

Doped Manganites Beyond Conventional Double-Exchange Model

A.S. Moskvina, I.L. Avvakumov

Department of Theoretical Physics, Ural State University,
Ekaterinburg, 620083, Russia

Abstract

The problem of adequate electronic model for doped manganites like $La_{1-x}Sr_xMnO_3$ remains controversial. There are many thermodynamic and local microscopic quantities that cannot be explained by the conventional double-exchange model with dominantly $Mn3d$ location of doped holes. In such a situation we argue a necessity to discuss all possible candidate states with different valent structure of manganese and oxygen atoms, as well as different valent states of octahedral MnO_6 centers.

In frames of rather conventional quantum-chemical approach, crystal field and the ligand field model we address different types of MnO_6 centers, different types of $d-d$, and charge transfer transitions. We draw special attention to the so-called charge transfer states related to strong intra-center charge fluctuations. As we conjecture, namely these could become active valent states for doped manganites. We discuss some electric and magnetic properties of the electron MnO_6^{10-} , and hole MnO_6^{8-} centers with unconventional ${}^6A_{1g}-{}^6T_{1u}$ and ${}^4A_{2g}-{}^4T_{2u}$ valent manifolds, respectively.

We propose two idealized theoretical models for hole system in doped manganites. The first one implies an overall oxygen localization for the doped holes occupying the non-bonding $O2p$ orbitals. The second assumes a doping induced formation of the electron-hole Bose liquid, or a system of the electron MnO_6^{10-} , and hole MnO_6^{8-} centers. In a sense, this scenario resembles a well-known disproportionation reaction. In both cases one might expect non-trivial magnetic behavior with strong ferromagnetic fluctuations due to anomalously strong ferromagnetic coupling of non-bonding $O2p$ holes with $Mn3d$ electrons.

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1 Introduction

The discovery of the high- T_c superconductivity in doped cuprates and colossal magnetoresistance in doped manganites like $La_{1-x}Sr_xMnO_3$ have generated a flurry of ideas, models and scenarios of these puzzling phenomena, many of which are being developed up to date, although the situation remains controversial in both cases. Observation of various unconventional properties in doped cuprates, manganites, bismuthates with high- T_c 's, nickellates and many other oxides shows that we deal with a manifestation of novel strongly correlated states with a "metal-dielectric" duality, strong coupling of different (charge, spin, orbital, structural) degrees of freedom and non-Landau behaviour of quasiparticle. Moreover, for such *strongly correlated oxides* one observes many features typical for boson or boson-fermion systems. Finally, in all cases we deal with a specific role of nonisovalent substitution which appears to be a trigger mechanism to form a novel phase.

Current approach to manganites implies an applicability of conventional band model with some modifications resulting in what one calls the "double exchange plus Jahn-Teller" (DE+JT)

model [1]. The model is a generalization of the well-known double exchange model [2, 3] and implies a predominantly $Mn3d$ character of valent states both for parent and hole-doped system. Indeed, according to the conventional band theory calculations [4, 5] the conduction band of $LaMnO_3$ is derived mainly from Mne_g symmetry d -orbitals and is well separated from other bands. So, the low energy ($\hbar\omega \leq 4$ eV) physics of these materials is believed to be governed by Mne_g electrons, which are coupled by a strong Hund's coupling, J_H to Mnt_{2g} symmetry "core spins" and also interact with each other and with lattice distortions [4]. This model has been developed, in particular, with aim to relevantly describe the low frequency conductivity data [4]. An appropriate effective Hamiltonian could be represented as a sum of several terms

$$\hat{H} = \hat{H}_{KE} + \hat{H}_\mu + \hat{H}_{JT} + \hat{H}_{Hund} + \hat{H}_C, \quad (1)$$

$$\hat{H}_{KE} + \hat{H}_\mu = \sum_{i,j,a,b,\nu} t_{ij}^{ab} \hat{d}_{i\nu}^\dagger \hat{d}_{j\nu} + (h.c.) + \mu \sum_{i,a\nu} \hat{d}_{i\nu}^\dagger \hat{d}_{i\nu}, \quad (2)$$

$$\hat{H}_{JT} = -\lambda \sum_{i\nu} \hat{d}_{i\nu}^\dagger (\hat{\sigma}_x Q_2 + \hat{\sigma}_z Q_3) \hat{d}_{i\nu}, \quad (3)$$

where λ is a vibronic constant, $\hat{d}_{i\nu}^\dagger (\hat{d}_{i\nu})$ is a two-component (a, b) creation (annihilation) operator, $\sigma_{x,z}$ Pauli matrices, $Q_{2,3}$ are oxygen displacement modes for octahedral MnO_6 centers. The Hund coupling is written as follows

$$\hat{H}_{Hund} = \sum_{i,a} J_H (\hat{s}_i \cdot \hat{S}_i), \quad (4)$$

where \hat{S}_i represents the t_{2g} core spin and \hat{s}_i does the e_g one; \hat{H}_C describes the Coulomb correlation interaction.

Unfortunately, this approach is likely to preserve all the shortcomings of the conventional band models and cannot provide the correct description of the low energy physics for doped manganites. Indeed, the energy spectrum of MnO_6 center with one and two e_g holes has nothing to do with that of Mn^{3+} and Mn^{2+} , respectively. The authors [4] did not solve the Jahn-Teller problem, and \hat{H}_{JT} virtually appears to be simple low-symmetry crystalline field term. They neglect a rather strong exchange between Mn^{4+} spin cores. In addition, the strong intra-atomic Hund exchange coupling cannot be correctly described by the mean-field approximation, that results in some doubts about calculated temperature dependences. Traditional model approach reduces the role of the oxygen ions to the indirect effects of the $Mn3d - O2p$ covalent bonding resulting in crystal field effects and renormalization of the Mne_g and Mnt_{2g} orbitals.

In our opinion, conventional approach is questionable both in what concerns the electronic structure of valent states and electronic homogeneity in doped systems. There are many thermodynamic and local microscopic quantities that cannot be explained by the conventional double-exchange model.

It should be noted that unconventional behavior for the most part of strongly correlated oxides is generated by a nonisovalent substitution accompanied by strong fluctuations of the electric potential and considerable charge fluctuations. It seems highly probable that this substitution results in a stabilization of fluctuations of a novel strongly polarizable metallic-like phase that provides the most effective screening of charge inhomogeneity. Owing to the features of the pinning potential, the novel phase could hardly resemble the conventional phase states of the pure homogeneous systems. This could form a large non-adiabatic polaron or topological defect texture somewhat like a vortex. The topological order endows the doped manganite with tremendous amount of robustness to various unavoidable "real-life" material complications, such as impurities

and other coexisting broken symmetries. Such a situation in manganites implies a necessity to examine different valent states of manganese and oxygen atoms, as well as different valent states of a slightly distorted octahedral MnO_6 center being the basic unit for crystalline and electron structure.

Specific property both of $Mn3d$ and $O2p$ holes in manganites is in their strongly correlated nature, so the conventional (*metallic – like*) text-book band models like LDA or even its recent modification LDA+U cannot provide a relevant description of electronic structure and energy spectrum. This situation implies a making use of *dielectric – like* quantum-chemical approach as the most relevant basis for realistic description both of local intra-center and nonlocal intercenter correlations. Natural candidate for an effective center in manganites is slightly distorted octahedral MnO_6 center being the basic unit for crystalline and electronic structure.

In the doped manganites we have to deal with strong fluctuations of the crystal fields. Moreover, in these systems one might expect strong fluctuations, up to the sign reversal, of the charge transfer energy Δ_{pd} , *e.g.* due to the substitution driven fluctuations of Madelung potential. Such fluctuations result in a crucial modification of conventional electron structure and energy spectrum for the cation-anion centers with possible stabilization of the charge transfer (CT) states, or the oxygen location of holes. The Figure 1 illustrates such a situation for the hole MnO_6^{8-} center. The Δ_{pd} parameter in the mixed valence systems appears to be the variable order parameter, in contrast to conventional oxides (fluorides,...), where it is quenched at certain positive value. It seems, many doped oxides such as cuprates, manganites represent systems with the self-organized fluctuations of this parameter. Many conventional approaches such as band model, crystal field theory and ligand field theory should be significantly modified to describe these systems with mixed, or strictly speaking, indefinite valence, and the strong fluctuations of electron potential comparable with its mean value.

