, 1.95, 2.06 eV in $PrBa_2Cu_3O_6$ [32] is a direct evidence of strongly localized long-lived states related to self-trapped excitons or their derivatives. Thus, cuprates are believed to be unconventional systems which are unstable with regard to a self-trapping of the low-energy charge transfer excitons with a nucleation of electron-hole droplets being actually the system of coupled electron CuO_4^{7-} and hole CuO_4^{5-} centers having been glued in lattice due to a strong electron-lattice polarization effects.

The system of strongly correlated electron CuO_4^{7-} and hole CuO_4^{5-} centers appears to be equivalent to an electron-hole Bose liquid (EHBL) in contrast with the electron-hole Fermi liquid in conventional semiconductors. A simple model description of such a liquid implies a system of local singlet bosons with a charge of $q = 2e$ moving in a lattice formed by hole centers. Local boson in our scenario represents the electron counterpart of Zhang–Rice singlet, or two-electron configuration $b_{1g}^2\,{}^1A_{1g}$. Naturally, that conventional electron CuO_4^{7-} center represents a relaxed state of composite system: «hole CuO_4^{5-} center plus local singlet boson», while the «nonretarded» scenario of a novel phase is assumed to incorporate the unconventional states of electron CuO_4^{7-} center up to its orbital degeneracy. In cuprates we deal with the electron/hole injection to the insulating parent phase due to a nonisovalent substitution as in $La_{2-x}Sr_xCuO_4$, $Nd_{2-x}Ce_xCuO_4$, or change in oxygen stoihiometry as in $YBa_2Cu_3O_{6+x}$, $La_2CuO_{4-\delta}$, $La_2Cu_{1-x}Li_xO_4$. Such a substitution provokes the nucleation of EH droplets and shifts the phase equilibrium from the insulating state to the unconventional electron-hole Bose liquid, or, in other words, induces the insulator-to-EHBL phase transition. Hence, the formation of EHBL in cuprates can be considered as the first order phase transition. The doping in cuprates gradually shifts the EHBL state away from half-filing. It is clear that the EHBL scenario makes the doped cuprates the objects of *bosonic* physics. There are numerous experimental evidence that support the bosonic scenario for doped cuprates [33]. In this connection, we would like to draw attention to the little known results of comparative high-temperature studies of thermoelectric power and conductivity which unambiguously reveal the charge carriers with $q = 2e$, or two-electron(hole) transport [34]. The well-known relation $\partial\alpha/\partial \ln\sigma = \text{const} = -k/q$ with $|q| = 2|e|$ is fulfilled with high accuracy in the limit of high temperatures (~ 700–1000 K) for different cuprates ($YBa_2Cu_3O_{6+x}$, $La_3Ba_3Cu_6O_{14+x}$, $(Nd_{2/3}Ce_{1/3})_4(Ba_{2/3}Nd_{1/3})_4Cu_6O_{16+x}$).

Conclusions

We have developed a model approach to describe charge fluctuations and different charge phases in strongly correlated $3d$ oxides. In frames of $S = 1$ pseudospin formalism different phase states of the system of the metal-oxide M centers with three different valent state $M^{0,\pm}$ are considered on the equal footing. Simple uniform mean-field phases include an insulating monovalent M^0 phase, mixed-valence binary (disproportionated) $M^{\pm}$ phase, and mixed-valence ternary («under-disproportionated») $M^{0,\pm}$ phase. We consider two first phases in more details focusing on the problem of electron/hole states and different types of excitons in M^0 phase and formation of electron-hole Bose liquid in $M^{\pm}$ phase.

Our consideration was focused mainly on a number of issues seemingly being of primary importance for the various strongly correlated oxides such as cuprates, manganites, bismuthates, and other systems with CT instability and/or mixed valence. These includes two types of single particle correlated hopping and the two-particle hopping, CT excitons, electron-lattice polarization effects which are shown to be crucial for the stabilization of either phase, topological charge fluctuations, nucleation of droplets of the electron-hole Bose liquid and phase separation effect. We emphasize an important role of self-trapped CT excitons in typical Mott–Hubbard insulators as candidate «relaxed excited states» to struggle for stability with ground state and natural nucleation centers for unconventional electron-hole Bose liquid which phase state include the superfluid. Pseudospin formalism has appeared to be very efficient to reveal and describe different aspects of essential physics for mixed-valence system. All the insulating systems such as M^0 phase may be subdivided to two classes: stable and unstable ones with regard to the formation of self-trapped CT excitons. The latter systems appear to be unstable with regard the formation of CT exciton clusters, or droplets of the electron-hole Bose liquid. The model approach suggested is believed to provide a conceptual framework for an in-depth understanding of physics of strongly correlated oxides such as cuprates, manganites, bismuthates, and other systems with charge transfer excitonic instability and/or mixed valence. We shortly discuss an unconventional scenario of the essential physics of cuprates that implies their instability with regard to the self-trapping of charge transfer excitons and the formation of electron-hole Bose liquid.