The unconventional oxygen nature of the doped holes manifests itself in many experimental observations. In this connection one should mention optical data [10] concerning the doping induced red shift of the anion-cation CT transitions, "arrested" Mn^{3+} -valence response in the $Mn K\beta$ emission spectra of $La_{1-x}Sr_xMnO_3$ to the doping in the $x < 0.3$ range founded in Ref. [11], anomalous magnitude of the effective magnetic moment per manganese ion that exceeds any thinkable theoretical value [12, 13].

In addition, one should note that traditional approach to the doped manganites with their colossal magnetoresistance as to conventional homogeneous media are incomplete and misleading. As for other strongly correlated oxides a phase separation and tendency to form different inhomogeneous structures seems to be a generic property of manganites [6, 7, 8, 9]. Nonetheless, a most part of the existing scenarios for the doped manganites corresponds to the usual effective-medium models and does not take account of their complicated inhomogeneous and, probably, phase-separated structure.

In present paper we discuss several candidate phase states of doped manganites with different valent structure of manganese and oxygen atoms, as well as different valent states of octahedral MnO_6 centers.

In Sec.II in the framework of the model of localized centers, crystal field and the ligand field model we address different types of MnO_6 centers, different types of $d - d$, and charge transfer transitions. We draw special attention to the so-called charge transfer states related to strong intra-center charge fluctuations. As we conjecture, namely these could become active valent states for doped manganites. Here we discuss some electric and magnetic properties of MnO_6 centers with unconventional valent manifold.

In Sec. III after short discussion of a conventional double-exchange model we present a novel

model of oxygen hole ferromagnetic metal.

In Sec. IV we address a novel mechanism for the insulator-metal transition that is well known for such standard semiconductors with filled bands as *Ge* and *Si*. Under certain conditions these reveal a nucleation of metallic electron-hole (EH) liquid resulting from exciton decay [27]. We speculate, that somewhat like this could take place in doped manganites where the electron-hole system should be equivalent to a Bose-liquid. In this section we briefly touch upon an issue of analogy with chemical disproportionation reaction, and experimental observation of different *Mn* valence states in manganites.

2 Electron structure of manganese ions and manganese-oxygen octahedral centers in manganites

Five *Mn3d* and eighteen *O2p* atomic orbitals in octahedral *MnO₆* complex form both hybrid *Mn3dO2p* bonding and antibonding e_g and t_{2g} molecular orbitals (MO), and non-bonding $a_{1g}(\sigma)$, $t_{1g}(\pi)$, $t_{1u}(\sigma)$, $t_{1u}(\pi)$, $t_{2u}(\pi)$ ones [14]. *Conventional* electronic structure of octahedral *MnO₆* complexes is associated with configuration of the completely filled *O2p* shells and partly filled *Mn3d* shells. *Unconventional* electronic configuration of octahedral *MnO₆* complexes is associated with a *charge transfer (CT) state* with one hole in *O2p* shells. The excited CT configuration $\tilde{\gamma}_{2p}^1 3d^{n+1}$ arises from the transition of an electron from the MO predominantly anionic in nature (the hole $\tilde{\gamma}_{2p}$ in the core of the anionic MO being hereby produced), into an empty *3d*-type MO (t_{2g} or e_g). The transition between the ground configuration and the excited one can be presented as the $\gamma_{2p} \rightarrow 3d(t_{2g}, e_g)$ CT transition. The CT configuration consists of two partly filled subshells, the ligand γ_{2p^-} , and the cation $3d(t_{2g}^{n_1} e_g^{n_2})$ shell, respectively. It should be emphasized that the oxygen hole having occupied the *non-bonding* γ_{2p} orbital interact *ferromagnetically* with $3d(t_{2g}^{n_1} e_g^{n_2})$ shell. This rather strong (up to ~ 0.1 eV) ferromagnetic coupling results in Hund rule for the CT configurations, and provides the high-spin ground states.

2.1 *Mn³⁺* ion and *MnO₆⁹⁻* center

2.1.1 Conventional electronic structure

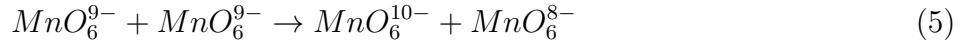
The typical high-spin ground state configuration and crystalline term for *Mn³⁺* in octahedral crystal field or for the octahedral *MnO₆⁹⁻* center is $t_{2g}^3 e_g^1$ and 5E_g , respectively. Namely this orbital doublet results in a vibronic coupling and Jahn-Teller (JT) effect for the *MnO₆⁹⁻* centers, and cooperative JT ordering in *LaMnO₃*. In the framework of crystal field model the 5E_g term originates from the ($3d^4 {}^5D$) term of free *Mn³⁺* ion.

Among the low-energy crystal field d-d transitions for the high-spin *Mn³⁺* ions one should note a single spin-allowed and parity-forbidden ${}^5E_g - {}^5T_{2g}$ transition at energy varying from about 2 eV to 2.5 eV depending on the crystalline matrix. So, this is 2.5 eV for the *Mn³⁺* impurity in perovskite *YAlO₃* [15]. The transition is magneto-optically active, and could manifest itself in the Faraday and Kerr effects. A detection of the spin- and parity-forbidden ${}^5E_g - {}^3T_{1g}$ transition with, probably, lower energy could be rather important in the *Mn³⁺* assignment. Some authors consider the orbital and parity-forbidden transition ${}^5E'_g - {}^5E''_g$ between two components of the 5E_g doublet splitted by the low-symmetry crystalline field to be an origin of a rather strong absorption observed in manganites near 1.5 eV. Such a rather big magnitude of the splitting for the 5E_g doublet agrees

well with observed magnitudes of the low-symmetry distortions for the MnO_6^{9-} octahedra of the order of 15% [16].

2.1.2 Intra- and inter-center charge transfer transitions for the MnO_6^{9-} centers. Small charge transfer excitons

A set of the intensive and broad absorption bands in parent manganites is related to the anion-cation $O2p - Mn3d$ charge transfer. In the framework of the MnO_6 center model this elementary CT process generates both intra- and inter-center CT transitions for the MnO_6^{9-} centers. The intra-center CT transitions, in turn, could be subdivided [17] to *localized electronic excitations* and *Frenkel excitons*, respectively. The inter-center CT transitions form a set of *small CT excitons*, which in terms of chemical notions represent somewhat like the *disproportionation* quanta



resulting in a formation of the bounded electron MnO_6^{10-} (e^-) and hole MnO_6^{8-} (h^-) small radius centers. A minimal energy of such an exciton or the disproportionation threshold turns out to be rather small (≤ 5.0 eV) as compared with appropriate purely ionic quantity which value equals to the electrostatic correlation energy $U_{dd} \approx 10$ eV.

Intracenter charge transfer transitions for the MnO_6^{9-} centers.

Conventional classification scheme of the charge-transfer transitions in the octahedral MnO_6^{9-} centers (intra-center CT transitions) incorporates the electro-dipole allowed $(t_{2g}^3 e_g^1)^5 E_g - (t_{2g}^4 e_g^1 \gamma_u)^5 T_{1,2u}$, $(t_{2g}^3 e_g^2 \gamma_u)^5 T_{1,2u}$ transitions from the odd oxygen $\gamma = 5t_{1u}, 6t_{1u}, 1t_{2u}$ orbitals to the even manganese $3dt_{2g}$ and $3de_g$ orbitals, respectively. Most probably, the minimal energy separation is related to the CT transition $1t_{2u} - e_g$ with formation of the excited Mn^{2+} -like $t_{2g}^3 e_g^2$ configuration. As for manganite $LaMnO_3$, the minimal energy of the allowed CT transitions is estimated to be $\Delta_{CT} \geq 4.0$ eV. In addition to the allowed CT transitions one should note a number of the parity-forbidden CT transitions, mainly the $1t_{1g} - t_{2g}, e_g$ ones with the lowest energy.

2.2 The hole MnO_6^{8-} center in doped manganites: conventional textbook model

The hole centers in manganites may be created as a result of the photo- or chemical doping as in $La_{1-x}^{3+} Sr_x^{2+} MnO_3$. In both cases the hole MnO_6^{8-} center can be chosen as a relevant model entity to describe a real distribution of the hole density.

Conventional model approach to the hole MnO_6^{8-} center implies $\Delta_{pd} > 0$ and the ground state with predominantly $Mn3d$ hole location (see Fig.1). The typical high-spin ground state configuration and crystalline term for Mn^{4+} in octahedral crystal field or for the octahedral MnO_6^{8-} center is half-filled configuration t_{2g}^3 and the orbital singlet term ${}^4A_{2g}$, respectively. In the framework of crystal field model the ${}^4A_{2g}$ term originates from the $(3d^3 {}^4F)$ term of free Mn^{4+} ion. Among low-energy crystal field d-d transitions for Mn^{4+} ions one should note a rather intense (oscillator strength $\sim 10^{-3}$) parity-forbidden ${}^4A_{2g} - {}^4T_{2g}$ transition at energy varying from about 2 eV to 2.6 eV depending on the crystalline matrix. The transition is magneto-optically active, and could manifest itself in the Faraday and Kerr effects. The very weak spin- and parity-forbidden ${}^4A_{2g} - {}^2E_g, {}^2T_{1g}$ transitions can be observed at lower energy $1.5 \div 2$ eV. The relatively weak orbital and parity-forbidden ${}^4A_{2g} - {}^4T_{1g}$ transition has energy about 3 eV.

The classification scheme for the CT transitions in octahedral MnO_6^{8-} centers is similar to that of MnO_6^{9-} centers, described above. As for manganite $LaMnO_3$ [18], the minimal energy of

the allowed CT transitions is estimated to be $\Delta_{CT} \sim 4.0$ eV. The luminescence measurements in [19] give the energies 2.6 eV and 3.1 eV for ${}^4A_{2g} - {}^4T_{2g}$ and ${}^4A_{2g} - {}^4T_{1g}$ transitions, respectively.

Very important information about the octahedral Mn^{4+} spectra with likely no problems of mixed Mn valence can be deduced from the magneto-optical studies of manganese pyrochlores $A_2^{3+}Mn_2^{4+}O_7$ ($A = In, Tl, Lu, Yb$) [20]. The authors observed two rather narrow magneto-optical features in the range 2.6 – 3.1 eV, related to the $d - d$ transitions ${}^4A_{2g} - {}^4T_{2g}$ and ${}^4A_{2g} - {}^4T_{1g}$, respectively, and two rather wide features near 3.7 – 3.9 eV and ≥ 4.3 eV, associated with CT transitions. This assignment agrees with data by Paulusz and Burrus [18], and Jung *et al.* for $CaMn^{4+}O_3$ [10].

2.3 The electron MnO_6^{10-} center in doped manganites: conventional scheme

The typical high-spin ground state configuration and crystalline term for Mn^{2+} in octahedral crystal field or for the octahedral MnO_6^{10-} center is a half-filled configuration $t_{2g}^3e_g^2$ and the orbital singlet term ${}^6A_{1g}$, respectively. In the framework of crystal field model this term originates from the $(3d^5S)$ term of free Mn^{2+} ion. It should be noted that for the $3d^5$ configuration the ${}^6A_{1g}$ term is the only spin-sextet one, so all the $d - d$ transitions from the ground state are spin- and parity-forbidden, therefore these are extremely weak (oscillator strength $\sim 10^{-7}$). Among low-energy crystal field $d - d$ transitions for Mn^{2+} ions one should note a sequence of ${}^6A_{1g} - {}^4T_{1g}$, ${}^4T_{2g}$, (${}^4A_{1g}$, 4E_g) transitions to be observed in the spectral range 2 ÷ 3 eV depending on the crystalline matrix. In manganese oxide $Mn^{2+}O$ these transitions are observed at ≈ 2.0 eV and ≈ 2.95 eV for ${}^4T_{1g}$ and ${}^4A_{1g}$, 4E_g , respectively [19]. All the transitions are magneto-optically active, and could manifest themselves in the Faraday and Kerr effects.

The classification scheme for the CT transitions in octahedral MnO_6^{10-} centers is similar to that of MnO_6^{9-} centers.

The many-electron state of the CT configuration is $\tilde{\gamma}_{2p}^1 : t_{2g}^4 e_g^2 ({}^5T_2) : {}^{2S+1}\Gamma$ or $\tilde{\gamma}_{2p}^1 : t_{2g}^3 e_g^3 ({}^5E) : {}^{2S+1}\Gamma$ (due to the transfer $\gamma_{2p} \rightarrow t_{2g}$ and $\gamma_{2p} \rightarrow e_g$, respectively). The symmetry selection rules for electro-dipole transitions permit only the following values of γ [14]: $\gamma = t_{1u}$ (two MO usually denoted as $t_{1u}(\pi)$ and $t_{1u}(\sigma)$) and $\gamma = t_{2u}$ (single MO). In accordance with thinkable variants of the combination of "intermediate" quantum numbers of the oxygen and manganese subsystems, six "one-electron" CT transitions (the lowest in energy) t_{2u} , $t_{1u}(\pi)$, $t_{1u}(\sigma) \rightarrow t_{2g}$ and t_{2u} , $t_{1u}(\pi)$, $t_{1u}(\sigma) \rightarrow e_g$ give rise to a lot of "many-electron" CT transitions, among which only six transitions of the ${}^6A_{1g} - {}^6T_{1u}$ type are electric-dipole allowed, and others are forbidden either by the quasimomentum selection rule (transitions of the ${}^6A_{1g} - {}^6\Gamma_u$ -type, $\Gamma \neq T_1$) or due to spin (transitions of the ${}^6A_{1g} - {}^4\Gamma_u$ -type; if $\Gamma \neq T_1$, they are doubly forbidden).

A rather detailed description of the optical and magneto-optical manifestation of similar transitions in isoelectronic octahedral centers FeO_6^{9-} for some ferrites is made in Ref.[21]. Due to a lower valence of cation Mn^{2+} the CT bands in MnO_6^{10-} can be shifted to bigger energies with the CT gap ~ 4.0 eV.

2.4 Unconventional MnO_6 centers. The valence crossover and pseudo-Jahn-Teller centers

2.4.1 Isolated MnO_6 centers

A significant magnitude of the CT energy $\Delta_{pd} \geq 2$ eV is a typical situation for the conventional transition metal oxides. However, this situation can be altered, in particular, for the intermediate (mixed) valence systems with strong fluctuations of electron potential, where an effective CT energy Δ_{CT} could reach very small values, and even to be negative one. Such a case implies close energies, or near-degeneracy, for two states with a hole localized predominantly on the $3d$ cation and the one localized on either purely oxygen orbital, respectively. This quasi-degeneracy or $Mn^{3+} - Mn^{4+}$ valence resonance (see Fig.1) could result in the formation of the hole MnO_6^{8-} pseudo-Jahn-Teller center, or small PJT polaron. The PJT polarons will manifest themselves in various physical effects.