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1. J.G. Bednorz and K.A. Müller, *Z. Phys.* **B4**, 189 (1986).
2. M. Imada et. al., *Rev. Mod. Phys.* **70**, 1039 (1998).
3. A.L. Shluger and A.M. Stoneham, *J. Phys.*: *Condens. Matter* **5**, 3049 (1993).
4. V.S. Vikhnin, S. Avanesyan, H. Liu, and S.E. Kaphan, *J. Phys. Chem. Solids* **63**, 1677 (2002).
5. J.E. Hirsch and S. Tang, *Phys. Rev.* **B40**, 2179 (1989).
6. A.S. Moskvin and Yu.D. Panov, *Phys. Rev.* **B68**, 125109 (2003).

7. P. Huai and Keiichiro Nasu, *J. Phys. Soc. Jpn*. **71**, 1182 (2002).
8. W.P. Su, J.R. Schrieffer, and A.J. Heeger, *Phys. Rev*. **B22**, 2099 (1980).
9. Y. Ando, A.N. Lavrov, S. Komiya et. al., *Phys. Rev. Lett*. **87**, 017001 (2001).
10. *Relaxations of Excited States and Photo-Induced Structural Phase Transitions*, K. Nasu (ed.), *Springer Series in Solid-State Sciences* **124** (1997), p.17.
11. M.Yu. Kagan, K.I. Kugel, and D.I. Khomskii, *JETP* **93**, 415 (2001).
12. T. Mizokawa, D.I. Khomskii, and G.A. Sawatzky, *Phys. Rev*. **B61**, 11263 (2000).
13. S.P. Ionov, G.V. Ionova, V.S. Lubimov, and E.F. Makarov, *Phys. Status Solidi* (b) **71**, 11 (1975).
14. R. Nataf, *Les Modeles en Spectroscopie Nucleaire*, Dunod, Paris (1965).
15. J.E. Hirsch, *Phys. Rev. Lett*. **87**, 206402 (2001); *Phys. Rev*. **B65**, 184502 (2002).
16. B.G. Dick and A.W. Overhauser, *Phys. Rev*. **112**, 90 (1958).
17. A.S. Moskvin, R. Neudert, M. Knupfer et. al., *Phys. Rev*. **B65**, 180512(R) (2002).
18. D.A. Varshalovich, A.N. Moskalev, and V.K. Khersonskii, *Quantum Theory of Angular Momentum,* World Scientific, Singapore (1988).
19. N.A. Mikushina and A.S. Moskvin, *Phys. Lett*. **A302**, 8 (2002); *arXiv:cond-mat/0111201*.
20. M. Boman and R.J. Bursill, *Phys. Rev*. **B57**, 15167 (1998).
21. A.S. Moskvin, *J. Phys. Conference Series* **21**, 106 (2005).
22. T.M. Rice, *Solid State Physics*, H. Ehrenreich, F. Seitz, and D. Turnbull (eds.), **32**, 1 (1977).
23. A.I. Kirilyuk, N.M. Kreines, and V.I. Kudinov, *Pisma Zh. Eksp. Teor. Fiz*. **52**, 696 (1990).
24. R. Micnas, J. Ranninger, and S. Robaszkiewicz, *Rev. Mod. Phys*. **62**, 113 (1990).
25. A.S. Moskvin, I.G. Bostrem, and A.S. Ovchinnikov, *JETP Lett*. **78**, 772 (2003).
26. A.S. Moskvin, *Phys. Rev*. **B69**, 214505 (2004).
27. G.G. Batrouni and R.T. Scalettar, *Phys. Rev. Lett*. **84**, 1599 (2000).
28. A.A. Belavin and A.M. Polyakov, *JETP Lett*. **22**, 245 (1975).
29. S.A. Kivelson and B.Z. Spivak, *Phys. Rev*. **B45**, 10490 (1992).
30. A.G. Green, *Phys. Rev*. **B61**, R16299 (2000).
31. Carsten Timm, S.M. Girvin, and H.A. Fertig, *Phys. Rev*. **B58**, 10634 (1998).
32. D. Salamon, Ran Liu, M.V. Klein et al., *Phys. Rev*. **B51**, 6617 (1995-II).
33. A.S. Alexandrov and N.F. Mott, *J. Superconductivity* **7**, 599 (1994); A.S. Alexandrov, *Physica* **C305**, 46 (1998).
34. I.A. Leonidov, Y.N. Blinovskov, E.E. Flyatau et al., *Physica* **C158**, 287 (1989); M.-Y. Su, C.E. Elsbernd and T.O. Mason, *J. Amer. Cer. Soc.* **73**, 415 (1990); E.B. Mitberg, M.V. Patrakeev, and A.A. Lakhtin et al., *J. Alloys and Compounds* **274**, 103 (1998).