One of the most probable bare electronic states for the hole PJT center MnO_6^{8-} are $(t_{2g}^3)^4 A_{2g}$ and $(t_{2g}^4 e_g^2 t_{2u})^4 T_{2u}$ one. Indeed, these even and odd states are most strongly coupled due to dipole-charge interaction with dipole-active displacement modes for MnO_6 octahedra that could result in a strong PJT effect with a multi-well adiabatic potential. Formally, such a center looks like a so-called charge transfer vibronic exciton (CTVE)[22], or charge transfer excitation $(t_{2g}^3)^4 A_{2g} - (t_{2g}^4 e_g^2 t_{2u})^4 T_{2u}$ strongly stabilized by a local dipole-active structural distortion. The important feature of such a PJT center, or CTVE, is the oxygen-manganese charge transfer which is self-consistently coupled with a local structural distortion. In other words, such a center could be described as a system of two coupled dipole moments generated by charge transfer and ionic displacements, respectively.

One should note that $(t_{2g}^3)^4 A_{2g}$ and $(t_{2g}^4 e_g^2 t_{2u})^4 T_{2u}$ states correspond to different $3d$ configurations: $3d^3$ and $3d^4$, familiar to Mn^{4+} and Mn^{3+} ions, respectively. This results in an unconventional $d - d$ spectrum for the hole PJT center MnO_6^{8-} , it will represent a superposition of $d - d$ transitions for Mn^{4+} and Mn^{3+} ions with relative intensity specified by the relative weights of bare electronic states in vibronic ground state. A Mn^{3+} -like $d - d$ spectrum for the hole PJT center MnO_6^{8-} has to be distinguished from the $d - d$ spectrum for the Mn^{3+} in the proper MnO_6^{9-} center. An occurrence of additional oxygen hole in the former center has to result in a screening effect with a lowering of the crystal field splitting parameter $10Dq$.

The Δ_{pd} sign crossover results in a peculiar interchange of valent $Mn3d$ holes to valent $O2p$ holes that generates a number of novel puzzling phenomena such as oxygen anionic magnetism, oxygen anionic metal, oxygen-oxygen CT transitions.

In optics the PJT center manifests itself in mid-infrared (MIR) absorption related to transitions between vibronic states for different sheets of adiabatic potential [14, 23, 24]. The MIR absorption band will be especially intensive when the allowed electro-dipole transition between the bare electronic states is possible.

Unconventional MnO_6^{10-} center: $Mn^{2+} - Mn^{1+}$ ionic-covalent resonance.

Similarly to the hole MnO_6^{8-} center we can expect formation of the electron MnO_6^{10-} PJT center given certain conditions. This is a center with nominal Mn valence resonating between Mn^{2+} and Mn^{1+} . The mid-infrared region transitions and Mn^{1+} -like d-d transitions represent a specific optical manifestation of the electron PJT center. The $Mn^{1+} 3d^6$ configuration has the high-spin ground state Hund term 5D , or crystalline term ${}^5T_{2g}$ for octahedral crystal field with a rather intense both optically and magneto-optically spin-allowed ${}^5T_{2g} - {}^5E_g$ transition. However, the most typical situation for octahedral centers with the $3d^6$ configuration corresponds to the competition of the high- and low-spin ground states with filled t_{2g} shell $(t_{2g}^6)^1 A_{1g}$. Then one observes a rather intense spin-allowed ${}^1A_{1g} - {}^1T_{1g}$ transition with energy $2 \div 3$ eV and ${}^1A_{1g} - {}^1T_{2g}$ at a slightly (~ 0.5 eV) higher energy. In addition, there exist numerous weak spin- and parity-

forbidden transitions.

2.4.2 The MnO_6 centers in a polarizable lattice

Above we implied an isolated MnO_6 center with varying Δ_{pd} parameter. However, for MnO_6 center in a polarizable medium, such as perovskite lattice we should account for additional polarization effects. The perovskite structure is typical for ferroelectrics like $BaTiO_3$, and incipient ferroelectrics or quantum paraelectrics such as $SrTiO_3$. Soft and highly polarizable perovskite lattice together with valence instability or the ability of Mn to exhibit intermediate valence states involving the oxidation states Mn^{2+}/Mn^{4+} together with Mn^{3+} could result in the specific instability of the bare orbitally nondegenerate ground states like ${}^4A_{2g}$ in Mn^{4+} or ${}^6A_{1g}$ in Mn^{2+} with regard to the cation-anion charge transfer accompanied by strong electric dipole moment fluctuations. Indeed, in strongly polarizable media the GS orbital singlets like $(t_{2g}^3 e_g^4)A_{2g}$ in Mn^{4+} or $(t_{2g}^3 e_g^2)A_{2g}$ in Mn^{2+} could be strongly coupled with the charge transfer states like $(t_{2g}^4 e_g t_{2u})T_{2u}$ and $(t_{2g}^4 e_g^2 t_{2u})T_{1u}$, respectively, due to the dipole-dipole polarization interaction with a possible formation of a peculiar cloud of the electronic polarization of the lattice. The dipole moment related to the $A_g - T_u$ manifolds could attain a rather big value: $d_{AT} \approx eR_{MnO}\lambda$, especially for the enhanced covalency effects realized for rather low Δ_{pd} values.

Thus we come to the formation of the specific charge transfer dipole center in a polarizable lattice with the mixed ionic-covalent type of the chemical bonding (ionic-covalent resonance) and fluctuating reorienting dipole moment. This situation is the straightforward analog of above mentioned PJT effect due to vibronic coupling with dipole-active lattice displacements. Moreover, both effects supplement each other. In addition, it should be noted that close energy separation of even A_g -like and odd T_u -like states with large magnitude of appropriate dipole matrix element implies a large electron polarizability of such a center, so, a tend to clusterization. Anyway, one of the most important consequences of this dipole instability for the systems of MnO_6 centers implies the incorporation of the odd charge transfer states like $(t_{2g}^4 e_g t_{2u})T_{2u}$ and $(t_{2g}^4 e_g^2 t_{2u})T_{1u}$ to the active valent electronic states on equal footing with the bare ground state like $(t_{2g}^3)A_{2g}$ or $(t_{2g}^3 e_g^2)A_{2g}$, respectively.

Naturally, that for a correct self-consistent description of systems with the effective Δ_{pd} sign crossover, or ionic-covalent resonance, one should both substantially extend the valent electron manifold and include the lattice degrees of freedom. Moreover, because of the particular importance of polarization effects, rigorously speaking, we should introduce these to a modified effective Hamiltonian having abandoned an attempt to make use of the conventional scheme with effective correlation parameters like U_d and U_p .

2.5 Electric and magnetic properties of the charge transfer $T_{1u,2u}$ states and $A - T$ valent manifolds for MnO_6 centers.

The singlet Hund terms ${}^6A_{1g}$ and ${}^4A_{2g}$ for the centers MnO_6^{10-} and MnO_6^{8-} originate from the electronic configurations $t_{2g}^3 e_g^2$ and t_{2g}^3 , respectively. The orbital triplets ${}^6T_{1u}$ and ${}^4T_{2u}$ are typical for several configurations with the ligand-metal charge transfer. For the MnO_6^{10-} center one has the CT configurations $t_{2g}^4 e_g^2 t_{2u}$, $t_{2g}^4 e_g^2 t_{1u}(\pi)$, $t_{2g}^4 e_g^2 t_{1u}(\sigma)$, related to the transfer of the oxygen $t_{2u}, t_{1u}(\pi), t_{1u}(\sigma)$ electron into the predominantly $3dt_{2g}$ state. Similarly, the electronic configurations $t_{2g}^3 e_g^3 t_{2u}$, $t_{2g}^3 e_g^3 t_{1u}(\pi)$, $t_{2g}^3 e_g^3 t_{1u}(\sigma)$ correspond to the transfer of the oxygen electron to the cation e_g state.

Below we address some electric and magnetic properties of the charge transfer $T_{1u,2u}$ states and $A - T$ valent manifolds for MnO_6 centers.

2.5.1 Electric properties.

First, one should note the significant difference between the electron density distributions in the orbital singlet ${}^6A_{1g}({}^4A_{2g})$ and in the orbital triplet ${}^6T_{1u}({}^4T_{2u})$, respectively.

In the orbital triplet state ${}^6T_{1u}({}^4T_{2u})$ it is possible to introduce the effective orbital moment $\tilde{L} = 1$, which has the very simple matrix

$$\langle i | \tilde{L}_k | j \rangle = -i\epsilon_{ikj}. \quad (6)$$

on the basis of the $|x, y, z\rangle$ -states.

The effective quadrupole moment of the ${}^6T_{1u}({}^4T_{2u})$ term has the form

$$\hat{Q}_{ij}^\Gamma = Q_\Gamma (\widetilde{L_i L_j} - \frac{1}{3} \widetilde{L^2} \delta_{ij}), \quad (7)$$

where $\Gamma = E, T_2$, Q_Γ is the quadrupole parameter, $\widetilde{L_i L_j} = \frac{1}{2}(L_i L_j + L_j L_i)$.

The nonzero matrix elements of the effective dipole moment for the valent multiplet are written as follows:

$$\langle {}^6A_{1g}({}^4A_{2g}) | d_k | {}^6T_{1u}({}^4T_{2u}) j \rangle = d_{A-T} \delta_{kj}. \quad (8)$$

2.5.2 Magnetic properties

Effective magnetic moment.

One of the most important magnetic peculiarities for the charge transfer states like $(t_{2g}^4 e_g t_{2u})^4 T_{2u}$ and $(t_{2g}^4 e_g^2 t_{2u})^6 T_{1u}$ is related to a nonquenched orbital magnetic moment. In common, the effective magnetic moment of the MnO_6 center can be written as follows

$$\vec{M} = \beta_e (g_S \vec{S} + g_L \vec{L}), \quad (9)$$

where $g_S \approx 2$ is the spin g -factor, g_L is the effective orbital g -factor, which is represented as the sum of the $Mn3d$ - and $O2p$ -contributions

$$g_L = g_L^{3d} + g_L^{2p}. \quad (10)$$

The values of the parameters g_L for all six different charge transfer configurations of the MnO_6^{10-} and MnO_6^{8-} centers resulting in ${}^6T_{1u}$ terms were calculated in [21]. The main charge-transfer configuration $t_{2g}^4 e_g^2 t_{2u}$ for the MnO_6^{10-} -center turns out to have the negative effective orbital g -factor

$$g_L = g_L^{3d} + g_L^{2p} = -\frac{1}{2} - \frac{1}{4}. \quad (11)$$

The effective spin-orbital interaction has the standard form

$$V_{SO} = \lambda \vec{L} \vec{S}, \quad (12)$$

where $\lambda = \lambda^{3d} + \lambda^{2p}$ is the effective spin-orbital constant. The magnitude of these parameters for all above addressed electronic configurations of the MnO_6^{10-} and MnO_6^{8-} centers were calculated in [21]. For the main charge transfer configuration $t_{2g}^4 e_g^2 t_{2u}$ of the MnO_6^{10-} center

$$\lambda = \frac{1}{20} \xi_{3d} + \frac{1}{10} \xi_{2p} > 0. \quad (13)$$

This corresponds to the antiparallel (antiferromagnetic) orientation of the spin and the orbital momenta in the ground state of the term $(t_{2g}^4 e_g^2 t_{2u})^6 T_{1u}$. With the negative value of the orbital g -factor this corresponds to the parallel (ferromagnetic) orientation of the spin magnetic moment and the orbital magnetic moment. The maximal value of the total magnetic moment is

$$M(^6T_{1u}) = 5\beta_e + 0.75\beta_e = 5.75\beta_e, \quad (14)$$

that significantly exceeds the pure spin value.

Magnetic anisotropy.

The source of the single-ion orbital magnetic anisotropy for the MnO_6 centers is the low-symmetry crystal field, which can be described by the effective Hamiltonian

$$\hat{H}_{LSCF} = \sum_{ij} K_{ij} (\widetilde{L}_i \widetilde{L}_j - \frac{1}{3} \widetilde{L}^2 \delta_{ij}). \quad (15)$$

Here K_{ij} are the effective constants of the single-ion orbital magnetic anisotropy. The magnitudes of these parameters can vary in a sufficiently wide region, taking the values $0.01 \div 0.1$ eV for the low-symmetry lattice distortions being of the order of $0.01 \div 0.1$.

Two-ion orbital anisotropy is determined by the quadrupole-quadrupole interaction and also can take large values. Thus, the MnO_6 centers in the case of the model manganite can exhibit large magnetic anisotropy, compared with that of the rare-earth compounds.

3 Unconventional model approaches to electron structure of doped manganites

3.1 The oxygen hole ferromagnetic metal

One of the simplest unconventional model approaches to the hole doped manganites like $La_{1-x}Sr_xMnO_3$ implies purely oxygen location of the doped holes. This result in an unconventional system with two, $Mn3d$ and $O2p$, non-filled shells. An appropriate effective Hamiltonian could be represented as a sum of several terms

$$\hat{H} = \hat{H}_{KE} + \hat{H}_\mu + \hat{H}_{LSCF} + \hat{H}_{exch} + \hat{H}_C + \hat{H}_{imp}, \quad (16)$$

$$\hat{H}_{KE} + \hat{H}_\mu = \sum_{i,j,\alpha,\beta,\nu} t_{ij}^{\alpha\beta} \hat{p}_{i\alpha\nu}^\dagger \hat{p}_{j\beta\nu} + (h.c.) - \mu \sum_{i,\alpha\nu} \hat{p}_{i\alpha\nu}^\dagger \hat{p}_{i\alpha\nu}, \quad (17)$$

where α, β labels different (x, y, z) $O2p$ orbitals, $t_{ij}^{\alpha\beta}$ are $O2p - O2p$ transfer integrals, μ chemical potential.

$$\hat{H}_{LSCF} = \sum_{i\alpha,\beta\nu} b_{\alpha\beta}(i) \hat{p}_{i\alpha\nu}^\dagger \hat{p}_{i\beta\nu}, \quad (18)$$

where $b_{\alpha\beta}(i)$ are the low-symmetry crystalline field parameters. The exchange coupling incorporates the $d - d$, $p - p$ and the strongest $p - d$ contributions, and is written as follows

$$\hat{H}_{exch} = \sum_{i,j} [J_{ij}^{dd}(\hat{S}_i \cdot \hat{S}_j) + J_{ij}^{pd}(\hat{s}_i \cdot \hat{S}_j) + J_{ij}^{pp}(\hat{s}_i \cdot \hat{s}_j)], \quad (19)$$

where \hat{S}_i represents the Mn^{3+} spin and \hat{s}_i does the $O2p$ hole one. The terms H_C and H_{imp} describe the intra- and inter-site Coulomb $O2p - O2p$ interaction and electrostatic interaction with Sr^{2+}

induced impurity potential. One should note that despite a wide-spread opinion the correlation effects for oxygen holes could be rather strong [25]. These should provide a coexistence of the two (manganese and oxygen) non-filled bands.

This Kondo lattice ($p - d$) model with ferromagnetic $p - d$ coupling immediately explains many unconventional properties of the hole doped manganites. First of all, at low hole content we deal with hole localization in impurity potential. Then, given further hole doping a percolation threshold occurs accompanied by insulator-anionic oxygen metal phase transition and ferromagnetic ordering both in oxygen and Mn sublattices, due to a strong ferromagnetic Heisenberg pd exchange. However, it should be noted that ferromagnetic sign of pd exchange is characteristic of non-bonding p and d orbitals.

The oxygen hole doping results in a strong spectral weight transfer from the intense $O2p - Mn3d$ CT transition bands to the $O2p$ band developed. The Mn^{3+} $d - d$ transitions will gradually shift to the low energies due to a partial $O2p$ -hole screening of the crystalline field. In a whole, optical data evidence in favor of the oxygen hole scenario. In addition, one might point to the two exciting experimental facts. Firstly, an "arrested" Mn^{3+} -valence response in the $Mn K\beta$ emission spectra of $La_{1-x}Sr_xMnO_3$ to the doping in the $x < 0.3$ range founded in Ref. [11] is consistent with creation of predominantly oxygen holes. Secondly, this is observation of anomalously large magnitude of saturated magnetic moments in ferromagnetic state for different doped manganites [12, 13].

Coexistence of two non-filled non-bonding bands is a rather unconventional phenomenon for usual homogeneous systems. Anycase this implies a quasi-degeneracy in energy and instabilities in the system.

In connection with the oxygen location of doped holes in manganites we should note the probable manifestation of the specific correlations inherent in almost filled electron shells [25]. Indeed, the conventional approach to the electron structure of the cation-anionic clusters like CuO_4 -centers implies allocation of a rather small number (one, two) of valent holes against the non-degenerate structureless (rigid) cation-anionic background with full neglect of appropriate correlational coupling "valent hole - many-electron background". However, such a coupling could play an important role, in particular, for anions like oxygen with almost filled $2p$ -shell, resulting in many quantitative and qualitative effects, including the $O2p$ -hole localization. Firstly, this implies a nonrigid degenerate structure for anionic $O2p^6$ background with internal degrees of freedom. Valent hole(s) moves around this nonrigid background. Namely such a situation occurs in a generalized "shell-droplet" model for nuclei after Bohr and Mottelson [26]. It seems, a rather similar picture one observes for clusters with the Jahn-Teller effect when an electron moves around nonrigid nuclear configuration. Partly, this resembles familiar transition from the rigid-ion model to the shell model in lattice dynamics.

The simplest "single-doublet" model was proposed by Hirsch et al. [25] who assumed an occurrence of the doublet structure of isolated anionic $O2p^6$ background in copper oxides and made use of the pseudo-spin formalism. Unfortunately, this very fruitful approach remained to be only interesting idea despite the ever growing interest in electronic structure and correlations in different oxides. The detailed theoretical treatment of the unconventional anionic oxygen hole model is needed to provide an appropriate description of the optical, magnetic, and many other physical properties.

3.2 The electron-hole Bose liquid (“disproportionation”) scenario in manganites

Above we considered two opposite versions of charge fluctuations in the hole doped manganites with hole localization either on $Mn3d$ or $O2p$ orbitals. Proceeding from symmetry and energetic consideration we may conjecture the non-isovalent substitution in doped manganites like $La_{1-x}Sr_xMnO_3$ should result in an inhomogeneous mixture of different phase states with predominant weight of a phase providing the most efficient screening of the charge inhomogeneity, in particular, either metallic, or metallic-like phase. In this connection we consider below a mixed valence phase being the analog of the well known in solid state chemistry disproportionation reaction, or, in a sense, electron-hole liquid in semiconductors like Ge and Si .

3.2.1 Electron-hole Bose liquid in manganites

Parent manganites such as $LaMnO_3$ are antiferromagnetic insulators with the charge transfer gap. Phase transition to novel hypothetically metallic state could be realized due to a mechanism familiar to such semiconductors with filled bands as Ge and Si where given certain conditions one observes a formation of metallic EH-liquid as a result of the exciton decay [27]. Fundamental absorption band in parent manganites is formed both by the intracenter $O2p - Mn3d$ transfer and by the small intercenter charge transfer excitons, which in terms of chemical notions represent somewhat like the disproportionation quanta with threshold ~ 3.5 eV, resulting in a formation of electron MnO_6^{10-} and hole MnO_6^{8-} centers. 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, become unstable regarding the decay (dissociation) to electron and hole centers, and we come to the system of electrons and holes, which form a so-called electron-hole plasma. Maximally dense EH plasma corresponds to overall disproportionation with transition to novel phase state with mixed valence which could be named as EH liquid [27]. EH liquid in conventional semiconductors like Ge , Si is a two-component *Fermi-liquid* whereas EH liquid in manganites would represent a system of strongly correlated electron and hole centers which is equivalent to a *Bose-liquid*.

An instability of parent manganite $LaMnO_3$ with regard to overall disproportionation like (5) was strikingly demonstrated recently by Zhou and Goodenough [16]. The transport (thermo-electric power and resistivity) and magnetic (susceptibility) measurements showed that $LaMnO_3$ above the cooperative Jahn-Teller orbital-ordering temperature $T_{JT} \approx 750$ K transforms into charge-disproportionated paramagnetic phase with $\mu_{eff} = 5.22\mu_B$ and cooperative charge transfer of many heavy vibronic charge carriers.

Strong variation of the $LaMnO_3$ Raman spectra with increasing laser power [28] could be related to the photo-induced nucleation and the volume expansion of the EH Bose-liquid, especially, as at a rather big excitation wavelength $\lambda = 514.5$ nm, or $\lambda = 632.8$ nm the absorption is considerably stronger in domains of novel phase than in parent lattice.

Effective nucleation of the EH Bose-liquid in manganites could be provoked by a non-isovalent substitution since this strongly polarizable or even metallic phase in contrast with parent insulating phase provides an effective screening of charge inhomogeneity.

Even the most relevant quantum-chemical approach to the description of the EH liquid in manganites comes across a number of essential difficulties related to a strong overlap and coupling of the neighbouring MnO_6 centers, and anomalously strong fluctuations of the electron potential to be comparable with the potential itself.

Such an approach starts first of all from effective center with a number of active valent states which form a *valent* multiplet. Then we introduce a pseudo-spin formalism and an effective pseudo-spin Hamiltonian for the system of centers. Various pseudo-spin models are based on familiar quantum and classical Heisenberg and Ising models and are widely used for description of the charge, spin, orbital and structural ordering in systems with "local" moments. Such an approach looks like a conventional variational treatment with trial functions and effective parameters which magnitude could be fitted from experiment or numerical quantum-chemical *ab-initio* calculations for rather small model system.

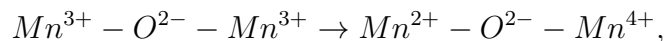
Optimal situation to take account of charge, dipole and quadrupole fluctuations could be provided if we start from the MnO_6 centers, and include to the valent multiplet of the *effective* electron and hole MnO_6 center the even orbital singlets ${}^6A_{1g}$, ${}^4A_{2g}$ and the odd orbital triplets ${}^6T_{1u}$, ${}^4T_{2u}$, respectively. Such effective centers with the ${}^6A_{1g} - {}^6T_{1u}$, ${}^4A_{2g} - {}^4T_{2u}$ valent multiplets could provide optimal simulation for the complex response of the centers to different fluctuations of potential. From the other hand, such a model allows to describe a rather subtle electron density distribution, and many other static and dynamic properties of the EH Bose-liquid. A conventional parametrization approach to appropriate effective Hamiltonian does not imply the detailed information about a microstructure of different states involved. However, such an information is essential for quantitative or semi-quantitative evaluation of different effective parameters and different terms in the Hamiltonian. The relevant choice of electronic configurations for the even ${}^4A_{2g}$ and ${}^6A_{1g}$ terms of the hole and electron centers in our case naturally corresponds to t_{2g}^3 and $t_{2g}^3 e_g^2$ ones, respectively. For the odd orbital triplets ${}^4T_{2u}$, ${}^6T_{1u}$ the most probable candidates are the low-lying CT configurations $t_{2g}^3 e_g^1 t_{2u}$ and $t_{2g}^4 e_g^2 t_{2u}$, respectively.

One should emphasize the specific role of the long-range electrostatic multipole interactions for the EH Bose-liquid. They can favor stabilization of an inhomogeneous vortex-like distribution of charge and orbital density.

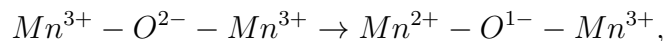
3.2.2 "Chemical" approach to an EH Bose-liquid and Mn valence problem

A simplified "chemical" approach to an EH Bose-liquid as to a disproportionated phase [29] naively implies an occurrence of Mn^{4+} and Mn^{2+} ions. However, such an approach is very far from reality. Indeed, the electron MnO_6^{10-} and hole MnO_6^{8-} centers are already the mixed valence centers, as in the former the Mn valence resonates between +2 and +1, and in the latter does between +4 and +3.

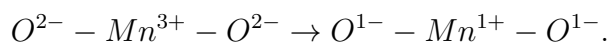
In this connection, one should note that in a sense disproportionation reaction (5) has several purely ionic counterparts, the two rather simple



and



and, finally, one rather complicated



Thus, the disproportionation (5) threshold energy has to be maximally close to the CT energy parameter Δ_{pd} . Moreover, namely this is seemingly to be one of the main parameters governing the nucleation of EH Bose-liquid in oxides.

So far, there has been no systematic exploration of exact valence and spin state of Mn in these systems. In thermoelectric power experiments (TEP) Hundley and Neumeier [30] find that more hole-like charge carriers or alternatively fewer accessible Mn sites are present than expected for the value x . They suggest a charge disproportionation model based on the instability of $Mn^{3+} - Mn^{3+}$ relative to that of $Mn^{4+} - Mn^{2+}$. This transformation provides excellent agreement with doping-dependent trends exhibited by both TEP and resistivity.

Using electron paramagnetic resonance (EPR) measurements Oseroff *et al.* [31] suggest that below 600 K there are no isolated Mn atoms of valence +2, +3, +4, however they argue that EPR signals are consistent with a complex magnetic entity composed of Mn^{3+} and Mn^{4+} ions.

Park *et al.* [32] attempted to support the Mn^{3+}/Mn^{4+} model, based on the Mn 2p x-ray photoelectron spectroscopy (XPES) and $O1s$ absorption. However, the significant discrepancy between the weighted Mn^{3+}/Mn^{4+} spectrum and the experimental one for given x suggests a more complex doping effect. Subias *et al.*[33] examined the valence state of Mn utilizing Mn K-edge x-ray absorption near edge spectra (XANES), however, a large discrepancy is found between experimental spectra given intermediate doping and appropriate superposition of the end members.

The valence state of Mn in Ca-doped $LaMnO_3$ was studied by high-resolution Mn $K\beta$ emission spectroscopy by Tyson *et al.* [11]. No evidence for Mn^{2+} was observed at any x values seemingly ruling out proposals regarding the Mn^{3+} disproportionation. However, this conclusion seems to be absolutely unreasonable. Indeed, electron center MnO_6^{10-} can be found in two configuration with formal Mn valence Mn^{2+} and Mn^{1+} (not simply Mn^{2+} !), respectively. In its turn, the hole center MnO_6^{8-} can be found in two configuration with formal Mn valence Mn^{4+} and Mn^{3+} (not simply Mn^{4+} !), respectively. So, within the model the Mn $K\beta$ emission spectrum for Ca-doped $LaMnO_3$ has to be a superposition of appropriately weighted $Mn^{1+}, Mn^{2+}, Mn^{3+}, Mn^{4+}$ contributions (not simply Mn^{4+} and Mn^{3+} , as one assumes in Ref.2). Unfortunately, we do not know the Mn $K\beta$ emission spectra for the oxide compounds with Mn^{1+} ions, however a close inspection of the Mn $K\beta$ emission spectra for the series of Mn -oxide compounds with Mn valence varying from 2+ to 7+ (Fig.2 of the cited paper) allows to uncover a rather clear dependence on valence, and indicates a possibility to explain the experimental spectrum for Ca-doped $LaMnO_3$ (Fig.4a) as a superposition of appropriately weighted $Mn^{1+}, Mn^{2+}, Mn^{3+}, Mn^{4+}$ contributions. It should be noted that an "arrested" Mn -valence response to the doping in the $x < 0.3$ range founded in Ref. [11] is also consistent with creation of predominantly oxygen holes.

This set of conflicting data together with a number of additional data [34] suggests the need for an in-depth exploration of the Mn valence problem in this perovskite system. However, one might say, the doped manganites are not only systems with mixed valence, but systems with indefinite valence, where we cannot, strictly speaking, unambiguously distinguish Mn species with either distinct valence state.

3.2.3 Effective model Hamiltonian

The effective model Hamiltonian describing the system of clusters MnO_6^{8-} and MnO_6^{10-} with the valent manifolds $^4A_{2g} - ^4T_{2u}$ and $^6A_{1g} - ^6T_{1u}$, respectively, can be presented as a sum of several terms

$$\hat{H} = \hat{H}_{QLBG} + \hat{H}_{orb} + \hat{H}_{sp} + \hat{H}_{so} + \hat{H}_{vibr}. \quad (20)$$

Here \hat{H}_{QLBG} is the effective Hamiltonian for quantum lattice Bose-gas, which accounts for quantum transfer of the electron (hole) centers (the effective kinetic energy of the bosons) and the effective repulsion of these bosons (see below).

The term \hat{H}_{orb} is responsible for the crystal field effects, multipole-multipole interaction, pure orbital part of the exchange interaction of the centers and the orbital Zeeman energy.

$$\hat{H}_{orb} = \hat{H}_{CF} + \hat{H}_{multi} + \hat{H}_{orb.ex.} + \hat{H}_{orb.Zeem.}, \quad (21)$$

Note that the effective crystal field Hamiltonian \hat{H}_{CF} includes both high-symmetry (cubic) term, which is responsible for the ${}^6A_{1g} - {}^6T_{1u}$ (${}^4A_{2g} - {}^4T_{2u}$) splitting, and low-symmetry term \hat{H}_{LSCF} . Here, one should note the important role of the long-range multipole-multipole terms in (21), leading to stabilization of the inhomogeneous structures.

The spin Hamiltonian \hat{H}_{sp} accounts for a spin-spin exchange interaction and spin Zeeman effect. The term \hat{H}_{so} accounts for the spin-orbital interaction. At last, \hat{H}_{vibr} is responsible for the vibronic effects, which in presence of the orbital (quasi)degeneracy of the valent manifold have the (pseudo)Jahn-Teller-like character.

Note that the oxygen holes occupying the non-bonding orbitals provide a strong ferromagnetic exchange with neighboring manganese ions resulting in formation of strongly coupled $Mn-O-Mn$ ferromagnetic clusters.

The detailed analysis of the effective Hamiltonian (20) represents itself extremely complex and challenging problem for further investigation. Below we shortly discuss one simple version of such a Hamiltonian.

3.2.4 Simple double-exchange model with triplet bosons

In the simplest model of the manganite as an electron-hole Bose liquid one can restrict himself with orbital singlets ${}^6A_{1g}$ and ${}^4A_{2g}$ for the electron MnO_6^{10-} and hole MnO_6^{8-} centers, respectively. In the absence of the external magnetic field the effective Hamiltonian of this model takes the form of the Hamiltonian of the quantum lattice Bose-gas of the triplet bosons (QLTBG)

$$\begin{aligned} \hat{H} = \hat{H}_{QLBG} + \hat{H}_{ex} = & -\frac{1}{2} \sum_{\langle ij \rangle} \tau_{ij} \vec{T}_i^\dagger \vec{T}_j + \sum_{\langle ij \rangle} V_{ij} N_i N_j - \mu \sum_i N_i \\ & - \frac{1}{2} \sum_{\langle ij \rangle} J_{ij}^{hh} \vec{S}_i \vec{S}_j - \sum_{\langle ij \rangle} J_{ij}^{hb} \vec{s}_i \vec{S}_j - \frac{1}{2} \sum_{\langle ij \rangle} J_{ij}^{bb} \vec{s}_i \vec{s}_j - \sum_i J_{ii}^{hb} \vec{s}_i \vec{S}_i. \end{aligned} \quad (22)$$

Here $T_{\alpha i}^\dagger$ denotes the spin $S = 1$ and the spin projection α boson creation operator at the i -th site; $T_{\alpha i}$ is the corresponding annihilation operator. The boson number operator $N_i = \vec{T}_{\alpha i}^\dagger \vec{T}_{\alpha i}$ at the i -th site due to the condition $V_{ii} \rightarrow +\infty$ (*hardcore boson*) can take values 0 or 1. The summation indices $\langle ij \rangle$ denote sum over the nearest neighbors.

The operators $T_{\alpha i}^\dagger$ and $T_{\alpha i}$ in the $|NSM\rangle$ representation have the following matrix elements [36] :

$$\begin{aligned} \left\langle 0 \frac{3}{2} m \left| T_{\alpha i} \right| 1 \frac{5}{2} m' \right\rangle &= (-1)^{\frac{3}{2}-m} \begin{pmatrix} \frac{3}{2} & 1 & \frac{5}{2} \\ -m & \alpha & m' \end{pmatrix} \left\langle \frac{3}{2} \left\| T \right\| \frac{5}{2} \right\rangle, \\ \left\langle 1 \frac{5}{2} m \left| T_{\alpha i}^\dagger \right| 0 \frac{3}{2} m' \right\rangle &= (-1)^{\frac{5}{2}-m} \begin{pmatrix} \frac{5}{2} & 1 & \frac{3}{2} \\ -m & -\alpha & m' \end{pmatrix} \left\langle \frac{5}{2} \left\| T \right\| \frac{3}{2} \right\rangle. \end{aligned}$$

Here $\left\langle \frac{5}{2} \left\| T \right\| \frac{3}{2} \right\rangle = \left\langle \frac{3}{2} \left\| T \right\| \frac{5}{2} \right\rangle = \sqrt{6}$ is the reduced matrix element for these operators. One can deduce that

$$(\vec{T}^\dagger \vec{T}) = N; \quad (\vec{T} \vec{T}^\dagger) = \frac{3}{2}(1 - N)$$

It is noteworthy that the presence of the triplet creation/annihilation operator with the relations shown above, generally, does not permit to introduce pseudo-spin formalism conventionally used in the case of QLSBG.

The first term in (22) corresponds to the kinetic energy of the bosons, τ_{ij} is the transfer integral. The second one reflects the effective repulsion ($V_{ij} > 0$) of the bosons, located on the neighboring sites.

The chemical potential μ is introduced to fix the boson concentration

$$n = \frac{1}{N} \sum_i \langle N_i \rangle \quad (23)$$

The last term in (22) is the Heisenberg exchange interaction of the spins of the hole centers with each other (term with J^{hh}), spins of the hole centers with the bosons' spins, located on the nearest sites (term with J^{hb}), and term with J^{bb} accounts for the exchange of the boson spins.

The very last term in (22) stands for the intra-center exchange between the boson spin and the spin of the hole center. In order to account the Hund rule one should consider it to be infinitely large ferromagnetic. After taking the limit $J_{ii}^{hb} \rightarrow +\infty$ the spin part of the (22) takes the form

$$\hat{H}_{ex} = -\frac{1}{2} \sum_{\langle ij \rangle} J_{ij}^{hh} \vec{S}_i^h \vec{S}_j^h - \sum_{\langle ij \rangle} J_{ij}^{he} \vec{S}_i^h \vec{S}_j^e - \frac{1}{2} \sum_{\langle ij \rangle} J_{ij}^{ee} \vec{S}_i^e \vec{S}_j^e. \quad (24)$$

Here we introduced the operators of the "hole center spin" and "electron center spin"

$$\vec{S}^h = (1 - N)\vec{S}; \quad \vec{S}^e = N\vec{S}.$$

New exchange parameters J^{eh} and J^{ee} are related with the old ones by the linear equations

$$J_{ij}^{eh} = \frac{2}{5} J_{ij}^{hb}, \quad J_{ij}^{ee} = \frac{9}{25} J_{ij}^{hh} + \frac{6}{25} J_{ij}^{bh} + \frac{4}{25} J_{ij}^{ee}.$$

At last, let us introduce the hermitian operators

$$\vec{T}^x = \frac{1}{2}(\vec{T} + \vec{T}^\dagger); \quad \vec{T}^y = \frac{i}{2}(\vec{T} - \vec{T}^\dagger)$$

instead of T and T^\dagger .

Thus the Hamiltonian will take its final form

$$\begin{aligned} \hat{H} = & \sum_{\langle ij \rangle_\alpha} \tau_{ij} (\vec{T}_{\alpha i}^x \vec{T}_{\alpha j}^x + \vec{T}_{\alpha i}^y \vec{T}_{\alpha j}^y) + \sum_{\langle ij \rangle} V_{ij} N_i N_j - \mu \sum_i N_i \\ & - \frac{1}{2} \sum_{\langle ij \rangle} J_{ij}^{hh} \vec{S}_i^h \vec{S}_j^h - \sum_{\langle ij \rangle} J_{ij}^{he} \vec{S}_i^h \vec{S}_j^e - \frac{1}{2} \sum_{\langle ij \rangle} J_{ij}^{ee} \vec{S}_i^e \vec{S}_j^e. \end{aligned} \quad (25)$$

One can easily see that the exchange parameters J^{hh} , J^{eh} and J^{ee} play the different role: the exchange integral J_{eh} together with the parameter V lead to set the different spin multiplicity of the neighboring sites and thus favor the diagonal long-range order (DLRO) – charge ordered phase. The exchange parameters J_{ee} and J_{hh} , vice versa, make spin multiplicity of the neighboring sites to be the same, which establishes droplet phase.

Generally, this model can be considered as Bose-analogue of the double-exchange model [2].

Tentative analysis of this model allows to predict possible phase states with rather conventional diagonal long-range order (antiferromagnetic insulating, ferromagnetic metallic), and unconventional nondiagonal long-range order with superfluidity of triplet bosons and ferromagnetic ordering [37].

4 Conclusions

A problem of adequate electronic model for doped manganites remains controversial. In such a situation we argue a necessity to discuss all possible candidate states both for isolated MnO_6 centers, and respective systems. Above we have mainly addressed unconventional charge transfer states for MnO_6 centers with oxygen holes. The experimental observation of spectral changes in optical absorption and anomalously large effective magnetic moments in doped manganites both at low ($T \ll T_C$) and high ($T \gg T_C$) temperatures [12, 13] provides a clear support for such a "oxygen-hole" scenario with the well developed fluctuations of the sign of the $O2p - Mn3d$ charge transfer energy. We propose two idealized theoretical models to describe manganites with unconventional hole behavior. The first implies an overall oxygen localization for the doped holes. The second assumes formation of the electron-hole Bose liquid, or a system of the electron MnO_6^{10-} , and hole MnO_6^{8-} centers. In a sense, this scenario resembles well-known disproportionation reaction. In both cases one might expect non-trivial magnetic behavior with strong ferromagnetic fluctuations due to anomalously strong ferromagnetic coupling of non-bonding $O2p$ holes with $Mn3d$ electrons.

Electron-hole Bose liquid in doped manganites represents the system of triplet local bosons moving in the lattice of the hole $S = 3/2$ MnO_6^{8-} centers which reveals complex phase diagram both with diagonal and off-diagonal order.

Actual electronic structure in doped manganites is believed to be strongly inhomogeneous with static and dynamic fluctuations of different phases including the above addressed ones. In this connection our consideration allows to uncover some unusual properties of such fluctuations.

An absence of the adequate physical model for the novel phase to be developed in manganites upon the doping hampers the further progress in complete understanding and description of the unconventional inhomogeneity in these systems. Anyway, making use of either experimental data as a trump in favor of either theoretical model should be made with some caution if a phase homogeneity of the samples under examination is questionable.

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Figure captions

Fig.1. Diagram of optically active levels for the MnO_6^{8-} center with varying Δ_{pd} parameter.

